

## Fundamental Study on Crystal Growth Process of Hydrothermally Synthesized PZT Poly-crystals

水熱合成法を用いた PZT 多結晶膜の結晶成長に関する基礎検討

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### 1. Introduction

Our laboratory has been fabricating a variety of devices as cavitation sensors, hydrophone, and small ultrasonic motor, by carrying out the deposition of poly-crystalline lead zirconate titanate (PZT) film, using hydrothermally synthesizing method.<sup>1-3)</sup> The hydrothermally synthesizing method is known as a fabrication technique for a variety of materials including metals and crystals. In this study, the hydrothermally synthesizing method is used to deposit PZT poly-crystalline film on titanium substrates. Additionally, this hydrothermal PZT thick film has many favorable features as follows: the film can be deposited on concave or convex titanium substrates; it is hard to be peeled from the surface of the titanium substrate, poling process and annealing process are not required.<sup>4, 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. In order to solve this problem, we considered the relationship between deposition time and deposition thickness of hydrothermally synthesized PZT poly-crystalline film.

In this study, we evaluate the influence of the deposition time in the crystal growth process of the hydrothermally synthesized PZT poly-crystalline film on its characteristics.

### 2. Hydrothermally synthesizing method for PZT

Deposition process of PZT poly-crystalline films on Ti substrate is consist of two stages. First, PZT nuclei is deposited on a Ti substrate using an autoclave, 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.<sup>6)</sup> Conditions in hydrothermal synthesizing method are the concentration of the solution, temperature, pressure and time. The structure of our apparatus for hydrothermal deposition of PZT poly-crystalline film is shown in Fig. 1.

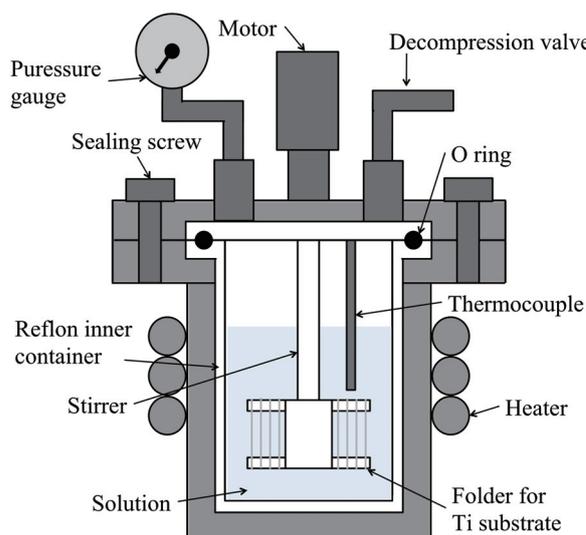


Fig. 1 Schematic view of our reaction apparatus for improved hydrothermal method

### 3. Experimental methods

We evaluate the influence of crystal growth process of PZT poly-crystalline films deposited on the titanium substrate using 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. First, The temperature and pressure under nucleation process were 160  $^{\circ}\text{C}$  and 0.5 MPa. The Ti substrates were fixed on a stirrer plate which is made of Teflon, and the stirrer was kept in the solution. The stirrer was rotated by a motor at 150 rpm. Deposition time was 24 h. The temperature and pressure under crystal growth process were 140  $^{\circ}\text{C}$  and 0.3 MPa. The stirrer was rotated at 150 rpm. Deposition times

were 3, 6, 12, 19 and 24h. Starting materials for the hydrothermal synthesis were shown in Table 1. Table 2 shows the setting conditions of the apparatus for hydrothermal synthesis.

Table 1 Source materials for hydrothermal synthesis of PZT poly-crystalline film

Source materials	Volume
ZrOCl <sub>2</sub> · 8H <sub>2</sub> O <sub>aq</sub> (0.25 mol/l)	60 ml
Pb(NO <sub>3</sub> ) <sub>2aq</sub> (0.5 mol/l)	100 ml
KOH <sub>aq</sub> (4 mol/l)	200 ml
Rutile-type TiO <sub>2</sub>	1 g

Table 2 Synthesis condition of hydrothermal method for poly-crystalline PZT film.

	Nucleation process	Crystal growth process
Temperature [°C]	160	140
Pressure [MPa]	0.5	0.3
Stirring speed [rpm]	150	150
Deposition time [h]	24	3, 6, 12, 19, 24

#### 4. Experimental Results

The morphology and microstructure of hydrothermally synthesized PZT were investigated by a scanning electron microscope (SEM: JEOL, JSM-5500). The PZT had a poly-crystalline structure, as shown in Fig. 2. Figure 3 shows the sizes of PZT poly-crystals deposited on Ti substrate in crystal growth process, and Fig.4 shows thickness of PZT poly-crystalline films deposited on Ti substrates in crystal growth process, that is changed by the deposition time (3, 6, 12, 19, 24 hours). We confirmed that the thickness of the PZT poly-crystalline film becomes larger with the increase of the deposition time in crystal growth process. However, we confirmed that crystal size has not significantly changed.

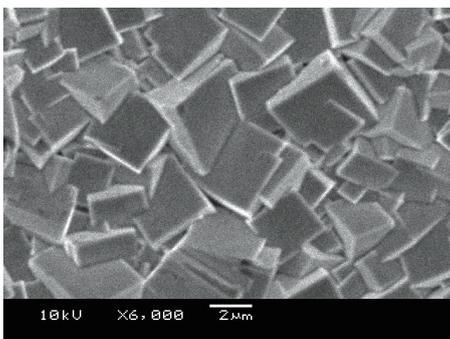


Fig. 2 SEM photograph on surface of PZT poly-crystalline film with deposition time of 24 hours in crystal growth process

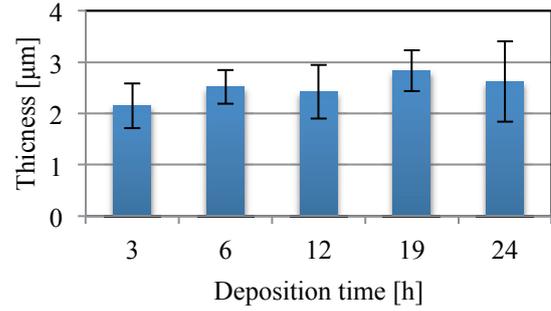


Fig. 3 Relationship between deposition time and the size of the synthesized PZT poly-crystalline films

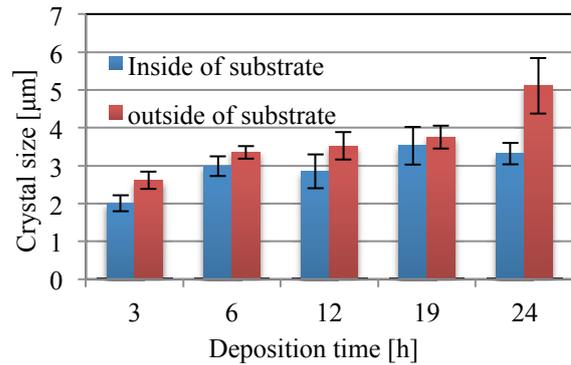


Fig. 4 Relationship between deposition time and film thickness of the synthesized PZT poly-crystals

#### 5. Conclusions and Future Works

We confirmed that the thickness of the PZT poly-crystals deposited become larger with the increase of the deposition time in crystal growth process. However, we confirmed that crystal size has not significantly changed. In this paper, we considered the effect of deposition time of crystal growth process by using PZT poly-crystalline film with deposition time at 24h in nucleation process. We will consider the influence of changing deposition time of nucleation process in the crystal growth process of the hydrothermally synthesized PZT poly-crystalline film in our future works.

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