Chemical vapour deposition of Al₂O₃ on titanium oxides

E. Fredriksson, J.-O. Carlsson

► To cite this version:

E. Fredriksson, J.-O. Carlsson. Chemical vapour deposition of Al₂O₃ on titanium oxides. Journal de Physique IV Proceedings, 1993, 03 (C3), pp.C3-557-C3-562. 10.1051/jp4:1993377 . jpa-00251434

HAL Id: jpa-00251434

<https://hal.science/jpa-00251434>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chemical vapour deposition of Al_2O_3 on titanium oxides

E. FREDRIKSSON and J.-O. CARLSSON

*Thin Film and Surface Chemistry Group, Institute of Chemistry, Uppsala University, Box 521,
751 21 Uppsala, Sweden*

Abstract

The morphology of chemically vapour deposited $\alpha\text{-Al}_2\text{O}_3$, developed on different titanium oxides, was studied. Ti_2O_3 , Ti_3O_5 and TiO_2 were used as substrate materials. The titanium oxides and the $\alpha\text{-Al}_2\text{O}_3$ were grown by the $\text{TiCl}_4/\text{H}_2/\text{CO}_2$ and the $\text{AlCl}_3/\text{H}_2/\text{CO}_2$ processes, respectively, usually at 1000°C and 6.7×10^3 Pa. No considerable difference in morphology of $\alpha\text{-Al}_2\text{O}_3$ on the different titanium oxides were obtained. The $\alpha\text{-Al}_2\text{O}_3$ grains were larger on Ti_2O_3 than on Ti_3O_5 and TiO_2 .

1. Introduction

Layers of Al_2O_3 , grown by CVD from $\text{AlCl}_3/\text{H}_2/\text{CO}_2$ gas mixtures, have been subject to an extensive research during the last two decades [1-4]. The process involves a hydrolysis reaction of AlCl_3 with water:

The water is produced *in situ* by the "water gas shift reaction", which is the rate-determining step of the process [5]:

The net reaction is thus:

At temperatures above about 950°C this process produces hard, wear-resistant and chemically inert layers of Al_2O_3 , which are used as protective layers on cemented carbide cutting tools [e.g. 6,7].

Al_2O_3 crystallizes in several different modifications among which the rhombohedral $\alpha\text{-Al}_2\text{O}_3$ (ABAB.. stacking sequence of the oxygen atoms), known as corundum, is the thermodynamically stable phase [8]. $\kappa\text{-Al}_2\text{O}_3$, which is orthorhombic (with an ABAC.. stacking sequence), is the next most commonly occurring modification at these temperatures [9]. $\kappa\text{-Al}_2\text{O}_3$ is metastable and transforms irreversibly to the α -phase at sufficiently high temperatures. In the industrial production of Al_2O_3 on cemented carbide cutting tools an intermediate layer of TiC (or TiN) is mostly employed. An oxidized TiC surface promotes the formation of $\alpha\text{-Al}_2\text{O}_3$ while a TiC surface free from titanium oxides favours the formation of the κ -phase [10,11]. TEM investigations of TiC/ Al_2O_3 interfaces have shown that aluminium oxide samples with good adhesion are

pore-free and consist mainly of κ - Al_2O_3 while samples with poor adhesion to the TiC surface contain many pores and α - Al_2O_3 [10,12,13]. Although the TEM studies have not confirmed any titanium oxides in the TiC/ Al_2O_3 interface it has been suggested that the porous interface is a consequence of a reduction of Ti_2O_3 or Ti_3O_5 into TiO [10].

Previous studies of Al_2O_3 deposited on silica, have shown that κ - Al_2O_3 is grown initially but during the CVD process a $\kappa \rightarrow \alpha$ - Al_2O_3 phase transformation occurs [14,15]. In addition to an increased deposition temperature the phase transformation rate is enhanced by small impurities of e.g. Si, C and air leaks into the CVD system [14,15]. Silicon present in the gas phase may result in the formation of whiskers and other odd-shaped morphologies consisting of α - Al_2O_3 [15-17].

The present study was intended to examine possible differences in phase content and morphology of aluminium oxide layers deposited by the $\text{AlCl}_3/\text{H}_2/\text{CO}_2$ process on single-phase samples of different titanium oxides that can be formed on an oxidized TiC surface. The titanium oxides were deposited on silica from $\text{TiCl}_4/\text{H}_2/\text{CO}_2$ gas mixtures.

2. Titanium oxides

In contrast to aluminium oxide, which has only one well-established stoichiometry, namely Al_2O_3 , titanium oxides exist in numerous stoichiometries ranging from Ti to TiO_2 [18-21]. In the composition range $\text{TiO}_{1.5}$ - TiO_2 there exist a series of oxides with the generic formula $\text{Ti}_n\text{O}_{2n-1}$. This series includes Ti_2O_3 which is rhombohedral and isomorphous with α - Al_2O_3 , Ti_3O_5 , which exists in several monoclinic polymorphs (e.g. α -, β - and γ -) and the triclinic Magnéli phases which are crystallographic shear structures with n ranging from 4 to about 60. TiO_2 occurs in three polymorphs at atmospheric pressure. Rutile is tetragonal and the only thermodynamically stable modification, while both anatase and brookite are orthorhombic.

All these titanium oxides can be described as being built up by TiO_6 octahedra or rutile slabs, and are thus more or less structurally related to each other. The interatomic distances in and between the TiO_6 octahedra of the different phases differ, however. Since α - Al_2O_3 is isostructural with Ti_2O_3 there may exist epitaxial conditions between these two phases and to a lesser extent also between α - Al_2O_3 and the more oxygen-rich titanium oxides. κ - Al_2O_3 on the other hand display an ABAC.. stacking sequence of the oxygen atoms and hence a lesser pronounced epitaxial relationship with the titanium oxides can be expected.

3. Experimental

3.1 Experimental procedure

The deposition experiments were performed in a horizontal hot-wall CVD system [15]. Silica was normally used as substrate material. The contamination level in the CVD system was minimized as specified previously [14,15]. For a more detailed description of the experimental procedure see [14,15,22]. The titanium oxides were deposited from $\text{TiCl}_4/\text{H}_2/\text{CO}_2$ gas mixtures as listed in table 1.

Table 1.
Process conditions used for depositing the titanium oxides

Phase	TiCl ₄ (%)	H ₂ (%)	CO ₂ (%)	Temp. (C)	Pressure (Pa)	Linear gas flow velocity, cm/s
Ti ₂ O ₃	7.5	86.5	6.0	1000	6.7x10 ³	33
Ti ₃ O ₅	6.8	81.0	12.2	1000	6.7x10 ³	26
TiO ₂	0.01	0.33	99.66	1050	2.0x10 ⁴	51

The Al₂O₃ layers were grown during 2 hours from an AlCl₃/H₂/CO₂ (2.7%/90.5%/6.8%) gas mixture in connection with the titanium oxide depositions (Ti₂O₃, Ti₃O₅, (ca. 50 nm thick) or as a separate step (TiO₂ (0.3 μm thick)). A temperature of 1000°C and a pressure of 6.7x10³ Pa were utilized in all the Al₂O₃ deposition experiments.

3.2 Film characterization

The phases grown were identified by means of X-ray diffraction (XRD) utilizing a Philips powder X-ray diffractometer with a 1710 control unit and CuKα radiation. The morphologies of the layers were investigated by Scanning Electron Microscopy (SEM), (JEOL, JSM 840). For examination of surface impurities X-ray photoelectron spectroscopy (XPS) and scanning Auger microprobe (SAM) analysis were performed with a PHD 5500 instrument using MgKα radiation.

4. Results and Discussion

4.1 Titanium oxide deposition

XPS analysis showed that Si was present in the titanium oxide films (less than 3%). The amount of silicon was higher at the surface than closer to the substrate. Simultaneous deposition of titanium oxide on sapphire substrates yielded no silicon which indicates that the silicon, found in the titanium oxides deposited on silica, originated from the silica substrate. The silicon is conceivably released as SiCl_x during the early stage of the deposition process when the silica substrate is exposed to the TiCl₄/H₂/CO₂ gas mixture. The SiCl_x reacts instantaneously with the water produced by the water gas shift reaction (2) and results in SiO₂. These reactions proceed as long as the silica substrate is exposed to the gas phase until an intact titanium oxide layer is formed. The SiO₂ is then forwarded by the growth front during the subsequent deposition process and will remain on the titanium oxide surface.

4.2 Aluminium oxide deposition

The aluminium oxide layers, obtained on intact titanium oxide films on silica, consisted of the α-phase irrespective of the titanium oxide phase. No silicon was detected. The preferred orientation of α-Al₂O₃ varied, however. Ti₂O₃ favoured the [1106] direction while on Ti₃O₅ and TiO₂ a more random growth

developed. Additionally, "lower" titanium oxides (more titanium rich) and occasionally Al_2TiO_5 [23] were detected. The lower titanium oxides are probably formed during the initial stage of the aluminium oxide deposition. Due to the slow kinetics of the water gas shift reaction (2) and to the high H_2/CO_2 molar ratio, all water formed is consumed by the AlCl_3 during the subsequent hydrolysis reaction. As long as the titanium oxide is exposed to the excess H_2 in the gas phase a reduction of the initial titanium oxide into lower oxides (more titanium rich) may occur. Al_2TiO_5 is most likely a consequence of a solid state reaction between the titanium oxide and the aluminium oxide.

The morphology of $\alpha\text{-Al}_2\text{O}_3$ grown on intact layers of the different titanium oxides are shown in figs. 1a-c.

Fig. 1
The morphology of $\alpha\text{-Al}_2\text{O}_3$ developed on different titanium oxides; a) Ti_2O_3 , b) Ti_3O_5 , c) TiO_2 .

The layers are uniform but cracks are frequently observed. The morphologies of the different aluminium oxide samples are almost identical and differ merely in grain size. On Ti_2O_3 larger grains of $\alpha\text{-Al}_2\text{O}_3$ were developed than on the other titanium oxides. This might be due to a more pronounced epitaxial relationship between the isostructural $\alpha\text{-Al}_2\text{O}_3$ and Ti_2O_3 phases.

The morphology of $\alpha\text{-Al}_2\text{O}_3$ shown in figs. 1a-c is similar to that of $\alpha\text{-Al}_2\text{O}_3$ developed on TiC-coated cemented carbides and quite different from the morphology of $\alpha\text{-Al}_2\text{O}_3$ initiated by a κ - to $\alpha\text{-Al}_2\text{O}_3$ phase transformation [14,15,22].

Fig. 2 shows a cross-section of $\alpha\text{-Al}_2\text{O}_3$ deposited on a TiO_2 /silica substrate. Close to the silica pores can be observed. These probably originate from the volume contraction involved upon reduction of the TiO_2 to lower titanium oxides or the formation of Al_2TiO_5 .

Fig. 2

Fractured cross-section of α - Al_2O_3 deposited on a TiO_2 /silica substrate, showing pores in the α - Al_2O_3 /initial TiO_2 interface.

5. Concluding remarks

Although Si was detected in the titanium oxide layers it is not believed that the presence of this silicon controlled the phase content of the deposited aluminium oxide layer. As explained in section 4.1 the silicon is most likely present as SiO_2 and annealing of metastable aluminium oxide modifications has shown that SiO_2 stabilizes the κ -phase [24]. Furthermore, the morphological examination disclosed no odd-shaped outgrowth or whiskers, which are readily obtained if silicon is present in the gas phase. Conclusively, the titanium oxides determined the phase composition of the aluminium oxide layers.

References

- [1] Silvestri, V. J., Osburn, C. M. and Ormond, D. W., *J. Electrochem. Soc.*, 125 (6) (1978) 902.
- [2] Kamoshida, M., Mitchell, I. V. and Mayer, J. W., *Appl. Phys. Lett.*, 18 (7) (1971) 292.
- [3] Funk, R., Schachner, H., Triquet, C., Kornmann, M. and Lux, B., in Blocher Jr, J. M., Hintermann, H. E. and Hall, L. H. (eds.), *Proc. 5th Int. Conf. CVD*, The Electrochem. Soc., New Jersey, U. S. A., 1975, p. 469.
- [4] Iida, K. and Tsujide, T., *Jpn. J. Appl. Phys.*, 11 (6) (1972) 840.
- [5] Lindström, J.N. and Schachner, H., in Hintermann, H. E., *Proc. 3rd Eur. Conf. CVD*, 1980, p. 208.
- [6] Lindström, J., Jonsson, B. and Ohlsson, F., *U. S. Patent 3,837,896*, 1974.
- [7] Lux, B., Funk, R., Schachner, H. and Triquet, C., *U. S. Patent 3,836,392*, 1974.
- [8] Kronberg, M. L., *Acta Metall.*, 5 (1957) 507.
- [9] Liu, P. and Skogsmo, J., *Acta Crystallogr.* B47 (1991) 425.
- [10] Chatfield, C., Lindström, J. and Sjöstrand, M. E., *J. Phys. Colloq.* C5(50) (1989) 377.
- [11] Danzinger, M., Haubner, R. and Lux, B., *J. Phys. IV Colloq.* C2 (1991) 579.
- [12] Vuorinen, S. and Skogsmo, J., *Thin Solid Films*, 193/194 (1990) 536.
- [13] Chatfield, C., *Int. J. Refr. Met. Hard. Mater.*, 9(3) (1990) 132.

- [14] Fredriksson, E. and Carlsson, J.-O., *J. Phys. Colloq.* C5(50) (1989) 391.
- [15] Fredriksson, E. and Carlsson, J.-O., *Surf. Coat. Technol.*, 56(1993)165.
- [16] Schmitt, T., Altena, H. and Lux, B., in Bloem (ed.), *Proc. 4th Eur. Conf. CVD*, Eindhoven, The Netherlands, 1983, p. 421.
- [17] Altena, H., Colombier, C., Lebl, A., Lindström, J. and Lux, B. in Bloem, J. (ed.), *Proc. 4th Eur. Conf. CVD*, Eindhoven, The Netherlands, 1983, p. 428.
- [18] Murray, J. L. and Wriedt, H. A. in Murray, J. L. (ed.), *Phase Diagrams of Binary Titanium Alloys*, ASM International, Sec. Print. 1990.
- [19] Hyde, B. G. and Andersson, S. *Inorganic Crystal Structures*, John Wiley & Sons, New York, 1989.
- [20] Rice, C. E. and Robinson, W. R., *Acta Crystallogr.*, 33 (1977) 1342.
- [21] Andersson, S., Collén, B., Kuylenstierna, U. and Magnéli, A., *Acta Chem. Scand.*, 11 (1957) 1641.
- [22] Fredriksson, E. *Thesis, Acta Univ. Ups., Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science*, 419. 35pp., Uppsala. ISBN 91-554-3040-6.
- [23] *XRD Data set 23-1078*.
- [24] Iler, R. K., *J. Am. Ceram. Soc.*, 47 (7) (1964) 339.