

Preparation of Oriented PZT Films via Sol-Gel Method and Their Dielectric and Piezoelectric Properties

Yutaka Ohya, Tomoharu Tamakoshi, Takayuki Ban and Yasutaka Takahashi

Department of Materials Science and Technology, Gifu University

Yanagido 1-1, Gifu 501-1193, Japan

Fax: 81-58-230-1893, e-mail: ohya@apchem.gifu-u.ac.jp

Oriented PZT films with composition of $\text{Pb}_{1.3}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ were prepared by a sol-gel, spin-on procedure on Pt/Ti/SiO₂/Si substrate. The coating solution was prepared using Ti and Zr alkoxides and lead acetate with diethanolamine. The coated film was fired at 700°C. The coating and firing cycle was repeated 5 to 7 times to obtain the PZT films of about 1 μm thick. The TiO₂ and PbO buffer coatings were applied between the substrate and first PZT coating to prepare random and <100> oriented films, respectively, while <111> oriented films resulted without the buffer layer. The thinner PbO coating resulted in the higher extent of the <100> orientation, though moderate thickness of TiO₂ layer was necessary to form the random PZT film. The resultant films were dense and the grain grew in a columnar manner. Dielectric constant of the films ranged from 1050 to 1500 depending the orientation. The higher value was obtained for <100> oriented film. The present films exhibited typical ferroelectric nature of P-E hysteresis. The resultant Pr value was ranged from 13 to 22 μC/cm² and the highest was obtained for <111> oriented film. The piezoelectric displacement and a 'butterfly' type displacement due to a domain reorientation of the prepared films could be detected.

Key words: PZT film, orientation, dielectric properties, piezoelectric properties

1. INTRODUCTION

Lead zirconate titanate (PZT) ceramics are widely used for their superior dielectric, ferroelectric and piezoelectric properties¹⁾. Among their very large application fields, the ferroelectric and dielectric properties of films are extensively studied. The very attractive properties of piezoelectricity of the films also began to be reported. There are two categories of the measurement of the piezoelectricity, displacement of the films on applying voltage and charge on loading^{2,3)}. The displacement of the film was measured by means of a laser interferometer^{4,5)} and an atomic force microscope⁶⁾.

The preparation of PZT film with a preferred orientation was another subject of interest. A sol-gel route has an advantage of easy fabrication of <111> preferred films on a <111> platinized silicon wafer. In the same manner, <100> oriented films were also fabricated by the tailored thermal treatment⁷⁾ and buffer layer⁸⁾. After the analysis of Chen^{8,9)}, the <111> and <100> oriented films were well understood and dielectric and ferroelectric properties of the oriented PZT films were reported^{7,10)}.

Since the solid solution series of PZT are anisotropic, dielectric and piezoelectric properties are also anisotropic. The PZT single crystal is not available now, the systematic investigation of these values have been calculated only by the tensor operations by Du et al.^{11,12)} For the further application of PZT films, the preparation of oriented films and evaluation of their dielectric and piezoelectric properties are of a great importance.

In this paper, we presented our results on investigation about preparation of 1 μm thick PZT films and their dielectric and piezoelectric properties.

2. EXPERIMENTAL

The PZT film was prepared via a sol-gel method¹³⁾. Starting reagents used were (CH₃COO)₂Pb·3H₂O, (C₃H₇O)₄Ti, and (C₄H₉O)₄Zr. They are dissolved into *i*-propanol with an equimolar amount of diethanolamine (DEA) to (Zr plus Ti) as a stabilizing agent. A composition of the solution of PZT was $\text{Pb}_{1.3}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and the concentrations were 0.5 and 0.75 mol/L. In order to control the film orientation, a buffer layer of TiO₂ or PbO was examined. The sol for TiO₂ coating was prepared from (C₃H₇O)₄Ti and DEA as an *i*-propanol solution of 0.1 to 0.5 mol/L. The sol of 0.1 to 0.5 mol/L for PbO coating was also prepared using (CH₃COO)₂Pb·3H₂O and DEA.

The coating was conducted by a spin-on method on a <111> platinized silicon wafer. After deposition, the substrate was dried followed by rapid heating at 700°C for 30 min. This procedure was repeated 5 to 7 times to obtain the film with about 1 μm thickness. The random and <100> oriented films were fabricated by using the buffer layer of TiO₂ and PbO, respectively.

The microstructure of the resultant films was observed by an SEM and the crystalline orientation was examined by an XRD.

The dielectric and ferroelectric properties of the films were measured by an impedance analyzer (HP-4192A) and a Sawyer-Tower circuit at 60Hz, respectively. After poling at room temperature, piezoelectric displacement was measured using a micro-laser interferometer (DS-80, Canon Inc., Tokyo, Japan). A resolution of the micro-laser interferometer used is 0.08 nm and a size of the measuring spot is 10 x 20 μm according to its

instruction manual. The film was placed on a metal rod (1 mm in diameter) and a ceramic ball (1 mm in diameter), and the measuring spot was set just above the ball. Therefore a bending effect of the substrate on the measurement could be minimized.

3. RESULTS AND DISCUSSION

3.1 Preferred orientation

The $\langle 111 \rangle$ orientation of the PZT film could be easily obtained by rapid heating the film as widely observed. The present film was about 200 nm for each deposition using 0.75 mol/L sol. And the 5 depositions resulted in 1 μm thick PZT films. The $\langle 100 \rangle$ orientation was achieved by PZT deposition on an internal PbO layer. Figure 1 represented the XRD profiles of PZT films fabricated on the PbO layer from different sol concentrations, 0.1 to 0.5 mol/L. Though the film exhibited not a perfect $\langle 100 \rangle$ orientation, the excellent $\langle 100 \rangle$ orientation resulted when the thinner PbO was deposited using the sol of 0.1 mol/L. This film was used in following experiments. This deposition thickness of PbO layer expected to be about a few ten nanometers or thinner and the result corresponded to the description of the previous report. This $\langle 100 \rangle$ oriented film was about 0.8 μm by seven depositions using the sol of 0.5 mol/L.

A random orientation of PZT film also fabricated using TiO_2 as a buffer layer. In this case thinner coating about 10 nm thick caused the $\langle 111 \rangle$ orientation of the film, as shown in Fig. 2. By increasing thickness of the TiO_2 layer to 20-30 nm using the sol of 0.25 mol/L, the random orientation film could be formed. The XRD peak intensity ratios of PZT on TiO_2 buffer layer from the sols of 0.25 and 0.5 mol/L were almost the same as those of a JCPDS card of random orientation PZT. The film thickness was about 1 μm by 5 depositions. The used film for the following experiment was that formed on TiO_2 from 0.25 mol/L sol.

3.2 Microstructure of the films

SEM microphotographs of the films were shown in Fig. 3. The three films were dense and a columnar structure of PZT was observed. An array of pores along each deposition layer was obvious. We have already pointed out that repetition of thin film deposition sometimes caused the columnar structure¹⁴. In order to examine the relation of the coating thickness and the columnar structure, a single thick coating onto the 1 μm random columnar PZT was conducted. The conditions for the single thick coating were from a sol of 1.5

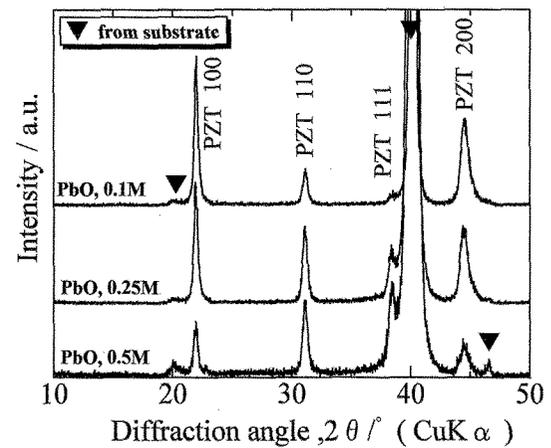


Fig.1 XRD profiles of $\langle 100 \rangle$ oriented PZT films on thin PbO buffer layer.

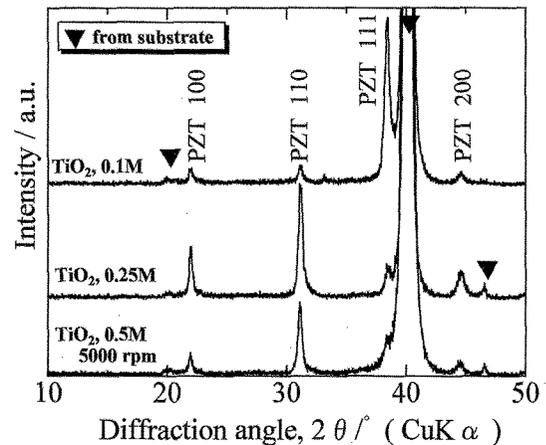


Fig.2 XRD profiles of random oriented PZT films on thin TiO_2 buffer layer.

mol/L, low revolution speed of spin-on, 1000 rpm, and rapid heating at 700°C.

Figure 4 is the resultant SEM micrograph of the film. A rather porous layer with randomly oriented grains covered the columnar dense layer. The thick coating, about 1.2 μm in this case, was not columnar and porous. The repetition of thin coatings, about 200 nm in this case, was very effective to obtain the dense and columnar structure.

The buffer layers were not obvious in all films,

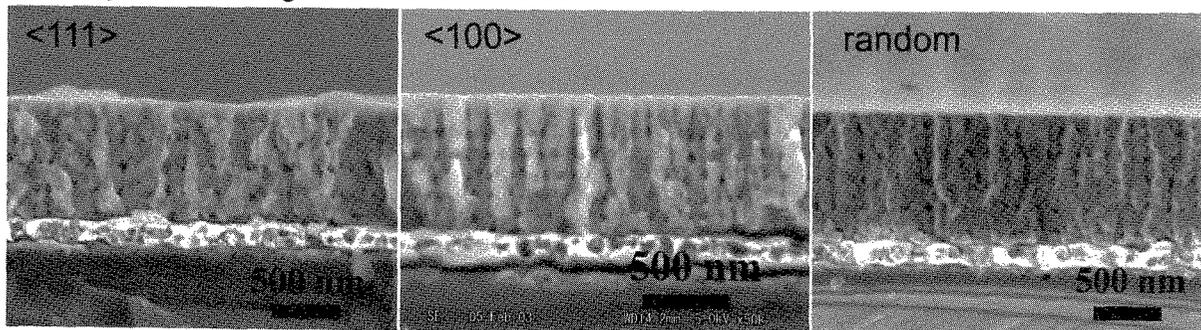


Fig.3 FE-SEM microphotographs of PZT films.

because the layers were thin and/or reacted to form solid solutions with PZT.

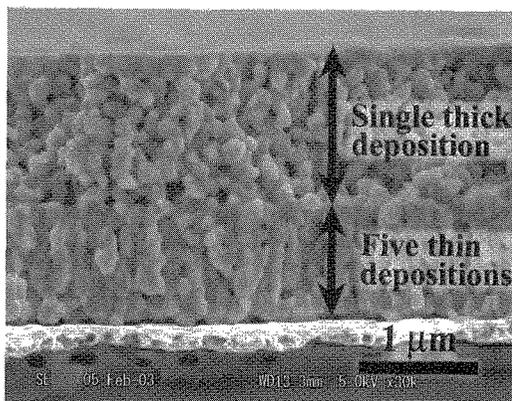


Fig.4 FE-SEM micrograph of film with thin and thick multi-depositions.

3.3 Dielectric and ferroelectric properties of the films

The polarization-voltage hysteresis curve of the <100> oriented film was shown in Fig. 5. The film and the other films exhibited a typical saturated hysteresis loop and the ferroelectric property of the film was confirmed. Table I represent the typical values of the dielectric and ferroelectric properties.

The dielectric constant of <100> orientation film, about 1500, was larger than that of <111> orientation. And remanent polarization of <111> direction was larger than that of <100> direction. This tendency was the same as report of Aoki⁷⁾. But the present dielectric values were larger. The dielectric constant of the thin and thick multi-deposition film, sample in Fig. 4, was

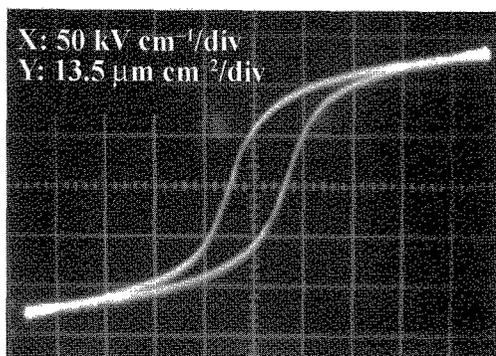


Fig.5 Polarization-voltage hysteresis curve of <100> oriented film at 60 Hz.

Table I Dielectric (@ 1 kHz) and ferroelectric (@ 60 Hz) properties of the films.

Orientation	ϵ_r	$\tan\delta$	P_r $\mu\text{C}/\text{cm}^2$	E_c kV/cm
<111>	1200	0.05	22.3	35.5
<100>	1500	0.08	15.6	34.0
random	1050	0.03	17.2	34.0
random*	650	0.03	13.2	41.0

*: thin and thick multi-deposition, sample in Fig. 4.

low and dielectric constant of the porous layer was evaluated as 490 assuming a series connection of capacitors of the dense ($\epsilon_r = 1050$) and porous layers. The porosity of the film reduced the dielectric constant to half of the dense film. Our present dense films fabricated by repetition of thin depositions had a large value.

3.4 Piezoelectric properties

The displacement of the film was measured by the micro-laser interferometer against an application of AC voltage. For the PZT films poled less than 5 kV/mm, no displacement was observed, when amplitude of AC voltage was less than 5 V_{p-p} , which was almost the same as the E_c value of the PZT films at its peak. The considerable in-phase sinusoidal displacement was observed when the poling field was 5 kV/mm or the applied AC voltage was larger than 5 V_{p-p} . Applying AC voltage of 5 V_{p-p} and larger, the displacement became clear, even the film was not poled.

Figure 6 showed results of the displacement of dense and randomly oriented film, which was poled at 10 kV/mm for 30 min at RT. The displacement increased as increasing the applied AC voltage. When the amplitude of AC voltage became as large as 10 V_{p-p} , the displacement sinusoid of the film became distorted and, at 15 V_{p-p} , the displacement wave showed a double in the frequency. At this voltage a domain switching in the ferroelectric PZT film occurred. And at AC voltage of 20 V_{p-p} , the amplitude of displacement became larger. The beginning of the distorted sinusoidal was almost the same among the films with <111>, <100> and random

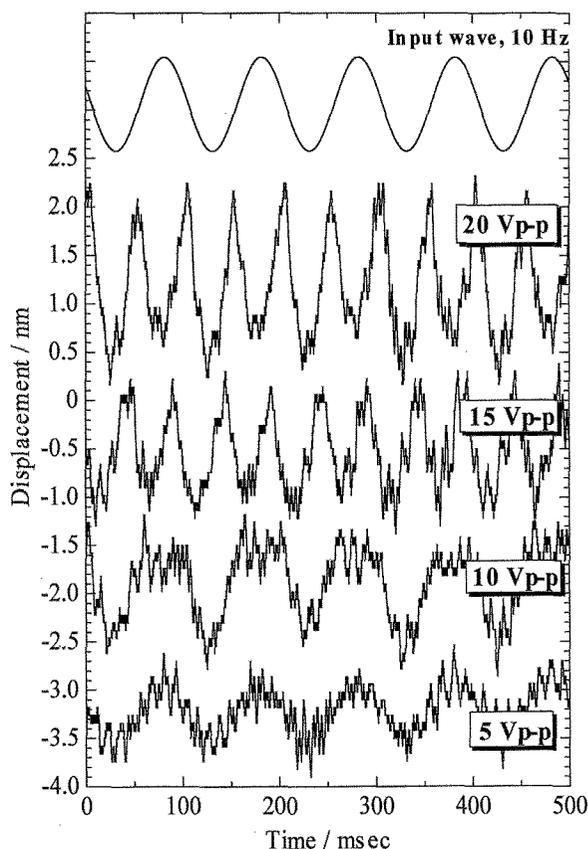


Fig.6 Displacement of random and dense oriented film measured at 10 Hz.

orientation, about $10 V_{p-p}$; this voltage was about double of the E_c values shown in Table I.

At the AC voltage application of $5 V_{p-p}$, the displacements of the PZT films, which were poled by 10 kV/mm, were calculated with some error as 140, 130 and 120 pm/V for $\langle 100 \rangle$, $\langle 110 \rangle$ and random orientation films, respectively. Although the order of the values corresponded to the calculated data by Du et. al.^[12], precise measurements were required before saying the validity.

Figure 7 showed the displacement against the applied AC voltage of $20 V_{p-p}$. A butterfly type character due to the domain switching was obvious for all specimens. The hysteresis of $\langle 100 \rangle$ oriented film was rather thin. When the measurement was carried out increasing the applied voltage from 5 to $20 V_{p-p}$, the butterfly type hysteresis became clear at $15 V_{p-p}$. This value corresponded with the result shown in Fig. 6. A direction of the butterfly was the same even when the voltage increased. And a bending effect of the substrate was not appeared by the supporting substrate with a ceramics ball, although Iijima^[9] indicated the bending effect of substrate during the displacement measurement using AFM.

For $\langle 100 \rangle$ oriented film and also $\langle 111 \rangle$ film, the butterflies were not symmetrical. The non-symmetrical curves were clearly observed when the lower AC voltage was applied. The effect of poling remained after the application of much higher voltage than the value of E_c in Table I.

4 CONCLUSION

The $\langle 111 \rangle$ and $\langle 100 \rangle$ oriented PZT films as well as random orientation were fabricated via the sol-gel spin-on method on platinumized Si wafer. The resultant films were very dense and columnar due to the repetition of thin (≈ 200 nm) coatings. On the other hand, the thick deposition caused the porous and random orientation. The measured ϵ_r values were large, about 1500 for $\langle 100 \rangle$ direction owing to the dense and columnar structure of the film.

Piezoelectric displacement of the film was measured using the micro-laser interferometer. When the applied AC voltage was about the same as the E_c value, the in-phase displacement was obvious. When the applied AC voltage became double of the E_c , the displacement curve distorted. And finally domain switching, or butterfly type displacement-electric field hysteresis curve, could be observed.

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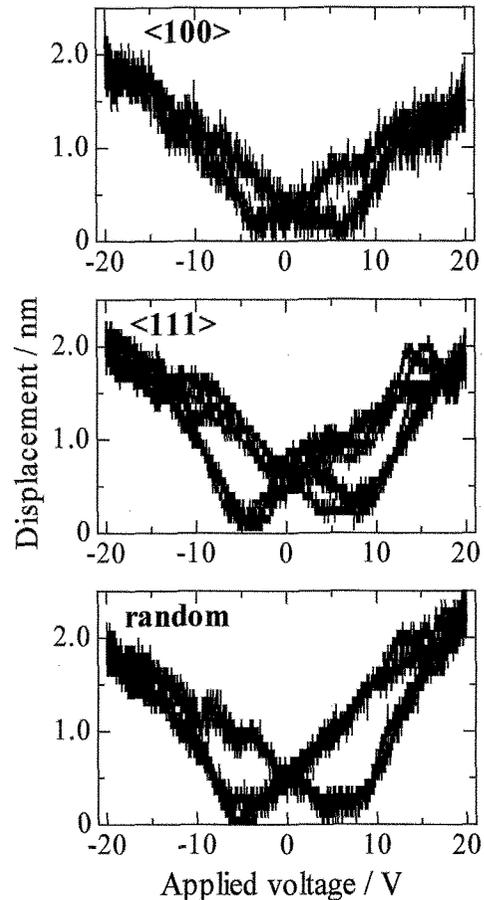


Fig.7 Displacement-voltage hysteresis curves measured at 10 Hz.

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