Preparation of piezoelectric PZT micro-discs by sol-gel method

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This paper describes a modified sol-gel method to prepare PZT discs of nearly 1 μ m thickness without repeating any process. The method is based on the subdivision of the PZT precursor into small areas prior to sintering. The subdivision is realised by pouring the precursor solution into a ZnO mold. Ultrasonic transducers were fabricated using the PZT disc and the piezoelectricity of the PZT disc in GHz ranges were discussed.

Keywords: PZT, sol-gel method, ultrasonic transducer, piezoelectricity

1. Introduction

Because of its very large electromechanical coupling factor, lead zirconate titanate (PZT) ceramics has widely been used as ultrasonic transducers and actuators. Presently, PZT films are extensively investigated for device miniaturisation, enhanced device performance and integration with semiconductor circuitry ⁽¹⁾.

Various techniques such as sputtering $^{(2)}$ (3) and MOCVD $^{(4)}$ have been applied to the PZT film deposition. Amongst them, sol-gel method $^{(5)}$, deposition process of which is very simple, is one of the most attractive techniques; PZT films with highly piezoelectric properties can be prepared by the method. In fact, PZT films deposited by the sol-gel method have successfully been applied to develop ultrasonic devices operating in UHF and SHF ranges $^{(6)}$ (7), where mechanically thinned ceramic plates are of no use.

One of the drawbacks of the sol-gel method is that the film thickness obtained by a single batch is limited to circa 0.1 μ m, which means that both spin-coating and prebaking processes should be repeated (see Fig. 1) for preparing thicker films. This drawback originates from a large internal stress induced in the film during heating process; the residual stress causes cracks and limits the film thickness to about 1 μ m resulting in poor productivity of the films.

To deal with this problem, lateral relaxation of the internal stress has been proposed, in which a thick PZT precursor layer is subdivided into small areas prior to the heating process⁽⁸⁾; for high frequency applications, the required area for PZT films is usually very small. For example, Ref.⁽⁹⁾ demonstrated that crack-free PZT films of nearly 1 μ m thickness can be deposited in a single step by subdividing a thick PZT precursor with chemical etching. Although the films showed strong piezoelectricity, they were not reproducible because the



Fig. 1. PZT preparation by sol-gel method with repeated precursor solution coating and prebaking processes $^{(6)}$.

film thickness varies widely; it is difficult to spin-coat PZT solution of sufficient thickness onto a flat surface.

This paper describes another approach to prepare thick PZT films by the sol-gel method, where PZT precursor is subdivided by a procedure similar to the lift-off process; PZT precursor solution is poured into a mold fabricated by a sputter-deposited ZnO film, which is removed after the heating process.

In the following sections, the fabrication process is described in detail and ultrasonic properties of the fabricated films are discussed.

2. Preparation of PZT micro-discs

Figure 2 shows the modified preparation process for the PZT films.

First, a Pt/Ti layer is deposited on a Si substrate as a buffer layer, which prevents Pb ions from diffusing into the Si substrate as well as accelerates the crystallisation of PZT films. The Pt/Ti layer also acts as a bottom electrode for the ultrasonic transducers described later. A ZnO film is sputter-deposited on the Pt/Ti layer (Fig. 2 (1) \sim (2)).

Secondly, an array of pits, which acts as a mold for PZT precursor solution, is formed in the ZnO film by



Fig. 2. Modified preparation process of PZT films.

conventional photolithography using an acetic acid solution (33wt%) as an etchant (Fig. 2 (3) ~ (4)). In the present experiment, the thickness and diameter of each pit are 1.2 μ m and 200 μ m, respectively.

Thirdly, PZT precursor solution is poured into the ZnO mold by spin-coating (Fig. 2 (5)). As the solution, CFP-1 ⁽¹⁰⁾ of Kanto Chemical Co., Inc. (nominal composition; Pb/Zr/Ti = 105:52:48) was employed.

After drying, the precursor gel is etched along the rims of the ZnO mold (Fig. 2 (6) ~ (7)) to prevent the precursor and ZnO mold from chemically reacting. The patterning for the gel etching is performed by conventional photolithography, where OMR83 of Tokyo Ohka Kogyo Co., Ltd. was used as a photoresist because of its chemical stability against alcohol. As an etchant, the solvent for the precursor solution, 2-methoxyethanol (CH₃O(CH₂)₂OH), was employed ⁽⁹⁾.

Figure 3 shows thus fabricated and prebaked PZT discs at 450°C for 60 min. Gaps are clearly seen between the precursor and the mold although the centre of each disc does not exactly agree with that of the mold.



Fig. 3. PZT discs and molds after prebaking. Radius of each pit and disc is 100 μ m and 80 μ m, respectively.

After prebaking, the ZnO mold is removed by acetic acid solution (Fig. 2 (9)). Note that the resist layer

burns and disappears during the prebaking process.

Finally, the precursor discs are sintered at 650° C for 60 min. in O₂ ambient gas (Fig. 2 (10)).

Figure 4 shows the sintered PZT discs, for which the rim-etching procedure (Fig. 2 (6) \sim (7)) was omitted; around the PZT discs, one can see some residua which are resistant to acetic acid solution.



Fig. 4. PZT discs fabricated omitting rim-etching procedure.

XRD analysis showed that the discs contain ZnOderived compounds, while the residua contain PZTderived compounds as shown in Table 1. This means that the thermal diffusion occurred during the prebaking process leaving the residua.

Table 1. Compounds detected by XRD analysis.

without rim	-etching procs.	proposed method		
	residua			
PZT region	(ZnO region)	PZT disc region		
PZT	ZnO_x	PZT		
$ZnPbO_x$	PZT	$PbTiO_x$		
$ZnTiO_x$	ZnPbO_x			
PbO_x	$ZnTiO_x$			
	PbO_x			

Figure 5 shows the sintered PZT discs, for which all the processes shown in Fig. 2 are applied (without omitting the rim-etching procedure (Fig. 2 (6) \sim (7))). By applying the rim-etching procedure, it is seen that no residue is left. In addition, no ZnO-derived compound was detected by XRD analysis. Hence, it is concluded that the diffusion problem is completely avoided by the rim-etching procedure.

The thickness of the fabricated PZT disc was about 0.7 μ m. Although cracks are still observed on a surface, they may be removed by reducing the disk area a little bit more.



Fig. 5. Fabricated arrayed PZT discs by the present method.

The fabrication process is summarised in Table 2.

Fable 2. F	Preparation	conditions	for	PZT	films.
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Substrate	Pt/Ti/Si
PZT precursor solution	CFP-1 (Kanto Chemical Co., Inc.)
	Pb: Zr: Ti = 105: 52: 48
Etchant	2-methoxyethanol
for PZT precursor	$(CH_3O(CH_2)_2OH)$
Drying	$150^{\circ}C \ 30 \ min.$
Prebaking	$450^{\circ}C$ 60 min.
Sintering	$650^{\circ}C$ 60 min.

3. Piezoelectricity

Piezoelectricity of the PZT discs is discussed by fabricating ultrasonic transducers, where a top Al electrode is fabricated using the lift-off technique. The PZT disc transducer behaviour was characterised by observing ultrasonic pulse echo trains reflected at the bottom surface of the Si substrate. The measurement system and the transducer configuration used in the experiment are shown in Figs. 6 and 7 respectively, where the PZT disc transducer is polarised by superimposing DC bias on RF signals.

Figure 8 shows the observed pulse echo responses in the time domain, where the bias voltage V_B is fixed at 15 V. By the Fourier transform of the first pulse echo observed in the time domain, the frequency response of the insertion loss was obtained as shown in Fig. 9.

The minimum insertion loss of 45.2 dB is obtained at f = 2.2 GHz, clearly showing the piezoelectricity of the PZT disc in GHz ranges. The measured minimum loss was about 10 dB larger than that estimated using material constants for PZT-5H bulk materials⁽¹¹⁾. The increase in the minimum insertion loss may be due to the ohmic loss of a bottom Pt/Ti electrode.



Fig. 6. Measurement system.



Fig. 7. PZT transducers under testing.



Fig. 8. Ultrasonic pulse echo trains. (DC bias : $V_B = 15$ V)

4. Conclusion

This paper described a modified sol-gel method to prepare PZT discs of nearly 1 μ m thickness without repeating any process. The method is based on the subdivision of the PZT precursor into small areas prior to sintering. The subdivision is realised by pouring the precursor solution into a ZnO mold. It was also shown that etching of the precursor gel along the rims of the ZnO mold is effective in preventing the precursor and



Fig. 9. Frequency dependence of insertion loss of the round-trip echo.

ZnO mold from chemically reacting each other. Ultrasonic transducers were fabricated using the PZT disc and the piezoelectricity of the PZT disc in GHz ranges were discussed.

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