Hydrolysis corrosion of alumina thin films produced by pulse DC reactive magnetron sputtering at various operating pressures

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ABSTRACT
Alumina thin films were prepared by pulsed DC reactive magnetron sputtering using operating pressures that were varied from 3 to 20 mTorr. The films were immersed in DI water at temperatures of 55 °C and 65 °C for 30 min to study their hydrolysis corrosion behaviors. Unlike bulk crystalline Al2O3 materials, sputtered alumina films fabricated at operating pressures of 7 mTorr and higher were found to react with DI water within minutes, even under mild conditions. X-ray diffraction (XRD) and spectroscopic ellipsometry (SE) showed that the as-sputtered films had amorphous structures with various degrees of porosity within the films. The calculated porosity was found to increase from 17% to 25% as the operating pressure increased from 3 to 20 mTorr, respectively. Field-emission scanning electron microscopy (SEM) was employed to characterize the morphologies of the corroded films. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy showed the presence of hydroxide-containing functional groups on surfaces of alumina films, suggesting that the corrosion was due to a hydrolysis reaction. X-ray photoelectron spectroscopy (XPS) revealed distinct features in the non-corroded and corroded sample groups. For the corroded group (7–20 mTorr), the Al 2p peak showed two transitions, at 74.2 and 75.5 eV, attributed to Al–O and Al–OH, respectively. The O 1s peak intensities associated with the hydroxide content of samples in this group were found to be stronger than those associated with the lattice oxygen. The O 1s signal from adsorbed water at 533.7 eV became much stronger in corroded samples. The results also show that films fabricated at higher operating pressures yielded higher levels of pre-adsorbed hydroxide. Corrosion may progress through collective processes, including the formation of soluble aluminum hydroxide complex species and Al–O bond breaking during the proton transfer reactions between adsorbed water and hydroxide.

1. Introduction

Alumina (Al2O3) is considered a thermally stable material with high strength, chemical inertness and excellent electrical insulating properties [1,2]. Crystalline alumina materials have two main phases, α-Al2O3 (corundum) and γ-Al2O3 (spinel). Both phases are generally assumed to be water-insoluble at room temperature. Thus, they are used as anti-corrosion materials in many applications. Several research groups have studied the reactivity of alumina with water [3–7]. Corrosion of alumina was normally found at elevated temperature by exposing it to water vapor [3,4] or under extreme conditions such as an alkaline solution at 150–200 °C [5]. Some reports have shown that γ-Al2O3 can react with water at 25 °C resulting in the formation of bayerite. However, the reaction rate is so slow that bayerite crystallization can only be...
detected after several days or weeks [6,7].

Assuming the physical properties of their bulk-crystalline counterparts, alumina thin films are widely used as protective coatings, diffusion barriers and insulating layers in semiconductor devices [8–11]. Magnetron sputtering is one of the most common processes adopted in the microelectronic industries for producing alumina films. This is because of the ease of controlling deposition, the capability for large-area coating and the cost-effectiveness. However, sputtered alumina thin films can have distinctive structures and properties not found in crystalline Al$_2$O$_3$ materials. These properties can be significantly altered by sputtering parameters such as operating pressure, substrate temperature and sputtering power [12–15]. Our groups have previously reported the effects of operating pressure on inhomogeneity of oxide thin films prepared by pulsed DC reactive magnetron sputtering [16]. A recent study by V. Dokmai et al. demonstrated that the corrosion of alumina thin films, produced by radio-frequency (RF) sputtering using the operating pressure of 20 mTorr, can take place under mild conditions [17]. The use of chemical inhibitors was suggested to control the corrosion reaction in DI water. This shows that the reactivity of these films in water should not be overlooked, especially when they are used as corrosion protection layers. Since many manufacturing steps involve the immersion of parts containing alumina thin films in water, it is crucial to gain more understanding of the corrosion resistance of these films. This work investigates the corrosion resistance of sputtered alumina thin films fabricated using various operating pressures in warm water. We focus on the effects of operating pressure on inhomogeneity of the films. Correlation between a film’s porosity and its susceptibility to hydrolysis corrosion is discussed.

2. Experimental

Alumina thin films were deposited on silicon wafers using pulsed DC reactive magnetron sputtering (AJA International, Inc.; ATC 2000-F) at room temperature. A high purity aluminum target (99.995%; KJ Lesker) was mounted on a sputtering cathode. The cathode was tilted at 40° to the normal of the substrate’s surface at a distance of 80 mm to produce highly uniform films. Prior to deposition, the chamber was pumped to a base pressure of $5 \times 10^{-7}$ Torr using a mechanical rotary pump (Alcatel) and a turbo-molecular pump (Shimazu, TMP-803-LM). A silicon substrate was sequentially cleaned in an ultrasonic washer with acetone, isopropanol and deionized water, then dried under a nitrogen atmosphere. The substrate was also cleaned with an argon plasma using an RF power of 25 W and operating pressure of 10 mTorr for 15 min to ensure contamination-free surfaces. The Al target was pre-sputtered in an oxygen atmosphere and sputtered with a Cu-K$_\alpha$ source at a grazing incidence of 0.4°. 

The crystal structures of the as-deposited films were determined by grazing incidence X-ray diffraction (GIXRD; RIGAKU TTRAX III) operated with a Cu-K$_\alpha$ source at a grazing incidence of 0.4°. The X-ray diffraction intensities were measured at incident angles between 20°–80° at 2° intervals. The thicknesses and optical properties of the as-deposited samples were analyzed using a spectroscope ellipsometer (SE; VASE2000 J A. Woollam Co.). The ellipsometric spectra $\Psi$ and $\Delta$ values were measured in the wavelength range of 350–1650 nm at 5 nm intervals at incident angle of 70°. The Tauc-Lorentz (TL) function was used with the optical model to determine the optical properties of the films.

The films were immersed in deionized (DI) water at 55°C and 65°C for 30 min to study their hydrolysis corrosion characteristics. The surface morphologies of both as-deposited and treated films were investigated via field-emission scanning electron microscopy (SEM; Hitachi SU8030). Functional groups on the film surfaces were examined using a Fourier transform infrared (FTIR) spectrometer (Thermo Scientific Nicolet iS 10) equipped with an IR source, DTGS KBr detector, and KBr beam splitter. The FTIR spectrum was recorded using the attenuated total reflectance (ATR) mode in the range of 4010 to 800 cm$^{-1}$, with a spectral resolution of 4 cm$^{-1}$. The chemical state and atomic composition of the prepared samples were analyzed using X-ray photoelectron spectroscopy (XPS; Kratos AXIS ultra DLD) on a unit equipped with a monochromatic Al K$_\alpha$X-ray source. Survey scans were used to assess any impurities as well as relative composition, collected using a pass energy of 80 eV. More detailed elemental scans were made using a pass energy of 20 eV. The C 1s peak at 285 eV was used as the reference line. Spectroscopic data were processed using Vision 2 software (Kratos Analytical, Ltd.). The areas of deconvoluted Gaussian peak fits were used to determine the composition contents of the samples. The percentage is shown on an atomic basis.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-deposited films prepared using various operating pressures, 3, 10 and 20 mTorr. No Bragg peak was observed in any sample, indicating neither the crystalline Al$_2$O$_3$ phases nor (oxy)hydroxide crystals such as gibbsite ($\alpha$-Al(OH)$_3$), bayerite ($\beta$-Al(OH)$_3$) and boehmite ($\gamma$-AlOOH) were present. The 2θ peak at 51.5° represented the (100) plane of the Si substrate. This indicated that as-deposited samples were amorphous, which agrees well with other reports of sputtered alumina films [18,19].

Table 1 summarizes the deposition conditions for the alumina films used in this study.

<table>
<thead>
<tr>
<th>Beige pressure (Torr)</th>
<th>$5 \times 10^{-7}$</th>
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<tbody>
<tr>
<td>Operating pressure (mTorr)</td>
<td>3, 5, 7, 10, 15 and 20</td>
</tr>
<tr>
<td>Ar flow rate (sccm)</td>
<td>15</td>
</tr>
<tr>
<td>O$_2$ flow rate (sccm)</td>
<td>2</td>
</tr>
<tr>
<td>DC power (Watts)</td>
<td>200</td>
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<tr>
<td>Time (min)</td>
<td>30</td>
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<tr>
<td>Substrate temperature (°C)</td>
<td>Room temperature</td>
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Fig. 1. XRD patterns of alumina films deposited at various operating pressures.
where \( A, E_0, C, E_g \) and \( E \) represent the amplitude, the peak transition energy, the broadening constant, the optical band gap and the photon energy, respectively. After the \( \varepsilon_2 \) determination, \( \varepsilon_1 \) was considered through the Kramers-Kronig relation, defined as follows [20]:

\[
\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi
\]

Subsequently, the refractive index (\( n \)) of the determined films as a function of the wavelength (\( \lambda \)) can be calculated as follows:

\[
n(\lambda) = \frac{1}{2} \left( \sqrt{\varepsilon_1(\lambda)^2 + \varepsilon_2(\lambda)^2} + \varepsilon_1(\lambda) \right).
\]

\[
\lambda = \frac{1240}{E}
\]

The model perfectly fitted all measured spectra, as shown in Fig. 2a. The index dispersions of the films were extracted from the model. The dispersions of refractive indices were then plotted as a function of the operating pressure, as presented in Fig. 2b. The results show that refractive index decreased as the operating pressure was increased. In general, the refractive index is related to the porosity of the thin film according to Eq. (4) [16,21].

\[
\text{Porosity} = \left( 1 - \frac{n_p^2}{n^2} \right) \times 100
\]

where \( n_p \) is the refractivity of the obtained porous thin films and \( n \) is the refractive index of bulk Al\(_2\)O\(_3\).

Fig. 2c shows the refractive index at 550 nm of samples fabricated at various operating pressures. The refractive index was found to decrease from 1.66 to 1.59 as the operating pressure increased from 3 to 20 mTorr, respectively. Using the effective refractive index of bulk corundum, Al\(_2\)O\(_3\), of 1.8 as a reference [22], the calculated porosity was found to increase from 17% to 25% as the operating pressure increased from 3 to 20 mTorr, respectively. The dependency the porosity on the operating pressure is believed to be related to the energy of particles in the sputtering system. Higher operating pressures made the atoms of gasses in sputtering system, which later transfer their energy to the sputtered atoms, have lower kinetic energy due to the decreased length of their mean free path [23]. This consequently left the sputtered atoms with low mobility when they arrived at the substrate [24]. As a result, the films deposited at higher operating pressures had higher degrees of porosity in the structure, while those deposited at lower operating pressure were found to be denser.

Correlations between corrosion resistance and an alumina film’s inhomogeneity resulting from different operating pressure used during fabrication is evidenced in Fig. 3. For films produced using low operating pressures of 3 and 5 mTorr, corrosion was not observed after 30 min of immersion in DI water at 55 °C and 65 °C. This is likely due to the low water-permeability of these denser films. As the operating pressure was increased during the sputtering process, the films became more prone to corrosion. Extensive corrosion was observed when operating
Fig. 3. SEM images of as-deposited and DI water-immersed samples at 55 °C and 65 °C for 30 min a) 3 mTorr as-deposited, b) 3 mTorr 55 °C, c) 3 mTorr 65 °C, d) 5 mTorr as-deposited, e) 5 mTorr 55 °C, f) 5 mTorr 65 °C, g) 7 mTorr as-deposited, h) 7 mTorr 55 °C, i) 7 mTorr 65 °C, j) 10 mTorr as-deposited, k) 10 mTorr 55 °C, l) 10 mTorr 65 °C, m) 15 mTorr as-deposited, n) 15 mTorr 55 °C, o) 15 mTorr 65 °C, p) 20 mTorr as-deposited, q) 20 mTorr 55 °C, and, r) 20 mTorr 65 °C.
pressures of 10 mTorr and higher were used. The corrosion of alumina was also found to be dependent on temperature. For a sample produced at a 7 mTorr operating pressure, corrosion was not observed when the DI water temperature was at 55 °C. As the DI water temperature was raised to 65 °C, extensive corrosion was clearly detected. This is due to the increase in kinetics of the reaction as temperature increases.

ATR-FTIR was performed to complement the characteristics of adsorbed species at the alumina films’ surface with spectral information that emphasizes the hydroxyl content. Fig. 4a and b show the FTIR spectra of alumina films produced at various operating pressures before and after immersion in DI water at 55 °C and 65 °C, respectively. The FTIR spectra of the as-deposited samples (without DI water treatment) are provided for reference. The absorption band at 1065 cm⁻¹ was attributed to the vibration of the Al–OH functional group [25]. This indicated that alumina was hydrolyzed by water. The band at 1636 cm⁻¹ corresponded to the bending mode of adsorbed water [26]. The peaks at 1420 cm⁻¹, 1490 cm⁻¹, 2344 cm⁻¹ and 2361 cm⁻¹ were attributed to the carbonate group [27], which may have resulted from the dissolution of background carbon dioxide from the atmosphere into the DI water. The vibrations near 2900 cm⁻¹ shown in some samples were associated with the aliphatic C–H stretching modes of hydrocarbon contamination [28]. The large band from 3000 cm⁻¹ – 3600 cm⁻¹, centered around 3300 cm⁻¹, was the result of both adsorbed water and OH functional groups attached to the alumina film. When the DI water temperature was at 55 °C, the bands at 1065 cm⁻¹ and 1636 cm⁻¹ were almost undetectable for samples produced at 3–7 mTorr operating pressures. At a DI water temperature of 65 °C, these peaks started to appear in the 7 mTorr sample. These results correlated well with the SEM images shown in Fig. 3, where corrosion started to appear in the sample fabricated at a 7 mTorr operating pressure that was treated with 65 °C DI water. It was also observed that the intensity of the peaks at 1065 cm⁻¹ and 3300 cm⁻¹ became higher for films fabricated at greater operating pressures (10 mTorr–20 mTorr). This suggests higher affinity for hydrolysis reactions in these films.

XPS was employed to examine the chemical composition and the pre-adsorbed hydroxide content in pristine alumina films. Fig. 5 shows the XPS spectra of an alumina film fabricated at a 5 mTorr operating pressure. The survey scan (Fig. 5a), the high resolution Al 2p peak (Fig. 5b), and the O 1s peak (Fig. 5c) represent general features found in all samples. The C 1s peak at 285 eV, shown in the survey scan, resulted from inevitable adventitious carbon that was used to charge correct the spectra. The Al 2p peak was located at a binding energy of 74.6 eV [29, 30]. An O 1s spectrum can be deconvoluted into three components. Its first component at a binding energy of 531 eV corresponds to the lattice oxygen atoms [29–34]. The peak at a binding energy of 532.2 eV was associated with adsorbed hydroxide at the surfaces of alumina films [17, 30–34]. In photoemission, the surface OH group distinguishes itself through a positive binding energy (BE) shift of O 1s relative to the bulk lattice O. This energy shift, ΔE, has been reported to vary between 1.0 and 2.0 eV [33–37]. We observed a similar ΔE of 1.2–1.3 eV in this experiment. An additional small peak was shown, near 533.7 eV, which was likely contributed by water or other weakly adsorbed species on the surface [30,32,34,38]. The XPS spectra of all samples in the current work are in the Supplementary Material.

Fig. 6 shows XPS spectra of alumina films after immersion in DI water at 55 °C for 30 min. Fig. 6a and b represent typical features of Al 2p and O 1s spectra, respectively, from the non-corroded samples (3–5 mTorr). Whereas, Fig. 6c and d represent XPS spectra of the corroded samples (7–20 mTorr). After DI water immersion, distinctions in the deconvoluted XPS peaks can be observed in the two groups. For the non-corroded group (Fig. 6a), the Al 2p peak appeared similar to the as-deposited sample (Fig. 5b), e.g., the peak corresponding to the Al–O binding energy. However, the O 1s (Fig. 6b) peak intensity contributed by the OH hydroxyl group (at 532.2 eV) appeared to have higher magnitude than that of the as-deposited sample. The intensity of the peak at 533.8 eV, which was contributed by water or other weakly adsorbed species, appeared to be similar to those of the as-deposited samples. For the corroded group, the Al 2p peak was shown to be clearly distorted. It can be deconvoluted into two peaks at binding energies of 74.2 eV and 75.5 eV, which are believed to arise from Al–O–Al and Al–OH clusters, respectively (Fig. 6c). This is in agreement with the work of A. Celebioglu et al., where the Al 2p peak of water-treated Al₂O₃ tubes show the high BE component at 75.5–75.8 eV [34]. The Al 2p peak, with two transitions observed here, is also similar to that reported for bayerite (β-Al(OH)₃), where structural hydroxyls existed in the crystal structure [32]. The splitting of Al 2p indicated a distinct coordination adopted from Al atoms coming either from the bulk (octahedral local environment as in Al₂O₃) or from the interface region (where the hydrolysis reactions occurred) [39,40]. These peaks were common in films fabricated at operating pressures of 7 mTorr and higher, indicating hydrolysis reactions in these samples. Although leaching of surface atoms was not evident in the SEM image of the 7 mTorr sample, the XPS result implied that corrosion had already begun in this sample. This is also supported by the FTIR absorption band at 1065 cm⁻¹ attributed to the vibration of the Al–OH functional group in these samples (Fig. 4). The peaks associated with OH and H₂O, shown in Fig. 6d, became much stronger compared to those of the non-corroded group. One can also notice that the OH peak intensities of samples in the corroded group

![Fig. 4. ATR-FTIR spectra of alumina films before and after being treated with DI water at (a) 55 °C and (b) 65 °C.](image_url)
(7–20 mTorr) became higher than those associated with the lattice oxygen. The XPS spectra of all samples in the current study are in the Supplementary Material.

Fig. 7 shows the chemical composition of alumina films fabricated at various operating pressures before and after immersion in DI water at 55 °C. For the as-deposited samples, the Al:O ratios were found to slightly deviate from the stoichiometric values for crystalline Al₂O₃, which was typical for amorphous alumina films deposited via a reactive magnetron sputtering technique [13]. The Al:O ratios were found to be marginally different among the samples (within 2%) as the operating pressure increased from 3 to 20 mTorr (Fig. 7a). However, the content of oxygen associated with hydroxide was found to increase from 32% to 34.5% as the operating pressure was increased from 3 to 7 mTorr. The O 1s hydroxide content then reached a level of approximately 36–38% for films fabricated at higher operating pressures (Fig. 7b). The level of oxygen associated with adsorbed water in these films was found to be in the range of 3.6%–4.8%. After treating with DI water at 55 °C, the Al:O ratios were found to significantly deviate from the stoichiometric condition, except for the films fabricated at lower operating pressures of 3 and 5 mTorr (Fig. 7c). Fig. 7d shows that the hydroxide content in these films increased significantly in the corroded films. For films fabricated at operating pressures of 7 mTorr and higher, the content of oxygen associated with hydroxide and adsorbed water was found to range from 48.2%–58.5% and 10.5%–19.8%, respectively.

As evidenced by the FTIR and XPS results, the film fabricated at a 7 mTorr operating pressure started to be hydrolyzed by warm DI water. The corrosion became clear when the DI water temperature reached 65 °C, as shown in the SEM micrograph (Fig. 3i). The higher level of porosity and pre-existing hydroxyl radicals in this sample together with higher temperature seemed to cause the hydrolysis reaction. Denser films fabricated at lower operating pressures of 3 and 5 mTorr have lower levels of pre-adsorbed hydroxide, which consequently resulted in more corrosion resistance.

The results show that alumina films fabricated at various operating pressures yielded different levels of porosity and pre-adsorbed hydroxide in the films. These different interface characteristics in alumina films play a significant role in the mechanisms of interfacial reactions. We postulate that the hydrolysis corrosion mechanism of these films passes through four stages: (i) deposition of films with various degrees of porosity resulting from different operating pressures, (ii) termination of film surfaces with hydroxyl groups and adsorbed water molecules, (iii) leaching of surface atoms due to these collective effects, including the formation of a soluble Al(OH)₄ species due to hydrolysis reactions and breaking of Al–O bonds resulting from hydrogen bond induced stretching during the proton transfer reactions between adsorbed water and hydroxide, and (iv) continuation of hydrogen bond formation and multiple H₂O adsorption on subsequent layers of alumina, which resulted in further straining and breaking of Al–O bonds. Fig. 8 shows a schematic representation of the proposed mechanism. Fig. 8a illustrates the surface of as-sputtered alumina films, where dangling bonds are present in the as-sputtered alumina film. Unlike crystalline alumina, amorphous alumina films possess much higher levels of active dangling bonds within the structure. S. K. Lee et al. [41, 42] used a solid-state nuclear magnetic resonance (NMR) technique to study the local atomic structures of amorphous alumina thin films. These studies showed that the alumina films were composed of three Al coordination species: the four-coordinated Al (⁴⁴Al), the five-coordinated Al (⁵⁵Al) and the six-coordinated Al (⁶⁶Al). Among these, ⁴⁴Al and ⁵⁵Al represent the dominant species (92–95%) within the structure. This suggests that alumina films are more reactive than previously thought. In such studies, the potential utility of amorphous alumina films as surface catalysts was proposed. The active ⁴⁴Al and ⁵⁵Al species in amorphous alumina films readily serve as adsorption sites for subsequent exposure to molecular species. Fig. 8b shows surface hydroxyl groups terminating on the as-sputtered alumina film. Upon exposure to the atmosphere, hydroxyl groups are rapidly formed. Several experimental and theoretical studies [43–46] presented evidence for dissociative chemisorption of water on the surface of alumina. The surface hydroxyl groups can be
in the form of terminal OH and bridge OH groups. These active surface hydroxyl groups on the oxide film dissociate in aqueous solutions and form electric charges as depicted in Fig. 8c. The surfaces can be positively or negatively charged when the film is immersed in a solution having a lower or higher pH than its point of zero charge (PZC), respectively. The presence of pre-adsorbed hydroxide also helps reduce the incubation time (the time required for the surface potential to change) in the solution [47]. Since the PZC of the amorphous alumina film was reported to be in the range of pH 5.7 [48], the neutral pH of DI water causes negative charges to build up on the surface of alumina films. At pH levels above the PZC, hydroxyl ions adsorb onto the surface and interact with alumina directly. The corrosion of alumina could occur through a hydrolysis reaction, where hydroxyl ions form soluble Al (OH)$_4$ species, as shown in Eq. (5) [17].

$$\text{Al}_2\text{O}_3 + 2\text{OH}^- + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_4^-$$  (5)

The involvement of the hydroxyl ion in the corrosion of amorphous alumina films is implied in the experimental study by V. Dokmai et al. [17]. In this study, a sputtered alumina film was subjected to vacuum ultraviolet treatment to deliberately form Al–O–H functional groups on its surface. The hydroxide-covered film was found to easily corrode in DI water even at 40 °C. On the contrary, when Zn$^{2+}$ or PO$_4^{3-}$ ions were introduced in the DI water to undergo a ligand exchange reaction with the alumino group (Al–OH), corrosion was suppressed [17]. The poor corrosion resistance of the amorphous films fabricated at higher operating pressures observed in our experiments is believed to be related to the presence of hydroxyl groups terminating on the surface of the sputtered alumina film. According to the O 1s spectra, the level of oxygen associated with the pre-adsorbed hydroxide in the as-deposited samples has been shown to increase from 32% to 37.8% as the operating pressure is increased from 3 to 20 mTorr (Fig. S-2). Higher coverage of hydroxyl groups on the surface can lead to a decrease in adsorption energy of water on alumina surfaces [46]. According to the molecular dynamics simulation of the interaction of water with Al$_2$O$_3$ using density functional theory by Hass et al. [46], at a high coverage of OH groups on alumina surfaces, many of the surface Al–O bonds can be greatly strained or broken, making some second-layer Al more accessible to H$_2$O. In such a regime, the simulation revealed rapid water-catalyzed dissociation and proton transfer reactions between adsorbed water and hydroxide. Fig. 8d shows a continuation of hydrogen bond formation and multiple H$_2$O adsorption on subsequent layers of alumina, which resulted in further straining and breaking of Al–O bonds. Greater degrees of porosity in alumina films fabricated at higher operating pressures also allows high permeability for water to adsorb onto the larger

Fig. 6. XPS spectra of alumina films treated with DI water at 55 °C (a–b) films fabricated at 5 mTorr representing the non-corroded group (a) Al 2p peak, (b) O 1s peak, (c–d) films fabricated at 15 mTorr representing the corroded group (c) Al 2p peak, (d) O 1s peak.
Fig. 7. Chemical composition of alumina films fabricated at various operating pressures (a) atomic compositions of as-deposited films, (b) Al–O, OH and H₂O contents of as-deposited films, (c) atomic compositions of 55 °C DI water-treated films, and (d) Al–O, OH and H₂O contents of 55 °C DI water-treated films. The calculation was based on the areas of deconvoluted O 1s XPS peaks.

Fig. 8. Schematic representation of hydrolysis corrosion in amorphous alumina films: (a) as-deposited alumina films with different degrees of porosity, (b) termination of film surfaces with hydroxyl groups, (c) leaching of surface atoms due to collective effects, including the formation of a soluble Al(OH)₄⁻ species and breaking of Al–O bonds resulting from hydrogen bond induced stretching, and (d) continuation of hydrogen bond formation and multiple H₂O adsorption on subsequent layers of Al.
surface area and enhance corrosion.

All experimental findings show that the operating pressure used during the sputtering process plays an important role in controlling the degree of porosity of deposited films. Higher operating pressures lead to structures with greater degrees of porosity, which consequently were more easily hydrolyzed and corroded in warm water, and vice-versa. Thus, chemical stability in sputtered alumina films cannot always be assumed. Our results show that fabricating alumina films at lower operating pressures is more suitable for applications requiring anti-corrosion properties. Emphasis should be made on sputtered alumina films, which consequently were deposited by an RF sputtering method as masks for some technological applications such as optical coatings with anti-glare or hydrophilic properties. Emphasis should be made on sputtered alumina films prepared by pulsed dc reactive magnetron sputtering, Thin Solid Films 520 (2012) 2689–2694., https://doi.org/10.1016/j.tsf.2011.11.040.

4. Conclusions

In this report, we described the effects of operating pressure used during a sputtering process on inhomogeneity and hydropysis corrosion of alumina films. The alumina films were fabricated via a reactive DC magnetron sputtering process using various operating pressures. For alumina films produced at operating pressures of 7 mTorr and higher, corrosion was found within 30 min after they were treated with warm DI water. The higher degree of porosity in these films resulted in a greater level of pre-adsorbed hydroxide, which consequently caused hydropysis corrosion. The hydropysis reaction was confirmed through the FTIR and XPS results of the corroded samples. This study emphasizes that the reactivity of sputtered alumina films with water cannot be disregarded. Nonetheless, microscopically rough alumina films may find use in some technological applications such as optical coatings with anti-glare or anti-reflective properties. Understanding the effect of operating pressure on corrosion gained from this study will lead to better design of alumina films with controllable roughness. Further studies should examine other sputtering parameters that may affect corrosion resistance properties of sputtered alumina films.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jceramint.2020.12.108.

References


