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Vibration properties of lead zirconate titanate thick film transducer fabricated by ultrasonic assisted hydrothermal method

超音波アシスト水熱合成法を用いて成膜した
PZT 厚膜振動子の振動特性評価

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1. Introduction

Lead zrconate titanate is widely used for ultrasonic transducers due to its excellent piezoelectricity. The hydrothermal method is one of the methods for PZT film deposition[1,2]. In order to promote the hydrothermal reactions, we proposed an ultrasonic assisted hydrothermal method[3], which accelerate the chemical reaction by the agitation effect and the cavitation generated by an ultrasonic transducer. A 7.5 μm thickness PZT film could be deposited on titanium substrate by this method, which is 2.5 times thicker than the conventional hydrothermal method.

For much thicker film thickness which is essential for high power output, it was required to repeat the syntheses. In such repetitive deposition, the precursor solution needs to be altered because the titanium ions are not supplied from the surface of the titanium substrate, differently from the first deposition.

In this research, we tried to find the optimum precursor solution conditions for thicker film thickness on repetitive deposition.

2. Experiment of PZT Film Deposition

To apply the ultrasonic irradiation, a Langevin-type transducer was attached to the hydrothermal container (Taiatsu Techno Co., Ltd. TAF-SR 300ml). The Langevin transducer contained four PZT rings whose diameter was 20 mm and the thickness was 2.5 mm. The input voltage was 300 $V_{P\text{-}P}$, and the driving frequency was controlled around 31.0 kHz to maximize the input power. For this purpose, the driving current was measured using the current probe (Tektronix TCPA300) and the lock-in amplifier (NF LI5630). The distance between the titanium substrate and the tip of the transducer was 5 mm.

The synthesis condition is shown in **Table 1**. The condition I is for the first deposition directly on the Ti substrate. It is the same condition as the previous research[3]. However, in the second deposition, the condition I could only deposit 3.0 μm PZT film which was much thinner than the first deposition (7.5 μm). It was because the surface of the titanium substrate was covered by the first deposited film and titanium ions were not supplied from the substrate surface. Therefore, in this research, we changed the ratio of TiO_2 and $ZrCl_2O\cdot 8H_2O$, as shown in **Table 1**, in order to compensate for Ti^{4+} ions from the substrate. First, we adopted the condition II for the second deposition. The cross-sectional SEM image of the condition II deposition after the first deposition is shown in **Fig. 1**. The entire thickness was 20.7 μm, so the second deposited film thickness on condition II was 13.2 μm. From XRD pattern in **Fig. 2**, it was clarified that the crystal structure with condition II was rhombohedral. It means that the chemical component has zirconium-rich.

Table 1 Deposition condition of PZT

Hydrothermal Method	Condition I	Condition II	Condition III
$ZrCl_2O\cdot 8H_2O$ 1 mol/L	6.86 mL	4.26 mL	3.40 mL
$Pb(NO_3)_2$ 1 mol/L	11.48 mL		
TiO_2(Rutile-type) + H_2O	0.13 g + 5.15 g	0.34 g + 7.75 g	0.41 g + 8.61 g
KOH 4 N	26.38 mL		
Solution Volume	50 mL		
Temperature	160℃		
Reaction Time	24 h		
Cooling Time (Water)	1.5 h		
Ultrasonic Assist Time	18 h (from the beginning)		

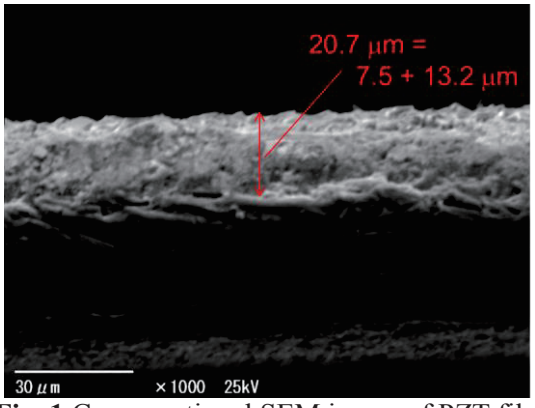

Fig. 1 Cross-sectional SEM image of PZT film deposited with condition II

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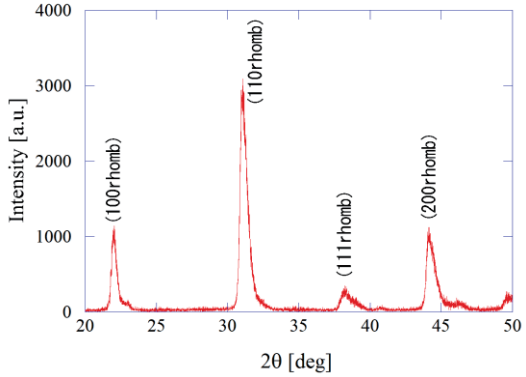

Fig. 2 XRD pattern of the PZT film deposited with condition II

We increased the ratio of Ti^{4+} / (Ti^{4+}+Zr^{4+}) by adopting the condition III in **Table 1**. The cross-sectional SEM image and the XRD result are shown in **Fig. 3** and **Fig. 4**. The film thickness increase by the second deposition with condition III was 23.6 μm. The XRD pattern indicated that the PZT film has not only rhombohedral but also tetragonal crystal. It is considered that this combined composition is similar to the morphotropic phase boundary (MPB) which realizes the excellent high piezoelectricity.

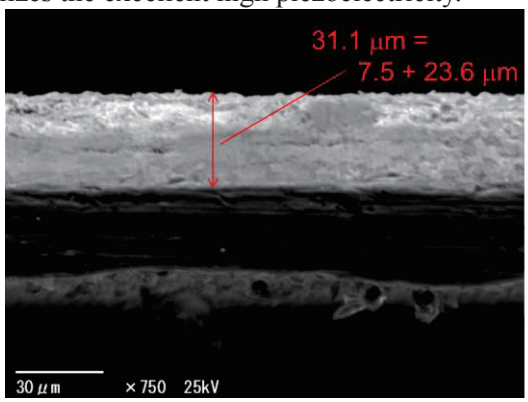

Fig. 3 Cross-sectional SEM image of the PZT film deposited with condition III

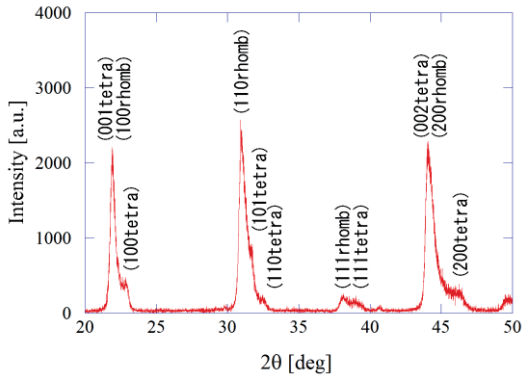

Fig. 4 XRD pattern of the PZT film deposited with condition III

3. Measurement of Properties of PZT Film

We fabricated the piezoelectric transversal effect transducer with the PZT film deposited on condition I and condition III in this order. It had the rectangular shape and the size of 4.5 mm×1 mm ×0.1 mm. The frequency response of the vibration velocity at the tip is shown in **Fig. 5**. The saturated velocity was 2.5 $m_{P\text{-}P}$/s at 8 $V_{P\text{-}P}$. This voltage is one-tenth of the required voltage for the similar transducer fabricated with the conventional hydrothermal method[5].

4. Conclusion

For the second deposition of the PZT films on the titanium substrate, we found that the ionic concentration, Ti^{4+} / (Ti^{4+}+Zr^{4+}) plays on important role about the film thickness. Over 30 μm thickness was demonstrated with the two successive depositions. By using this thick PZT film, the piezoelectric transducer was fabricated and the vibration properties were examined.

For further improvement of this PZT film, various ratio, Ti^{4+} / (Ti^{4+}+Zr^{4+}) is being studied now.

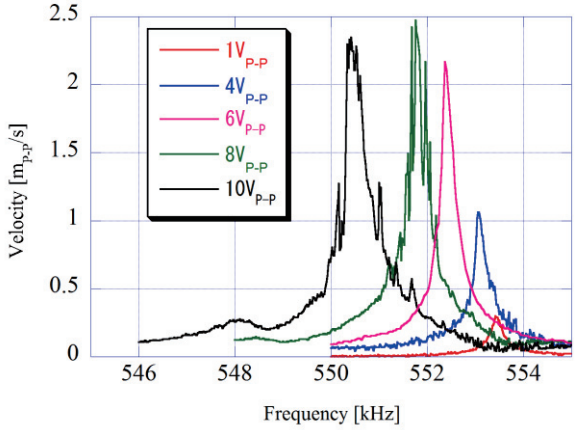

Fig. 5 Vibration velocity of the transducer at the tip

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