Comparison of the cohesive and delamination fatigue properties of atomic-layer-deposited alumina and titania ultrathin protective coatings deposited at 200 °C

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Abstract
The fatigue properties of ultrathin protective coatings on silicon thin films were investigated. The cohesive and delamination fatigue properties of 22 nm-thick atomic-layered-deposited (ALD) titania were characterized and compared to that of 25 nm-thick alumina. Both coatings were deposited at 200 °C. The fatigue rates are comparable at 30 °C, 50% relative humidity (RH) while they are one order of magnitude larger for alumina compared to titania at 80 °C, 90% RH. The improved fatigue performance is believed to be related to the improved stability of the ALD titania coating with water compared to ALD alumina, which may in part be related to the fact that ALD titania is crystalline, while ALD alumina is amorphous. Static fatigue crack nucleation and propagation was not observed. The underlying fatigue mechanism is different from previously documented mechanisms, such as stress corrosion cracking, and appears to result from the presence of compressive stresses and a rough coating–substrate interface.

Keywords: fatigue, ALD, harsh environment, titania, alumina, ultrathin coatings

1. Introduction
The development of effective ultra-thin passivation solutions is actively pursued given its significant impact on a wide range of promising technologies, including flexible printed electronics [1] (organic light emitting diodes for displays and solid state lighting, organic photovoltaics and organic electrochromics), chemical microelectromechanical system (MEMS) sensors [2], and silicon-based stretchable electronics for bio-implants [3]. For these applications, the ultra-thin coatings must provide permeation barriers with water vapor transmission rates as low as $10^{-6}$ g m$^{-2}$ per day and oxygen transmission rate as low as $10^{-5} - 10^{-3}$ cm$^3$ m$^{-2}$ per day [4–7]. Atomic layer deposition (ALD) is a very promising technique for dense, pinhole-free, conformal, highly uniform thin films that can be deposited at low temperatures ($<100$ °C), a requirement for deposition on polymers [8]. Various types of ALD coatings were shown to be effective ultra-barriers, including neat alumina ($\text{Al}_2\text{O}_3$), titania ($\text{TiO}_2$) and nanolaminates [4–7]. Importantly enough, this deposition technique is compatible with large-scale, roll-to-roll applications (spatial ALD) [9, 10].

A major limitation with the current state-of-the-art ultra-barrier technologies for flexible and/or stretchable...
Figure 1. Inclined SEM images of (a) Si microresonator coated with 22 nm of ALD TiO$_2$ and (b) notch area before test. The scalloping results from the deep reactive ion etching process. The defects observed in (b) slightly away from the notch root at the top of the film’s thickness (see white arrow) are related to the Si device fabrication process [22]. No fatigue damage was observed in that particular area, where stresses are much lower than at notch root [13]. (c) High magnification inclined SEM image of the sidewall coated with ALD TiO$_2$, showing that the TiO$_2$ coatings are likely to be crystalline.

...applications is the lack of understanding of the mechanisms responsible for the degradation of the barrier properties as a result of mechanical loading (especially cyclic loading), exposure to harsh environments (including aqueous and physiological environments), and, more critically, combination thereof. The aforementioned ALD metal oxide coatings are inherently brittle, and are ultra-strong mainly because they are ultra-thin. For example, critical onset strains for cracking in ALD alumina were shown to be inversely proportional to the square root of thickness, and typically reach a few% for thickness in the 5–50 nm range [11]. Vaha-Nissi et al [12] clearly demonstrated the deterioration of the barrier properties of ALD alumina after straining of 2 and 3%. Also, Baumert and Pierron [13–15] highlighted the occurrence of fatigue-induced crack channeling and delamination of ALD alumina coatings on Si thin films for strain amplitudes below the coatings’ critical onset strains. These strain values are inherently large for brittle materials (compared to thicker films or bulk brittle materials), but still provide considerable constraints for flexible and stretchable devices. Strategies involving depositing the brittle inorganic layers on more compliant ones have been developed to circumvent this issue, which are also the essence of stretchable electronics [1, 16, 17]. However, another issue with ALD alumina lies with its poor stability in aqueous environments. While Chang et al [18] showed that ALD alumina coatings improve the oxidation resistance of Cu in air, several other reports have shown that ALD alumina degrades when exposed to water, including possible dissolution [4, 19]. Garcia et al [4] argue that ALD alumina coatings, especially deposited at low temperatures, have significant hydrogen contents, making their composition reminiscent of oxy-hydroxides that are more prone to reaction with water. Metal oxide capping layers [20], including ALD titania [19], significantly improved the stability of ALD alumina in aqueous environments.

Given its excellent stability in aqueous environments and its excellent water permeation rates (as promising as ALD alumina) [7], ALD titania coatings were the focus of this present study. Particularly, the fatigue degradation properties of 22 nm-thick ALD titania deposited on Si thin films were characterized and compared to that of previously investigated 25 nm-thick ALD alumina [13–15]. Both the cohesive and delamination fatigue rates of ALD alumina were shown to be roughly one order of magnitude larger in a ‘harsh’ environment (80 °C, 90% relative humidity (RH)) compared to a ‘mild’ one (30 °C, 50% RH) [13–15]. The decreased fatigue performance in the more humid environment (partial pressure of water is about 20 times larger in the harsh environment) may be related to the aforementioned reaction of water with oxy-hydroxides present in the alumina. Hence the goal of this study was to establish whether ALD titania is more fatigue resistant than ALD alumina, particularly in humid environments, in an effort to further understand the role of environment on the governing fatigue mechanism.

2. Methods

2.1. Fatigue testing of ultrathin coatings

Baumert and Pierron [13–15] recently demonstrated the use of Si MEMS resonators to measure the cohesive and interfacial fatigue properties of ALD ultrathin coatings. The 10 µm-thick, monocrystalline Si micro-resonators consist of a notched beam and a mass with two comb drives for electrostatic actuation and capacitive sensing of the motion (see figure 1). The fatigue properties of the ALD coatings can be characterized by driving the coated micro-resonators at resonance under strain amplitudes, $\varepsilon$, that are large enough to cause fatigue damage in the ultrathin coatings (at the notch location, along the thickness of the Si film) without causing significant damage in the Si structure (in part thanks to the beneficial effect of the coating) [21]. Specifically, the evolution of the resonant frequency ($f_0 \sim 40$ kHz, measured with a precision of ~0.2 Hz) throughout a fatigue test is used to calculate cohesive and delamination fatigue rates based on accurate finite element models (FEM) and physically sound cracking scenarios [15]. The FEM quantifies the effect of cracking (both channel cracks and delamination cracks, with delamination width, $\lambda$, on the micro-resonators’ $f_0$. While in situ scanning electron microscope (SEM) fatigue tests have not been attempted in this study (in part because the
environment test plays a significant role in the fatigue process), a fatigue test that was interrupted multiple times for SEM inspection revealed the formation of a channelled crack across the micro-resonator’s thickness within a few million cycles followed by delamination of the coating from the Si substrate from the channelled crack’s edges occurring over much larger numbers of cycles [15]. The simplifying cracking scenario therefore assumes simultaneous crack channeling (in case of more than one crack), followed by delamination at the location of the fully extended channel cracks. The crack channeling rates are then calculated based on the initial portion of the $f_0$ evolution plot and the FEM results (giving the relationship between $f_0$ and the length of a channel crack), while the delamination rates are calculated based on the rest of the $f_0$ evolution plots. The delamination rates result from a linear fit of the calculated delamination widths, $\lambda$, as a function of cycles, for $\lambda$ between 0 and 70% of $\lambda_{\text{max}}$ ($\lambda_{\text{max}}$ is assumed to be 5h in these plots, with h the coating thickness) [15].

The fatigue rates can then be plotted as a function of $e_a$, or as a function of the nominal strain energy release rate amplitudes for either crack channeling ($G_{a,ch}$) or delamination ($G_{a,del}$), given by

$$G_{a,ch} = 2\epsilon_a^2 h E'$$

(1)

$$G_{a,del} = 0.5\epsilon_a^2 h E'$$

(2)

for this particular coating/substrate configuration (with similar elastic moduli) [23], with $h$ the coating thickness, and $E'$ the plane strain elastic modulus ($E' = E/(1 - \nu^2)$, with $E$ the elastic modulus and $\nu$ the Poisson’s ratio). Both $e_a$ and $G_a$ values remain constant during each test [15]. These equations ignore the residual tensile stresses in the coatings [24]. This assumption is reasonable given that $e_a$ (ranging from ~1 to 2%) is much larger than the tensile residual strains (approximately 0.2% for both alumina and titania coatings) [15, 24]. In addition to cyclic loading, static fatigue tests can also be performed with these devices, using external actuation [15].

2.2. Atomic-layered deposition of titania

The Si micro-resonators were coated with 22 nm of titania at 200 °C, using the plasma-enhanced ALD (PEALD) process. An initial nucleation layer of PEALD alumina was deposited on top of the devices using a Fiji Cambridge Nanotech ALD system. Trimethylaluminum (TMA) was used as the Al precursor with argon (Ar) as the carrier gas. Al precursor pulses of 0.06 s were followed by 10 s of purging Ar flow. Oxygen plasma was then generated by flowing 20 sccm of oxygen and applying an RF electric field of 300 W. This process was repeated for five cycles resulting in approximately 5 Å of alumina. The titania layer was then deposited on top of the alumina nucleation layer also by PEALD. Tetrakis(dimethylamido)titanium (TDMAT) was used as the Ti precursor also with Ar as the carrier gas. Ti precursor pulses of 0.2 s were followed by 10 s of purging Ar flow. Again oxygen plasma was then generated with 20 sccm of oxygen and an RF electric field of 300 W. This was repeated for 400 cycles resulting in approximately 22 nm of titania atop the alumina nucleation layer.

The targeted thickness of the titania coating was confirmed via SEM examination of a broken micro-resonator (not shown here). Figure 1(c) shows a high magnification SEM image of the titania coating along the sidewall of the Si micro-resonators, at the notch location (the horizontal striations are due to the deep reactive ion etching process of the Si layer). The granular surface aspect strongly suggests that these titania coatings are crystalline, with grains smaller than 50 nm, which is consistent with previous studies showing that ALD titania is crystalline for deposition temperatures above 200 °C [24]. This surface roughness was not observed for the ALD alumina coatings (also deposited at 200 °C) [13, 15, 21] that are known to be amorphous at this deposition temperature [8, 25] (crystallization of ALD alumina occurs at annealing temperatures of 750–800 °C) [24]. No cross-sectional transmission electron microscopy of thin slices of the coated micro-resonators were attempted to confirm these results, given the challenging specimen preparation procedure [26, 27]. However, based on the SEM images and the above literature data, it is likely that the titania coatings are crystalline and the alumina coatings amorphous.

No chemical composition characterization or impurity analysis was performed on the titania and alumina coatings, in part because most characterization techniques require large flat areas for the measurements not available on the Si micro-resonators. Hydrogen concentrations above 5% are expected for the alumina coatings because of the low temperature deposition [8, 25].

3. Results and discussion

3.1. Resonant frequency evolution curves

Figure 2(a) shows four representative $f_0$ evolution curves from the 22 fatigue tests that were performed on the titania-coated micro-resonators (12 fatigue tests at 30 °C, 50% RH, and 10 fatigue tests at 80 °C, 90% RH). Similarly to the alumina-coated devices, the overall trend is a decrease in $f_0$, resulting from the coating’s fatigue damage [13, 15], followed by a plateau (except for a few devices that fail before a plateau is reached). However, a significant difference between the two coatings is the much larger numbers of cycles for the titania-coated devices necessary to reach a plateau at 80 °C, 90% RH. While the plateau in $f_0$ was typically reached in less than 1–2 × 10⁶ cycles for the alumina-coated devices [15], it can take more than 10⁹ cycles for the titania-coated devices. As shown in figure 2(b), the total decrease in $f_0$, $\Delta f_0$, as a function of $e_a$ is similar for both coatings at 80 °C, 90% RH (the trend lines represent linear fits). Hence the decrease in $f_0$ is significantly slower for the titania-coated devices (as it takes many more cycles to reach the same total decrease in $f_0$), suggesting lower fatigue rates for titania compared to alumina in the harsh environment. In addition, the $f_0$ evolution in the plateau region is different for the two coatings. Most of the alumina-coated devices exhibit a small (albeit measurable)
increase in $f_0$ in the plateau region (six out of seven at 30 °C, 50% RH, three out of four at 80 °C, 90% RH) [21]. In contrast, most of the titania-coated devices (except for four specimens) do not exhibit any increase in $f_0$ in the plateau region. A possible interpretation of the increase in $f_0$ in the plateau region for the ALD alumina-coated devices could be related to the slow corrosion of these coatings exposed to adsorbed water layers, not occurring for ALD titania.

Another notable difference between the two coatings is the lower $\Delta f_0$ values for similar $\varepsilon_a$ at 30 °C, 50% RH for the titania-coated devices. Based on the linear fits for that environment, the threshold $\varepsilon_a$ value below which no fatigue damage occurs (i.e. no decrease in $f_0$) for the titania coatings is 1.15%, whereas it is 0.95% for the alumina coatings. The ~10% difference in thickness between the two coatings is unlikely to account for this result, given that the threshold value for alumina only increases from 0.95 to 1.2% when the thickness is decreased by 50%, from 25 to 12.6 nm [13].

A series of static fatigue tests were also performed to assess whether the observed decrease in $f_0$ was related to cyclic loading. Specifically, six static tests were performed for static applied strains, $\varepsilon_s$, ranging from 0.9 to 1.8%, and test durations ranging from 35 min to 3 h. The $f_0$ was measured before and after the static tests. None of the static tests resulted in any measurable decrease in $f_0$, while total decreases as large as ~110 Hz (for similar test durations) could be measured under cyclic loading for $\varepsilon_a \sim 1.8\%$ (see figure 2(b)). Two additional static tests ($\varepsilon_a = 1.6\%$ and 1.2% for 40 min each) were also performed after a short amount of cyclic loading. The decrease in $f_0$ after the cyclic loading was 36 and 11 Hz for each specimen. The static tests resulted in no further decrease in $f_0$, clearly suggesting that cyclic loading is responsible for the observed fatigue behavior.

3.2. Fatigue crack predictions and observations

The observed decrease in $f_0$ was confirmed to be related to fatigue damage in the coating, in the form of both fatigue crack channeling and delamination. Figures 3(a) and (b) show the predicted numbers of cracks as a function of $\varepsilon_a$ at 30 °C, 50% RH, and 80 °C, 90% RH, respectively, for different delamination lengths on each side of the channel cracks, $\lambda$. These predicted numbers are based on the linear fits from figure 2(b) and the FEM results [15] (using $E = 150$ GPa for titania) [28]. These predictions were compared to SEM observations of devices that did not fail during the fatigue tests, from which the number of cracks could be estimated. A crack that does not appear to have propagated through the entire micro-resonator thickness (10 $\mu$m) only counts as the thickness fraction where the crack is present, as its effect on $\Delta f_0$ is proportional to this fraction ($\Delta f_0 \ll f_0$) [15].

Figure 4 shows representative images of five fatigued titania coatings at the notch location, at 30 °C, 50% RH (figures 4(a)-(f)) and 80 °C, 90% RH (figures 4(g)-(j)). Clear signs of fatigue damage in the coatings can be seen compared to images of the untested coatings (figures 1(b) and (c)). Specifically, the fatigued coatings exhibit channel cracks through the thickness of the Si device with evidence of delamination between the coating and the Si sidewall on the sides of the channel cracks (see e.g. figures 4(b) and (d)). The rough features along the channel cracks are likely the result of compression-induced delamination of the coating [15]. The estimated numbers of cracks based on SEM observations match the predicted ones (from FEM) for delamination lengths on each side of the channel cracks, $\lambda$, that are about 5–10 times the coating’s thickness $h$ ($h_{\text{TiO}_2} = 22$ nm), i.e. for $\lambda$ ranging between ~100 and 200 nm (see figure 3). These $\lambda$ values appear to be consistent with SEM.
Figure 3. Predicted (lines) and measured (circles) number of cracks in ALD titania coatings, as a function of $\varepsilon_a$, at (a) 30°C, 50% RH and (b) 80°C, 90% RH.

Figure 4. Inclined SEM images of notch area after fatigue test at 30°C, 50% RH (ALD titania): (a), (b) $\varepsilon_a = 1.68\%$, (c), (d) $\varepsilon_a = 1.84\%$, and (e), (f) $\varepsilon_a = 2.07\%$. Inclined SEM images of notch area after fatigue test at 80°C, 90% RH (ALD titania): (g), (h) $\varepsilon_a = 1.05\%$ and (i), (j) $\varepsilon_a = 1.47\%$. Inclined SEM images of notch area after fatigue test at 80°C, 90% RH (ALD alumina): (k), (l) $\varepsilon_a = 2.19\%$. 
images of the damage surrounding the channel cracks, thereby validating the numerical model.

Overall, the numbers of fatigue cracks as a function of $\varepsilon_a$ are similar for alumina and titania coatings (except for the larger $\varepsilon_a$ threshold value at 30°C, 50% RH, as mentioned above). However, there is a significant difference between the two coatings, related to the effect of environment on the fatigue damage appearance. The fatigued alumina coatings had much rougher features (‘swelling’, see figures 4(k) and (l)) surrounding the channel cracks in the harsh environment compared to the mild environment [13]. This trend is not observed for titania coatings, as illustrated with figure 4(a) ($\varepsilon_a$ = 1.68% at 30°C, 50% RH) and (i) ($\varepsilon_a$ = 1.47% at 80°C, 90% RH). This result along with the abovementioned difference in $f_0$ evolution plots clearly suggest that the environmental effects on the fatigue properties of ALD titania are not as pronounced as with ALD alumina, as shown next.

3.3. Fatigue crack growth rates

Figures 5(a) and (b) show the calculated fatigue crack channeling growth rates for both ALD titania ($h_{\text{TiO}_2} = 22$ nm) and ALD alumina ($h_{\text{Al}_2\text{O}_3} = 25$ nm) as a function of $\varepsilon_a$ and $G_{a,\text{ch}}$ (see equation (1)), respectively, while figures 6(a) and (b) show the calculated fatigue delamination rates, also as a function of $\varepsilon_a$ and $G_{a,\text{del}}$ (see equation (2)). The lines correspond to the power fits for each condition. Because there are only four data points for alumina in the harsh environment (with a narrow range in $\varepsilon_a$ and $G_a$), the power fits between the fatigue rates and $G_a$ obtained from a larger set of fatigue experiments of the alumina-coated devices (including three other thicknesses [14, 15]) were also plotted in figures 5(b) and 6(b). These fits were obtained from a larger range of $G_a$ values (from $\sim$0.3 to $\sim$8 N m$^{-1}$ in figure 5(b) and from $\sim$0.07 to $\sim$2 N m$^{-1}$ in figure 6(b)). The calculated rates, especially the delamination rates (ranging from $10^{-7}$ to $10^{-3}$ Å per cycle), are much smaller than the interatomic distances, suggesting that the delamination front does not advance uniformly along the length of the channeled crack [15]. Hence these rates are average delamination rates along the channeled cracks. The large scatter in the data is also likely the result of the simplifying assumptions that are made to calculate these average rates based on the measured $f_0$ evolution plots. Despite this scatter, figures 5 and 6 show that, while the fatigue rates are similar for both materials in the mild environment (with slightly smaller delamination rates for titania), they are about one to two orders of magnitude larger for alumina compared to titania in the harsh environment.

The critical energy release rates cannot be easily determined with this technique [15]. The critical energy release rate for ALD alumina was calculated to be $G_{c,\text{Al}_2\text{O}_3} = 29.3 \pm 6.1$ N m$^{-1}$ [29], which is about six times more than the maximum $G_{a,\text{ch}}$ value in this study. No corresponding values for ALD titania could be found in the literature. Likewise, the interface fracture energies, $\Gamma$ (i.e. critical strain energy release rate for Si/ALD coating material systems) are not known, and could range anywhere from 1 N m$^{-1}$ (the maximum $G_{a,\text{ch}}$ in this study) to more than 10 N m$^{-1}$ in the case of a tough interface [30]. The small calculated fatigue rates could therefore also be a result of the relatively small applied driving forces. It should be noted that these driving forces would be much larger for the same applied strain amplitudes, $\varepsilon_a$, if the substrate was much more compliant than the coatings (i.e. polymer substrate instead of Si) [30].

3.4. Discussion

The results shown in this study demonstrate that ALD titania ultrathin coatings are more fatigue resistant than ALD alumina in harsh/humid environments. As mentioned in the introduction, ALD titania is more stable in aqueous
environments than alumina. Therefore, the mechanical fatigue properties of ALD ultrathin coatings may be intricately coupled to the coatings’ chemical stability in the environment. The observed ‘swelling’ for the fatigued alumina coatings at 80 °C, 90% RH [13, 15] that was not observed for ALD titania is consistent with this conclusion and could be related to the corrosion of alumina. An important consideration is to determine whether the structure (i.e. crystalline versus amorphous) or the chemical composition of the coatings (including impurities, such as H) is the governing factor in the improved fatigue resistance observed in the crystalline titania coatings compared to the amorphous alumina coatings. For example, crystalline alumina is very stable in presence of water. As mentioned in the introduction, low temperature, amorphous ALD alumina is not stable in water, which may be because of the large H contents in the coatings [4]. Additional characterization and testing would be necessary to unambiguously address this issue, such as characterizing the amount of H in the titania coatings, or performing fatigue experiments on ALD titania coated devices for both amorphous titania (deposition temperature <200 °C) and crystalline titania (deposition temperature ≥ 200 °C).

The effects of humidity on the subcritical cracking or delamination of ceramics that behave like glass are well known. In these cases, stress corrosion cracking occurs due to absorption of water molecules by the strained bonds at the crack tip (Si–O–Si in the case of SiO2), leading to time dependent crack extension above a threshold strain energy release rate (G0) that depends on the humidity level [31]. However, it is important to note that this time-dependent crack extension mechanism is unlikely to account for our fatigue results. As mentioned in section 3.1, six static fatigue tests (in laboratory air) performed at static strains, εs, ranging from 0.9 to 1.8% did not result in any fatigue damage of the titania coatings (see figure 2(b)), suggesting that cyclic loading is required to nucleate fatigue cracks. In addition, static fatigue tests performed after a short cyclic loading period on two devices (whose purpose was to nucleate a short channeling crack i.e. not fully extended throughout the device’s thickness, based on the measured decrease in f0) did not result in any additional fatigue damage (i.e. no further decrease in f0). These results clearly suggest that time-dependent crack extension (either channel crack or delamination crack) does not occur for these ultrathin coatings under these loading conditions. One possible explanation for the absence of stress corrosion cracking is the fact that the small applied driving forces in this study (see figures 5 and 6) may be below the threshold values G0.

Instead, we hypothesize that the observed interfacial fatigue behavior results from compression-induced degradation of the interface fracture energy, Γ, which is the sum of two terms:

$$\Gamma = G_0 + \Delta G$$  \hspace{1cm} (3)

with G0 the intrinsic interface fracture energy and ΔG an additional term resulting from frictional sliding of contact asperities behind the crack front. Specifically, we hypothesize that the ΔG term is reduced during cyclic loading as a result of reduced frictional sliding due to repeated contacts of the crack faces during the compression parts of the loading, leading to further crack extension. The observed environmental effects may instead result from the effects of humidity on reducing G0 [31], which would be more pronounced in the case of an unstable coating such as alumina. In other words, G0 may be similar for both coatings in the mild environment, whereas G0 for alumina may be smaller than G0 for titania in the harsh, humid environment. Accordingly, this mechanism may only be preponderant when the aforementioned stress corrosion cracking mechanism is
not activated and when rough interfaces (leading to frictional sliding) undergo compression during cyclic loading.

Further experiments would be required to test this hypothesis, such as performing similar fatigue experiments on Si micro-resonators with smooth sidewalls. In that case $\Gamma$ and $G_0$ would be equal. Measuring $\Gamma$ as a function of the environment would also be beneficial, although these measurements can be challenging for such thin coatings [32]. For applications such as flexible and stretchable electronics mentioned in the introduction, the fatigue degradation properties of ALD titania should be directly characterized on soft substrates to account for the importance of substrate’s compliance (and roughness) on the strain energy release rate calculations, their critical values (especially $\Gamma$), and the corresponding crack growth rates. Particularly, it would be useful to establish whether additional fatigue mechanisms, such as stress corrosion cracking, would occur for ALD coatings on polymer substrates under similar maximum applied strains (~2%), given that the strain energy release rates would be much larger than that of the Si micro-resonators.

4. Conclusions

In conclusion, this study highlights a promising candidate, ALD titania deposited at 200°C, as a reliable, more fatigue resistant, ultrathin protective coating compared to ALD alumina deposited at 200°C. The fatigue rates are comparable for both materials in a mild environment while they are one order of magnitude larger for ALD alumina compared to ALD titania in a humid environment. Static fatigue crack nucleation and propagation was not observed. The results suggest that protective coatings that are more stable in humid environments, such as crystalline ALD titania, are more fatigue resistant, an important result for the development of robust ultrathin passivation layers.

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