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SULFUR CONCENTRATION IN NANOPOROUS ALUMINA MEMBRANE Studied by TA and XPS

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Abstract

Nanoporous alumina membrane prepared by anodic oxidation using sulfuric acid electrolyte was subjected to TG-DTA and X-ray Photoelectron Spectroscopy (XPS or ESCA) to further study the distribution of sulfur. In XPS study, Ar^+ ion bombardment was performed on the sample to etch the surface at a rate of 3 nm min^{-1}. As a result, sulfur was found to be concentrated within a depth of 3nm from the surface. The S content of the surface was found to be 2.7±0.5 wt%, and that at a depth of ca. 3 nm and ca. 10 nm was found to be as low as about 0.6±0.11 wt% (5.37±1.0 wt%→ 1.26±0.2wt% SO_2). In TG-DTA, the mass loss of 7.3% was in fair agreement with that calculated on XPS results (7.1±1.2%).

Keywords: amorphous alumina, mesopores, nanoporous alumina membrane, TG-DTA, XPS

Introduction

Nanoporous alumina membranes are attracting much attention as templates for producing nanomaterials such as carbon nanotubes [1] and metal nanowires [2], because the pores are controllable by the conditions of preparation. The authors have prepared nanoporous alumina membranes by anodically oxidizing high purity aluminum in sulfuric acid, and have reported on their morphological change and thermal properties [3–6]. However, this material was found to contain carbon and sulfur, and to discharge carbon dioxide and sulfur dioxide on heating to temperatures higher than ca. 950°C. EDS results showed uniform distribution of S [7]. This is not in agreement with the above results. Hence, further study was found necessary to confirm our previous results.

The present paper reports on the distribution of sulfur studied by XPS (or ESCA; Electron Spectroscopy for Chemical Analysis) and TG-DTA.

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Experimental

The amorphous as-prepared alumina obtained by anodizing aluminum in sulfuric acid electrolyte was used as the sample. As reported previously [5], this sample is about 150 μm in thickness and has cylindrical pores about 25 nm in diameter. The as-prepared sample contains about 11% by mass of SO_2 as determined by EDS.

XPS measurements were made with ESCA 5600Ci (manufactured by ULVAC PHI, Inc.) under ultrahigh vacuum of $6.6\cdot10^{-9}$ Torr ($8.8\cdot10^{-7}$ Pa) using MgK_α X-ray source (1253.6 eV) with a hemispherical analyzer. Argon ion etching gun directly attached to the XPS analysis chamber was used for Ar^+ ion bombardment of the sample over an area of 4 mm^2 (total sample area: 16 mm^2) for 1 min (depth: ca. 3 nm) and 3 min (depth: ca. 10 nm).

TG-DTA was performed using vertical furnace type TG-DTA 2000S (manufactured by MAC SCIENCE Co., Ltd.) in a flow of gaseous N_2 at a rate of 250 mL min^{-1} (200 mL min^{-1} inside sleeve and 50 mL min^{-1} outside sleeve) and at a heating rate of 20°C min^{-1}. Runs were made on samples before and after Ar^+ ion bombardment.

Results and discussion

Figure 1 shows the X-ray photoemission spectra of the original sample (a), the sample subjected to Ar^+ ion bombardment for 1 min. (b), and the sample subjected to ion bombardment for 3 min (c). It can be seen that the original sample (spectrum (a)) clearly shows the presence of sulfur as seen by the signals for S2s, S2p, and S3s. However, at a depth of 3 nm (spectrum (b)) and 10 nm (spectrum (c)), the signals for sulfur become extremely weak. Furthermore, spectrum (a) also indicates that the sample surface contains carbon contamination (C1s, 284.5 eV) in addition to Al and O. After Ar^+ etching, carbon peaks considerably decrease the intensity.

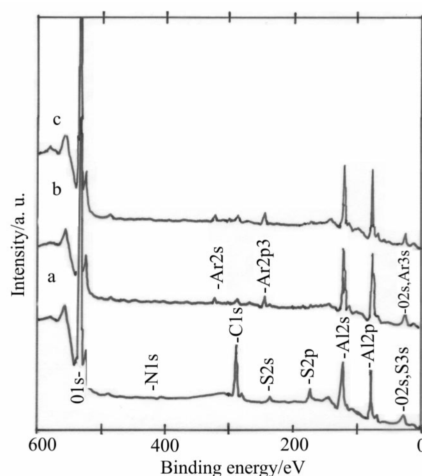

Fig. 1 X-ray photoelectron spectra for a – original sample, b – sample after Ar ion bombardment for 1 min and c – sample after Ar ion bombardment

The average near-surface composition of the sample and the samples subjected to Ar^+ ion bombardment was calculated using the XPS peak intensities and the corresponding XPS sensitivity factors of the Al2p, S2p, and O1s. The sensitivity factors for Al2p, S2p, and O1s are 10.894, 31.131, and 35.015, respectively. The results are summarized in Table 1.

Table 1 Atomic concentration of the samples

	Element / wt%		
	Al2p	S2p	O1s
Original	33.74	2.69	63.57
3–nm depth	37.51	0.55	61.94
10–nm depth	37.91	0.63	61.46

Although the results obtained in Table 1 include experimental error (S content for the original sample and the ion-bombarded sample are 2.69±0.51 wt% and 0.55±0.11 to 0.63±0.12 wt%, respectively, it can be understood that sulfur found in the surface greatly decreases at a depth of 3 to 10 nm. The wall thickness of the cylinder is 25 nm, and this signifies that the impurity sulfur is concentrated within a narrow thickness of less than 3 nm from the inner surface of the cylinder. That is, the layer thickness of the layer is about 0.12, and this is in fair agreement with the results reported on layer thickness ratio (0.1 to 0.12) of membranes prepared from oxalic acid [8, 9]. The original amorphous sample may be assumed to mainly contain amorphous alumina ($Al(OH)_3$) and SO_3. Since the molar ratio for S and Al is 0.084 and 1.250, the content of $Al(OH)_3$ and SO_3 can be calculated as 6.72 and 97.51 wt%, yielding a total of 104.2 wt%. However, if the same assumption should be made for the results obtained at 10 nm depth, the total mass results too high as to yield 111.1 wt%. Thus, by assuming that a part of amorphous alumina crystallizes, and by adjusting that 28 mol % of Al is present in the form of crystallized Al_2O_3, for instance, the resulting components are 20.65 wt% Al_2O_3, 77.79 wt% $Al(OH)_3$, and 1.57 wt% SO_3 to yield a total of 101.8 wt%.

In Fig. 2 are shown the XPS spectra for (a) C1s, (b) O1s, and (c) Al2p. The peak of C1s for all the samples yields a unique value of 284.5 eV. However, the O1s peak for the original sample shifts from 531.5 eV to the lower energy side (531.0 eV), and the Al2p peak shifts from 74.1 eV to the higher energy side (74.4 eV). This suggests that oxygen atoms after ion bombardment become anionic to form a stronger bonding with Al ions [10], which implies the formation of crystalline phase, such as γ-Al_2O_3. Bose *et al*. [11] reports that binding energy (BE) for Al2p shifts to the higher energy side from 74.07 eV (gamma boehmite (AlOOH)) to 74.11 eV (γ-Al_2O_3), and to 74.58eV (γ-Al_2O_3), whereas BE for O1s shifts from 531.38 eV (γ-AlOOH) to the lower 531.14 eV (γ-Al_2O_3). Since γ-AlOOH is regarded to be precursor of γ-Al_2O_3, the removal of S by Ar ion bombardment accelerates the crystallization of AA.

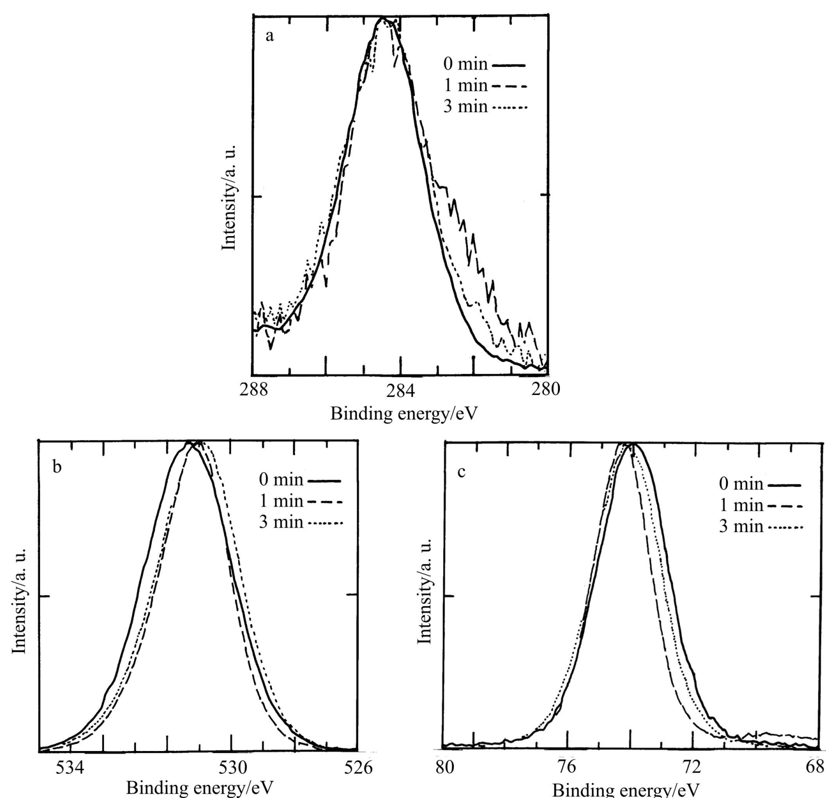

Fig. 2 X-ray photoelectron spectra showing shift for a – Cls, b – Ols and c – Al2p, of original sample (0 min), sample after Ar ion bombardment for 1 min (1 min) and sample after Ar ion bombardment for 3 min (3 min)

Figure 3 shows the TG-DTA curves of the original sample and the sample subjected to Ar ion bombardment for 3 min. Details are given in Table 2.

According to Fig. 3, it can be understood that the first exo-endothermic reaction occurring on the original sample no longer takes place, but only the endothermic peak is observed. This supports our previous discussion that the exothermic reaction represent the disordering of the atomic arrangement caused by the migration of sulfur atoms and crystallization [3]. That is, as stated above, Ar^+ bombardment had already caused disarrangement of the surface and allowed sulfur discharge to cause partial crystallization. The total mass loss for the original sample is 11.5 wt%, which is in agreement with the EDS data. The total mass loss for the sample subjected to ion bombardment is 9.5 wt%. Since the surface of the sample subjected to ion bombardment is highly active and easily adsorb hydroxyl groups and hydrocarbon, the mass loss to about 900°C is eliminated from the calculation. That is, the mass loss to ca. 940°C for the original sample is 5.4 wt%, and the same for the latter sample is 11.0 wt%. The normalized mass losses are then 8.7 and 3.5 wt% for the original sam-

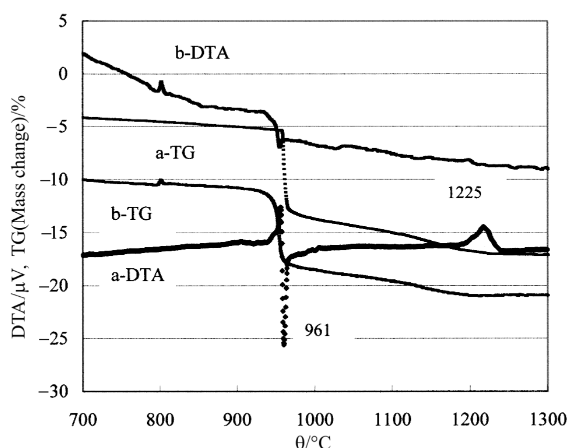

Fig. 3 TG curves for original sample (a-TG) and Ar^+-ion bombarded sample (b-TG); DTA curves for original sample (a-DTA) and Ar^+-ion bombarded sample (b-DTA)

ple, and those for the ion-bombarded sample are 7.3 and 3.4 wt%. According to XPS results, the content of sulfur as SO_2 is 5.4 (±1.0) wt% and 1.3 (±0.2) wt% for the original and the ion-bombarded samples; i.e., the SO_2 concentration is reduced to about 24 % by bombarding. This is in good agreement with the TG results. Since the area of Ar ion bombardment is 1/4 of the total area of the sample, 3/4 of the sample remain unchanged, and assuming 1/4 of the sample loses SO_2, the mass loss is calculated to be 7.1 (±1.2) wt%. This is in fair agreement with the observed value of 7.3 wt%.

Table 2 TG-DTA for the original sample and the sample subjected to 3 min Ar ion bombardment

	1st Ex-En		2nd Ex	
	Original	After ion bombarding	Original	After ion bombarding
		TG		
Ti/°C	951	939	1209	1201
Tf/°C	983	980		
Mass loss/%	8.2	6.5	3.3	3.0
Normalized/%	8.7	7.3	3.5	3.4
		DTA		
T_p 1*/°C	950	940	1224	1213
T_p 2**/°C	961	956		

* Exothermic peak, ** Endothermic peak

Conclusions

The distribution of sulfur in nanoporous alumina membrane prepared by anodic oxidation of aluminum in sulfuric acid electrolyte was investigated by TG-DTA and X-ray photoelectron spectroscopy (XPS). By employing Ar^+ ion bombardment, sulfur was found to be concentrated within a depth of 3 nm from the surface (2.7±0.5 wt% S on the surface and about 0.6 wt% S at a depth of ca. 3 nm and ca. 10 nm, or 5.4±1.0 wt%→ 1.3±0.2 wt% SO_2). Furthermore, O1s peak for the original sample shifts from 531.5 eV to the lower energy side (531.0 eV), and the Al2p peak shifts from 74.1 eV to the higher energy side (74.4 eV). This suggests that oxygen atoms after ion bombardment become anionic to form a stronger bonding with Al ions. According to TG-DTA, the mass loss (7.3%) was in agreement with the loss calculated on XPS results (7.1±1.2 %), and it supported our previous results that sulfur discharge initializes crystallization of amorphous alumina.

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