Microstructure and Stress-Induced Phase Transformation of Sol-Gel Derived Zirconia Thin Films

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ゾル-ゲル法で作製したジルコニア薄膜の微構造と応力誘起相変態

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Zirconium oxide thin films were fabricated using a sol-gel method. The sols were prepared using zirconium alkoxide and acetate. An alcoholic solution of the alkoxide and an aqueous solution of the acetate were dip-coated on a glass substrate and fired at 600°C. Both films were crystallized as the tetragonal phase, which was detected by an XRD and an electron beam diffraction of an ion-thinned section. On the other hand, the electron beam diffraction of the film prepared by crushing in a mortar, exhibited the monoclinic phase, which was transformed by stresses applied during sample preparation for TEM. The SEM observation showed a grain size of 30-50 nm. The TEM micrographs exhibited contrasts of less than 10 nm size in a single grain of about 30 nm. [Received February 13, 2006; Accepted April 19, 2006]

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1. Introduction

Zirconium oxide ceramic has been extensively studied and used in a wide range of applications. The ceramics were traditionally utilized as refractories, heaters, oxygen sensors, a solid state electrolyte, and as tough-ceramics.¹⁾⁻³⁾ Besides these applications, ZrO_2 thin film has also been investigated as an insulating layer in silicon technology for its high permittivity and low leakage properties.^{4),5)} Other applications include protection coatings for stainless steel⁶⁾ and ceramic membranes.⁷⁾ Thus, the thin film applications of ZrO_2 are becoming increasingly important.

 ZrO_2 films were often deposited by vapor-related methods such as sputtering,⁴⁾ pulsed laser deposition.⁵⁾ We have been studying a sol-gel deposition of the ZrO_2 film prepared using zirconium alkoxide as a starting reagent and stabilized by the addition of ethanolamine.^{6),7)} These ZrO_2 films have been used as a solid electrolyte,⁸⁾ a matrix of organic dye,⁹⁾ and as an insulating layer for transparent oxide thin film transistors.¹⁰⁾ In order to improve the electrical and optical properties, characterization of the films and the effects of the film process on the resultant film structure are of great importance.

One of the most interesting characters of ZrO_2 is its crystalline phases. The metastable tetragonal phase appears when the grain size is less than a certain critical value. The critical grain size for transformation from metastable tetragonal to monoclinic at room temperature was determined to be 6 to 23 nm, by measurements using XRD, TEM, and Raman spectrometry.¹¹⁾⁻¹³⁾ Here we report the result of the microstructural investigation and tetragonal to monoclinic phase transformation of the sol-gel ZrO₂ films deposited on a heat resistant glass substrate.

2. Experimental procedure

Two sols were prepared using zirconium alkoxide and zirconium acetate. Zirconium tetra-*n*-butoxide (Mitsuwa Chemical Co., Osaka) was mixed with 2-propanol and then double molar diethanolamine was added into the solution as a solstabilizer. A pale yellowish, transparent sol with a concentration of up to 0.5 mol/L was obtained and a solution of 0.3 mol/L was used for experiments. The sol can be handled in an ambient atmosphere without any gelation or precipitation.

Zirconium acetate (Aldrich, USA) is water soluble and often used as starting reagent for the sol-gel method.^{14),15)} We used zirconium acetate as another starting material. Using thermogravimetric analysis, a nominal formula of the starting acetate was determined as $Zr(OCOCH_3)_{1.5}(OH)_{2.5}$. After filtration of the aqueous solution, a non-ionic surfactant of 0.1 vol% was added in order to improve the wettability of the solution onto a glass substrate. The prepared aqueous solution of 0.3 mol/L was used for experiments.

The substrate used was heat resistant glass, Corning #1737 or #7059. A dip-coating method was used for film deposition. The glass substrate was immersed into the sol and withdrawn at a speed of 6 cm/min. After coating, the film was dried at 110° C and then rapid-heated at $300-700^{\circ}$ C for 30 min, mainly at 600° C. This coating-drying-heating cycle was then repeated.

The resultant film was characterized by means of an X-ray diffractometer (XRD, RAD-2R, Rigaku, Tokyo), a spectrometer (U-4000, Hitachi, Tokyo), a scanning electron microscope (FE-SEM, S-4300, Hitachi), and a transmission electron microspore (TEM, H-8100, Hitachi). For the TEM specimens, two different methods, i.e., simple crushing and an ion-thinning method, were examined. Conductive carbon was coated on the ion-thinned section for TEM observation.

3. Results and discussion

3.1 Crystalline phase and optical transmittance of the films

Figure 1 shows the XRD profile of the ZrO_2 film from the alkoxide solution heated at 600°C. The film was deposited eight times. The film crystallized and peaks could be indexed as the tetragonal phase, for convenient identification. The difference in the crystallization between the starting reagents was the crystallization temperature. The film from the acetate solution was crystallized by heating at 400°C. This temperature was low compared with the film from the alkoxide solu-



Fig. 1. XRD profile of ZrO_2 film from alkoxide derived sol, deposited 8 times and heated at 600°C.



Fig. 2. Transmittance of ZrO₂ films heated at 600°C.

tion, which was crystallized by heating at 500°C. The difference in the crystallization temperature was attributed to the difference in decomposition temperature of the alkoxide derived gel and the acetate gel. The former decomposed at about $500^{\circ}C$,⁹⁾ while the latter decomposed by heating at 400°C. All films from the acetate solution heated 400° to 700°C could be indexed as the tetragonal phase. The tetragonal phase at low temperature was common among zirconia films with small crystallite size, or low crystallinity.

The results of the measurements using the spectrometer for the films heated at 600°C are shown in **Fig. 2**. The films were eight depositions of the alkoxide solution and three depositions of the acetate solution. Both films were transparent. The existence of interference bands in the figure clearly indicates that the film was uniform in optical thickness. The interference bands could be used for estimating the refractive index and film thickness. The refractive indexes of the films shown in the figure were calculated as 2.06 (at 544 nm) and 1.89 (at 719 nm) for the films from alkoxide and acetate, respectively. The film from the alkoxide solution had a slightly highervalue. Film porosity related to the refractive index was calculated using the Lorentz-Lorenz equation below.¹⁶

$$1 - p = \frac{(n_{\rm f}^2 - 1) (n_{\rm c}^2 + 2)}{(n_{\rm f}^2 + 2) (n_{\rm c}^2 - 1)}$$

Where p, n_f , and n_c are the porosity, refractive index of the film, and refractive index of the crystal (pore free film), respectively. There is a problem for practical application of this equation in determining the film porosity, i.e., there is no data for the refractive index of pore-free film. Because of this,



Fig. 3. SEM micrographs of ZrO_2 films deposited 3 times and heated at 600°C, prepared using (a) alkoxide derived sol and (b) acetate derived sol.

data for Baddeleyite¹⁷⁾ (monoclinic ZrO₂, α =2.13, β =2.19 and γ =2.20) was used after averaging the optical anisotropy, being n_c =2.17. Wavelength dispersion of the refractive index was neglected, though Baddeleyte exhibits strong dispersion. The porosity of the films was calculated as 6% and 14% for films from alkoxide and acetate, respectively. Considering errors in the estimation, we can conclude that the present ZrO₂ films, especially the film from the alkoxide sol, were dense.

The thickness of the films was also estimated using the results of the spectrometer. The single coating thicknesses of the films were about 50 and 30 nm for film prepared using alkoxide and acetate, respectively. The difference in the thickness was caused by the difference in viscosity of the solution, though we have not measured the values yet.

3.2 Microstructure of the films

Figure 3 shows cross sectional FE–SEM micrographs of the films prepared using alkoxide and acetate solution and fired at 600°C. Both films were deposited three times. The thickness of the film was about 150 and 100 nm, for films from alkoxide and acetate, respectively. The grain size of the films was almost the same at 30–50 nm. There was little difference due to the starting reagents. Both films seemed to be very dense and no pores were distinguishable. The SEM observation of the film suggested less porosity than that estimated using the refractive index, above. This is mainly due to an oversimplification on the estimation of porosity using the refractive index, or ignoring the effect of dispersion of the index.

TEM micrographs of the thin section prepared using the alkoxide derived sol are shown in Fig. 4. Micrographs of the crushed fragment are shown in Fig. 4(a). Those of ion-thinned and carbon coated section are shown in Fig. 4(b). TEM micrographs of a crushed fragment of the film prepared using the acetate derived sol are shown in Fig. 5. The microstructure was quite different from that observed by SEM. The TEM observation revealed that the films consisted of three deposited layers. The grains of 30-50 nm size, which was identified by SEM, were not obvious. Also, small regions of 10 nm or less in size, which were not observed by SEM, were recognized. The extent of lattice fringe of the high magnification photos, shown in Figs. 4(a) and 5, and a dark field image, in Fig. 4 (b), clarified the grain of 30-50 nm, which was observed by SEM. The structure, i.e., TEM contrasts of less than 10 nm inside 30-50 nm size grains, was independent of the starting reagents and preparation methods of thin sections, though the coated carbon layer on the ion-thinned section somewhat obscured recognition of the 10 nm size region. It was concluded that the small regions revealed crystalline inhomogeneity inside the grains. Another possibility of this TEM contrast of about 10 nm was the existence of pores inside the grain. However, the low porosity of the film contradicts this idea.





(b)

Fig. 4. TEM micrographs of (a) crushed ZrO_2 films from alkoxide derived sol, deposited 3 times and heated at 600°C, and (b) ion-thinned ZrO_2 section from alkoxide derived sol, deposited 3 times and heated at 600°C.



Fig. 5. Micrographs of crushed ZrO_2 film from acetate derived sol, deposited 3 times and heated at 600°C.

The electron beam diffraction patterns of the ZrO_2 sections were very interesting. The patterns from the crushed fragment and ion-thinned section are shown in **Fig. 6**. The ZrO_2 film was prepared using the alkoxide derived sol. Calculated *d*-spacings from the diffraction rings are listed in **Table 1**, together with JCPDS data of the tetragonal and monoclinic phases. The diffraction pattern from the ion-thinned section was identified as the tetragonal phase, whereas that from the crushed fragment was the monoclinic phase. In the Fig. 6, the diffraction patterns of the film prepared using alkoxide are



Fig. 6. Electron beam diffraction patterns of ZrO_2 films from alkoxide derived sol: (a) ion-thinned section, (b) crushed fragment.

 Table 1.
 Electron Diffraction Patterns from Ion-Thinned Section and Crushed Fragment, and Corresponding JCPDS Data

Electron Diffraction				hkl and d-spacing (PDF files No.)			
Ion-thinned		Crushed		Monoclinic (37-1484)		Tetragonal (50-1089)	
#	d / Å	#	d / Å	hkl	d / Å	hkl	d / Å
		1	3.62	110, 010	3.70, 3.64	-	-
		2	3.09	111	3.16	-	-
1	2.95	3	2.84	111	2.84	011	2.95
2	2.58	4	2.59	200, 020, 002	2.62, 2.61, 2.54	002, 110	2.58, 2.54
3	2.13	5	2.17	112, 201, 121	2.21, 2.19, 2.18	012	2.10
		6	2.02	211, 202	2.02, 1.99	-	-
4	1.81	7	1.81	220, 022, 221	1.85, 1.82 1.80	112, 020	1.81, 1.80
		8	1.70	003	1.69	-	-
5	1.55	9	1.55	131, 203	1.55, 1.54	013, 121	1.55, 1.54

shown, and that from the crushed fragment of the acetate derived film shows the same result. The tetragonal ZrO_2 film was transformed into monoclinic by crushing during preparation for TEM observation, or the stress-induced transformation of metastable tetragonal to stable monoclinic phase occurred. The diffraction pattern, unfortunately, was not accurate enough to evaluate the percentage of transformed grains.

The transformation from metastable tetragonal to stable monoclinic is well recognized as a toughening mechanism of partially stabilized zirconia ceramics.³⁾ Though the stressinduced transformation of pure ZrO_2 thin film does not seem to be extraordinary, direct observation of the transformation is rare and is thus presented here. These results suggest that the stress-induced toughening mechanism may be applicable to pure and small-grained ZrO_2 ceramics. As to the crystalline inhomogeneity inside the grain, a monoclinic variant in the tetragonal grain was not the origin of the contrast because such contrast also exists in the tetragonal grains.

Usually fine ZrO_2 powder remains as tetragonal metastable phase when the size is less than about 20 nm. The grain size of the present film is larger than 30 nm and exceeds the critical size as shown in the SEM photographs in Fig. 3. Regarding the stabilizing effects of such large grains, constraint by the substrate and crystalline inhomogeneity of less than 10 nm inside the grain can be deduced. Further investigations are now in progress.

4. Conclusion

The ZrO_2 films were successfully prepared using zirconium alkoxide and also zirconium acetate. The films using the

acetate and alkoxide as starting reagents were crystallized as the tetragonal phase by heating at 400°C and 500°C, respectively. The transformation of the tetragonal phase into the monoclinic phase by crushing and stress-induced transformation was confirmed. The films exhibited fine 10 nm inhomogeneity inside grains of about 30–50 nm.

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