Basic Consideration on Relationship between Deposition Time and Crystal Growth Process for Hydrothermally Synthesized PZT Poly-crystals

Ozeki Seiya [1, 2] and Takeuchi Shinichi [1]

[1] Graduate School of Engineering, Toin University of Yokohama
[2] Faculty of Health Sciences, Tsukuba International University

I. Introduction

A hydrothermally synthesizing method is known as manufacturing techniques, for crystal, metals etc.. Recently, synthesis of piezoelectric materials such as lead zirconate titanate (PZT), potassium niobate ($KNbO_3$), and potassium sodium niobate (KNN) has been reported using a hydrothermally synthesizing method.[1, 2] We have been fabricated various devices with a PZT film on a Ti substrate by using a hydrothermally synthesizing method for example, cavitation sensor3), hydrophone,[3-6] ultrasound probe,[7] and ultrasound micromotor.[8]

Hydrothermally synthesis uses chemical reaction that can not be achieved in atmospheric pressure by using an autoclave in high temperature and high pressure conditions. The hydrothermally synthesizing method for deposition of the normal PZT poly-crystalline film consists of the two processes of crystal growth process (CG) and nucleation process (NC).[9–11] At first stage, PZT nuclei are deposited on a Ti substrate, and at next stage, the crystals are grown up to the required thickness, respectively.[9–12]

However, a deposition rate of hydrothermally synthesized PZT poly-crystals is about 2 μm / 24 h in our laboratory. Therefore, there is a problem that it takes a long time for deposition of the hydrothermally synthesized PZT poly-crystalline film with required thickness. In order to solve this problem, we considered on the relationship between deposition time and deposited thickness of the hydrothermally synthesized PZT poly-crystalline film in NC.[13]

In this study, we evaluate the influence of the deposition time in the CG of the hydrothermally synthesized PZT poly-crystalline films on their characteristics.

II. Hydrothermally synthesized PZT poly-crystalline film

The hydrothermally synthesized PZT poly-crystalline film is deposited on the Ti substrate from the starting material solutions. **Table 1** shows

[1, 2] Ozeki Seiya and [1] Takeuchi Shinichi

[1] Graduate School of Engineering, Toin University of Yokohama. 1614 Kurogane-cho, Aoba-ku, Yokohama 225-8503, Japan

[2] Faculty of Health Sciences, Department of Medical Care Technology, Tsukuba International University. 6-20-1, Manabe, Tsuchiura-shi, Ibaraki-ken 300-0051, Japan

Table 1. Source materials of hydrothermally synthesizing method for the PZT poly-crystalline film.

Material	Concentration [mol/L]	Quantity
$ZrOCl_2 \times 8H_2O$	0.25	60 mL
$Pb(NO_3)_2$	0.5	100 mL
KOH	4	200 mL
TiO_2	Powder	1 g

source materials for the hydrothermal synthesis of the PZT poly-crystalline film. The hydrothermal synthesis proceeds according to the following Eq (1),

$$Pb^{2+} + (1-x)Zr^{4+} + xTi^{4+} + 6OH^-$$
$$\rightarrow Pb(Zr_{1-x}, Ti_x)O_3 + 3H_2O \qquad (1)$$
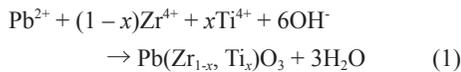
Pb^{2+} and Zr^{4+} ions are supplied from the starting material solution, Ti^{4+} ions are supplied from TiO_2 particles in the starting material solution and dissolved Ti substrate.[14] KOH solution at a concentration of 4 mol / L it was used as a mineralizer.

Additionally, hydrothermally synthesized PZT poly-crystalline film has various favorable features as follows: the film can be deposited on the tiny sized or the complex shaped Ti substrates; it is hard to be peeled from the surface of the Ti substrate, poling process and annealing process are not required.[15, 16]

The relationship among deposition time, temperature, and pressure are important conditions for the hydrothermal synthesis of the PZT poly-crystalline films. The hydrothermally synthesized PZT poly-crystalline film has deposited on the Ti substrate by using special apparatus (the autoclave) for hydrothermal synthesis in our laboratory. **Figure 1** shows the schematic diagram of the apparatus for hydrothermal synthesis using in our laboratory.

The hydrothermally synthesizing apparatus has stirring blades for stirring the solution. It is possible to adjust the stirring speed between 15 to 245 rpm.[13] Ti substrates for deposition of the PZT poly-crystalline film are fixed to the stirring blades as shown in **Figure 2**. It is easy to from
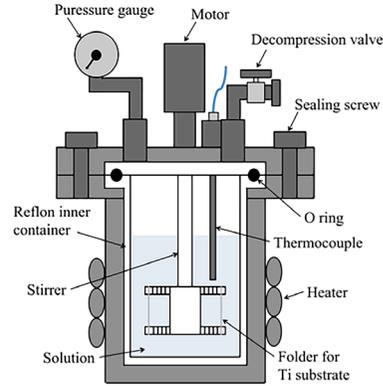
Figure 1. Schematic diagram of the hydrothermally synthesizing apparatus.
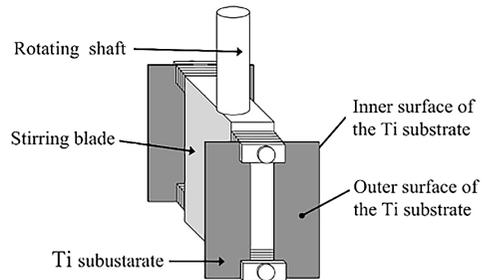
Figure 2. Schematic diagram of the stirring blade for our hydrothermally synthesizing apparatus.

impurity on the surface of the deposited films in the conventional hydrothermally synthesizing method. The lead oxide other than PZT was deposited as the impurity on the surface of deposited PZT poly-crystalline film at the temperature lower than 80 °C at high pressure.[16–18] The deposition of impurities was avoided by decreasing the pressure to atmospheric pressure rapidly within 5 min with a decompression valve, retrieving the PZT film from the autoclave before the temperature decreased to less than 99 °C, and rapidly cooling the Ti substrate with water.[13, 17, 18] Using the autoclave allows the deposition of stable PZT poly-crystalline film on the Ti substrate in our laboratory.

III. Experiment method

The thickness, width, and length of the Ti sub-

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

	Process	
	NC	CG
Temperature [°C]	160	140
Pressure [MPa]	0.5	0.3
Stirring speed [rpm]	245	150
Deposition time [h]	24	3, 6, 12, 19, 24

(a)   (d)

(b)   (e)

(c)   (f)

Figure 3. SEM image of the surface of the hydrothermally synthesized PZT poly-crystalline films deposited on the Ti substrate. (a) inner surface of the hydrothermally synthesized PZT poly-crystalline film (deposition time in CG: 0 h, in only NC) (b) deposition time in CG: 3 h. (c) deposition time in CG: 6 h. (d) deposition time in CG: 12 h. (e) deposition time in CG: 19 h. (f) deposition time in CG: 24 h.

strate samples are 0.05 mm, 25 mm and 20 mm respectively. Setting temperature and pressure in the NC were 160 °C and 0.5 MPa. The Stirring speed was set at 245 rpm. The 20 sheets of the Ti substrate were equipped to the stirring blade and immersed into the material solution. Subsequently, the setting temperature and pressure of the hydrothermally synthesizing apparatus in the CG was 0.3 MPa of 140 °C. The stirring speed was set to 150 rpm. Deposition times were changed to 3, 6, 9, 12, 19, and 24 h. The 4 sheets of Ti substrates were used at each condition of deposition times. ***Table 2*** shows the setting conditions of our hydrothermal synthesis.

IV. Results and Discussions

Evaluation in crystal growth was performed by using a scanning electron microscope. (SEM; JEOL, JSM-5500). ***Figure 3*** shows the SEM image of a typical hydrothermally synthesized PZT poly-crystalline film at NC (a) and the hydrothermally synthesized PZT poly-crystalline films at each time in CG (b), (c), (d), (e), (f). From these images, the size of crystals diameter has increased with increase of the deposition time.

In addition, ***Figure 4*** shows the relationship between the deposition time and crystal diameter in the hydrothermally synthesized PZT poly-crystalline film. It was found from the SEM images in CG and NC as shown in ***Fig. 3*** that the size of crystals diameter has significantly changed by
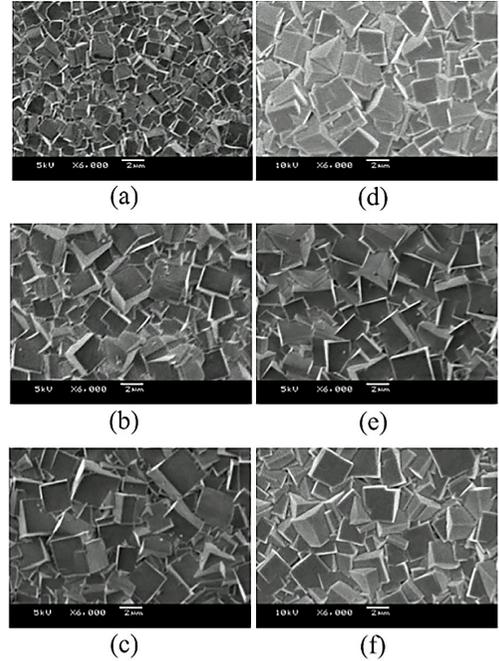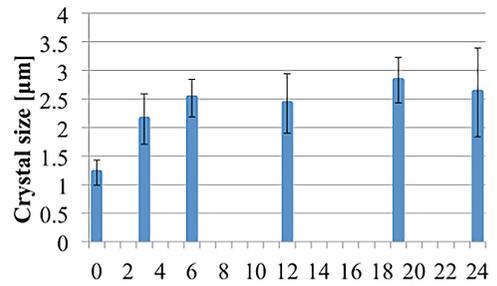

Figure 4. Relationship between deposition time and the size of the deposited PZT poly-crystals.

the deposition time. However, the crystal size did not always depend on the deposition time in GC, significantly as shown in ***Fig. 4***.
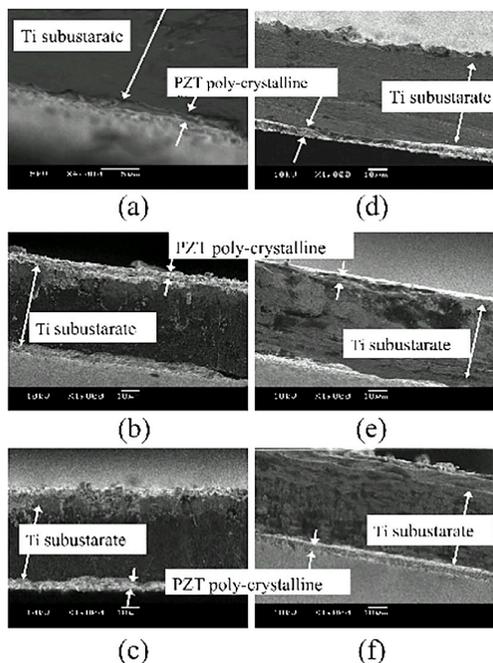
Figure 5. SEM image of the cross section of Ti substrate and the hydrothermally synthesized PZT poly-crystalline filmz after different deposition time on CG and 24 h in NC (stirring speed: 150 rpm). (a) deposition time in CG: 0 h (only NC). (b) deposition time in CG: 1 h. (c) deposition time in CG: 2 h. (d) deposition time in CG: 3 h. (e) deposition time in CG: 4 h. (f) deposition time in CG: 5 h. (g) deposition time in CG: 6 h. (h) deposition time in CG: 12 h. (i) deposition time in CG: 18 h. (j) deposition time in CG: 24 h.
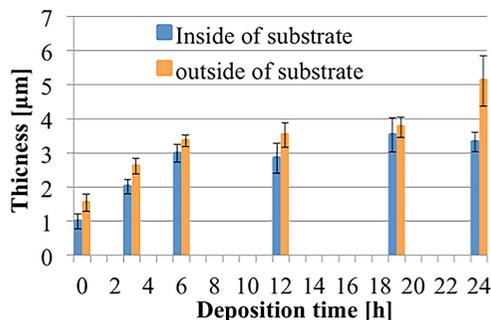

Figure 6. Relationship between deposition time in CG and deposited PZT poly-crystalline film thickness (deposition time in NC: 24 h).

Figure 5 shows the cross section SEM images of the hydrothermally synthesized PZT poly-crystalline films, and *Figure 6* shows the relationship between the deposition time and thickness of the hydrothermally synthesized PZT poly-crystalline film in CG. The thickness of the hydrothermally synthesized PZT poly-crystalline film did not increase during at 6 to 19 h, but they increased during at 3 to 6 h and 19 to 24 h. The thickness of the deposition PZT poly-crystalline film on the outer surface of the Ti substrate was maximum for 24 h deposition. However, it was suggested that 6 h deposition was most effective it CG was repeated many times. In this study, we evaluated the deposition time of the hydrothermally synthesized poly-crystalline film on Ti substrate in CG. The crystal size did not change even by changing the deposition time in CG. It was found from these results that the increasing rate of the crystal diameter was almost saturated at 6 h. We think that the reason for this is balance of an etching and the crystal growth by strong alkali between subsequent 3 to 24 h, and deposition rate of hydrothermally synthesized PZT poly-crystalline was 3 μm / 6 h in CG.

We should evaluate the relationship between the stirring speed of the material solution and crystal growth by fixing the deposition time to 6 h in CG. Furthermore, we would like to consider on the effect of the synthesizing condition in NC on the deposited PZT poly-crystalline film in CG in our future works.

Acknowledgment

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