Proceedings of Symposium on Ultrasonic Electronics, Vol. 35 (2014) pp. 413-414
3-5 December, 2014

Fundamental study on control of deposition area for hydrothermally synthesized PZT poly-crystalline film

水熱合成法を用いた PZT 多結晶膜への成膜範囲の制御に関する基礎検討

Seiya Ozeki[1†], Toshinobu Abe[1], Minoru Kuribayashi Kurosawa[3] , and Shinichi Takeuchi[1] ([1] Grad. School of Eng., Toin Univ. of Yokohama; [2] Interdisciplinary Grad. School of Sci. and Eng., Tokyo Inst. of Tech.)
大関誠也 [1†]，阿部峻靖 [1]，黒沢実 [2] ，竹内真一 [1] ([1] 桐蔭横浜大院 医用工, [2] 東工大院 総合理工,)

1. Introduction

Our laboratory has been fabricating a variety of devices as cavitation sensors, hydrophone, and small ultrasonic motor, by carrying out the deposition of poly-crystalline PZT film, using a hydrothermal synthesis method.[1-3] The hydrothermal synthesis method is known as a fabrication technique for a variety of materials including metals crystals.[1] In this study the hydrothermal synthesizing method is used to deposit poly-crystalline film PZT on titanium substrates. Additionally, this hydrothermal PZT thick film has many favorable features as follows: the film can be deposited on concave or convex titanium substrates; it is hard to be peeled from the surface of the titanium substrate, poling process and annealing process are not required.[1] There is a problem that the hydrothermally synthesized PZT polycrystalline film is difficult to be deposited on only a portion of the surface of the titanium substrate. Therefore, this problem becomes significant limitation in manufacturing a device. It is important to develop the control technique of hydrothermally synthesized PZT film deposition area.

Hydrothermal PZT poly-crystalline film is deposited by chemical reaction between metal ions in the material solution for PZT and the surface of titanium substrate. So we thought that it is possible to control the deposition area of the hydrothermally synthesized polycrystalline film by inhibiting the synthesis of PZT poly-crystalline film by coating of Au membrane on the surface of the titanium substrate. Hydrothermal synthesis of the PZT polycrystalline film is carried out at high temperature and high pressure in the strong alkaline the material solution. Au is stable even in above severe condition. In addition, deposition area is necessary to control arbitrarily. We think that Au is suitable masking material to control the area of hydrothermally synthesized PZT film deposition.

2. Experimentals

2.1 Hydrothermal synthesis method and deposition conditions of PZT film

PZT poly-crystalline film has deposited on the titanium substrate by using dedicated apparatus for hydrothermal synthesis in our laboratory. The relationship among deposition time, temperature, and pressure is important to the hydrothermal synthesis of PZT polycrystalline films. Table 1 shows the setting conditions of the apparatus for hydrothermal synthesis. Table 2 shows source materials for hydrothermal synthesis of the PZT poly-crystalline film.

Hydrothermal synthesis method for deposition of normal PZT polycrystalline film consists of the two processes of crystal growth process and nucleation process. However, only nucleation process was performed in order to confirm whether nucleation is inhibited by Au masking technique or not.

Table 1 Conditions of Hydrothermally synthesis of PZT poly-crystalline film deposited on titanium substrate in this study

Conditions	NC
Temperature (℃)	160
Pressure (MPa)	0.5
Revolution speed of stirring blade (rpm)	150

Table 2 Source materials for hydrothermal synthesis of PZT poly-crystalline film

Source materials	Volume
$ZrOCl_2 \cdot 8H_2O_{aq}$ (0.25 mol/l)	90 ml
$Pb(NO_3)_{2aq}$ (0.5 mol/l)	150 ml
KOH_{aq} (4 mol/l)	300 ml
Rutile-type TiO_2	1 g

2.2 Masking process by using Au sputtering

We investigated only inhibition of deposition of the hydrothermal PZT film by using Au masking technique in this time. At first, Au was sputtered on both of front and rear surfaces of the titanium substrate by using the ion sputtering apparatus. The thickness, width, and length of the titanium substrate used in this study were 0.05 mm, 10 mm, and 15 mm, respectively. Thickness of sputtered Au membrane was set to 0.5 μm. Thereafter, we tried to deposit hydrothermal PZT on the titanium substrate with sputtered Au surface.

3. Evaluation of hydrothermal PZT film with Au sputtered surface by SEM and XRD

Figure 1 shows the photograph of Ti substrate with Au sputtered surface before and after deposition of the hydrothermal PZT film. Left side of the picture was the Ti substrate with Au sputtered surface after deposition of hydrothermal PZT film. Right one was the Ti substrate with Au sputtered surface before deposition of hydrothermal PZT film. It was found in the left sample in Fig. 1 that deposition of hydrothermal PZT film was prohibited by sputtered Au membrane in almost area. However, hydrothermal PZT was deposited on the left and top sides of the left sample where Au membranes were removed due to washing process.

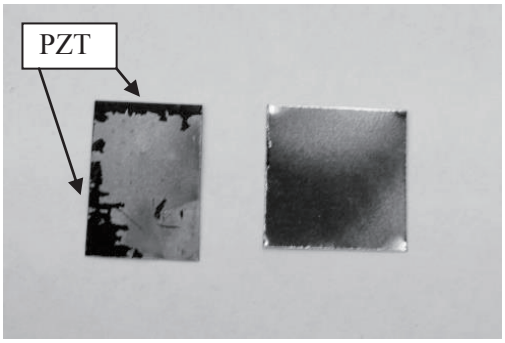

Fig.1 Photograph of Ti substrate with Au sputtered surface before and after deposition of hydrothermal PZT film

Figure 2 shows a SEM image of the interface between the PZT deposited area and the PZT not deposited area on the surface of Au sputtered Ti substrate. Deposited PZT polycrystals were observed in the right half area of the image. Something like crystals were observed in the left half. Density of the crystals in left half area is higher than and those in right half area. Figure 3 shows three X-ray diffraction (XRD) data. Fig.3 (a) is XRD data of bulk Au, (b) shows that of hydrothermal PZT deposited on Ti substrate without Au sputtered surface and (c) shows that with Au sputtered surface.

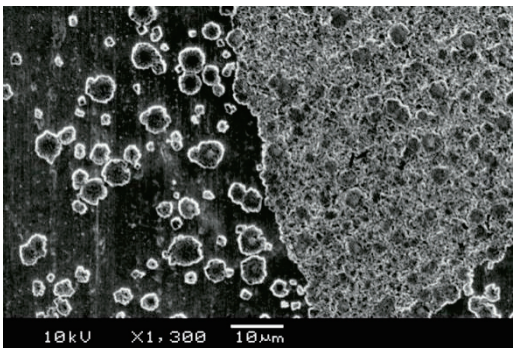

Fig.2 SEM image of the interface between the PZT deposited area (Right area) and the PZT not deposited area (left area) on the surface of Au sputtered Ti substrate

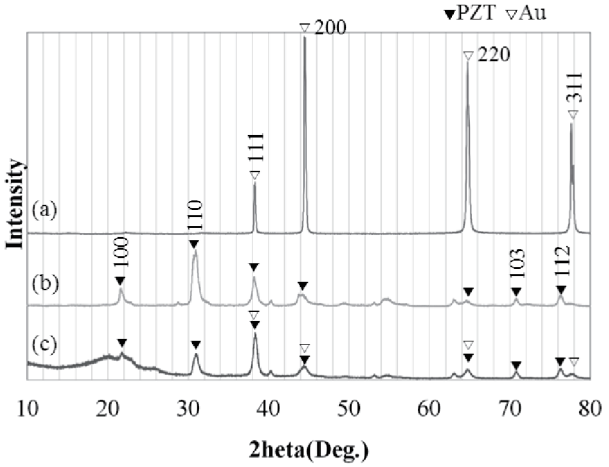

Fig. 3 X-ray diffraction (XRD) data in this study (a) XRD data of bulk Au, (b) XRD data of hydrothermal PZT deposited on Ti substrate without Au sputtered surface , (c) XRD data of hydrothermal PZT deposited on Ti substrate with Au sputtered surface.

4. Conclusions

It is thought from the results of XRD and SEM image that nucleation of hydrothermal PZT was inhibited by masking with sputtered Au membrane. However, masking by using Au sputtering is insufficient. Consequently, we observed the hydrothermal PZT polycrystals on the Ti substrate by masked with Au sputtered surface. We think that masking process was insufficient. We should modify our masking technique for deposition of hydrothermal PZT in future.

References

1. M.Ishikawa.: Jpn. J. Appl. Phys. **47** (2008) 7673.
2. M. Shiiba: Jpn. J. Appl. Phys. **50** (2011) 07HE02.
3. T. Abe, T. Moriya, T. Irie and S. Takeuchi : Res. Bull. TOIN Univ. Yokohama 29 (2013) pp. 13-17.(In Japanese)