

## Preparation of Pb(Zr,Ti)O<sub>3</sub> thin films with graded composition profiles by RF-sputtering

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Pb(Zr,Ti)O<sub>3</sub> (PZT) thin films with graded composition profiles were prepared by multi-target RF-sputtering aiming to enhance the piezoelectric properties by active domain motion. PZT thin films were epitaxially grown on (100)Pt/(100)MgO substrates and their composition was modulated from Zr/Ti=30/70 to 53/47 or from 53/47 to 30/70. XRD measurements revealed that Pb(Zr<sub>0.70</sub>Ti<sub>0.30</sub>)O<sub>3</sub> thin films with uniform composition showed clear *a/c* domain structure, while Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub> films showed perfect *c*-axis orientation. In the case of the graded compositional PZT films, clear *a/c*-axis orientation was observed, suggesting the films are composed of modulated domain structure along the thickness. The transverse piezoelectric properties were calculated from the displacement of the unimorph cantilevers. The PZT thin films with the graded composition profiles show larger piezoelectricity than that of uniform compositional PZT films. Furthermore, for the graded compositional PZT films, piezoelectric coefficient of *e*<sub>31</sub> gradually increased with increasing applying voltage, indicating the domain motion is superimposed on the lattice motion.

Key words: PZT, ferroelectric, thin films, graded composition

### 1. INTRODUCTION

In recent years, Pb(Zr,Ti)O<sub>3</sub> (PZT) thin films have attracted considerable attention as functional MEMS materials for microsensors and microactuators since they have superior ferroelectric, dielectric, pyroelectric and piezoelectric properties. Especially, for the development of microactuators, the piezoelectric thin films with high transverse piezoelectric coefficient are required to realize low-voltage drive microactuators.

Since piezoelectric strain is originated with both lattice motion and domain motion which are strongly related to the crystalline structure, it is expected that the piezoelectricity of thin films can be modified by optimization of crystalline structure. In the case of the PZT ceramics, it is well known that the crystalline structure depends on Zr/Ti ratio, and composition of morphotropic phase boundary (MPB) shows the largest piezoelectricity. However, our previous study revealed that the crystalline and domain structures of the PZT films, especially epitaxial films, are much different with bulk ones.<sup>[1,2]</sup>

In this study, we prepare compositionally graded PZT films to enhance piezoelectricity, especially by promoting domain motion. Graded ferroelectric devices (GFD) have been intensively studied as tunable microwave capacitors.<sup>[3-5]</sup> In the case of epitaxial PZT thin films, graded composition of Zr/Ti ratio induces modulation of crystalline phase and domain structure, which may lead to promotion of active domain motion and enhancement of piezoelectricity. In this paper we report the deposition of epitaxial PZT films with graded Zr/Ti composition and their piezoelectric properties.

### 2. EXPERIMENTAL

#### 2.1 PZT deposition

PZT films were deposited by multi-target rf magnetron sputtering technique. Substrates used were (100)MgO single crystals, which were coated with (100)Pt about 0.1 μm in thickness as bottom electrodes. PZT films with the thickness of 1.0~1.5 μm were deposited under Ar/O<sub>2</sub>(=19.5/0.5) mixed gas atmosphere of 0.45 Pa, where the substrates were heated up more than 600 °C. Deposition was carried out by applying rf power of 200 W to each ceramic target of 3 in. in diameter. In this study, we use the PZT target with Zr/Ti ratio of 30/70 and 53/47, in which 20 mol% excess PbO was added for the compensation of the lead re-evaporation from the films. For the deposition of graded composition PZT films, rf power of each target is modulated during the film growth. We prepared two types of compositionally grade PZT films with Zr/Ti ratio from 30/70 to 53/47 (PZT(30→53)), or from 53/47 to 30/70 (PZT(53→30)), respectively, by modulating rf power as the composition is linearly changed. The compositional profiles of the films were illustrated in Fig. 1. For the comparison, the uniform composition PZT films of 30/70 and 53/47 were also prepared.

Crystalline structure of the prepared PZT films was investigated using 2θ/θ and 4-circle X-ray diffraction (XRD) measurements.

For the measurements of the electric properties, we deposited Pt top electrode of 0.3 and 0.5 mm in diameter

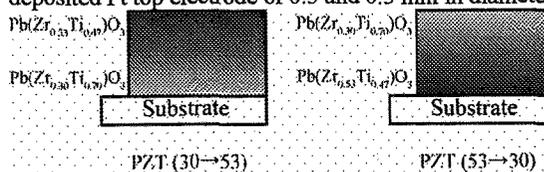


Fig.1. Schematic illustration of composition profiles

by sputtering. The relative dielectric constant of the films was measured by an impedance analyzer at a frequency of 1 kHz.  $P$ - $E$  hysteresis loops were also observed by a Sawyer-Tower circuit by applying sine-wave voltages at a frequency of 1 kHz. Remanent polarization ( $P_r$ ) and coercive field ( $E_c$ ) were measured from observed loops.

## 2.2 Piezoelectric properties

Transverse piezoelectric properties were evaluated from the tip displacement of the unimorph cantilevers composed of the PZT thin film and the MgO substrate.<sup>[6]</sup> Pt electrode with the thickness less than 10 nm was sputtered over the surface of the PZT films with covering one end of the beam for the contact of the Pt bottom electrode. Since a MgO single crystal is easily cleaved, we cleaved the MgO substrates to rectangular-shaped beams with the size of about 15mm  $\times$  2mm and clamped the edge of the beam using a small vise to prepare unimorph cantilevers. Schematic illustration of the measurement system is depicted in Fig.2. Piezoelectric vibration was generated by applying sine wave voltage between upper and bottom electrodes, and the tip displacement was measured using laser Doppler vibrometer. The frequency of input sine wave was 500–700Hz which was much lower than the mechanical resonant frequency of the cantilever. Since PZT films deposited by sputtering are inherently poled along downward direction from top electrode to bottom electrode, we applied negative unipolar voltage onto the top electrode without poling treatments.<sup>[7]</sup>

## 3. RESULTS AND DISCUSSION

### 3.1 Crystal structure of PZT thin films

The surface and cross-sectional morphology of the PZT films were observed by scanning electron microscopy (SEM) (S-4500 Hitachi). Very smooth structure could be confirmed in the absence of specific structure of grain boundary. Crystalline structure of the prepared PZT films was investigated using  $2\theta/\theta$  XRD measurements. The  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  (PZT(53)) films are oriented along  $c$ -axis and no other phase are observed. On the other hand,  $\text{Pb}(\text{Zr}_{0.30}\text{Ti}_{0.70})\text{O}_3$  (PZT(30)) films show clear  $a/c$ -axis orientation, and have  $a/c$  domain structure.

Figure 3 shows the SEM micrographs of the PZT films with graded composition profiles. Although grain-like structure is observed, the smooth surface was confirmed.

Figure 4 shows XRD patterns of the PZT films (30 $\rightarrow$ 53) and (53 $\rightarrow$ 30), respectively. From this result, we

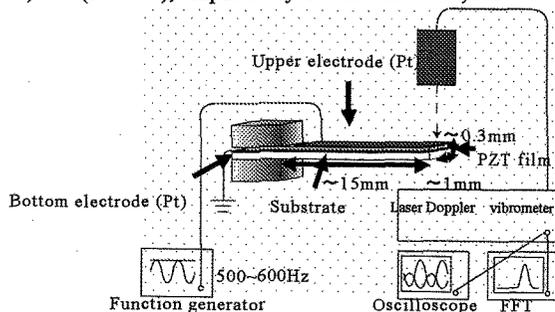


Fig.2. Schematic illustration of the measurement systems for transverse piezoelectric properties.

confirmed that the PZT thin films with both graded composition profiles have  $a/c$ -axis orientation like PZT(30).

Reciprocal space map of (204)PZT(30 $\rightarrow$ 53) obtained by the 4-circle XRD measurements is shown in Fig. 5. The measurements revealed that the graded compositional PZT films were epitaxially grown with  $a/c$  domain structure. Almost same pattern was observed in the inverse profile PZT(53 $\rightarrow$ 30). The lattice constants of  $a$ - and  $c$ -axes of both graded PZT films were calculated by the reciprocal space maps and these values were almost same independent of the direction of composition gradient.

### 3.2 Dielectric properties

The relative dielectric constant of the PZT films are listed in Table.1 The relative dielectric constants of all PZT films are relatively low due to the epitaxial growth along  $c$ -axis. In addition, the PZT(30) and (30 $\rightarrow$ 53), as well PZT(53) and (53 $\rightarrow$ 30) shows almost same values, respectively. This result implies that the dielectricity depends on the composition of the interface of the substrate.

The  $P$ - $E$  hysteresis loop of each film shows excellent ferroelectricity. For the uniform composition PZT(53), a remanent polarization ( $P_r$ ) is 35  $\mu\text{C}/\text{cm}^2$  and a coercive field ( $E_c$ ) is 85 kV/cm, while the graded PZT(30 $\rightarrow$ 53) shows  $P_r$  of 35  $\mu\text{C}/\text{cm}$  and a  $E_c$  of 100 kV/cm. On the other hand, for the  $\text{Pb}(\text{Zr}_{0.30}\text{Ti}_{0.70})\text{O}_3$  film and the PZT film (53 $\rightarrow$ 30), large fatigue was observed. On the surface of these films, we could observe clear cracks where the films are partially peeled off from the substrates. These cracks should cause the fatigue of the  $P$ - $E$  hysteresis loops.

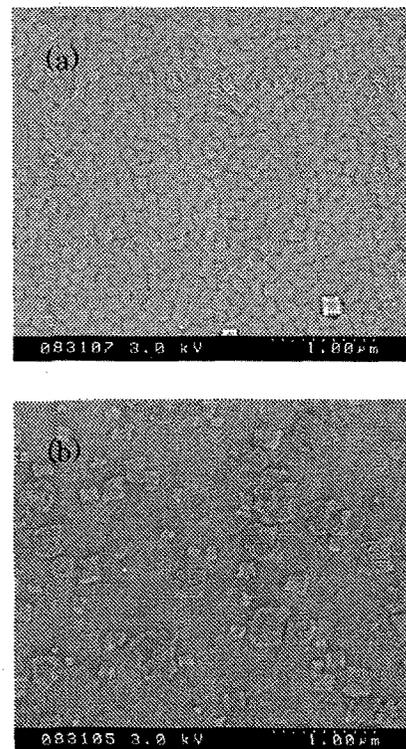


Fig. 3. SEM images of thin films with graded composition profiles (a) PZT(53 $\rightarrow$ 30) (b) PZT(30 $\rightarrow$ 53)

Table.1. The relative dielectric constant and dielectric loss of PZT thin films

composition	$\epsilon_r$	$\tan \delta$
PZT(53)	264	0.03
PZT(30)	170	0.31
PZT (30→53)	169	0.05
PZT (53→30)	208	0.03

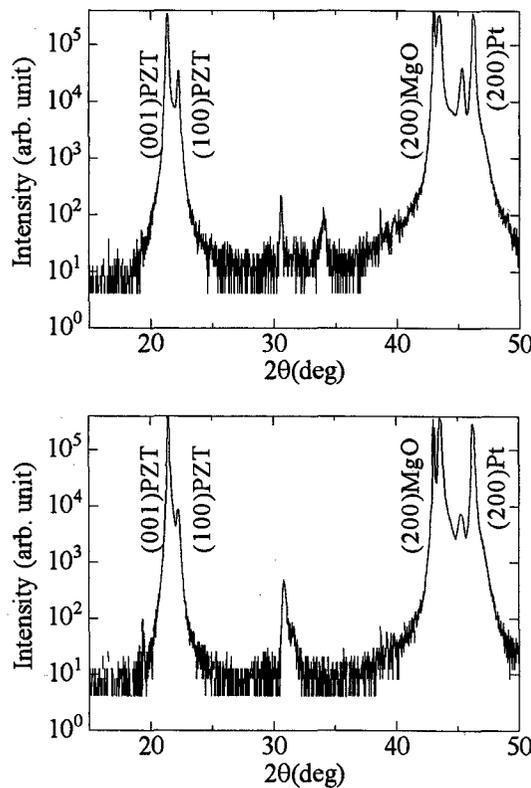


Fig.4. XRD patterns of thin films with graded composition profiles (a) PZT(53→30) (b)PZT(30→53)

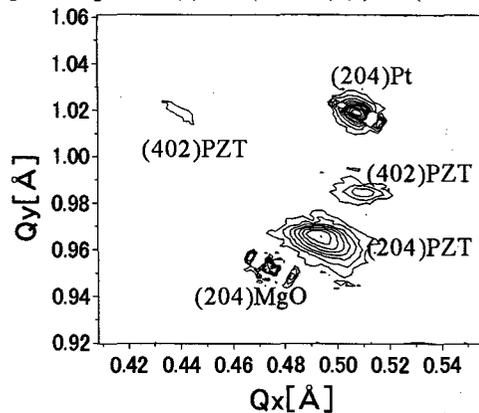


Fig.5. Reciprocal space maps of (204)PZT(30→53)

### 3.4 Comparison of piezoelectric property

The tip displacement of the cantilever was measured as a function of applied voltage applying unipolar sine-wave signals of 500 Hz and the results are shown in Fig.6. In the case of the PZT(53) thin films, tip displacement exhibit proportional relationship as shown in Fig.6. This result indicates that the piezoelectric strain of the PZT(53) is caused by simple lattice motion of

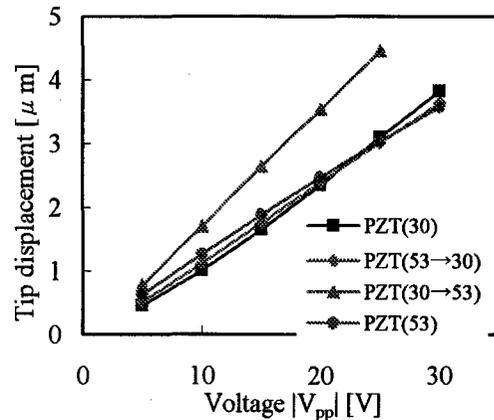


Fig.6. Tip displacement of PZT(53) thin films as a function of applied voltage

elongation and shrinkage along the polar axis because the PZT(53) films are oriented along  $c$  axis. On the other hand, For PZT(30) and graded PZT thin films, tip displacement shows obvious non-linear relationship and slope of the displacement increases with the applied voltage as shown in Fig.6. This result suggests that the domain motions are superimposed on the lattice motion.

Transverse piezoelectric properties of  $e_{31}$  were calculated from the piezoelectric displacement of Fig.6. Since the thickness of the substrate is much thicker than that of PZT films, the  $e_{31}$  can be calculated by simple equation as follows,

$$e_{31} \approx -\frac{(h^s)^2}{3s_{11}^s L^2 V} \delta \quad (1)$$

Where  $V$  and  $L$  are the applied voltage and the length of cantilever, and  $h^s$  and  $s_{11}^s$  are the thickness and the elastic compliance of the MgO substrate, respectively.<sup>[6]</sup> The value of  $d_{31}$  is popular parameter for the design of the piezoelectric devices using piezoelectric films, however it is necessary to estimate elastic property of the piezoelectric films. The measurements of the elastic properties of thin film materials are not as easy as bulk materials because of very thin thickness of films as well as the existence of the substrates. On the other hand,  $e_{31}$  represents the proportional constant of the piezoelectric stress generated by the transverse electric field and this parameter can be derived without the value of the elastic properties of the piezoelectric thin films as shown in eq. (1). Assuming the unimorph actuator is ideal cantilever, elastic compliance  $s_{11}$  is given by reciprocal of the Young's modulus. The Young's modulus of the (100)MgO was reported as 248 Gpa. Figure 7 shows the transverse piezoelectric coefficient  $e_{31}$  of the PZT films as a function of applied voltage.

PZT(53) shows almost constant  $e_{31}$  which is independent of the applied voltage. On the other hand,  $|e_{31}|$  of the PZT(30) and the graded compositional PZT films increase with applied voltage, and especially at high applied voltage, the  $|e_{31}|$  of the graded compositional PZT is higher than those of morphotropic composition PZT(53) films.

The PZT films with graded composition profiles have good piezoelectric property. PZT(53) whose composition is near the morphotropic phase boundary

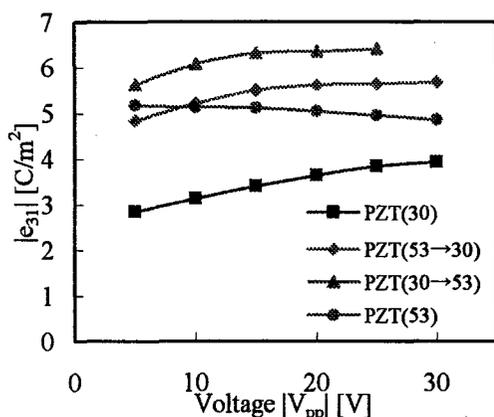


Fig. 7. Piezoelectric coefficient  $e_{31}$  of the PZT films as a function of applied voltage

have large and very stable transverse piezoelectric coefficient since their piezoelectricity is caused only by the lattice motion. On the other hand, the graded compositional PZT films have as large piezoelectric coefficient as PZT(53) at low applied voltage and then their piezoelectric coefficient increase with electric field. These results suggest that the lattice motion of the graded compositional PZT films is as high as morphotopic PZT films, while under higher electric field, domain motion is also induced like PZT(30) films. In consequence, large piezoelectricity could be obtained for the graded compositional PZT films due to the large lattice motion as well as domain motion.

#### 4. CONCLUSIONS

In this study, we prepared PZT thin films with graded composition profiles by multi-target RF-sputtering to enhance piezoelectric properties by inducing active domain structure. From 4-circle XRD measurements, we confirmed that the graded compositional PZT films of both  $Zr=30 \rightarrow 53$  and  $53 \rightarrow 30$  have clear  $a/c$  domain structure. Piezoelectric coefficient  $e_{31}$  of PZT thin films with graded composition profiles is larger than those of PZT thin films with uniform composition. The large piezoelectricity of the graded compositional PZT films is attributed to the domain motion, of which effect is prominent especially at the high electric field.

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