A Comparative Study of the Mechanical and Tribological Properties of Thin Al₂O₃ Coatings Fabricated by Atomic Layer Deposition and Radio Frequency Sputtering

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1. Introduction

Alumina coatings are widely used for a vast range of technological applications like diffusion barriers and for protection against corrosion, wear, and heat.¹⁻³ As an example, thin alumina layers are used as passivating layers in metal–oxide–semiconductor (MOS) devices, solar cells, storage devices, smartphones, and so on, while hard thick alumina coatings are widely used in cutting tools to increase their high-temperature oxidation resistance.⁴⁻⁶ Alumina is also widely used as high refractive index layer in multilayer interferential filters for several optical applications because of its high UV transparency.⁷ Al₂O₃ coatings deposited by atomic layer deposition (ALD) have attracted considerable attention in the past years due to the ability to coat complex geometries with very high aspect ratios for application in several technological fields. ALD coatings are also a viable approach to mitigate fretting wear in nuclear reactor components.⁸

For all the applications, the mechanical properties of the alumina layers have to preserve the underlying substrate or the device’s stability.

The mechanical performances of alumina are strongly dependent on its structure and alumina is known to exist in the amorphous form and in a number of polymorphic metastable phases (transition phases) prior to the thermodynamically stable α phase. The temperature-dependent sequence is amorphous → γ → δ → θ → α. While the amorphous form has a lower hardness and a lower chemical and thermal resistance, the rhombohedral α-phase Al₂O₃ (corundum) presents undoubtedly superior chemical and mechanical stability, higher oxidation resistance at higher temperatures, higher hardness, and wear resistance.⁹ However, the synthesis of α-phase alumina is not straightforward and requires very high substrate temperatures, e.g., commercial

Thin Al₂O₃ films (150 nm thick) are deposited by atomic layer deposition (ALD) and radio frequency sputtering on Si substrates and submitted to annealing in N₂ atmosphere at 900 °C for 90 min. X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM–EDS), nanohardness, and fretting wear measurements are used to infer the structural, morphological, mechanical, and wear properties of the as-deposited and annealed films. Results show a higher hardness for the annealed coatings, being the hardness of the annealed ALD coating the highest (18.8 GPa). The measured mechanical properties convey clear trends of stiffening and hardening associated with selected process (ALD versus sputtering) and post-processing (annealed versus unannealed).

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α-alumina is generally grown by chemical vapor deposition (CVD) at a temperature of about 1000 °C. Physical vapor deposition (PVD) techniques allow for lower growth temperatures, but often additional expedients are used for the same purpose, such as the introduction of Cr₂O₃ seed layers, plasma assistance, pulsed techniques or high substrate bias even though some authors report the formation of the alpha phase even at 480 °C.

Despite its inferior mechanical properties, the γ-phase attracts the attention of researchers because of its stronger catalytic properties which make it suitable as a catalyst carrier due to the higher specific surface area (100–400 m² g⁻¹), tendency to disperse the active phase, and acid–base properties. Even if not as high as the α-phase, the γ-phase alumina can present good hardness and chemical resistance, which are useful for applications as a mechanical barrier while the amorphous metastable PVD alumina layers with lower hardness can be used as dielectric layer, barrier layer, and optical layer. Crystalline PVD γ-alumina coatings have also been investigated for applications as a mechanical barrier, while the amorphous metastable PVD alumina layers with lower hardness can be used as dielectric layer, barrier layer, and optical layer. Crystalline PVD γ-alumina coatings have also been investigated for applications as a mechanical barrier, while the amorphous metastable PVD alumina layers with lower hardness can be used as dielectric layer, barrier layer, and optical layer.

Other high-temperature forms of alumina derived from γ-Al₂O₃ also play an important role both as catalyst and as catalytic support. Moreover, the other transition aluminas possess lower surface area, less structural disorder, and higher thermal stability, and low tendency to adhesion due to their low surface free energy.

Postannealing is therefore often required to increase the mechanical performances of alumina coatings.

The aim of this work is to report on a comparative study of the mechanical and wear characteristics of 150 nm-thick coatings obtained by two different thin film deposition techniques: RF sputtering and ALD. The study was performed on as-grown (unannealed) coatings and on coatings annealed at 900 °C. The coatings were characterized by X-ray diffraction (XRD) measurements to evaluate the microstructural differences got by the two different techniques and the variations induced by the thermal annealing process. Also, the influence of deposition techniques and postannealing on the hardness and fretting wear of the resulting films was assessed. Clear trends concerning alumina hardening and stiffness associated with selected process (ALD versus sputtering) and postprocessing (annealed versus unannealed) are given. The main technological goal was to achieve good hardness at a thickness of interest of about 150 nm. While such a thickness value is a relatively high value for ALD, coatings of such a thickness may be desirable to create a conformal barrier layer with high strength on complex geometries. This is the case of barrier layers in Generation IV (Gen-IV) fission nuclear systems, for example, to withstand corrosion from liquid metal (e.g., lead) used as coolant. In this regard, our preliminary studies on ALD alumina coatings for protection of alloys in nuclear applications were focused on coatings with a thickness of few hundreds nanometers. Therefore, our purpose was to investigate the technological viability of fabricating coatings with a thickness not less than 150 nm primarily for usage as mechanical barriers.

2. Results and Discussion

Figure 1 shows the XRD diffraction patterns of the annealed sputtered (labeled as “Sample 4”) and annealed ALD ("Sample

![Figure 1](https://www.advancedsciencenews.com/pss-a)
coatings deposited on Si substrates. The XRD measurements of the as-grown coatings ("Sample 1" and "Sample 3") showed an amorphous structure for both coatings (not shown here), that is in accordance with the amorphous structure usually found on as-deposited sputtered and ALD samples,\textsuperscript{36} despite the ALD alumina growth process is generally carried out on preheated substrates. For conventional sputtered coatings, to get the crystalline $\gamma$-phase, the substrate temperature should be generally greater than 500°C in case of magnetron sputtering process,\textsuperscript{37–41} even if some reports show crystalline gamma phase at temperature as low as 290°C in case of pulsed magnetron sputtering (PMS).\textsuperscript{42}

The XRD diffraction pattern of annealed ALD sample shows a mixed of transition $\theta$ and $\delta$ aluminas, corresponding to the indicated JCPDS cards. The annealed sputtered sample shows a lower crystallinity, with a $\gamma$ phase (JCPDS card 29-003).

Figure 2a,b show the SEM micrographs of the annealed coatings (Sample 2 and Sample 4) deposited by ALD and sputtering, respectively. A very smooth, pin-hole free surface was observed for the ALD sample, as opposed to the sputtered coating, considerably rougher at glance and presenting some pits. Annealed sputtered sample (Sample 4) showed a quite homogeneous and compact morphology with an average grain size of less than 20 nm.

These results are also confirmed by AFM analysis, as shown in Figure 3a,b, which report the AFM images of the annealed ALD and sputtered coatings, respectively. The root mean square (RMS) roughness ($R_q$) estimated on a $5 \times 5 \mu m^2$ is about 1 and 6 nm for ALD and sputtered coatings, respectively.

Representative nanoindentation loading/unloading curves are shown in Figure 4, and the resulting average hardness and Young's Modulus are shown in Table 1. It should be noted that the resulting maximum penetration depth was in the range of 10–16 nm for all the coatings, except for the as-grown sputtered sample. For this sample, the maximum depth was around 20 nm, i.e., about 13% of the sample thickness, that is only slightly higher than the 10% (Bückle's rule) recommended to avoid substrate contribution on the measured values.\textsuperscript{43} Nanoindentation measurements were conducted to provide a technological comparison between ALD versus sputtering grown samples, and annealed versus nonannealed ones. In this respect, while the $H$ and $E$ value may not be accurate in absolute terms, the analysis is legitimate for comparative purposes. Bückle's criterion was respected as a first approximation by choosing a load range ensuring a penetration depth around 10% (between 10–20 nm for all cases), considerably greater than the samples RMS in case of ALD samples and great enough for sputtered coatings. Again for a comparative study this was deemed acceptable and the tabulated values need to be considered lower-bound estimates.

To refine the investigation, both a FEM study and a depth sensing dynamic study would aid in the identification of the
The average hardness of both as-grown samples deposited by the two techniques is in agreement with the values reported in the literature for amorphous coatings, i.e., in the range from 5 to 12 GPa. Higher hardness values, in the range 8–20 GPa, are then usually found on transition alumina coatings. Accordingly, both high temperature annealed coatings showed a higher hardness with respect to the corresponding unannealed films, as expected due to the transition from a totally amorphous alumina film to a crystalline structure containing the harder transition phases.

At the same time, a variation in the plastic deformation behavior was observed in samples deposited by the two techniques and subjected to subsequent thermal treatment. From a qualitative point of view, the graphs reported in Figure 4 clearly evidence a broader widening in the load–displacement curves of the sputtered and unannealed samples with respect to the ALD-grown and annealed ones, thus indicating a more intense plastic deformation and lower stiffness. This is quantitatively reflected in the corresponding values of the elastic modulus, being higher in the ALD samples and increasing after the annealing treatment, thus being related to an increased coating stiffness.

The different mechanical properties demonstrated in the sputtered coatings (lower hardness and Young’s modulus) with respect to the ALD-grown samples are a consequence of their poorer crystallization and lower density (less compactness), as evidenced by XRD and SEM analyses, respectively. Indeed, a higher fraction of crystalline phase and improved film compactness are known to give rise to higher hardness, that is in line with the behavior observed in our samples. The low hardness and Young’s modulus found in our sputter-deposited samples suggest a growth regime that is similar to the one indicated as “zone 4” in Bobzin et al., inducing the formation of poor crystalline films with a low content of γ-phase within a predominant amorphous structure. In that previous work, the alumina deposition was conducted starting from a pure aluminum target, and the aforementioned “zone 4” was found when the target was sputtered under a poisoned mode, i.e., when the metal target surface was almost completely oxidized. Under such circumstances, the mobility of the depositing species on the substrate is reduced, due to the main production of AlO molecules (heavier than Al species) and to the decrease in exothermic reactions between aluminum and oxygen, thus producing a less crystalline material. In our process, the deposition was conducted from an oxide target, and the substrate effect from the softer substrate really causes a critical departure from the usual Buckle’s approximation is a reasonable modeling assumption here. The substrate effect from the softer substrate really causes a critical departure from the usual Buckle’s rule only for superhard coatings (H > 80). As reported in Veprek-Heijman and Veprek, the substrate effect could then become relevant at less than 10% deformation (even at 3% deformation for that matter) but that range of penetration depth is prevented for our systems because of overlapping with the roughness of the surface, as mentioned earlier, defeating the purpose of a simpler analysis. In this respect, the development of accurate higher order models for the systems under investigations would be a complex endeavor.

The surface profile of the fretting wear mark of the tested sputtered specimens under 15 N load is shown in Figure 5. In the samples, wear occurred by a localized removal of coating, minimal debris accumulation, and the subsequent displacement toward the edge of the mark forming an arrangement of successive zones called a “shark whale” pattern.

The flatter central zone has a width of 0.18–0.20 mm equal to the double of the elongation of fretting swing. It is noted that the onset of the substrate effect, but this is beyond the current scope of this article. When considering the (comparative) goal of the study and that the Si substrate is not considered exceedingly soft (H about 12.5 GPa), with a ratio E/Es close to 1 or even higher (being Es the Young modulus of the film and E = 180 GPa the measured Young modulus of the substrate), the Buckle’s approximation is a reasonable modeling assumption here. The substrate effect from the softer substrate really causes a critical departure from the usual Buckle’s rule only for superhard coatings (H > 80). As reported in Veprek-Heijman and Veprek, the substrate effect could then become relevant at less than 10% deformation (even at 3% deformation for that matter) but that range of penetration depth is prevented for our systems because of overlapping with the roughness of the surface, as mentioned earlier, defeating the purpose of a simpler analysis. In this respect, the development of accurate higher order models for the systems under investigations would be a complex endeavor.

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dimensions of the mark are smaller though deeper for nonannealed alumina coatings.

Fretting wear can be quantified by means of the fretting wear coefficient (K) defined as lost volume per unit applied normal load per unit sliding distance in (mm³Nm⁻¹).

Volume loss is calculated from the cross-sectional area of displaced material, obtained from the profilometric measurement along the normal direction to the sliding motion, multiplied by the fretting scar length. It is noted that this methodology can be a source of error due to an incorrect estimation of the volume. The evaluation of the eroded area is based on the assumption that the baseline has been correctly made on the surface profile of the sample and that the scar has a regular shape.⁴⁹

Looking at Table 1, it can be seen that the fretting coefficient is lower for sputtered films than for ALD ones and that this value increases after annealing. The values obtained are the lower boundary line of the optimal range indicated for wear resistances values in Kato and Adachi.⁵⁰

Sometimes, however, the mere numerical value does not give a full understanding of the phenomenon. To discuss the results of fretting wear, it is essential to identify the sliding regime developed during the test.⁵¹ In fact, the morphology and the shape of the trace resulting from the fretting damage give indications about the regime itself. The sliding amplitude already corresponds to a different deterioration mechanics. The traces on the not annealed sputtered sample can be explained basing on the partial slip mechanism.

It has a very deep trace but considerably narrow about 0.25 mm. In the partial slip motion regime wear occurs only where there is sliding, that is, in the annular area surrounding the stick area. In this area there is the maximum contact pressure and the continuous rubbing can cause the nucleation of cracks. In the central area, on the contrary, there is the minimum Herzian pressure; therefore, there are no relevant phenomena other than a deformation by compression. In the transition zone between the sliding area and the sticking area as the test time increases, the cracks propagate until the coating failure due to fatigue. This is also the case of the 15 N test on as ALD deposited coatings where the surface profile shows a depression greater than the nominal thickness of the coating. Obviously the very narrow trace of the as-deposited sputtered film then leads to a relatively low fretting coefficient, though the test is destructive for the coating itself.

Figure 6a shows an optical photograph representative of the partial slipping phenomenon, in particular, it is the mark of sputtered coating. The annealed coatings show tracks greater but less deep. The typical image is represented in Figure 6b. In this case, a different regime, the gross slip regime (GSR) occurs, where the sliding amplitudes are sufficiently large to allow relative sliding of all contact points. In the gross slip regime the surface deterioration has an elliptical geometry with a large increase in surface roughness. Only annealing can be attributed to this variation of the fretting regime. The heat treatment causes a densification of the material, an increase in hardness, an increase in surface flatness and consequently a different fretting regime. Further studies and insights will be necessary to have a complete and clearer picture.

3. Conclusions

Alumina coatings (150 nm thick) were grown by ALD and RF sputtering on Si substrates. The mechanical and tribological properties of as deposited coatings and coatings annealed @ 900 °C were compared.

![Figure 5](image1.png)

**Figure 5.** The surface profile of the wear marks at 15 N for the as-deposited and annealed coatings. The d values represent the width of the wear track.

![Figure 6a and 6b](image2.png)

**Figure 6.** The optical images of the fretting wear marks central zone: a) sputtered coating; b) annealed sputtered coating.
The different crystalline and morphological properties observed in the various samples were reflected in the different mechanical properties of the films. The presence of mixed θ and δ-phases in case of annealed ALD samples and of the γ phase in case of annealed sputtered samples and the formation of a compact structure indeed resulted in coatings with higher hardness and Young’s modulus. The highest hardness of 18.8 GPa was observed in the case of ALD annealed coatings, which is quite a high value for such a thin layer if compared to many data reported in the literature. Interpretation of fretting results is less straightforward and needs further studies. Results show the great potentiality of thin ALD alumina layers for application as hard and antiwear coatings.

4. Experimental Section

Sample Preparation: A commercial plasma-assisted ALD (PEALD) apparatus with an integrated remote plasma source (Picosun Advanced R200, Finland) was utilized for the growth of Al2O3 films on the silicon substrate. The growth was performed by alternately exposing the trimethyl aluminum ((CH3)3Al, TMA precursors) and O2/Ar gas mixture plasma reactant. TMA was injected into the chamber through the carrier gas N2. The temperature of the TMA source was maintained at room temperature. Each cycle of the ALD process was as follows: TMA feeding (0.1 s), N2 purging (6 s), H2O feeding (0.1 s), and N2 purging (6 s). A number of 1250 cycles at a process temperature of 300 °C was repeated to get a final thickness of 150 nm for the Al2O3 coatings.

RF sputtered alumina coatings were deposited with a MRC 8620 plant starting from a 6 in., 99.999% purity Al2O3 target. Base pressure in the chamber was about 7 × 10⁻⁵ Pa. Alumina films were grown on Si substrates at a RF power of 300 W, Ar working pressure of 0.53 Pa, and room temperature (substrates were not intentionally heated during the sputtering process).

All the samples were annealed in a tubular furnace under N2 gas flow at 900 °C for 90 min, with a temperature ramp increase of 10 °C min⁻¹.

Sample Characterization: The thickness of sputtered alumina films (150 nm) was obtained by sputtering time, after having estimated the growth rate by fitting spectrophotometric transmittance and reflectance data obtained by a Perkin Elmer 950 UV-Vis–NIR spectrophotometer on reference thicker alumina films grown on fused silica substrates. The thickness of the annealed sputtered coatings was also confirmed by cross-sectional field emission scanning electron microscopy (FE-SEM) micrographs’ analysis. The thickness of ALD coatings was controlled by the number of cycles in which the reaction occurs and further inferred by ellipsometric measurements (HORIBA UVISEL 2).

XRD measurements were conducted by a RIGAKU Smartlab X-Ray diffraction system, while the morphology of the coatings was analyzed by a ZEISS 1530 FE-SEM and by Park XE-100 atomic force microscopy (AFM).

Nanoindentation measurements were conducted by an Anton Paar nanoindentor mod. TXXT-NHT2 equipped with a Berkovich diamond tip, at a maximum load of 0.1 mN and linear loading/unloading rates of 0.2 mN min⁻¹. Ten indentations at steps of 10 μm were performed on each sample, and the corresponding values of average hardness (H) and Young’s modulus (E) were reported with their standard deviation. Fretting measurements were conducted with a TriboCryo 1 system, in reciprocating mode at a sliding amplitude of 0.09 mm, time 10 min, distance 0.5 m (corresponding to 3555 cycles), and load of 15 N. The tests were conducted in air and ambient room conditions of temperature (23 °C) and humidity (50%). Stationary 100Cr6 steel counterface cylindrical pin had a diameter of 6 mm and a radius of curvature for hemispherical shape 25 cm. For a point contact between steel (Young’s modulus E = 213 GPa and Poisson’s ratio ν = 0.29) and Al2O3 (E = 390 GPa and ν = 0.22), the maximum Hertzian contact pressure calculated was 742.3 and 936.2 MPa for the two different loads and the maximum contact area diameter was 0.196 and 0.248 mm, respectively. In the same way, it was possible to calculate the depth of the maximum shear as 0.045 mm.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

atomic layer deposition, mechanical properties, radio frequency sputtering, thin Al2O3 coatings, tribological properties

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