Ultrasonics 53 (2013) 837–841

Contents lists available at SciVerse ScienceDirect

Ultrasonics

journal homepage: www.elsevier.com/locate/ultras

# Study on optimizing ultrasonic irradiation period for thick polycrystalline PZT film by hydrothermal method

Kanako Ohta [a,*], Gaku Isobe [a], Peter Bornmann [b], Tobias Hemsel [b], Takeshi Morita [a]

[a] The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8563, Japan
[b] Faculty of Mechanical Engineering, University of Paderborn, Pohlweg 47-49, 33098 Paderborn, Germany

ARTICLE INFO

*Article history:*
Received 16 August 2012
Received in revised form 3 December 2012
Accepted 4 December 2012
Available online 23 December 2012

*Keywords:*
Piezoelectric material
PZT ceramics
Hydrothermal method
Ultrasonic irradiation

ABSTRACT

The hydrothermal method utilizes a solution-based chemical reaction to synthesize piezoelectric thin films and powders. This method has a number of advantages, such as low-temperature synthesis, and high purity and high quality of the product. In order to promote hydrothermal reactions, we developed an ultrasonic assisted hydrothermal method and confirmed that it produces dense and thick lead–zirconate–titanate (PZT) films. In the hydrothermal method, a crystal growth process follows the nucleation process. In this study, we verified that ultrasonic irradiation is effective for the nucleation process, and there is an optimum irradiation period to obtain thicker PZT films. With this optimization, a 9.2-μm-thick PZT polycrystalline film was obtained in a single deposition process. For this film, ultrasonic irradiation was carried out from the beginning of the reaction for 18 h, followed by a 6 h deposition without ultrasonic irradiation. These results indicate that the ultrasonic irradiation mainly promotes the nucleation process.


## 1. Introduction

Piezoelectric materials are widely used in devices such as ultrasonic motors and ultrasonic sensors and so on. For miniaturizing them, piezoelectric thin films are intensively being studied by a lot of researchers [1–4]. To improve the performance of ultrasonic medical devices using piezoelectric films, it is important to increase the piezoelectric constant, decrease the acoustic impedance and have the ability to output ultrasonic at an optimum frequency [5].

PZT has a high piezoelectric constant in general; however, from the point of view of acoustic impedance, the values for a human and PZT are respectively about $1.5 \times 10^6$ kg/m$^2$s and $30 \times 10^6$ kg/m$^2$s [6]. Moreover, in the case of a catheter, 50 μm thickness is required for outputting 30 MHz. However, this thickness range is too thin for fabricating bulk PZT and too thick for depositing as a film.

We have therefore made PZT using the hydrothermal method because it is known to yield thicker and denser PZT without the need for sintering, compared to PZT formed using conventional methods [7]. The hydrothermal method utilizes a solution-based chemical reaction. Synthesis is carried out around 150° C and pressure inside a closed vessel in the case of PZT thin film deposition. Due to the conditions used, it has unique advantages. It is a simple process, yields high-quality material, and offers the possibility of deposition on three dimensional substrates. Moreover, the low reaction temperature compared to the conventional deposition process allows PZT to be produced without sintering or polling treatment [8]. PZT synthesized by this method has therefore been widely studied [9,10].

However, for obtaining thick PZT films, the hydrothermal method requires a long deposition time and repeated synthesis. For obtaining thicker films in a single deposition, we have developed the Ultrasonic Assisted Hydrothermal Method (UAHTM) for promoting the chemical reaction [11,12]. Ultrasonic irradiation of the solution is considered to accelerate the chemical reaction, due to cavitation and acoustic streaming [13]. We have already verified the effect of ultrasonic assist for promoting the hydrothermal reaction [11,14]. However, details of the phenomena still remain to be clarified for much thicker films. In this study, the objective was to clarify the optimum conditions to obtain thicker PZT films in a single deposition using UAHTM.

As described above, the hydrothermal method is a solution-based chemical reaction under high temperature and pressure. The PZT films obtained are comparatively thicker and denser than PZT formed by conventional methods. However, the long deposition time is a serious problem. For example, Ishikawa showed that the deposition of 50-μm-thick PZT films by the hydrothermal method required repeating the process 20 times [15]. Such repetition is not realistic for practical applications.

## 2. Synthesis procedure

Our research group formulated a method using ultrasonic irradiation and investigated a new autoclave for this purpose. This

* Corresponding author. Tel.: +81 4 7136 4615.
*E-mail addresses:* ohta@ems.k.u-tokyo.ac.jp (K. Ohta), morita@k.u-tokyo.ac.jp (T. Morita).

0041-624X/$ - see front matter 
http://dx.doi.org/10.1016/j.ultras.2012.12.003

autoclave enables us to irradiate the chemical solution directly with ultrasonic waves. As shown in Fig. 1, a bolted Langevin PZT ultrasonic transducer was attached to a hydrothermal container (Taiatsu Techno Co., Ltd. TAF-SR type 300 ml) in the autoclave. It should be noted that this transducer is different from the one used in our previous study [14] so the irradiation conditions used in this work are also different. This means that the effect of the ultrasonic irradiation was not the same in this study as in the previous one.

The driving frequency was controlled to follow the resonant frequency around 31.0 kHz and the input voltage was 300 $V_{p\text{-}p}$. Current was measured by a current probe (Tektronix TCPA300) for changing the driving frequency, and the function generator (NF WF1974) was controlled by a PC through a GPIB interface.

Using this autoclave and transducer, PZT was deposited on oxidized titanium substrate oxidized at 600° C for 5 min; the starting materials are shown in Table 1 [14]. The gap between the tip of the transducer and the substrate was 5 mm. Our objective therefore was to clarify the optimum irradiation period for a thick film.

## 3. Effect of UAHTM

### *3.1. Irradiating ultrasonic beginning or later*

As mentioned in introduction, the ultrasonic irradiation promotes the chemical reaction. The PZT film deposited by UAHTM was denser as shown in Fig. 2. In this study, we focused on the difference in grain size, and it can be seen that the grains in Fig. 2b are smaller than those in Fig. 2a. The film becomes thicker by continuous piling up of grains. Therefore, when the deposition time is constant, the number of grains and their size are important for a thicker film. In this case, the ultrasonic assist makes the grains smaller while the number of grains increases. Moreover, it is expected that changing the irradiation time affects the number and size of the grains.

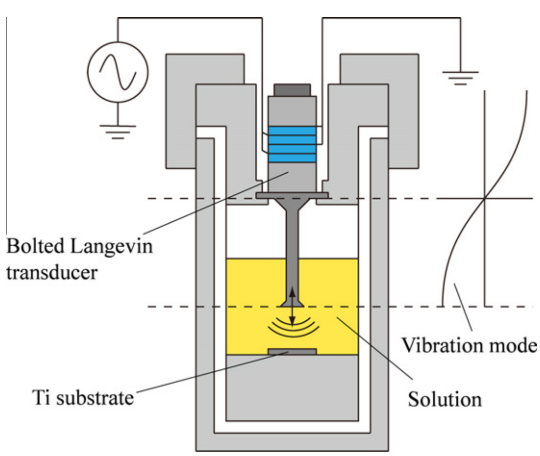


**Fig. 1.** Ultrasonic assisted hydrothermal method.

**Table 1**
Conditions for depositing PZT.

| Hydrothermal method | |
|---|---|
| $ZrCl_2O{\cdot}8H_2O$ | 0.604 g |
| $Pb(NO_3)_2$ | 2.070 g |
| $TiO_2$ (rutile type) | 0.100 g |
| $H_2O$ | 37.50 ml |
| K0H (8 N) | 12.50 ml |
| Solution volume | 50 ml |
| Titanium substrate | 17 mm × 25 mm × 50 μm |
| Temperature | 140° C |

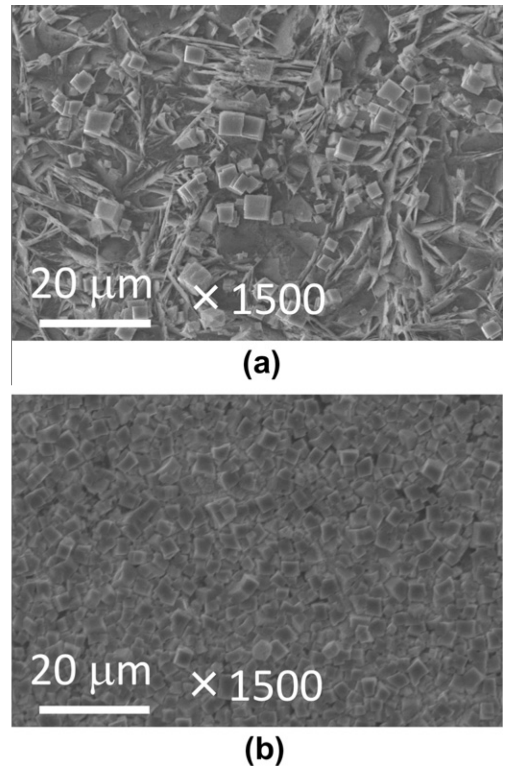


**Fig. 2.** Surface images of PZT (a) without ultrasonic assist and (b) with ultrasonic assist.

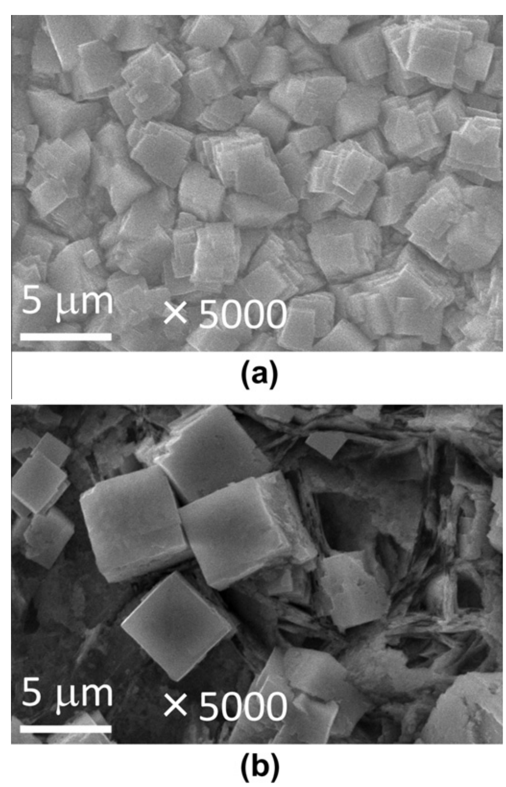


**Fig. 3.** Surface images of PZT (a) irradiated at the first of the deposition and (b) irradiated at the end of the deposition.