Sol-gel Preparation of a PZT Thick Film from a Solution Containing Polyvinylpyrrolidone and Its Application for a Micro Ultrasonic Sensor

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Abstract

A relatively thick PZT film without any cracks is obtained by sol-gel method with single-step spin coating. PZT solution containing PVP and acetylacetone is prepared in the laboratory. The key point is incorporating PVP into a solution, which realizes a highly stable viscosity and allows the formation of crack-free PZT films of several thousands angstroms. Acetylacetone is chelating reagent to suppress the rapid hydrolysis reaction. A film of 3000 Å without any cracks is obtained on a $Pt/Ti/SiO_2/Si$ substrate by non-repetitive, single-step spin coating. The resultant film is almost single-phase perovskite PZT and it exhibited *P-E* hysteresis typical of ferroelectrics. Remanent polarization *P*r and coercive field *E*c values are 48 μCcm^{-2} and 100 $kVcm^{-1}$ respectively. Piezoelectricity is preliminarily confirmed by applying an impulsive vibration. For an example of application of PZT films, an ultrasonic sensor array of diaphragm type is fabricated by a micro machining process.

Keywords: PZT, Sol-gel method, PVP(polyvinylpyrrolidone), acetylacetone, ultrasonic sensor

1 INTRODUCTION

Sol-gel method comprises coating solution containing raw material on a substrate, pre-baking for evaporation of solvent and post-annealing for crystallization. Since the process can be carried out in ambient atmospheric pressure and does not need expensive apparatuses, sol-gel method is very attractive and many research papers related to this method have been published [1].
It has been already reported that a perovskite PZT (lead zirconate titanate : $Pb(ZrTi)O_3$) film can be prepared by sol-gel method. However, as far as using commercial specific solutions, cracks are liable to occur in the post-annealing process when the thickness of the PZT film is larger than several hundred angstroms. Therefore, forming many thin layers of film successively is usually done in order to prevent cracks in MEMS research, in which the thickness of several microns is required [2]. However, many time repetition of spin coating, pre-baking and post-annealing is time consuming and laborious process, which also increases the probability of contamination. Considering these circumstances, depositing a thick film at once without any cracks is strongly being desired for the purpose of successful industrialization of sol-gel PZT films.

In this research, PZT films are deposited on $Pt/Ti/SiO_2/Si$ (0.18/0.06/1/500 μm) substrates by single-step spin coating using a $Pb(NO_3)_2$-$Zr(OC_3H_7^n)_4$-$Ti(OC_3H_7^i)_4$ solution containing polyvinylpyrrolidone (PVP) and acetylacetone ($CH_3COCH_2COCH_3$) [3]. This solution is not commercial but prepared in the laboratory. The key point is incorporating PVP into a coating solution, which realizes a highly stable viscosity and allows the formation of crack-free PZT films of several thousands angstroms. Acetylacetone is chelating reagent to suppress the rapid hydrolysis reaction. PZT films obtained from this solution are surely without cracks, and several times as thick as those obtained from commercial solutions.
Crystalline structure and the ferroelectric characteristics of the obtained film are experimentally examined. For an example of application of PZT films, an ultrasonic sensor array is fabricated by a micro machining process.

2 PREPARATION OF SOL-GEL SOLUTION

In order to obtain a relatively thick PZT film by single-step sin coating, the sol-gel solution containing PVP is prepared in the laboratory.
The molar composition of the solution is as follows:
$Pb(NO_3)_2$:$Zr(OC_3H_7^n)_4$:$Ti(OC_3H_7^i)_4$:PVP:acetylacetone:
$CH_3OC_2H_4OH$:*n*-C_3H_7OH=1.1:0.53:0.47:1:0.5:22:0.98,
where $CH_3OC_2H_4OH$ and *n*-C_3H_7OH are solvent.
The mechanism of formation of crack-free film is that PVP suppress the rapid dehydration and condensation reaction during heating and annealing, which leads to relax the intrinsic stress of the film.

The preparation process flow is shown in **Fig.1**. The molar composition and weighing value of reagents are shown in **Table 1**.
First, $Pb(NO_3)_2$ is dissolved in $CH_3OC_2H_4OH$ with stirring for 1 hour. Then PVP is added and stirred until it is completely dissolved, which takes about 3 hours. Next TPZR solution, which comprises $Zr(OC_3H_7^n)_4$ and

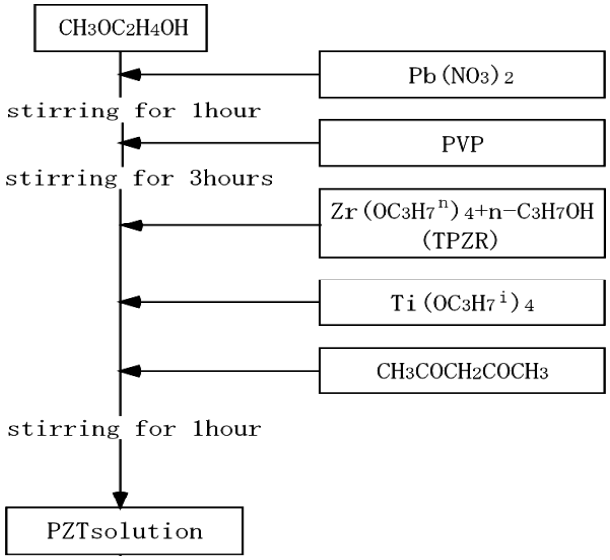


Fig.1 Preparation process flow of PZT solution

Table 1 Molar composition and weighing value of reagents

	Molar composition	Weighing value
Pb	1.1	5.1 g
Ti	0.47	1.87 g
$CH_3OC_2H_4OH$	22	24.31 ml
TPZR	0.53	3.25 g
Acetylacetone	0.5	0.72 ml
PVP	1	1.56 g

n-C_3H_7OH, is added and stirred for 1 minute. And $Ti(OC_3H_7^{i})_4$ solution is added and stirred for 1 minute. Then acetylacetone is added and stirred until it is completely dissolved, which takes about 1 hour. The resultant solution is transparent and shows a highly stable viscosity.

3 DEPOSITION OF PZT FILM BY SOL-GEL METHOD

As the substrate on which the PZT film is to be deposited, an oxidized silicon substrate is prepared. SiO_2 layer acts as an insulator on which the lower electrodes are fabricated. It is known that perovskite PZT is generated on the (111) oriented surface of Pt (platinum), which acts as the bottom electrode. This Pt layer is thought to play role of defining and assimilating the direction of crystalline growth of PZT.

As a test, PZT film is prepared by sol-gel method (the condition is the same as mentioned later in case of on $Pt/Ti/SiO_2$ surface) on bare silicon surface, however, cracks occurs severely and the film itself is very porous as shown in **Fig.2**. It means that direction of crystal grain is not assimilated and some internal stress is generated, which eventually causes cracks.

Considering this, similarly to other researches, $Pt/Ti/SiO_2$ surface is adopted in this research. First Ti (titanium) layer of 600 Å is deposited by sputtering method in order to increase the adhesion between Pt layer and SiO_2 surface of the substrate. Also, Ti atoms diffuse to the surface of Pt layer and form TiO_2, which acts as nucleation sites for PZT crystallization. Furthermore, the presence of TiO_2 can prevent Pb from diffusing into Pt layer [4]. Next, Pt layer of 800 Å is deposited on Ti layer by also sputtering method. Finally, $Pt/Ti/SiO_2/Si$ (0.18/0.06/1/500 μm) substrate is prepared.

Table 2 Condition of sol-gel preparation of PZT

Spin coating	500 rpm 5 s
	5000 rpm 60 s
Baking	120 ℃ 10 min
	350 ℃ 10 min
	650 ℃ 10 min

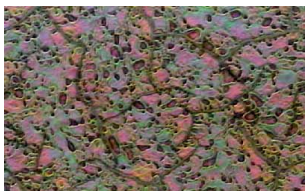


Fig.2 Optical microscope image of PZT film surface on bare Si

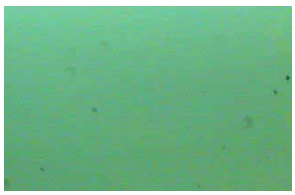


Fig.3 Optical microscope image of PZT film surface on $Pt/Ti/SiO_2$

The solution, of which preparation is explained in the previous chapter, is spin coated on the substrate at 500 rpm for 5 sec. and at 5000 rpm for 60 sec. The resultant film is heated successively at 120 °C and 350 °C on a hot plate, and at 650 °C in an electric furnace for 10 min. respectively. These conditions are shown in **Table 2**.

The optical microscope image of the surface of the resultant film is shown in **Fig.3**. It seems there are no cracks. The thickness of this film is checked by surface profiler and it is 0.3 μm (3000 Å), which is relatively thick compared with that obtained from a commercial solution (the example of the case of commercial solution is explained in the next chapter in detail).

4 CHARACTERIZATION OF PZT FILM

4.1 Crystalline Structure

The crystalline structure of the resultant PZT film is investigated by x-ray diffraction (XRD). The result of XRD pattern is shown in **Fig.4**. It is proved that the film is almost single-phase perovskite PZT without precipitation of pyrochlore. The perovskite structure plays important role in realizing good ferroelectric property. Ferroelectric material necessarily shows piezoelectric property.

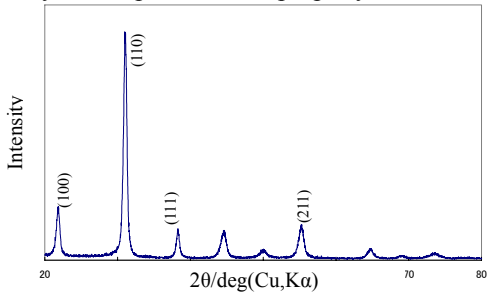


Fig.4 XRD pattern of PZT film

4.2 Ferroelectric Propertuy

The polarization-electric (*P-E*) field characteristics are examined at 60 Hz, where upper Pt electrodes of 0.2 mm in diameter are deposited onto the film. The film exhibited *P-E* hysteresis typical of ferroelectrics as shown in **Fig.5**. The remanent polarization *P*r and coercive field *E*c values are 48 μCcm^{-2} and 100 kVcm^{-1} respectively. Higher *P*r and lower *E*c are preferable in the point of view of ferroelectricity.

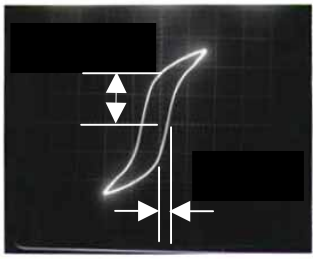


Fig.5 *P-E* hysteresis loop of PZT film

For reference, a PZT film is obtained from a commercial solution (Mitsubishi material, A6 type) at a spinning rate of 4000 rpm. The thickness is 0.07 μm by single-step spin coating. Coating process is carried out for three times and thickness of 0.21 μm is obtained. *P*r and *E*c of this film are 57 μCcm^{-2}, 120 kVcm^{-1} respectively. The comparison of these data with that obtained from the solution containing PVP is shown in **Table 3**.

It is proved from these results that the PZT film utilizing PVP is fairly thick, while keeping good ferroelectrics characteristics.

4.3 Preliminary Confirmation of Piezoelectricity

It is confirmed preliminary whether the resultant PZT film has piezoelectricity or not. The experimental setup is shown in **Fig.6**. A weight is put on the film surface and impulsive vibration is input to the substrate by hitting the table. Namely, the inertia force acting the weight generates the strain in PZT film in vertical direction. The voltage between upper and lower electrodes is measured by an oscilloscope.

This vibration is also measured by a commercial accelerometer simultaneously. The result of vibration measurement is shown in **Fig.7**.

Table 3 Chacteristics of PZT films

	Solution containing PVP	Commercial solution
Spinning rate	5000 rpm	4000 rpm
Number of spin coating	1 time	3 times
Thickness	0.3 μm	0.21 μm
Remanent polarization *Pr*	48 μccm-2	57 μccm-2
Coercive field *Ec*	100 kvcm-1	120 kvcm-1

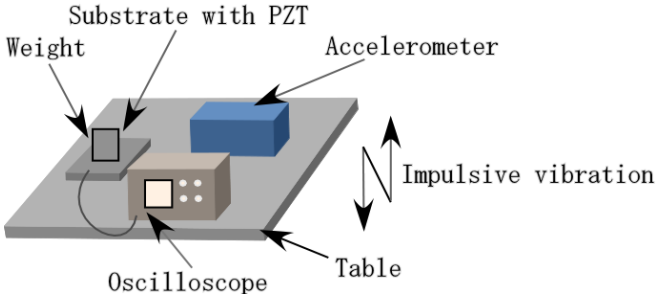


Fig.6 Experimental setup for piezoelectricity confirmation

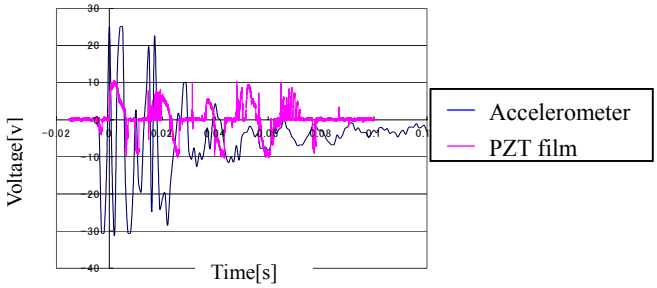


Fig.7 Result of vibration measurement

The signal from the PZT film does not coincide with that from the accelerometer and the difference between them is large. The reason of it is thought to be as follows: the positions of them were different, which means the input vibrations of them were different. Also, the weight is not adhered to the film surface completely on account of experimental condition.

Although the problem exists as mentioned above, it is proved that surely some signal is generated from the PZT film, which means this film has piezoelectricity.

5 STRUCTURE AND FABRICATION OF MICRO ULTRASONIC SENSOR

5.1 Design of micro ultrasonic sensor

In manufacturing a micro ultrasonic sensor of diaphragm type, a SOI substrate (Si: 3 μm, SiO_2: 1 μm, Si: 300 μm) is adopted, since the high reproducibility is expected and the thickness of the diaphragm can be uniformly kept. The cross section of the sensor structure is shown in **Fig.8**. The size of square diaphragm (515 μm) and the thickness of PZT (0.9 μm) are decided so as that the resonant frequency becomes to be around 100kHz.

The fabrication process flow is shown in **Fig.9**. The process is as follows: A SOI wafer is prepared and oxidized on both sides. Front side SiO_2 is to make an insulator layer for lower electrodes. Back side SiO_2 is to make a mask layer for anisotropic etching (see Fig.(1)).

The SiO_2 layer on the backside is patterned to make windows for forming the diaphragm. Bulk silicon is anisotropically etched by using TMAH (tetra methyl ammonium hydroxide) until the thickness of the silicon part becomes to be about 50 μm (see Fig.(2)). The reason of leaving relatively thick silicon is to keep the mechanical strength of the substrate enduring spin coating process of PZT sol-gel solution afterward.

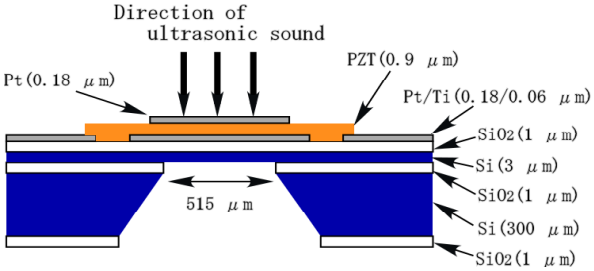


Fig.8 Cross section of ultrasonic sensor structure

Photoresist is spin-coated and patterned for the lower electrode. After that, Ti (0.06 μm) and Pt (0.18 μm) is deposited by sputtering and followed by a lift off process (see Fig.(3)).
PZT film of 0.9 μm is prepared by carrying out sol-gel process for three times, and is patterned by $HF:HNO_3:H_2O$=1:1:100 solution to reveal lower electrode for electrical contact (see Fig.(4)).
Photoresist is spin-coated and patterned for the upper electrode. After that, Pt (0.18 μm) is deposited by sputtering and followed by a lift off process (see Fig.(5)).
Front side is coated by Parylene film of 2 μm. The remained silicon part of 50 μm is etched away by using TMAH, while PZT is protected from TMAH by Parylene. SiO_2 layer of 1 μm is also etched away by using BHF. After that, Parylene film is removed by O_2 plasma ashing (see Fig.(6)).

An example of fabricated sensor device is shown in **Fig.10**. The characterization of resonant frequency, sensitivity, etc. of this sensor is under preparation.

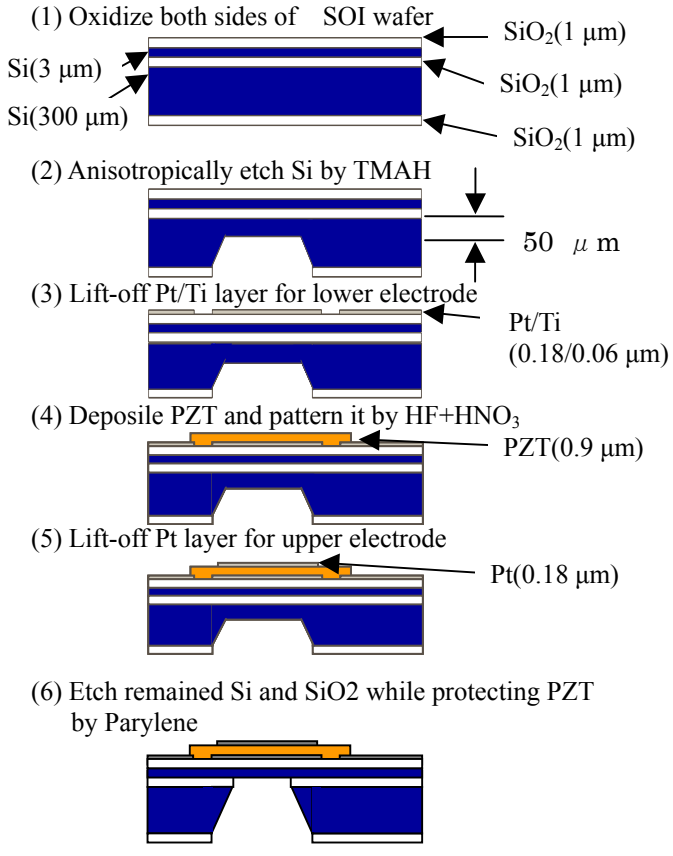
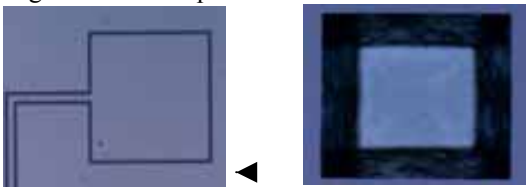


Fig.9 Fabrication process flow of ultrasonic sensor



(a) Front side (b) Back side

Fig.10 Image of fabricated ultrasonic sensor

6 CONCLUSION

PZT solution containing PVP(polyvinylpyrrolidone) and acetylacetone is prepared in the laboratory. By sol-gel method, a relatively thick PZT film of 3000 Å without any cracks is obtained on a $Pt/Ti/SiO_2/Si$ substrate by non-repetitive, single-step spin coating. The resultant film is almost single-phase perovskite PZT and it exhibited *P-E* hysteresis typical of ferroelectrics. Remanent polarization *P*r and coercive field *E*c values are 48 μCcm^{-2} and 100 $kVcm^{-1}$ respectively. For an example of application of PZT film, an ultrasonic sensor using this film is designed and fabricated.

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