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Analysis of Bending Displacement of Lead Zirconate Titanate Thin Film Synthesized by Hydrothermal Method

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Lead zirconate titanate solid-solution (PZT) films with various thicknesses were synthesized on titanium substrates by repeated hydrothermal treatments. Young's modulus and the density of the PZT film were measured by the vibrating-reed technique and Archimedes' method, respectively, and they were lower than those of PZT ceramic. We fabricated bimorph-type bending actuators using those films and analyzed the displacement induced by the electric field. It was found that the piezoelectric constant and electromechanical coupling factor of the PZT film were comparable to those of the ceramic, and also that the displacement was caused by the piezoelectric effect. The actuators were bent by applied voltage without poling, because the polar axes in the as-deposited film were aligned in the direction from the film surface to the substrate.

KEYWORDS: lead zirconate titanate, thin films, hydrothermal method, ferroelectrics, elastic constant

1. Introduction

Lead zirconate titanate solid solution (PZT) is a typical piezoelectric ceramic and is applied to such devices as actuators, ultrasonic motors, and sensors.[1] Piezoelectric actuators are useful for controlling small displacement more precisely than other actuators. However, the improvement of device efficiency, especially the control of a large displacement caused by a low applied voltage, is essential to expand the field of application. By using thin film actuators, it may be possible to improve the properties of actuators. Recently, PZT thin films have been synthesized by several methods, such as sputtering,[2] sol-gel coating,[3] chemical vapour deposition.[4] We have fabricated crystalline PZT films on titanium substrates by hydrothermal methods.[5,6] It was found that the bending actuator using this film showed a large electric-field-induced displacement without poling treatment. As a mechanism of this displacement, we have presented a possibility of the alignment of polar axes in the as-deposited PZT films,[6] but it is not yet fully confirmed. Furthermore, it is also necessary to measure the electrical and mechanical properties of PZT films for practical applications.

The purpose of the present study is to measure the elastic and electromechanical properties of the PZT film and to confirm the alignment of polar axes. First, PZT films with various thicknesses were fabricated on titanium substrates, and were formed into bimorph-type bending actuators. The electric-field-induced displacement of the actuators was measured and compared with that calculated from the theory of elasticity. Moreover, the alignment of polar axes was confirmed from the effect of poling treatments on the displacement.

2. Experimental

2.1 *Preparation of PZT thin films*

PZT thin films were fabricated through two hydrothermal processes. The first process was the nucleation of PZT on titanium substrates and the second process was the growth of PZT crystals from nuclei.[5] In the first process, the titanium substrate (Ti, $10\times50\times0.05$ mm^3), solutions of lead nitrate ($Pb(NO_3)_2$), zirconate oxychloride ($ZrOCl_2$) and potassium hydroxide (KOH, 8 N) were heated at 150°C for 48 h in a Teflon-lined autoclave. The Pb/Zr molar ratio was 2.29. The PZT nuclei layers were formed on both sides of the Ti substrate. The crystals were subsequently grown from the nuclei in the solutions containing $Pb(NO_3)_2$, $ZrOCl_2$, titanium tetrachloride ($TiCl_4$) and KOH at 120°C for 24 h in the second process. The molar ratio of Pb:Zr:Ti was 110:52:48 and the concentration of KOH was 4 N. In order to control the thickness of the PZT layer, the second process was repeated 1–5 times. The synthesized films with various thickness were analyzed by X-ray diffractometry (XRD). Density and thickness of the films were measured by Archimedes' method[7] and optical microscopy, respectively.

2.2 *Measurement of Young's modulus and electric-field-induced displacement*

To fabricate bimorph-type bending actuators, Au was first sputtered on the surfaces of PZT film as electrodes, and the substrate was cut off into strips (40×5 mm). Young's modulus of PZT film was measured by the vibrating-reed technique.[8] The displacement caused by the voltage across the electrodes was measured from the reflection angle of a He–Ne laser beam.[6] In order to understand the mechanism of displacement, the displacement-voltage curves were compared before and after poling displacement-voltage curves were compared before and after poling treatment. The poling treatment was performed by applying voltage (30 V) from the substrate to the PZT film surface, or in the opposite direction, for 10 minutes.

3. Results and Discussion

3.1 *Characterization of PZT films*

Figure 1 shows the changes in the thickness of PZT films with the number of repetitions of the second process. It was found that the thickness of PZT films increased by repeating the second process. The maximal rate of increase was obtained during the first treatment (the first process and the first application of the second

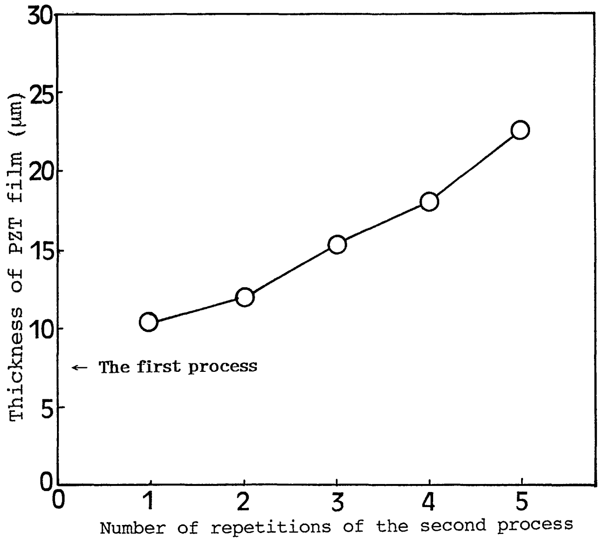

Fig. 1. Changes in the thickness of PZT films with the number of repetitions of the second process.

process), because it includes the thickness of the PZT film formed by the first process, which was about 7–8 μm, estimated from the weight change of the substrate. After the first treatment, the deposition rate was about 3 μm for each successive treatment. The thickness of films was restricted in the ordinary hydrothermal process, because it only makes use of the reaction between the substrate and solution. However, sufficient growth was achieved in this study by employing the sequence of two different processes where the components are supplied from solution for crystal growth. The deposited film was identified to be a single phase of PZT by XRD analyses, irrespective of the thickness. However the density measured by Archimedes' method (4.8 g·cm^{-3}) was much lower than the value of the ceramic (7.9 g·cm^{-3}).[9]

3.2 *Young's modulus of PZT film*

The elastic property of a composite beam consisting of a substrate and two identical films (Fig. 2) can be analyzed by the vibrating-reed technique.[8] Young's moduli of the substrate (Y_s) and of the film (Y_f) can be written[8] as

$$Y_s = 3.87 f_0^2 L^4 d_s \pi^2 t_s^{-2} \tag{1}$$

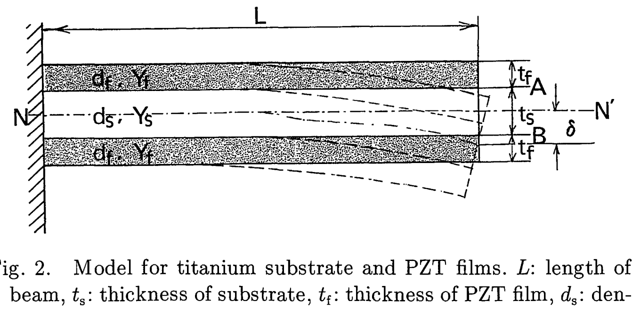

Fig. 2. Model for titanium substrate and PZT films. L: length of beam, t_s: thickness of substrate, t_f: thickness of PZT film, d_s: density of substrate, d_f: density of PZT film, Y_s: Young's modulus of substrate, Y_f: Young's modulus of PZT film, δ: bending displacement of free end of a cantilever, N-N': neutral axis, A, B: interfaces between substrate and PZT film.

$$Y_f = \frac{\dfrac{f_c^2}{f_0^2}\left(1+2\dfrac{t_f d_f}{t_s d_s}\right)-1}{8\left(\dfrac{t_f}{t_s}\right)^3+12\left(\dfrac{t_f}{t_s}\right)^2+6\left(\dfrac{t_f}{t_s}\right)} Y_s \tag{2}$$

where L=length of the substrate, f_0=resonant frequency of the bare substrate, f_c=resonant frequency of the composite beam, d_s=density of the substrate, d_f=density of the film, t_s=thickness of the substrate, and t_f=thickness of the film.

The PZT films prepared in the present study can be regarded as the composite beam above. The resonant frequencies of the bare titanium substrate and that with PZT films (the composite beam) were measured using the following system: a variable-frequency sinusoidal oscillator was connected to a small speaker to produce a mechanical driving vibration. One end of the specimen was fixed at the center of the moving membrane of the speaker. An optical dilatometer (Suntechno, optometric-15D) was used to detect the amplitude of vibration of the cantilever.

Figure 3 shows the changes in the amplitude of vibration as a function of applied frequency. The resonance was clearly observed and its frequency was changed by the deposition of PZT films. The length, breadth and thickness of the titanium plate were 34.5, 5 and 0.050 mm, respectively. The size of the composite beam was as follows: L=33.7 mm, t_s=0.050 mm, t_f=0.025 mm and breath=5 mm. By substituting resonant frequencies into eqs. (1) and (2), Young's moduli of the titanium substrate and of the PZT film were calculated as 1.28×10^{11} and 4.2×10^{10} N·m^{-2}, respectively. Young's modulus of titanium was larger than the value in the literature[10] depends on their manufacturing process. It

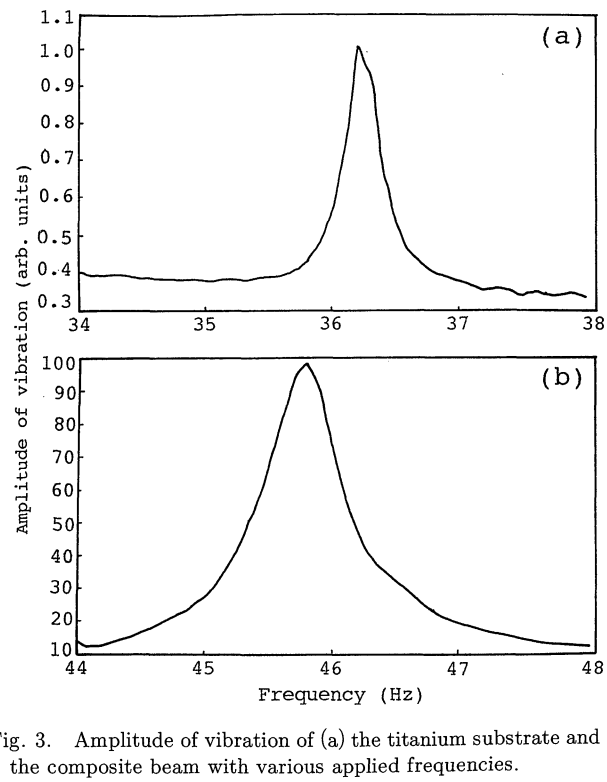

Fig. 3. Amplitude of vibration of (a) the titanium substrate and (b) the composite beam with various applied frequencies.

was found that Young's modulus of the PZT film was less than that of the PZT ceramic (7.246×10^{10} N·m^{-2}).[9]

3.3 *Analysis of displacement and piezoelectricity of PZT film*

The bending displacement of the composite beam was calculated from the balance of stress at interfaces A and B in Fig. 2. In this calculation, the following conditions were assumed: 1) two identical PZT films are completely fixed on the substrate, 2) the substrate and the films are homogeneous in their layers, 3) the neutral axis of the beam (N–N' in Fig. 2) neither expands nor shrinks when the beam bends, 4) the beam is bent only by the expansion or shrinkage of PZT films, 5) the radius of curvature of the bending beam is much longer than the length of the beam, and 6) the deformation of PZT films is caused by the piezoelectric effect.

The displacement (δ) of the actuator is given by

$$\delta=\frac{3L^2}{2t}\frac{Y_f(1-a^2)}{Y_sa^3+Y_f(1-a^3)}d_{31}E \qquad (3)$$

where t_f, t_s, Y_f and Y_s are the thicknesses and Young's moduli of the film and of the substrate, and E and d_{31} are the electric field and the piezoelectric constant of the film, respectively. Furthermore, t and a are given by $t=t_s+2t_f$ and $a=t_s/t$.

Figure 4 shows the displacement of the bending actuator as a function of the thickness of PZT film on one side. The applied voltage was 30 V between two electrodes. The displacement of the actuator was decreased with increasing thickness of PZT film. The solid line in Fig. 4 was calculated from eq. (3), using Y_s, Y_f, d_s, d_f, t_s, t_f, and L values measured for the PZT films. For d_{31}, the data of PZT ceramic[9] was used in the calculation. It was found that the observed data agreed well with the theoretical curve, indicating that the displacement was caused by the piezoelectric effect, and d_{31} of the PZT films synthesized by the hydrothermal method agreed with that of PZT ceramic.

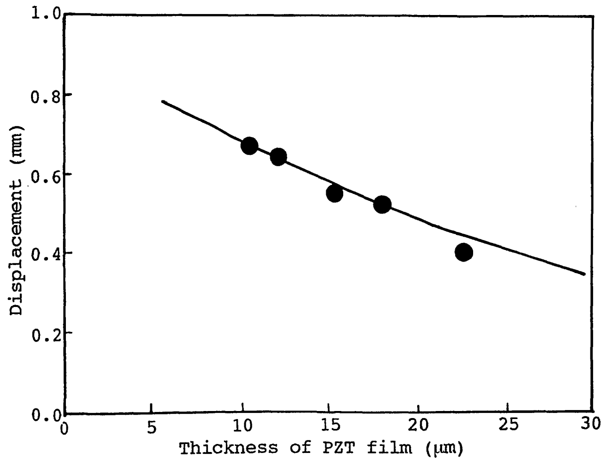

Fig. 4. Displacement of bimorph-type bending actuator by applied voltage (15 V/*film*) using PZT films with various thicknesses. Measured displacement (closed circles) and calculated curve (solid line).

The piezoelectric constant is given by $d_{31}=k_{31}(s_{11}\varepsilon_{33})^{1/2}$, where k_{31} is the electromechanical coupling factor, ε_{33} is the dielectric constant and s_{11} is elastic compliance which is the inverse of Young's modulus. The measured dielectric constant was about 380 at 1 kHz. By substituting the value of the piezoelectric constant, dielectric constant and elastic compliance into the equation above, the electromechanical coupling factor was estimated to be about 0.33. This value is comparable to that of ceramic (0.31),[9] but it can be regarded as very high if the low density of films is taken into consideration.

3.4 *Mechanism of displacement*

Based on the discussion in the previous section, it was concluded that the bending displacement of the actuator was caused by the piezoelectric effect, but that the poling treatment was not necessary before measurement. This indicated that the polar axes were aligned in the as-deposited films. To confirm this phenomenon, the effect of poling treatment on the displacement was investigated.

The displacement-voltage curves before and after the poling treatment are shown in Fig. 5. When the poling field (30 V/*film*) was applied from the substrate to both PZT surfaces, the displacement was decreased. However, it was recovered after a subsequent poling in the opposite direction. This suggests that the polar axes were originally aligned in the direction from the film surface to the substrate in PZT films. In the previous report,[6] we observed a drastic decrease in the dis-

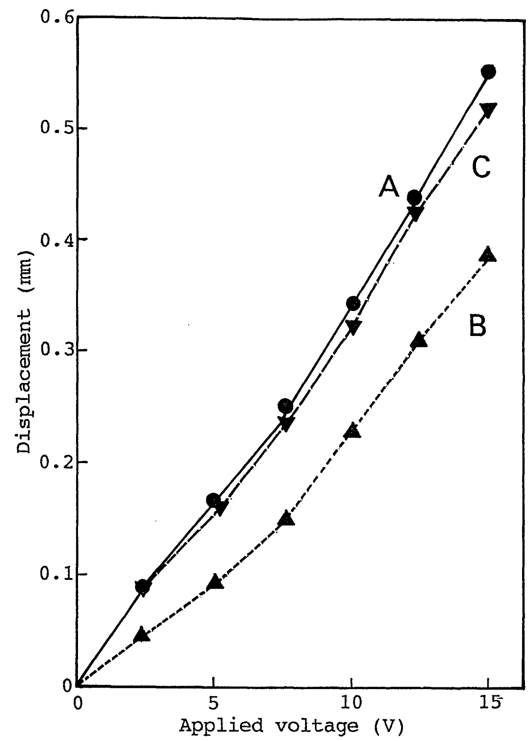

Fig. 5. Displacement-voltage curves of bimorph-type bending actuators before and after poling treatments. A: before poling (●), B: poling in the direction from the substrate to the surface of the fiims with 30 V/*film* for 10 minutes (▲), C: poling direction was opposite to B with same voltage and duration (▼).

placement with PZT films heated above the Curie temperature. From these results, it is concluded that the polar axes of as-deposited PZT films were aligned, giving rise to the electric-field-induced displacement due to the piezoelectric effect.

The temperature range of the hydrothermal conditions used in this study was lower than the Curie temperature of PZT, where the ferroelectric phase of PZT was stable. This distinguishes the hydrothermal method from other process, and a particular poling state may result in the high electromechanical coupling factor in spite of a low density.

4. Conclusions

The results obtained in this study are summarized as follows.

1. PZT films with various thicknesses were synthesized by repeated hydrothermal treatment. Bimorph-type bending actuators were fabricated using these films.
2. Young's modulus of PZT films was lower than that of ceramic, while the piezoelectric constant and electromechanical coupling factor were comparable to those of ceramic.
3. The electric-field-induced displacement was caused by the piezoelectric effect. The polar axes in as-deposited film were aligned from the film surface to the substrate.

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