PZT Thick Films Deposited by Improved Hydrothermal Method for Thickness Mode Ultrasonic Transducer

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ABSTRACT

The purpose of this study was to improve deposition rate of the hydrothermal method for lead zirconate titanate (PZT) thick film on titanium substrate. We developed a high-speed rotation substrate holder at a tangential velocity of about 0.8m/s in autoclave. A titanium substrate was fixed by the holder on the surface of a stirring bar. For the film deposition, powder of TiO$_2$ was used instead of the liquid TiCl$_4$. The deposition rate on titanium substrate was improved up to 7µm/24h. Piezoelectric constant $d_{31}$ of the hydrothermal PZT film was $-2.6 \times 10^{-11}$ V/m. This result was lower than that of PZT ceramics. However, this hydrothermal method obtained thick film and this film was confirmed to be polycrystalline PZT analyses of XRD and SEM. In addition, performance of thickness mode vibration of hydrothermal PZT 50µm thick film was investigated by radiating in water. The phase velocity of dilatational wave of the thickness mode vibration of the hydrothermal PZT film was 1800m/s and the electromechanical coupling factor was 47%.

INTRODUCTION

Lead Zirconate Titanate (PZT) is a promising ferroelectrics material with a variety of functional application such as micro actuators, ultrasonic transducers and others. There are a lot of studies on fabrication of PZT films by the sol-gel $^1$, the chemical vapor deposition $^2$, the sputtering $^3$, the aerosol deposition $^4$, the hydrothermal method $^5$, etc. Among these techniques, hydrothermal method has attracted considerable interest. This is because the hydrothermal method is available to deposit on concave and convex surface of titanium substrate, reaction temperature is less than 200°C, poling process and annealing process are not required, deposition over 10µm thick is available, peel-strength was 20MPa and over. This deposition process was utilized to fabricate novel application reports, such as a micro ultrasonic motor $^6$, a touch prove sensor $^7$, a tuning type vibrator $^8$, and fluidic device $^9$. The device application achieved in parallel with improvement of deposition process $^5$-$^13$. These literatures reported characteristic of films with changing the process conditions such as temperature, reaction time, etc. However, it was difficult to prepare thick film more than 20µm by the hydrothermal method. The hydrothermal process is performed in an autoclave. In the previous deposition process, a base material was placed in the solution statically $^6$-$^8$, or stirring speed was slow as it controlled for occurrence of turbulent flow in autoclave. We developed, however, a high-speed rotation substrate holder at a tangential velocity of about 0.8m/s in autoclave. The substrates were supported by the holder on a Teflon stirrer revolving at 245rpm in solution. In addition, TiO$_2$ powder was used instead of liquid TiCl$_4$. The thickness vibration mode around 18MHz using 50µm thick film was investigated.
DEPOSITION PROCESS

The hydrothermal method is carried out in solution including Pb\(^{2+}\), Zr\(^{4+}\) and Ti\(^{4+}\) to deposit PZT on a titanium substrate. The hydrothermal method consists of two steps, so-called, nucleation process and crystal growth process\(^6\). At the first reaction process, nucleic crystals of PZT are deposited on a titanium substrate at 160 °C. During the next reaction process, the nucleic crystals are grown up at 140 °C. The second reaction process is repeated several times. A flow chart illustrating the improved hydrothermal method of PZT thick films is shown in Fig.1.

A reaction apparatus for the hydrothermal process is shown in Fig.2. In a Teflon vessel, the solution and a titanium substrate were kept. The titanium substrate were held on a stirrer plate. The stirrer was rotated by a motor slued out of the autoclave. The stirrer was rotated at 245rpm; the tangential velocity of the substrate was about 0.8m/s.

Lead nitride, zirconium chloride oxide, and titanium oxide were used as starting reagents. The material changes from solution of TiCl\(_4\) to powder of TiO\(_2\). Potassium hydroxide was used as the mineralizer. The solution filled the six out of ten of the autoclave capacity. A composition of experiment was determined as shown in Table 1.

![Flowchart of improved hydrothermal method.](image1.png)

![Schematic view of a reaction apparatus for improved hydrothermal method.](image2.png)

Table 1 Composition of the solution for improved hydrothermal method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Quantity</th>
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<tbody>
<tr>
<td>ZrOCl(_2)·8H(_2)O</td>
<td>52ml (1N)</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>TiO(_2) 1g</td>
</tr>
<tr>
<td>Pb(NO(_3))(_2)</td>
<td>87ml (1N)</td>
</tr>
<tr>
<td>KOH</td>
<td>200ml (4N)</td>
</tr>
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EVALUATION OF HYDROTHERMAL PZT FILMS

PZT films morphology and microstructure were investigated by the scanning electron microscopy (SEM) and the energy dispersion X-ray spectrometry (EDS). The phase structure of the films was evaluated by the X-ray diffraction (XRD).

The deposit films had a polycrystalline structure, as shown in Fig.3. The surface of the film after crystal growth process was layer stuck. The grain size was about 5µm over. The film thickness was about 15µm. The polycrystalline PZT films were deposited at about 7µm/24h. The atomic ratio of Zr:Ti of crystal in the films was investigated with EDS. The atomic ratio of the film was Zr:Ti= 80:20 (fudge factor 0.04%). Figure 4 shows XRD patterns of the PZT film of the improved process with TiO₂ and the pervious process with TiCl₄. Each XRD pattern has same peaks. These patterns indicated the crystal structure of PZT.

PERFORMANCE AS VIBRATORS

BENDING MODE VIBRATION

On a titanium substrate size of 15mm × 5mm × 40µm, PZT films about 7µm thick were deposited on both surfaces by the mentioned method. The Au electrode was deposited on the both bare surface of the PZT films. The frequency response of this bimorph vibrator was measured as illustrated in Fig.5. The measurement of the vibration velocity of the bimorph vibrator was carried out with a laser Doppler vibrometer (LDV). Under the condition of a constant driving voltage, the vibration velocity was measured by sweeping the driving frequency at up direction.

The result of the frequency response is shown Fig.6. A mechanical resonance frequency of the bending mode was about 135Hz. The vibration displacement and the vibrator velocity were 1.8mm and 1.5m/s when the driving voltage was 20 Vp-p at the frequency of 135Hz.

The piezoelectric constant $d_{31}$ and young’s modules were calculated by the method mentioned in the previous paper from the resonance frequency and electric displacement. The piezoelectric
constant $d_{33}$ was $-2.6 \times 10^{-11}$ V/m and young’s modulus was $2.2 \times 10^{10}$ N/m$^2$. The density was 4.3 g/cm$^3$. The phase velocity of longitudinal wave in the hydrothermal PZT film was estimated to be about 2200 m/s from the density and young’s modulus.

**THICKNESS MODE VIBRATION**

On a titanium substrate size of 20 mm $\times$ 10 mm $\times$ 50 μm, a PZT film about 50 μm thick was deposited by the mentioned method. The Au electrode was deposited on the surface of the PZT film at 5 mm $\times$ 5 mm. The frequency response of the thickness mode vibrator was measured as shown in Fig.7. The measuring point was at center of the surface of the electrode. The measurement of the vibration velocity of the device was carried out with the laser Doppler vibrometer (LDV, bandwidth 20 MHz). Under the condition of a constant driving voltage, the vibration velocity was measured by sweeping the driving frequency at up direction.

The result of frequency response is shown Fig.8. A mechanical resonance frequency of the thickness mode was about 18 MHz. The vibration displacement and the vibrator velocity were 8 nm and 0.8 m/s when the driving voltage was 45 V$\text{p-p}$ at the frequency of 18 MHz. The electromechanical coupling factor of the hydrothermal PZT thick film was estimated 47% from Fig.8.

The phase velocity of the dilatational wave of the hydrothermal PZT film is given by

$$f_r = \frac{V}{2t}$$

where $V$ is the phase velocity of dilatational wave, $t$ is the thickness of the material, and $f_r$ is the resonance frequency.

It was about 1800 m/s. Furthermore, we mentioned that the phase velocity of the longitudinal wave in the hydrothermal PZT was about 2200 m/s. It can be thought that almost appropriate results were obtained by comparison between the two phase velocities.
CONCLUSIONS

We deposited a excellent quality polycrystalline of PZT films by holding substrate on surface of stirring bar and the starting material change from liquid of TiCl₄ to powder TiO₂. However, piezoelectric constant $d_{31}$ of hydrothermal PZT film was $-2.6 \times 10^{-11}$ V/m. This result was lower than that of PZT ceramics.

The performance of thickness mode vibration of the hydrothermal PZT film was investigated by a LDV. A mechanical resonance frequency of 50µm thick films was 18MHz in water. The vibration displacement and the vibrator velocity were 8nm and 0.8m/s when the driving voltage was 45 V p-p at the frequency of 18MHz. The electromechanical coupling factor and the phase velocity of the dilatational wave of the hydrothermal PZT film were 47% and 1800m/s.

ACKNOWLEDGEMENT

This work was supported by the Murata Science Foundation, 21th century of excellence program and Electronics Society of The institute of Electronics, Information and Communication Engineers.

REFERENCES