

Control of Deposition Area for Hydrothermally Synthesized Lead Zirconate Titanate Film by Masking with Au Sputtering

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We have previously used a hydrothermal synthesis method to fabricate various devices, including a cavitation sensor¹⁾, hydrophone,^{2, 3)} ultrasound probe,⁴⁾ and ultrasound micromotor,⁵⁾ from a lead zirconate titanate (PZT) film on a Ti substrate. The hydrothermal synthesis method is used to precipitate crystals at high temperatures and pressures. Recently, hydrothermal synthesis of piezoelectric materials, such as PZT, potassium niobate, and potassium sodium niobate, has been reported.^{6, 7)} Additionally, hydrothermally synthesized PZT polycrystalline films have various advantages: the film can be deposited on small or complex shaped Ti substrates; it adheres well to the surface of the Ti substrate; and poling and annealing are not required.^{8, 9)} However, it is difficult to deposit the PZT film on a specific portion of the

surface of the Ti substrate. This is a significant limitation in manufacturing piezoelectric devices with hydrothermally synthesized PZT polycrystalline films and it is important to develop a technique for controlling the film deposition.

In previous studies, the deposition area of the hydrothermally synthesized PZT polycrystalline film has been controlled by masking methods using a PTFE plate or PTFE film. However, these masking methods were not sufficient.^{10, 11)} In hydrothermal synthesis, the PZT polycrystalline film is deposited by the chemical reaction between metal ions in solution and the surface of the Ti substrate. Therefore, we expected that it would be possible to control the deposition area of the film by inhibiting the film synthesis through coating the surface of the Ti substrate with an Au film.¹²⁾ The hydrothermal

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We have previously fabricated various devices with lead zirconate titanate (PZT) film on Ti substrate by using a hydrothermal synthesis method. However, in hydrothermal synthesis, it is difficult to control the deposition area for PZT polycrystalline film. In this study, we propose a masking method with Au sputtering for controlling the deposition area for hydrothermally synthesized PZT polycrystalline film.

Table I. Source materials for the hydrothermal synthesis of PZT polycrystalline films.

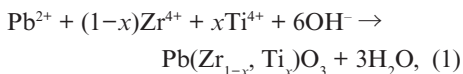
Material	Concentration [mol/L]	Quantity
ZrOCl ₂ ·8H ₂ O	0.25	60 mL
Pb(NO ₃) ₂	0.5	100 mL
KOH	4	200 mL
TiO ₂	Powder	1 g

Table II. Hydrothermal synthesis conditions for polycrystalline PZT films.

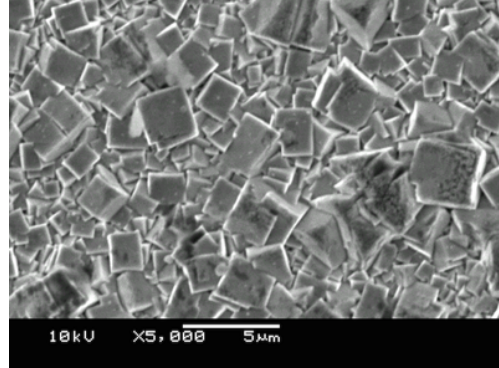
	NC
Temperature [°C]	160
Pressure [MPa]	0.5
Stirring speed [rpm]	160
Deposition time [h]	24

synthesis of the PZT polycrystalline film is carried out at high temperature and high pressure in a strongly alkaline solution. Au is stable even under these harsh conditions. In addition, it is necessary to control the deposition area arbitrarily.

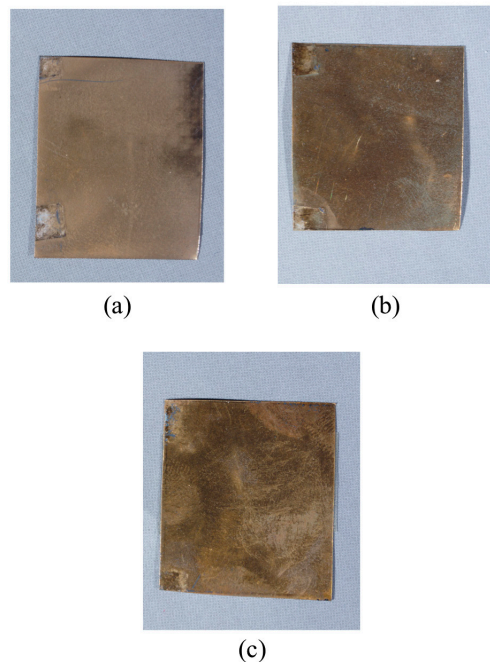
In this work, the PZT polycrystalline film was deposited on the Ti substrate by using dedicated apparatus for hydrothermal synthesis. The relationship among the deposition time, temperature, and pressure is important for the hydrothermal synthesis of the PZT polycrystalline films. Table I shows the source materials and Table II shows the setup of the apparatus. The hydrothermal synthesis proceeds according to the reaction in Eq (1).



Pb²⁺ and Zr⁴⁺ ions are supplied from the starting material solution, and Ti⁴⁺ ions are supplied from TiO₂ particles in the starting material solution and eluted from the Ti substrate.¹³⁾ Hydrothermal synthesis usually consists of

**Fig. 1.** SEM image of the surface of the PZT polycrystalline film deposited on the Ti substrate by hydrothermal synthesis.

the crystal growth process and nucleation process.¹⁴⁻¹⁶⁾ However, only the nucleation process was performed to confirm whether nucleation could be inhibited by the Au masking technique. First, we sputtered Au on the front and back surfaces of the Ti substrate. The thickness, width, and length of the Ti substrate were 0.05 × 20 × 25 mm, respectively. The thicknesses of the sputtered Au films were 0.1, 0.5, and 1.0

**Fig. 2.** Deposition on the Ti substrate of the Au film with thickness of (a) 0.1 μm, (b) 0.5 μm, and (c) 1.0 μm.

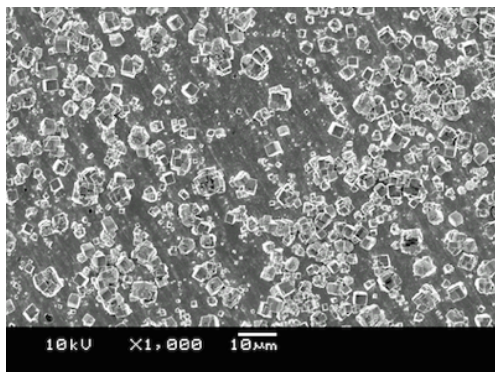


Fig. 3. SEM image of the surface of the PZT polycrystalline film after deposition of an Au film with a thickness of 0.1 μm on the Ti substrate.

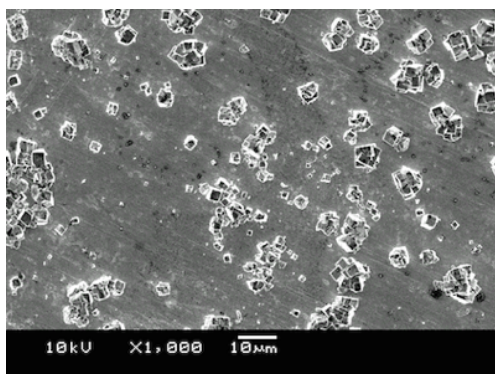


Fig. 4. SEM image of the surface of the PZT polycrystalline film after deposition of an Au film with a thickness of 0.5 μm on the Ti substrate.

μm . Subsequently, we attempted to deposit the hydrothermal PZT on the Au film on the Ti substrate. Figure 1 shows a scanning electron microscope (SEM) image of a hydrothermally synthesized PZT polycrystalline film for comparison.

Figures 2 (a)–(c) show the thickness (0.1, 0.5, and 1.0 μm) of the sputtered Au after hydrothermal synthesis. We confirmed a whitish dullness on the Au after PZT deposition. Figures 3–5 show SEM images of the sputtered Au surfaces after PZT deposition. Crystalline material was observed on the Au surface in Fig. 3, and small crystals were also confirmed on the Au surface in Figs. 4 and 5. However, the surface in Fig. 5 showed small sparsely distributed

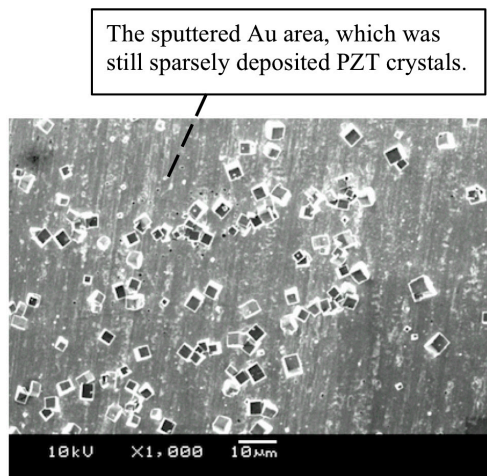


Fig. 5. SEM image of the surface of the PZT polycrystalline film after deposition of an Au film with a thickness of 1.0 μm on the Ti substrate.

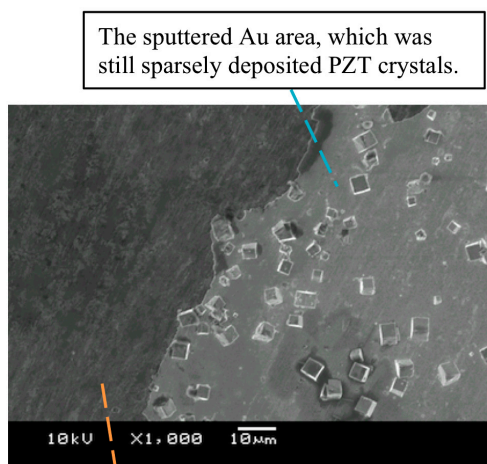


Fig. 6. SEM image of the boundary between the Ti substrate and peeling of Au with PZT crystals.

crystals, and the crystals were peeled away from the Ti substrate together with the sputtered Au by using carbon tape. Figure 6 shows an SEM image of the Ti substrate area after the peel of the sputtered Au film and the sputtered Au area, which was still sparsely deposited PZT crystals.

The SEM images indicate that the nucleation of hydrothermal PZT was inhibited by

masking with a sputtered Au film. However, some PZT crystals still formed on the Au mask, suggesting that this technique requires modification. We expect that this masking technique will eventually be applied to various devices, such as ultrasound sensors, hydrophones, and ultrasound micromotors with sophisticated structures.

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References

- 1) M. Shiiba, N. Kawashima, T. Uchida, T. Kikuchi, M. Kurosawa, and S. Takeuchi, *Jpn. J. Appl. Phys.* **50**, 07HE02 (2011).
- 2) M. Shiiba, N. Okada, T. Uchida, T. Kikuchi, M. Kurosawa, and S. Takeuchi, *Jpn. J. Appl. Phys.* **53**, 07KE06 (2014).
- 3) H. Kitsunai, N. Kawashima, S. Takeuchi, M. Ishikawa, M. Kurosawa, and E. Odaira, *Jpn. J. Appl. Phys.* **45**, 4688 (2006).
- 4) A. Endo, N. Kawashima, S. Takeuchi, M. Ishikawa, and M. K. Kurosawa, *J. Appl. Phys.* **46**, 4779 (2007).
- 5) S. Ozeki, T. Abe, T. Moriya, T. Irie, M. Kurosawa, and S. Takeuchi, *TOIN Inter. Symp. Eng. Abs. Book*, 2014, p. 108.
- 6) T. Morita, *Materials* **3**, 5241 (2010).
- 7) T. Maeda, T. Hemsell, and T. Morita, *Jpn. J. Appl. Phys.* **50**, 07HC01 (2011).
- 8) M. Ishikawa, M. K. Kurosawa, A. Endoh, and S. Takeuchi, *Jpn. J. Appl. Phys.* **44**, 4342 (2005).
- 9) T. Morita, T. Kanda, Y. Yamagata, M. Kurosawa and T. Higuchi, *Jpn. J. Appl. Phys.* **36**, 2998 (1997).
- 10) K. Yoshimura, N. Kawashima, S. Takeuchi, T. Uchida, M. Yoshioka, T. Kikuchi, and M. K. Kurosawa, *Jpn. J. Appl. Phys.* **47**, 4215 (2008).
- 11) T. Abe and S. Takeuchi, *TOIN Inter. Symp. Eng. Abs. Book*, 2012, p. 47.
- 12) S. Ozeki, T. Abe, M. K. Kurosawa, and S. Takeuchi, *Proc. Symp. Ultrasonic Electronics*, 2014, p. 413.
- 13) Y. Seto, N. Kawashima, M. K. Kurosawa, and S. Takeuchi, *Jpn. J. Appl. Phys.* **47**, 3871.
- 14) K. Shimomura, T. Tsurumi, Y. Ohba, and M. Daimon, *Jpn. J. Appl. Phys.* **30**, 2174 (1991).
- 15) T. Kikuchi, T. Tsurumi, Y. Ohba, and M. Daimon, *Jpn. J. Appl. Phys.* **31**, 3090 (1992).
- 16) Y. Ohba, K. Arita, T. Tsurumi, and M. Daimon, *Jpn. J. Appl. Phys.* **32**, 4095 (1993).
- 17) Y. Ohba, K. Arita, T. Tsurumi, and M. Daimon, *Jpn. J. Appl. Phys.* **33**, 5305 (1994).