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XPS analysis of surface layer of sol-gel-derived PZT thin films

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Abstract

The crystalline phase and composition of sol-gel-derived lead zirconate titanate (PZT) thin films were successfully analyzed by X-ray photoelectron spectroscopy (XPS). The crystalline phase was determined from deconvolution of Zr3d photoelectron spectra, in which the binding energy reflected the distance from the neighboring ions. The composition was estimated by using the calibration equations, which were induced from the relation between the photoelectron intensities and the molar ratio of ions. The surface layers with a thickness of several tens nm were found to be different crystallographically and compositionally from the inside of the films; they were composed of the rhombohedral phase, and Pb and Ti contents in them were less than those from the inside. The energy dispersive X-ray spectroscopic (EDS) analysis of the cross-section of the thin films confirmed for these findings.

Keywords: PZT; Sol-gel process; Spectroscopy; Surfaces; X-ray methods

1. Introduction

Lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT) thin film is one of the potential candidates for a cantilever of a scanning probe microscope, an infrared imaging device and a non-volatile ferroelectric memory. Among different film formation techniques,[1–3] a sol-gel process has many advantages such as compositional controllability and homogeneity. Nano-scale chemical and structural fluctuations of the thin film that occur due to hydrolysis of the starting material and vaporization of the organic component will possibly produce this effect on the ferroelectric properties of sol-gel derived PZT thin films.

We have reported that the crystalline phase and composition of PZT ceramics were possibly determined from the deconvolution of Zr3d photoelectron spectra[4] and calibration equations,[5] respectively, by X-ray photoelectron spectroscopy (XPS).[6,7] In this study, the surface crystallographic and compositional fluctuations along the depth direction of PZT thin films that were prepared via a sol-gel process have been investigated using XPS with the argon ion etching method.

2. Experimental

2.1. Sample preparation

Bulk PZT samples were prepared by conventional sintering; a mixture of lead oxide, zirconium carbonate and titanium oxide powders was compacted and sintered at 1230 °C. In the starting powders, 10 mol% of excess lead oxide was added to conteract the loss during sintering. The sintered samples were cut and the cut surfaces were polished for analysis by XPS. The compositions of the bulk samples were $PbZr_{0.80}Ti_{0.20}O_3$, $PbZr_{0.53}Ti_{0.47}O_3$ and $PbZr_{0.20}Ti_{0.80}O_3$, which were used as compositionally and crystallographically homogeneous samples.

PZT thin films were prepared through a sol-gel process. Lead acetate, zirconium tetra-*iso*-propoxide, titanium tetra-*iso*-propoxide and acetyl acetone were dissolved in ethyl alcohol, and then the solution was refluxed at 78 °C. Corning 7959 glass substrate was dipped into the solution and dried at 115 °C. After repeating the dipping and drying ten times, the substrate was heated at 350 °C for 10 min and then at 600 °C for 2 h. The nominal composition of the thin films prepared were Pb/Zr/Ti = 100/80/20 (No. 1), 100/53/47 (No. 2), 120/30/70 (No. 3), 120/53/47 (No. 4) and 140/53/47 (No. 5). The thin films were confirmed to be the desired PZT polycrystals by an X-ray diffraction analysis.

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2.2. XPS analysis

Photoelectron spectra of Pb4f, Zr3d and Ti2p were obtained using an X-ray photoelectron spectrometer (Shimadzu-Kratos XSAM800pci) equipped with Ar^+ ion etching gun. The probe X-ray and its power were MgKα line and 150 W. The current density of the Ar ion beam was about 200 $\mu A\ cm^{-2}$, which provided an etching rate of approximately 1 nm/min. All the photoelectron spectra obtained were smoothened and their area intensities determined. The binding energy shift originated from a charge-up was corrected by referring to the C1s peaks of hydrocarbons at 285.0 eV.

The Zr3d spectra were deconvoluted using a Gaussian fitting program into two pairs of elemental profiles: [A] at the binding energies of 182.3 ± 0.2 and 184.8 ± 0.2 eV (assigned for 3d5/2 and 3d3/2, peak intensity ratio 3:2) and [B] at 183.7 ± 0.2 and 186.0 ± 0.2 eV. The crystalline phase was then determined from the area ratio [B]/[A].[4] The [B]/[A] 0, 0.3 and 0.6 corresponded to the rhombohedral phase, the morphotropic phase boundary (abbreviated as MPB hereafter) and the tetragonal phase, respectively.

The composition of the thin films was analyzed using calibration Eqs. (1) and (2) that were obtained as reported elsewhere.[5]

$$X_{Zr}/(X_{Zr}+X_{Ti}) = 1.004\cdot I_{Zr}/(I_{Zr}+1.9\cdot I_{Ti}) - 0.113 \qquad (1)$$

$$X_{Pb}/(X_{Zr}+X_{Ti}) = 0.152\cdot I_{Pb}/(I_{Zr}+1.9\cdot I_{Ti}) + 0.377 \qquad (2)$$

where I_{Pb}, I_{Zr} and I_{Ti} represent XPS intensities of Pb4f, Zr3d and Ti2p, and X_{Pb}, X_{Zr} and X_{Ti} molar ratios of Pb, Zr and Ti atoms in PZT thin films. The composition along the depth direction was corrected after considering the difference of etching rates for Pb^{2+}, Zr^{4+} and Ti^{4+}.

The cross-sections of the thin films were analyzed by energy dispersive X-ray spectroscopy (EDS) to confirm the XPS results.

3. Results and discussion

3.1. Influence of argon ion etching on XPS analysis

The spectral and compositional changes in the XPS analysis through the ion etching were investigated using the sintered samples, of which both the crystalline phase and the composition must be invariable along the depth direction. The determination of the crystalline phase was found to be possible without any correction, since the argon ion etching bore little influence on the Zr3d spectra. The circle plots in Fig. 1 show the compositional changes in terms of Pb/(Zr + Ti) and Zr/(Zr + Ti) atomic ratios with the etching time. The Pb/(Zr + Ti) ratio abruptly decreased at an initial stage of etching (from 0 to 50 min), indicating that Pb was dominantly sputtered comparing to Zr and Ti. The Zr/(Zr + Ti) ratio increased slightly from 0 to 30 min. These are apparent changes that resulted due to the differences of etching rates among the ions. Therefore, the analyzed composition can be corrected by multiplying the coefficients that were deduced from these results. The correction coefficients are shown as solid lines in Fig. 1. Since the reliability of the calibration equations was ±1%[5] and the systematic error of the correction coefficient among the different compositions was 3%(±1.5%), the reliability of the composition determined by this method was estimated to be ±3%.

3.2. Crystalline phase of the film surface

From the XPS measuremetnts of the surface for all the thin films, no significant variation in Pb4f, Zr3d or Ti2p spectrum that would have originated from PbO,[8] ZrO_2, $PbZrO_3(OH)_{3-x}$,[9] TiO_2 or $PbTiO_3$[10] relevant to PZT was observed. Fig. 2 shows the changes of the Zr3d spectra and their deconvoluted profiles with the etching time for the thin films Nos. 1, 2 and 3, respectively. The crystalline phase at the etching time of 0 min was rhombohedral ([B]/[A] = 0) for all the films, indicating that the outermost surface of the thin films was in the rhombohedral phase. As the etching time increased, the

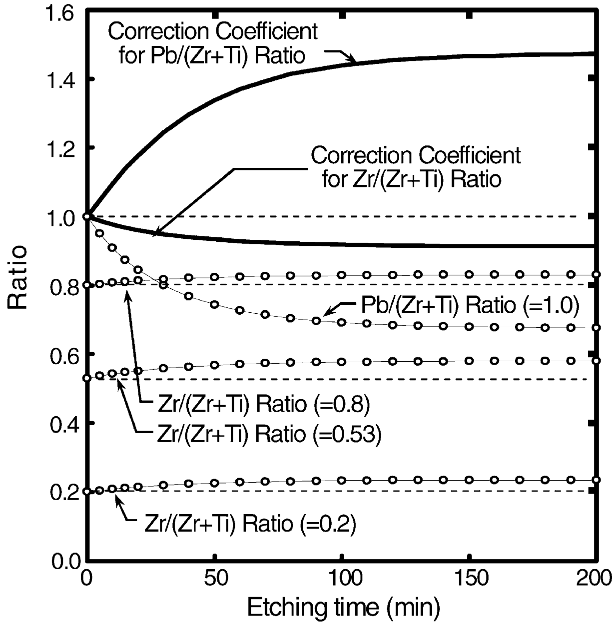

Fig. 1. Changes in the analyzed compositional ratios with increasing etching time for homogeneous PZT samples and the deduced correction coefficients.

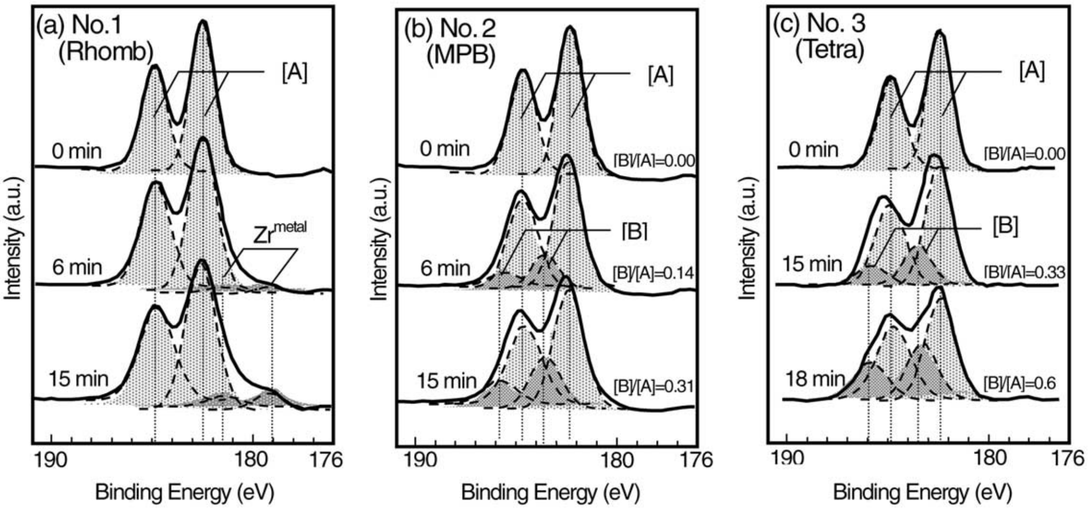

Fig. 2. Zr3d spectra and their deconvoluted profiles for the sol-gel-derived PZT thin films at various etching times.

spectra varied, and finally reached to the phases that were expected from the phase diagram[11] of their nominal compositions. For the thin films of Nos. 2 and 3, the [B]/[A] ratios monotonously increased before they reached to the constant values. It was concluded that the surface layer of 15–20 nm thick, which contained some of the rhombohedral phase, existed in the thin films. At the etching times of 6 and 15 min for the thin film of No. 1, another pair of the deconvoluted profiles at the binding energies of 188.9 and 181.4 eV appeared (Fig. 2(b)). This pair was assigned as metallic zirconium, suggesting that some of the Zr^{4+} ions were reduced to Zr^0. However, the [B] pair did not appear before and after the ion etching; that is, both the surface and the inside are in the rhombohedral phase.

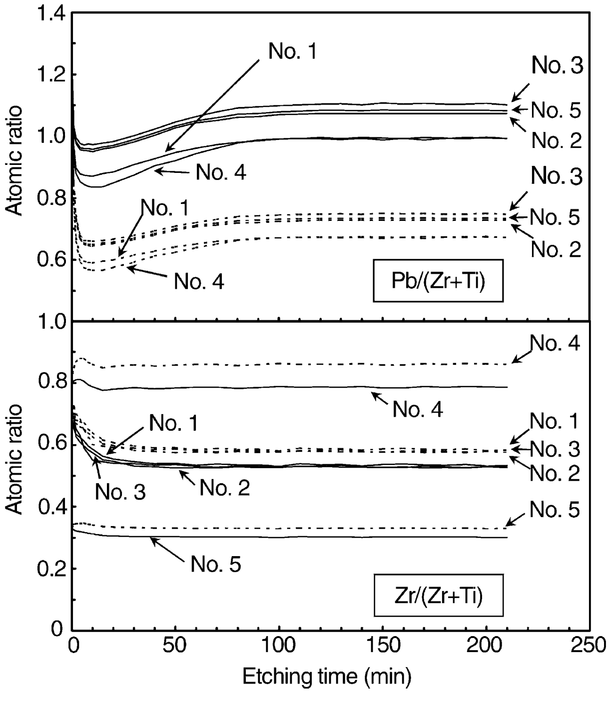

Fig. 3. Compositional variations at the surface of the sol-gel-derived PZT thin films as a function of etching time. Dotted lines denote the compositions that were obtained based on Eqs. (1) and (2), and solid lines denote the compositions after being corrected based on the correction coefficients in Fig. 1.

3.3. Composition of the film surface

As shown in Fig. 3, the Pb/(Zr + Ti) ratios at an etching time of less than 60 min and the Zr/(Zr + Ti) ratios at less than 30 min, corresponding to the surface regions less than 60 and 30 nm, respectively, were relatively high compared with that of the inside. These results showed a deficit of Pb and Ti in the surface of as-prepared thin films. Further inside, the compositional ratios became constant.

The crystalline phases and compositions for both the surfaces and the inside of the thin films are listed in Table 1. The Pb/(Zr + Ti) ratios were less than nominal ones for the excess-lead added thin films (Nos. 3–5); the Pb content was nearly equal to the sum of the Zr and Ti contents despite the excess addition. It was speculated that the excess Pb component could not be included at the crystal lattice and were excluded from the film surface via a liquid or gas phase during the heating treatment. A small part of the excess Pb component may exist at the grain boundary region. It was noteworthy that an intimate relationship between the crystalline phase and the composition was elucidated from both the results for the surface and the inside of the film, that is, the rhombohedral, MPB and tetragonal phases corresponding to $Zr/(Zr + Ti) > 53/47$, $Zr/(Zr + Ti) = 53/47$ and $Zr/(Zr + Ti) < 53/47$, respectively.[11]

Table 1
Crystalline phase and composition of sol-gel derived PZT thin films. The compositional notation, x/y/z, represents the atomic ratio of Pb, Zr and Ti

No.	Nominal composition	XPS results			
		Crystalline phase		Composition	
		Surface (nm)	Inside	Surface (nm)	Inside
1	100/80/20	Rhomb. (0–15)	Rhomb. (15)	83-87/80/20 (0–20)	98/77/23 (70)
2	100/53/47	Rhomb. + MPB (0–15)	MPB (15)	87-91/69/31 (0–30)	99/53/47 (70)
3	120/30/70	Rhomb. + Tetra. (0–20)	Tetra. (20)	97-99/35/65 (0–20)	106/28/72 (70)
4	120/53/47	Rhomb. + MPB (0–15)	MPB (15)	95-98/70/30 (0–30)	107/53/47 (70)
5	140/53/47	Rhomb. + MPB (0–15)	MPB (15)	98-100/70/30 (0–25)	109/53/47 (70)

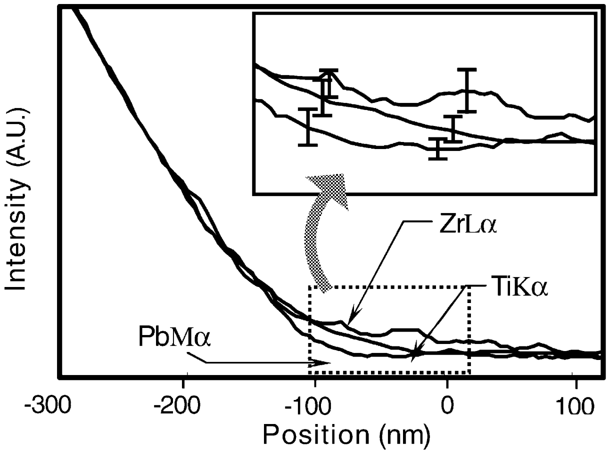

Fig. 4. Changes in signal intensities for Pb, Zr and Ti in EDS analysis along the cross-section of the sol-gel-derived PZT thin film. The horizontal axis expresses the depth from the film surface as a minus distance. The error bars denote the ranges of intensities observed for five repeted analyses.

According to the EDS line analysis for the thin film of No. 2 (Fig. 4), X-ray intensity of Ti is lower than that of Zr from 0 nm (utmost surface) to about −50 nm (50 nm inside from the surface), and the intensity of Pb is lower than that of Zr from 0 nm to about −100 nm. This result gave a confirmation for the above-mentioned XPS results.

4. Summary

The sol-gel-derived PZT thin films were analyzed by XPS together with an Ar ion etching method. Surface layers with thicknesses of several tens nm were found, of which Pb and Ti contents were lower than those from the inside and the crystalline phase was rhombohedral. The novel methods are very effective in the characterization of PZT thin films.

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