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Ordered structure and preferred orientation of boehmite films prepared by the sol–gel method

Aurelian Florin Popa^a, Sylvie Rossignol^b, Charles Kappenstein^{b,*}

^a Department of Inorganic Chemistry, University 'Al.I.Cuza', Iassy, Romania

^b UMR 6503, Laboratoire Catalyse par les Métaux, Université de Poitiers, 40 Avenue du Recteur Pineau, F-86022 Poitiers cedex, France

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Abstract

Several boehmite films were produced using the sol–gel route. The drying process, the film structure evolution and the final texture of the samples were investigated by means of combined X-ray diffraction and weight variation. A remarkable (010) preferred orientation (about 97% of the crystallites) was found for xerogel films with thickness ranging from 1.5 to 24 μm . The ordered structure is already present in the sol state and is appeared and enhanced during drying, before gelling. This phenomenon may be attributed to the particular boehmite structure that induces special crystallite organization in the aquagel. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The sol–gel chemistry provides an interesting alternative for the synthesis of inorganic oxides [1,2], and particularly, thin films that may have various applications. In the case of alumina porous films, available results reported mainly their use as separation membranes [3–5] and catalyst support coatings [6]. One possible way to prepare such films is the boehmite route which utilizes aluminum alkoxides as precursors; this offers some particular advantages such as low temperature

synthesis and the possibility to prepare homogeneous crack-free films. In this work the synthesis and the investigation of some boehmite films before and after drying are presented. Several papers have been already examined this topic in the past, therefore our work focuses mainly on the following points: (i) the films' weight evolution in time; (ii) changes in the sol structure monitored by X-ray diffraction; (iii) the quantification of boehmite crystallites ordering and (iv) a tentative interpretation based on the structural characteristics of ideal boehmite.

2. Experimental procedure

The boehmite sols were prepared according to a procedure developed by Yoldas [7]: the aluminum

* Corresponding author. Tel.: +33-5 49 45 38 60; fax: +33-5 49 45 40 20.

E-mail address: charles.kappenstein@univ-poitiers.fr (C. Kappenstein).

tri-*sec*-butoxide (97 wt%, Aldrich) precursor was hydrolyzed in excess of distilled water ($\text{H}_2\text{O}:\text{Al}(\text{O}^{\text{-sec}}\text{C}_4\text{H}_9)_3=100:1$) at 70 °C for 1 h, under vigorous stirring. Peptization was then initialized by adding HCl (37 wt%) in a $\text{Al}(\text{O}^{\text{-sec}}\text{C}_4\text{H}_9)_3:\text{HCl}$ molar ratio 10:1. Subsequently the temperature was raised to 90 °C and maintained at this level for 2 h. At the end of this process, a sol containing boehmite $\text{AlO}(\text{OH})$ in the range of 3.6–4 wt% is obtained.

Different sol quantities were then poured into beakers resulting in liquid sheets with respective thicknesses of 4.5, 12 and 21 mm and surfaces of 9 or 12 cm^2 . These samples were allowed to gel and dry at room temperature in an open area, while their weight was carefully monitored over time.

In order to investigate the structure after drying, four thin films were prepared by depositing different boehmite sol quantities on single crystal Si wafers exposing their (511) crystallographic face. After drying, the thickness of the films ranged from 1.5 to 24 μm . These samples were then analyzed by X-ray diffraction, on a theta–theta Siemens D 5000 diffractometer using Cu back-monochromatized K_α radiation (dwell time 2 s; step 0.04° 2-theta). The ‘Profile’ software (Socaim, France) was used to determine the precise breadth and position of the diffraction peaks. The size of the crystallites was determined from the peak integral width using the Scherrer equation,

after correction for instrumental broadening obtained with LaB_6 standard.

The theta–theta diffraction geometry was further utilized to follow the structure modifications of a sample from the beginning of the synthesis up to the drying stage.

The crystalline structure of boehmite was drawn using CaRIne 3.1 software on the basis of the atomic coordinates of ICSD file 2118, obtained from Ref. [8].

3. Results

Fig. 1 displays the weight loss over time at room temperature for four samples. After a defined weight loss, which corresponds to the so-called critical point [1], the drying rate decreases drastically. This phenomenon is related to gel drying mechanism that occurs after the sol–gel transition, as has already been reported elsewhere [9,10]. The weight loss corresponding to the critical point is in the range 93–95%, corresponding to boehmite content of 65–70 wt%. Before the critical point the drying rates per surface area ranged from 0.003 to 0.005 $\text{g cm}^{-2} \text{h}^{-1}$; therefore, they are of the same order of magnitude despite the important thickness differences (0.26–21 mm).

The dried samples prepared on Si wafers display a thickness in the range of 1.5–24 μm (i.e. 20 times less than the initial thickness). X-ray diffraction

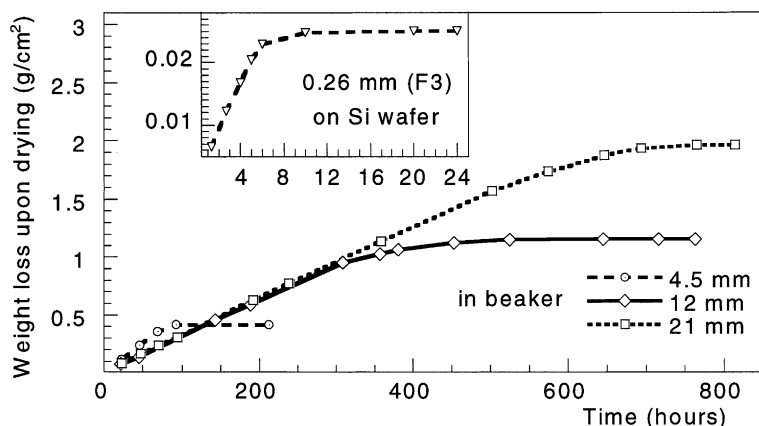


Fig. 1. Film weight loss during drying.

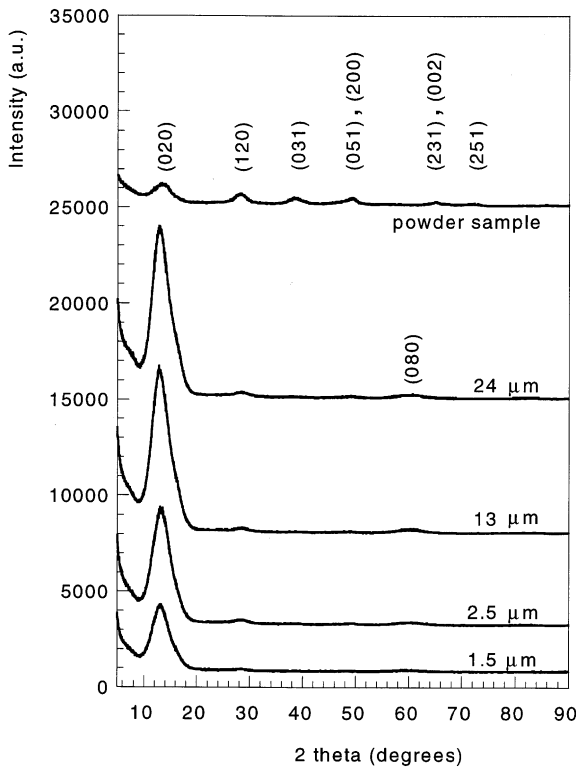


Fig. 2. X-ray diffractograms of dried films on Si wafers.

patterns indicate that they have a nano-crystalline boehmite structure (Fig. 2). The first obvious feature of these diffractograms is the strong enhancement of the (0 2 0) peak intensity, disclosing an important preferred orientation. By comparison, a ground sample synthesized under similar conditions displays a less intense (0 2 0) peak and

higher intensity for the remaining peaks (Fig. 2), in agreement with a random crystallite orientation. The results are summarized in Table 1. For the different films, the intensity ratio of the two most important peaks, (0 2 0) and (1 2 0), is 40–44 times larger than the expected ratio for a pure random orientation of a well crystallized boehmite 100:65 = 1.54 (PDF no. 21-1307). We can quantify the preferred orientation on the basis of a simple model, assuming two crystallite sets, a perfectly oriented and a randomly disordered one. If we admit that the powder sample contains only disordered crystallites, the oriented set represents in the films about 97% of the total number of crystallites. The (0 8 0) peak, which corresponds to the same family plane orientation as the (0 2 0) peak, also shows a similar enhancement (Table 1). This indicates that a large number of boehmite crystallites have their (0 1 0) plane in parallel position with respect to the substrate surface.

The structure evolution during the sol formation and the subsequent water elimination was monitored in the sol; the corresponding diffractograms are presented in Fig. 3. A sample taken after the first hour of synthesis at 70 °C contains primarily the aluminum oxyhydroxide in a mainly amorphous state and only a small amount of poorly developed boehmite germs are present (Fig. 3(a)), as indicated by the appearance of small features at the expected 2-theta positions, superimposed onto the amorphous profile. Under the synthesis conditions, oligomeric aluminum species (like monomeric $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, dimeric $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$, trimeric $[\text{Al}_3(\text{OH})_4(\text{H}_2\text{O})_9]^{5+}$ or $[\text{AlO}_4-$

Table 1
X-ray diffraction data of the dried films

Sample	Thickness (μm)	Intensity (0 2 0) (counts degree)	$I_{(020)}/I_{(120)}^a$	$I_{(080)}/I_{(120)}^b$	b (\AA) ^c	D_b (\AA) ^d	Preferred orientation (%)
F ₁	1.5 ± 0.1	5627	65 ± 6	2.0 ± 0.3	13.3 ± 0.1	19 ± 2	97.1
F ₂	2.5 ± 0.1	10 233	61 ± 5	1.8 ± 0.2	13.3 ± 0.1	19 ± 2	96.9
F ₃	13 ± 1	15 795	68 ± 5	1.6 ± 0.1	13.4 ± 0.1	19 ± 2	97.2
F ₄	24 ± 1	15 175	66 ± 5	1.5 ± 0.1	13.4 ± 0.1	19 ± 2	97.2
G	Powder sample	1182	1.87 ± 0.09	–	13.2 ± 0.2	26 ± 3	0
Reference	PDF 21-1307	–	1.54	0.09	12.227	–	–

^a Intensity ratio of the (0 2 0) to (1 2 0) peaks.

^b Intensity ratio of the (0 8 0) to (1 2 0) peaks.

^c b parameter.

^d Crystallite size in b direction.

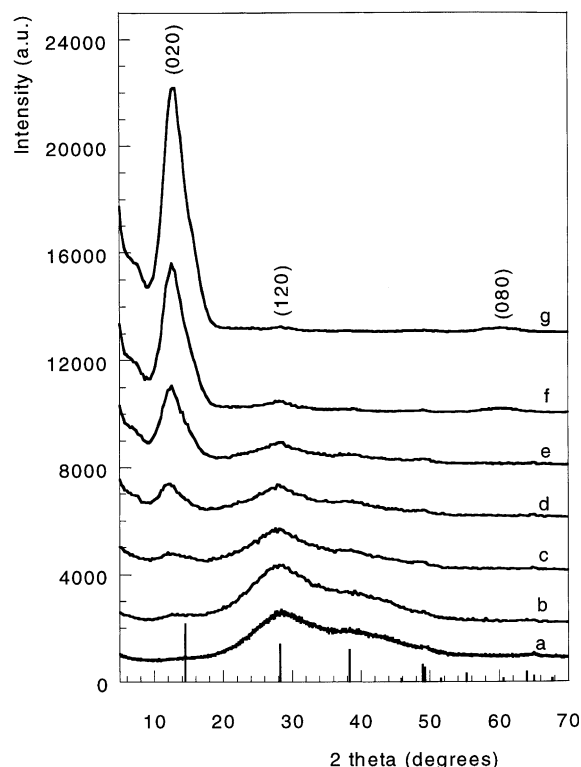


Fig. 3. Film diffractograms as a function of time: (a) after 1 h of synthesis at 70 °C; (b) after 3 h of synthesis (1 h at 70 °C and 2 h at 90 °C); (c) after drying for 49 min; (d) after drying for 62 min; (e) after drying for 74 min; (f) after drying for 85 min; (g) after drying for 96 min.

$\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) can also be present in the sol (as indicated by the ^{27}Al NMR and Raman spectra [11]) but they are in X-ray diffraction indiffrent. The diffractogram of a second sample, taken at the end of the synthesis, indicates no major changes (Fig. 3(b), thickness 260 μm). During the drying step at room temperature, the boehmite crystallizes at the expense of the amorphous phase or by consumption of the lower-molecular polymeric species [10]. After 49 min, the preferred orientation is already visible (Fig. 3(c)) and increases with time (Fig. 3(d)–(f)). After 96 min, only well ordered nano-crystalline boehmite is present, despite the presence of excess water; at this stage the film has a thickness of 180 μm and contains approximately 5.5 wt% boehmite. From this point on, the drying process continues

without any new X-ray detected structure modification.

From the (020) line position, the cell parameter b was determined (Table 1) and found to be in the range 13.3–13.4 Å, significantly larger than that of the well-crystallized boehmite. The increase in distance between the (010) planes of the boehmite can be attributed to the excess water content, partially located in intercalated position [12].

The crystallite dimension along the b axis can be obtained from the mean breadth of the (020) and (080) reflections; its value of 1.9 nm is equivalent to 1.5 unit cell in that direction.

The a and c parameters and the corresponding crystallite size cannot be obtained because of strong overlapping of the (200) with the (051) and the (002) with the (231) lines respectively. In the case of the ground powder sample, the parameters are $a_{\text{exp}} = 3.69$ Å and $c_{\text{exp}} = 2.86$ Å, practically identical to the ideal structure. The corresponding crystallite sizes are 4.9 and 7.8 nm respectively, which is equivalent to about 15 unit cells in the a direction and 30 unit cells in c direction [13]; therefore, the crystallites exhibit a platelet shape, with the thickness along the b axis.

4. Discussion

The absolute weight loss corresponding to the critical point of the samples is directly related to the quantity of the sol (Fig. 1). The drying time is approximately proportional to the thickness of the layer. At the end, the final water content of the gel is in the range 22–25 wt%, which corresponds to about 1 mol excess H_2O per mole of boehmite ($\text{AlO}(\text{OH}), 1\text{H}_2\text{O}$).

A preferred orientation effect has already been noticed in previous literature reports [14–16]. We can explain this peculiarity on the basis of the ideal boehmite structure presented in Fig. 4. The ideal cell (PDF no. 21-1307, orthorhombic, space group no. 63, Amam) is elongated in the b axis direction ($a = 3.700$ Å, $b = 12.227$ Å, $c = 2.868$ Å) and contains four formula units $\text{AlO}(\text{OH})$. The aluminum atoms are equivalent and present a deformed octahedral geometry with four oxide and two hydroxide neighbors; the $\text{AlO}_4(\text{OH})_2$ octahe-

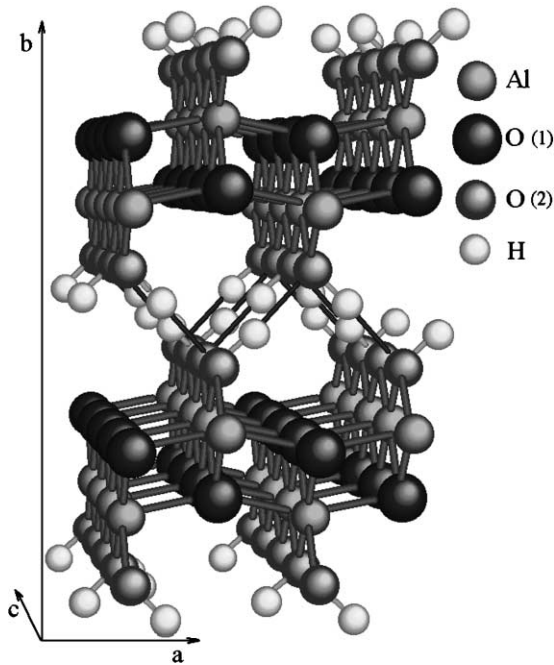
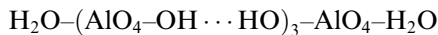


Fig. 4. Boehmite (γ -AlO(OH)) ideal structure.

drons are linked to one another edge to edge, resulting in AlO(OH) polymeric layers parallel to the (0 1 0) planes (\vec{a} , \vec{c} planes). These layers are stacked along the b axis and held together by multiple hydrogen bonds between the OH groups of each octahedron. Taking into account the crystallite size along the b direction, the layer stacking can be simply described by the following sequences including the presence of surface hydrogen bonded and aluminum coordinated water molecules:



or



The hydrogen bonds are weaker than the bonds inside the octahedron layers between aluminum and oxygen atoms and the direct consequence is the preferential growth of the boehmite crystallites in the a , c layers plane. This could explain the platelet shape as well as the important size differences in length, width and height.

The preferred orientation is probably induced by interactions between solvent molecules and the

surface OH groups of the (0 1 0) planes of boehmite via hydrogen bonds. These interactions can lead to a horizontal orientation of the hydrogen bonds layers when starting from the interfaces between sol sample and air, or between sol sample and internal substrate surface. They appear already in the sol state, in the course of the boehmite crystallite formation.

5. Conclusion

Highly ordered boehmite films have been synthesized using aluminum alkoxide as gel precursor. The present results prove that the strong preferred orientation appears prior to gelling; boehmite crystallites interact and organize themselves at the same time they are developing in the sol state. The shape and size of the crystallites as well as the film texture could be beneficial during an expected to-potactic transformation of boehmite into transition alumina, with respect to strains and cracks. By careful control of the calcination process conditions, we should be able to prepare high quality homogenous alumina films.

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References

- [1] C.J. Brinker, G.W. Scherer, Sol-gel Science, The Physics and Chemistry of Sol-gel Processing, Academic Press, New York, 1990.
- [2] J. Livage, C. Sanchez, F. Babonneau, Chem. Adv. Mater. (1998) 389.
- [3] A.F.M. Leenars, K. Keizer, A.J. Burggraaf, J. Mater. Sci. 19 (1994) 1077.
- [4] L. Cot, A. Ayrat, J. Durand, C. Guizard, N. Hovnanian, A. Julbe, A. Larbot, Solid State Sci. 2 (2000) 313.
- [5] Q. Fu, C.-B. Cao, H.-S. Zhu, Thin Solid Films 348 (1999) 99.

- [6] K. Haas-Santo, M. Fichtner, K. Schubert, *Appl. Catal. A* 220 (2001) 79.
- [7] B.F. Yoldas, *J. Mater. Sci.* 10 (1975) 1856.
- [8] N. Achiwa, N. Yamamoto, S. Kawano, *Annual report KURAA* 10 (1997) 8.
- [9] A.C. Pierre, D.R. Uhlmann, *J. Am. Ceram. Soc.* 70 (1987) 28.
- [10] A.C. Pierre, *J. Can. Ceram. Soc.* 59 (1990) 52.
- [11] T. Assih, A. Ayril, M. Abenoza, J. Phalippou, *J. Mater. Sci.* 23 (1988) 3326.
- [12] B.R. Baker, R.M. Pearson, *J. Catal.* 33 (1974) 265.
- [13] A.F. Popa, S. Rossignol, C. Kappenstein, presented at the 17th North American Catalysis Society Meeting, Horizons of Catalysis, Toronto, Ont., Canada, 3–8 June 2001.
- [14] D. Ouyang, C. Mo, L. Zhang, *Nanostruct. Mater.* 7 (1996) 573.
- [15] J. Campaniello, P. Berthet, F. d'Yvoire, A. Revcolevschi, *J. Mater. Res.* 10 (1995) 297.
- [16] J.-I. Fukasawa, K. Tsujii, *J. Coll. Interface Sci.* 125 (1988) 155.