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Deposition of alumina thin film by dual magnetron sputtering: Is it γ-Al_2O_3?

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Abstract

Alumina thin films were deposited by reactive dual magnetron sputtering at 550 °C on cemented carbide substrates. A Young's modulus of 315 GPa and a Vickers hardness of 2348 were determined by nanoindentation and were compared to reference materials. The crystal structure of such films is usually referred to as γ-Al_2O_3; however, the crystal structure of cubic γ-Al_2O_3 is not well defined, not even for bulk materials. The alumina grain size of the films was about 50 nm as measured by dark-field imaging in a transmission electron microscope. The energy-filtered electron diffraction patterns were segmented: one part showed an amorphous intensity distribution, not known for γ-Al_2O_3, the other part contained reflections arranged in rings, the brightest of which had lattice spacings of the (400) and (440) reflections of γ-Al_2O_3. Therefore, the structure of the thin films is referred to as pseudo γ-Al_2O_3. This nomenclature expresses that this phase is different from γ-Al_2O_3 but among the Al_2O_3 phases is most closely related to this phase. Differences between the two crystal structures are highlighted and discussed with respect to lattice spacings, intensities of the various reflections, chemical composition and other physical properties. The pseudo γ-Al_2O_3 films contained an Al/Ar mole fraction ratio of about 17 as determined by energy-dispersive X-ray spectroscopy.

Keywords: Thin films; Nanostructure; Ceramic material; Microstructures; Alumina

1. Introduction

The importance of alumina ceramics for various technological applications is well documented in the literature [1,2]. The 24 known alumina phases can be divided into two main series—see Table 1 [3]. The α-series contains α-, κ-, χ-Al_2O_3 with hexagonal closed-packed oxygen anions and rhombohedral symmetry. The γ-series contains η-, γ-, δ-, θ-Al_2O_3 and these phases are described as a defect spinel structure [4].

Corundum crystallizes in the α-Al_2O_3 phase and has been studied in detail by transmission electron microscopy (TEM) and X-ray diffraction (e.g. [5]). It is formed at 1000–1100 °C from γ-AlOOH (bohemite) by a sequence of phase transformations: γ-Al_2O_3 (at 300–500 °C), δ-Al_2O_3 (700–800 °C) and θ-Al_2O_3 (900–1000 °C).

In this paper we focus on the γ-Al_2O_3 phase. The unit cell of γ-Al_2O_3 originates from the cubic $MgAl_2O_3$ spinel, by removing Mg to retain the Al_2O_3 stoichiometry. The Al atoms partially occupy Mg sites of $MgAl_2O_3$ spinel, and thus vacant Al sites are present [6]. The atomic positions of γ-Al_2O_3 are given in the upper part of Table 2.

The most detailed experimental investigations on the structure of γ-Al_2O_3 (space group $Fd\bar{3}m$) bulk materials were carried out by Zhou and Snyder using X-ray and neutron diffraction [7]. They reported a large number of surprisingly small diffraction peaks for γ-Al_2O_3 (see Table 3c in Ref. [7]) and the *R* values of the Rietveld analysis

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Table 1
Crystal structures of alumina polytypes given by the ICDD® Database PDF1.

	Phase	Crystal system	Lattice parameter (Å)	PDF card
α-series	α-Al_2O_3	Rhombohedral	$a = 4.75$, $c = 12.99$	421468
	χ-Al_2O_3	Hexagonal	$a = 5.57$, $c = 8.64$	130373
	β-Al_2O_3	Hexagonal	$a = 5.46$, $c = 33.65$	100414
γ-series	η-Al_2O_3	Cubic	$a = 7.9$	040875
	δ-Al_2O_3	Monoclinic	$a = 11.74$, $b = 5.72$, $c = 11.24$, $\beta = 103.34$	110517
	δ-Al_2O_3	Tetragonal	$a = 7.94$, $c = 23.5$	160394
	γ-Al_2O_3	Cubic	$a = 7.9$	500741
	θ-Al_2O_3	Monoclinic	$a = 11.83$, $b = 2.9$, $c = 5.62$, $\beta = 104.1$	231009

Table 2
Atomic positions for γ-Al_2O_3. Data are based on (i) theoretical calculations for γ-Al_2O_3 described as a defect spinel structure and (ii) on a Rietveld analysis of the X-ray and neutron diffraction pattern determined from a disordered γ-Al_2O_3 crystal structure [6,7].

	Atom	Wyckoff site	X	y	Z	Probability
γ-Al_2O_3 [6]	Al	16d	0.5	0.5	0.5	1
	Al	8a	0.125	0.125	0.125	2/3
	O	32e	0.255	0.375	0.375	1
γ-Al_2O_3 [7]	Al	16d	0.5	0.5	0.5	0.58
	Al	8a	0.125	0.125	0.125	0.84
	Al	32e	0.0272	0.272	0.0272	0.17
	O	32e	0.2547	0.2547	0.2547	1

Table 3
Deposition parameters of analyzed thin films (samples #1–4) and properties of bulk materials (samples #5 and #6).

Sample #	Film deposition	Crystal structure	Bias potential (V)	Applied method
1	DMS Al_2O_3	γ-Al_2O_3	−150	SEM, AFM, XRD, TEM plan-view prepared, hardness,
2	DMS Al_2O_3	γ-Al_2O_3	−150	TEM cross-section prepared
3	DMS Al_2O_3	Amorphous	−40	TEM cross-section prepared, hardness
4	CVD α-Al_2O_3	α-Al_2O_3	–	XRD, hardness
5	Sapphire (0 0 0 1)	Trigonal rhombohedral	–	Hardness
6	WC-Co	Hexagonal	–	REM, hardness

[8], i.e. the squared differences between measured and calculated intensities, were 10%. This indicated that even for bulk material the understanding of the crystal structure was poor, particularly if one considers the large number of free parameters in the structural model used. Zhou and Snyder explicitly concluded a cubic crystal structure with a disordered Al sublattice. In Table 2, the atomic positions of Al and O determined by Zhou and Snyder are compared to those of γ-Al_2O_3 described as a defect spinel structure [6]. The combined X-ray and neutron diffraction is the key for understanding the disorder in detail. Zhou and Snyder further concluded that transition alumina like γ-Al_2O_3 or η-Al_2O_3 refers to the group of partially dehydrated aluminum hydroxides.

Various calculations [9–12] predicted the defect positions within the unit cell of γ-Al_2O_3, though without conclusive results. Neither electron, X-ray and neutron diffraction nor nuclear magnetic resonance (NMR) have revealed consistent values for the occupancy probability of tetrahedrally and octahedrally coordinated Al atoms in γ-Al_2O_3. As a consequence the model of a purely defect spinel structure does not explain the structure of γ-Al_2O_3 in detail. In summary, to the best of our knowledge we could not find a defined reference material for bulk γ-Al_2O_3 in the literature, for which convincing structural analysis with small Rietveld factors exists. Thus, the structural model of Zhou and Snyder is the most convincing model published so far.

The crystal structure of alumina thin films obtained from aqueous solutions was studied in detail by Levin et al. [3] using electron diffraction. The authors claimed the presence of the γ-Al_2O_3 phase but did not show any diffraction pattern corresponding to this alumina phase. French et al. [13] studied the same set of samples by electron energy loss spectroscopy (EELS) and investigated plasmon energies and the electron loss near edge structure (ELNES) of Al-*L* ionization edges. They concluded that the plasmon energy of γ-Al_2O_3 was the same as that of α-Al_2O_3 (26.1 eV). As a result, the α- and γ-Al_2O_3 phase cannot be distinguished by this method. No diffraction pattern of γ-Al_2O_3 is given either in Ref. [13] or in Ref. [14]. Another EELS analysis of γ-Al_2O_3 was reported by