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Protective Alumina Coatings by Low Temperature Metalorganic Chemical Vapour Deposition

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Abstract. Alumina thin films were processed from aluminium tri-iso-propoxide in a horizontal, with N_2 as a carrier gas, occasional addition of water in the gas phase, deposition temperature in the range 350-700°C, total pressure 0.67 kPa (2 kPa when water was used). The films do not diffract X-ray when prepared below 700°C. At 700°C, they start to crystallize as γ-alumina. EDS, EPMA, ERDA, RBS, FTIR and TGA revealed that films prepared in the range 350-415°C, without water in the gas phase, have an overall composition $Al_2O_{3-x}(OH)_{2x}$, with x tending to 0 with increasing temperature. Al_2O_3 is obtained above 415°C. When water is added in the vapour phase, the film composition is Al_2O_3, even below 415°C. Coatings deposited in these conditions show promising protection properties.

Introduction

Alumina in the form of thin coatings is a material of major technological interest for a wide panel of applications going from microelectronics to catalysis and metal surface protection. The present study was initiated to test the MOCVD technique to deposit high surface area alumina films on a non-flat, stainless steel substrate for catalytic applications. Working at moderate temperature (< 700°C) not to damage the steel structure, we could not yet prepare films porous enough to be efficient catalyst supports. First results [1] lead us to enlarge our purpose and to systematically study the MOCVD of alumina at moderate and low temperatures. Generally speaking, films composition, allotropic form, micro-structure and crystallinity can be adjusted by playing with the MOCVD experimental parameters. This particularly applies to alumina which besides several structural modifications of the pure oxide may also present compositional modifications of general formula $AlO_x(OH)_{3-2x}$.

Following Aboaf's pioneering works [2], aluminium tri-isopropoxide (ATI) has been the most used precursor as it is easy to use and despite problems due to ageing. Once melt, it remains liquid far below the melting temperature, so that it can be used as a liquid precursor. However, it has the inconvenience to transform into less volatile species on ageing and on being heated. Films of Al_2O_3 were claimed to be deposited at 693K [2], 673K-773K [3-5], 673K [6], 623K-773K [7], 623K-673K [8], below 603K [9], 573K [10], 523K-693K [11,12], 523K-673K [13]. Low-temperature deposition (598K-773K) from ATI was also used for preparing graded-index aluminium oxide thin films [14,15]. Corrosion resistance studies were performed on films grown at 623 K [16] or 693 K [17].

In the present study we have studied the dependence of both the nanostructure and the composition of films processed by ATI-MOCVD upon experimental parameters, mainly deposition temperature and occasional use of water vapour as a reactive atmosphere.

Experimental Part

Deposition of thin films was performed in a custom-made, hot-wall reactor [1]. ATI (Across Organics) was melted above 140°C, kept supercooled at 80°C, and heated at 110°C during deposition experiments. The precursor was renewed in the bubbler every 12 hours of use. Fixed experimental parameters are: total pressure 0.67 kPa; N_2 flow rate over ATI = 53 sccm; dilution N_2 flow rate = 590 sccm. When necessary, water vapour was introduced in the reactor by bubbling N_2 (35 sccm) in a water container maintained at 1°C. In this case, the overall pressure was set at 2 kPa. Deposition temperatures were in the range 350-700°C; deposition time between 10 minutes and 110 minutes. Films were deposited on degreased <100>Si wafers and on thermally grown silica on Si wafers.

The films were characterized by grazing-incidence X-ray diffraction (Seifert 3000 TT diffractometer, and by scanning electron microscopy (LEO 435 VP equipped with an EDS analyser). Elemental compositions were determined by EPMA (CAMECA SX-50). Both Al and O were directly determined and quantified by peak position determination. For ERDA and RBS analyses (Centre d'Etudes Nucléaires de Gradignan), the samples were irradiated with a 2.3 MeV He^+ beam under a tilt angle of 10°. TGA analyses (SETARAM TAG 24s, sensitivity = 0.5 µg). Samples consisted of two ~ 1.2 µm thick films grown on square SiO_2/Si platelets of ~ 1.5-2 cm^2. TGA conditions: dry air 0.2 l/min, heating rate: 5°C/min up to 150°C, 2°C/min up to 600°C.

Results and discussion

XRD. Deposited films were transparent. Films prepared below 700°C do not diffract X-rays. Wide diffraction peaks were observed for a film prepared at 700°C (Figure 1). The peak positions fit with the pattern reported for gamma-Al_2O_3 in the JCPDS file #10-425. Well-crystallized γ-Al_2O_3 formed upon annealing for 1 hour at 800°C under flowing N_2 [1].

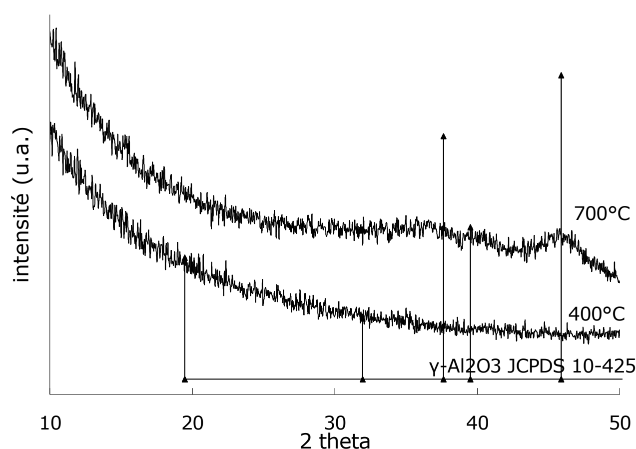


Figure 1. XRD patterns for the coating deposited at 700°C.

Elemental analyses. For films grown without water added in the vapour phase, the O/Al atomic ratio was measured by EPMA, EDS and RBS techniques in comparison with a standard of α-Al_2O_3. The results were expressed as the normalized ratio $R = [O/Al]_{sample}/[O/Al]_{alumina}$ (Figure 2). The samples prepared at 350°C have R values corresponding to AlO(OH). At 415°C and above, average R values correspond to Al_2O_3. Transition from O-rich to Al_2O_3-type films occurs between 380°C and 415°C. The mean H atomic concentration determined by ERDA is close to 25 at% for films deposited at 350°C (Figure 3). This is the expected value for AlOOH. At 415°C and above, it is less than 5 at%. EPMA revealed C traces for deposition at 350°C and 380°C and no C within the detection limit of the technique above 415°C. This rules out the possibility that the deposit consisted of partially hydrolyzed precursor $Al(OR)_{3-x}(OH)_x$, even at the lowest deposition temperatures investigated. From measured O/Al ratios and H concentrations, samples

prepared at 350°C have a composition compatible with the formula AlO(OH). Above 415°C, the composition is that of alumina Al_2O_3. The presence of OH groups below 415°C was further confirmed by transmittance FTIR spectroscopy.

From EDS and EPMA analyses, the films grown in the presence of water vapour have R ratios corresponding to Al_2O_3 within the experimental error range, whatever growth temperature in the range 350-550°C. FTIR spectroscopy confirmed the absence of OH groups.

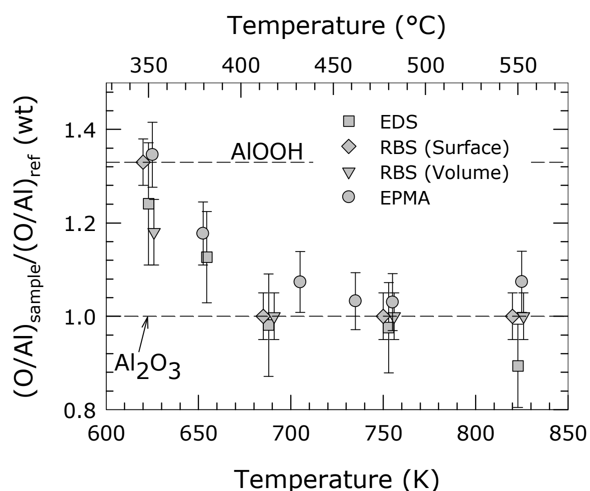


Figure 2. EDS, EPMA and RBS analyses of the O/Al ratio for films prepared without water in the gas phase.

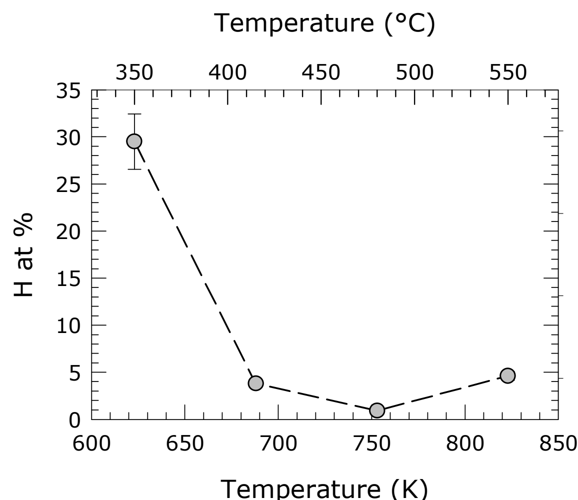


Figure 3. ERDA analyses of the H content for films prepared without water added in the gas phase.

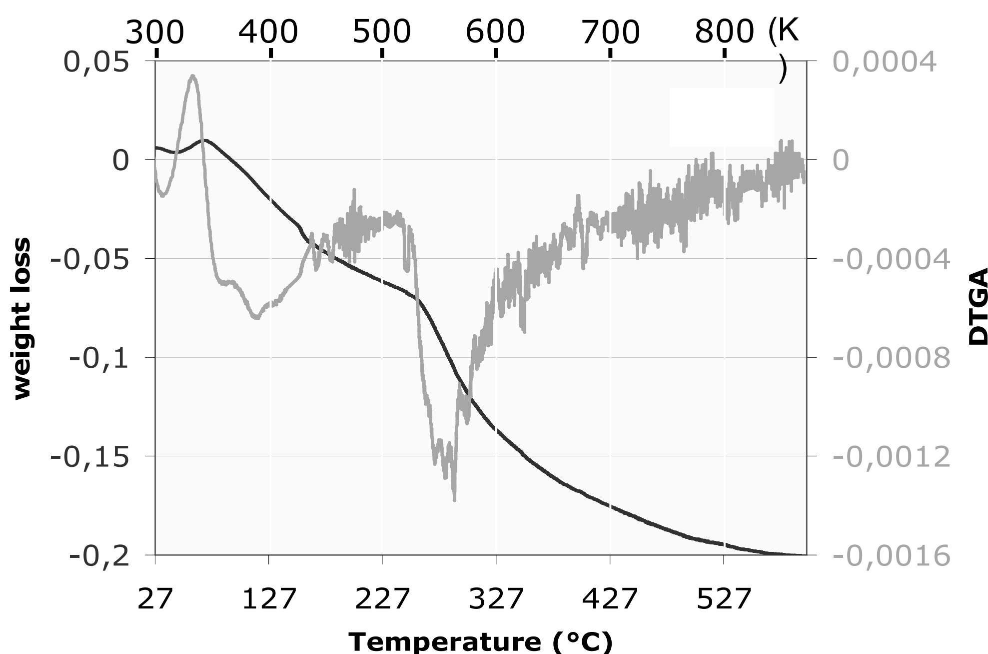
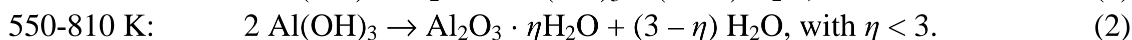


Figure 4. TGA (black) and DTG (grey) thermograms for the coating deposited at 350°C.

Thermal Gravimetric Analyses. Thermal gravimetric analyses were performed for films grown without water in the gas phase. Samples processed at 480°C and above do not lose weight on heating, thus confirming the composition Al_2O_3. The films processed at 350°C and 380°C lose weight. Weight loss takes place far below the preparation temperature.

The film prepared at 623 K (350°C) shows two weight losses (Figure 4): about 30 % of the total loss occurs between 343 K and 533 K, and the remaining 70 % above 533 K. The DTG curve shows two broad peaks at 388 K and 555 K. This behaviour can be interpreted from a study by Ram et al. [18]. These authors have shown that the thermal behaviour of amorphous boehmite does depend upon the number of hydration water molecules in the formula $AlO(OH) \cdot xH_2O$. Particularly, for $x > 1$, TGA reveals two nearly equal weight losses (18 % each), the one between 310 K and 550 K, the other between 550 K and 810 K. Corresponding DTA endotherm maxima are at 388 K and 715 K (heating rate of 20 K/min). The authors have attributed the high temperature endotherm to dehydroxylation of $Al(OH)_3$, which would have formed during the low temperature weight loss. Corresponding reactions are:

310-550 K: $AlO(OH) \cdot xH_2O \rightarrow Al(OH)_3 + (x - 1)\, H_2O$, (1)



550-810 K: $2\, Al(OH)_3 \rightarrow Al_2O_3 \cdot \eta H_2O + (3 - \eta)\, H_2O$, with $\eta < 3$. (2)

This process might well correspond to what occurs in our film deposited at 623 K. The two weight losses start at temperatures (343 K and 533 K) rather close to those reported for starting reactions (1) (310 K) and (2) (550 K). The formation of $Al(OH)_3$ upon heating at low temperature and its subsequent decomposition at higher temperature may explain why the film decomposes below its temperature of formation. The x H_2O molecules necessary to the formation of $Al(OH)_3$ according to reaction (1) may come from the film being kept several weeks without preventing against absorption of atmospheric water.

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