

# Fundamental Study on Nucleation Process of Hydrothermally Synthesized PZT Poly-crystalline Film

水熱合成法を用いた

PZT 多結晶膜の核形成に関する基礎検討

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## 1. Introduction

Recently, piezoelectric transducer has been used for generation and detection of ultrasound. in medical ultrasound equipment and ultrasound non-destructive inspection equipment. In our laboratory, we fabricated a piezoelectric transducer with PZT poly-crystalline film deposited on the titanium substrate by a hydrothermal synthesis method which is one of crystal growth technology. Fabrication of anti-acoustic cavitation hydrophone<sup>[1]</sup>, cavitation sensor<sup>[2]</sup> and coiled-stator-type micro ultrasound motor<sup>[3]</sup> with hydrothermally synthesized PZT piezoelectric transducer have been reported.

The hydrothermally synthesized PZT thick film has many favorable features as follows: the hydrothermal process is able to make crystalline films at low temperatures<sup>[4]</sup>; the films can be deposited on concave or convex Ti substrates with thickness of 10  $\mu\text{m}$ <sup>[5]</sup>; hydrothermally deposited PZT film is hard to be peeled from the boundary of Ti substrate, annealing process is not required<sup>[5]</sup>.

However, deposition rate of hydrothermal poly-crystalline PZT is 2  $\mu\text{m}$  / 24 hours in our laboratory. Therefore, there is a problem that it takes long time for deposition of the hydrothermally synthesized PZT poly-crystalline film with required thickness. Furthermore, relationship of the piezoelectric properties and deposition efficiency with respect to the deposition time has not been considered.

In this study, we evaluate the influence of the deposition time in the nucleation process of the hydrothermally synthesized PZT poly-crystalline film deposited on the titanium substrate of characteristics

## 2. Hydrothermal Synthesis Method for PZT Poly-crystalline Film

The structure of our apparatus for hydrothermal deposition of PZT poly-crystalline film is shown in Fig. 1. Deposition process of PZT poly-crystalline on Ti substrate is consist of two stages. First, PZT nuclei is deposited on a Ti

substrate using an autoclave shown in Fig. 1, and then the crystals are grown up to the required thickness, respectively. Process of forming a PZT nucleus on Ti substrate is called nucleation process. PZT nucleus growing up process on the Ti substrate is called as crystal growth process.

Conditions in hydrothermal synthesizing method are the concentration of the solution, temperature, pressure and time.

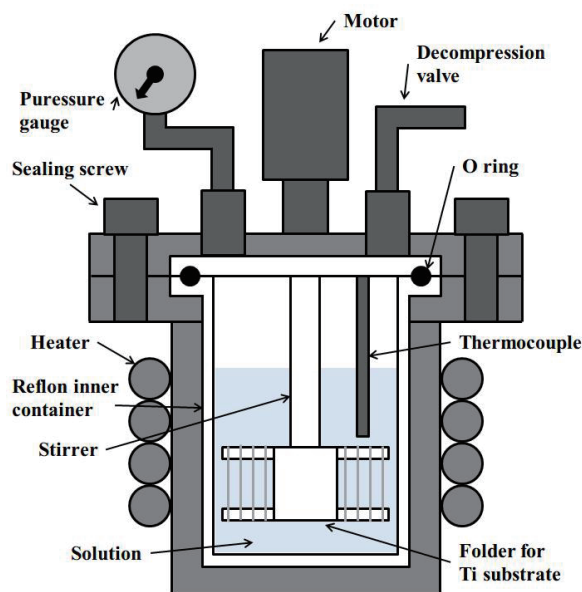


Fig. 1 Schematic diagram of a hydrothermally synthesizing apparatus for PZT poly-crystalline film on the Ti substrate.

## 3. Experimental

We evaluate the influence on nucleation process of PZT poly-crystalline film deposited on the titanium substrate using a hydrothermal synthesis by changing the deposition time. The thickness, the width, and the length of the Ti substrates are 0.05 mm, 25 mm and 20 mm respectively. The temperature and pressure under deposition conditions were 160  $^{\circ}\text{C}$  and 0.3 MPa. Starting materials for the hydrothermal synthesis were shown Table 1. The Ti substrates were fixed on stirrer plates which is made of Teflon, and the stirrers were kept in the solution. The stirrers were rotated by a motor at 150 rpm.

Table 1 Source materials of hydrothermal method for PZT film.

| Material                                  | Concentration | Quantity |
|---|---------------|----------|
| ZrOCl <sub>2</sub> · 8H <sub>2</sub> O aq | 0.25 mol/l    | 60 ml    |
| Pb(NO <sub>3</sub> ) <sub>2</sub> aq      | 0.5 mol/l     | 100 ml   |
| KOH aq                                    | 4 mol/l       | 200 ml   |
| TiO <sub>2</sub>                          |               | 1 g      |

#### 4. Experimental Results

PZT morphology and microstructure were investigated by scanning electron microscopy (SEM : JEOL, JSM-5500). The PZT had a polycrystalline structure, as shown in Fig. 2. Figure 3 shows size of PZT poly-crystalline deposited on Ti substrate, that is changing the deposition time (1 - 6, 12, 18, 24 hours). We confirmed that the crystal nuclei of the PZT poly-crystalline deposited on Ti substrate becomes larger with the increase of the deposition time in nucleation process. However, the growth rate is decreased when deposition time exceeds 6 hours.

Furthermore, the crystal structure of the PZT poly-crystalline was evaluated by X-ray diffraction (XRD : Rigaku, RINT 2000). Figure 4 shows XRD pattern of our PZT poly-crystalline. The XRD pattern of PZT poly-crystalline with deposition time at 2 hours and 24 hours indicated a good crystal structure of PZT. However, the XRD pattern of PZT poly-crystalline with deposition time at 1 hour did not show the crystal structure of PZT.

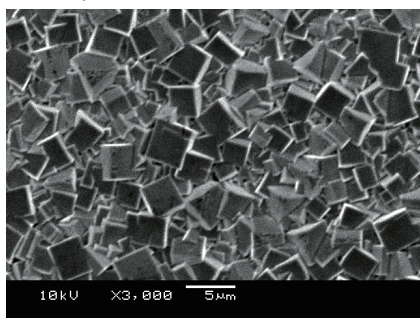


Fig. 2 SEM photograph on surface of PZT polycrystalline film with deposition time of 24 hours deposition hydrothermally synthesized.

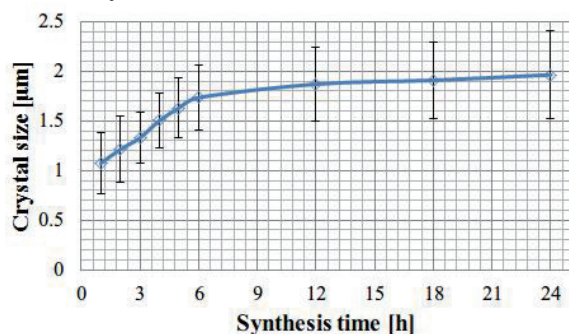


Fig. 3 Relationship between deposition time and the size of the PZT crystal nuclei.

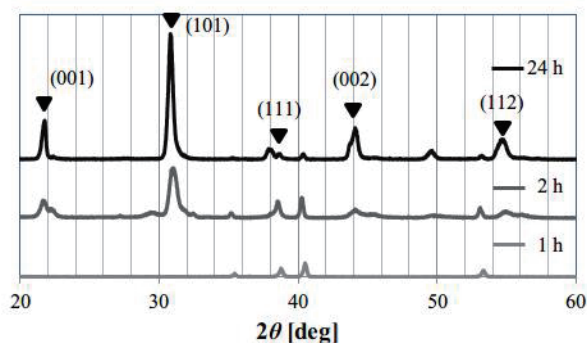


Fig. 4 XRD patterns of hydrothermally synthesized PZT polycrystalline films deposited on Ti substrate.

#### 4. Conclusion and Future Works

We confirmed that the crystal nuclei of the PZT polycrystals deposited on Ti substrate become larger with the increase of the deposition time in nucleation process. However, the growth rate is decreased when deposition time exceeds 6 hours. Furthermore, The XRD pattern of PZT poly-crystalline film with deposition time longer than 2 hours indicated a good crystal structure of PZT. Therefore, it was found in this experiment that deposition time longer than 2 hours is required to obtain good characteristics of hydrothermally synthesized PZT poly-crystalline film deposited on Ti substrate.

Future, we consider the effect of deposition time of hydrothermal synthesis method on the piezoelectric properties of PZT poly-crystalline film deposited on Ti substrate.

#### Acknowledgment

I would like to express my deepest gratitude to Mr. Kouichirou Saita of graduate of Toin University of Yokohama who made enormous contribution in this study.

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