Proceedings

Sensitivity of Piezoelectric Ultrasonic Microsensors with Sol-Gel Derived PZT Films Prepared through Various Pyrolysis Temperatures †

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Abstract: Sensitivity of piezoelectric-diaphragm type ultrasonic microsensors were investigated with sol-gel derived lead-zirconate-titanate (PZT) films prepared through various pyrolysis temperatures. The residual stress of the PZT film should be precisely controlled because the sensor diaphragms show static deflection by buckling and highly sensitive sensors have been realized on upward-buckled diaphragms whose buckling direction and deflection are determined by the stress. The films were prepared under pyrolysis temperatures in the range from 250 °C to 400 °C and for (100)- or (111)-orientation. Higher pyrolysis temperature resulted in lower film stress and larger buckling deflection of the diaphragms. The (111)-oriented films showed the higher sensitivity in the higher pyrolysis temperatures. The (100)-oriented films, however, showed the highest sensitivity in the lowest pyrolysis temperature (250 °C).

Keywords: PZT; sol-gel; pyrolysis temperature; residual stress; crystallographic orientation; ultrasonic sensor; sensitivity; diaphragm; buckling

1. Introduction

Piezoelectric ultrasonic microsensors on MEMS (microelectromechanical systems) structures have been developed especially for airborne ultrasonic applications to gesture recognition [1] or fingerprint sensing [2]. The authors have been developing piezoelectric MEMS array sensors using sol-gel derived PZT films [3]. Figure 1 illustrates a structure of our ultrasonic microsensor with the piezoelectric diaphragm. The diaphragm consists of a PZT capacitor and a thermally oxidized silicon (SiO_2) film. The SiO_2 film has strong residual stress on the silicon wafer and the stress is released by removing silicon under the diaphragm with resulting in the diaphragm buckling, as shown in Figure 1b,c. The authors reported that the buckling of the diaphragm strongly affects the sensitivity [4]; upward-buckled diaphragms show higher sensitivity than flat or downward-buckled ones. The sol-gel PZT has tensile residual stress, and it turns the buckling direction to upward [5] whereas it decreases the buckling deflection. Accordingly, the PZT stress should be precisely controlled in an adequate range to be small enough to yield a large buckling deflection but to be still large enough to turn the buckling direction upward. The authors previously reported that the preparation condition of the sol-gel PZT affects the buckling deflection of the PZT diaphragms [6]. In this work, the stress of the PZT films and the sensitivity of the sensors using the PZT films were investigated with sol-gel films prepared under various pyrolysis temperatures and for crystallographic orientations.

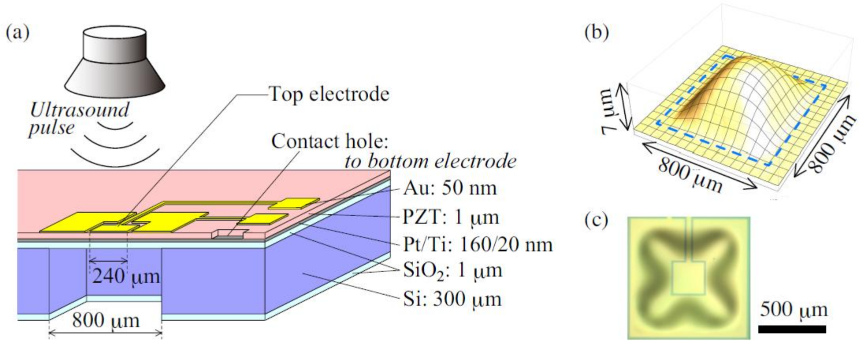

Figure 1. The sensor structure with a buckled diaphragm. (**a**) A schematic illustration of the sensor structure; (**b**) a profile of a buckled diaphragm; and (**c**) its photograph.

2. Experiments

A 2-inch silicon wafer with 1 μm-thick thermal oxide was the start substrate. Platinum film was deposited on the substrate by using rf magnetron sputtering in room temperature as the bottom electrode continuously following to titanium film deposition as an adhesion layer. The PZT film was deposited on the bottom electrode by using sol-gel method. The crystalline texture of the PZT films was determined by X-ray diffraction on Discover-8 (Bruker, Yokohama, Japan). The stress of the PZT film was determined using Stoney's formula [7] with bending profile of the wafer measured by a stylus profiler Dektak-XT (Bruker, Tokyo, Japan). After the stress evaluation, the wafer was processed to form the sensor structure; Top electrode of gold film was deposited by using rf magnetron sputtering, and the gold and PZT films were patterned to form the capacitor shape and the contact hole. The oxide film on the backside was etched to form windows and finally the substrate was vertically etched through the windows to form the thin diaphragm structure by using conventional Bosch process on RIE-400iPB (SAMCO, Kyoto, Japan). The buckling profile of the diaphragms was determined by using a laser profiler LT-9000 (Keyence, Kyoto, Japan). The sensitivity of the sensor was calibrated by using microphone Type-4831 (Brüel & Kjær, Tokyo, Japan).

Table 1 shows the preparation parameters of the PZT films. The sol-gel solution used here is a product of Mitsubishi Materials, E1-type (Pb/Zr/Ti = 115/52/48, 15% wt in 1-butanol solvent.) The films having 950 nm-thick are obtained by repeating the set of spin-coating and pyrolysis for totally 15 times, together with 3 or 4 crystallization anneals corresponding to type A or type B films; The type-A films have the first crystallization layer of 320 nm-thick, to be expected to prefer (111) orientation. The type-B films have the first crystallization layer of 60 nm-thick, to be expected to prefer (100) orientation. The spin coating and pyrolysis were carried out in normal air ambient. The pyrolysis temperature was set to 250, 300, 350, or 400 °C on a conventional hot plate. The crystallization anneals were carried out in a tube furnace at 650 °C in pure oxygen ambient, for 10 min except for the last annealing for 30 min.

Table 1. Preparation conditions of sol-gel PZT films.

(**a**) Sol-gel process parameters.				
	Process	**Condition**	**Time**	**Repetition**
(i)	Spin coating Pyrolysis	4,000 rpm T [◦C], air	20 s 10 min.	1 † or 5 times before annealing
(ii)	Annealing	650◦C, O_2	10 min *	3 or 4 † times
(**b**) Pyrolysis temperatures.				
***T* [◦C]**	**250**	**300**	**350**	**400**
(**c**) Annealed layers.				
	Type A	5th, 10th, 15th		
	Type B	1st, 5th, 10th, 15th		

* 30 min for the last annealing. † Type-b process.

3. Results and Discussion

Figure 2 shows the XRD patterns of the PZT films. The type-A films showed the orientation to (111) direction, except for the 400 °C-pyrolyzed case. The height of (111) peak once increases with increasing the pyrolysis temperature up to 300 °C, and decreases to 400 °C, which means the crystallographic orientation of the type-A films was affected by the pyrolysis temperature. On the other hand, all the type-B films showed preferred orientation to (100) direction.

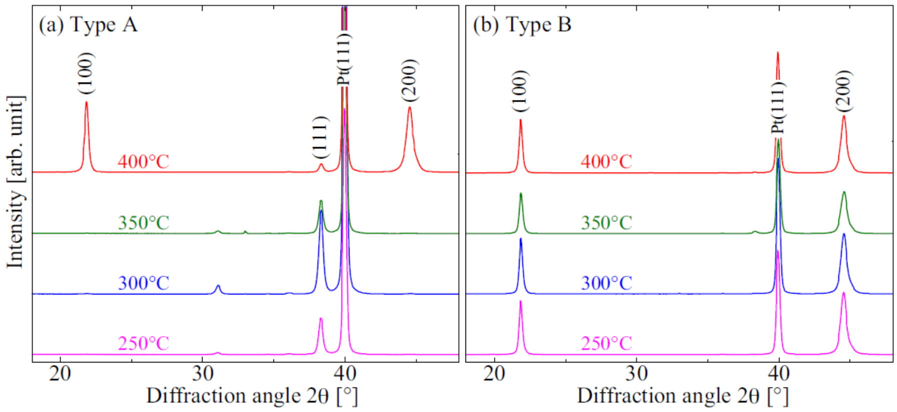

Figure 2. XRD patterns of the prepared PZT films through (**a**) type-A annealing schedule (320 nm-interface layer) and (**b**) type-B annealing schedule (60 nm-interface layer).

Figure 3 shows the in-plane tensile stress of the PZT films evaluated on the wafer. The (111)-oriented films show higher stress than the (100)-oriented ones, and the stress decreases with increasing the pyrolysis temperature in the both orientation cases. Figure 4 shows the buckling deflection of the sensor diaphragms fabricated from the wafers. The diaphragms with (111)-oriented PZT films show almost no buckling due to too strong PZT stress, whereas the (100)-oriented PZT films pyrolyzed over 250 °C shows the buckling deflection of 12–15 μm. This suggests that the PZT stress corresponding to the buckling limit of the diaphragm exists around 150 MPa. Diaphragms with 250 °C-pyrolyzed and (100)-oriented films show a scattered buckling deflection. This film has a scattered stress around the buckling-limit stress, and thus the buckling deflection of the diaphragms also scatters from no buckling (film stress above the buckling limit) to buckling with the deflection of 9 μm (film stress below the buckling limit).

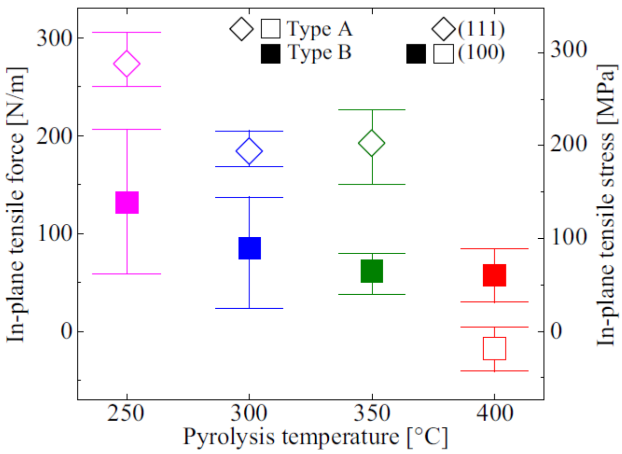

Figure 3. In-plane tensile force and stress of the prepared PZT films on wafers.

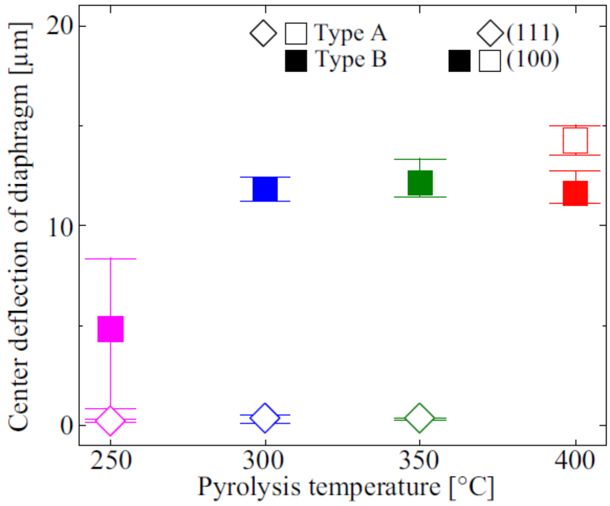

Figure 4. Diaphragm deflection versus PZT pyrolysis temperature.

Figure 5 shows the sensitivity of the sensors on the diaphragms with the PZT films. The sensors on diaphragms with no buckling shows low sensitivity less than 10 μV/Pa, whereas those with buckling show sensitivity over 10 μV/Pa. The 250 °C-pyrolyzed and (100)-oriented film sensors show much higher sensitivity around 50 μV/Pa than the other buckled-diaphragm sensors, although the buckling of the diaphragms is smaller than that of the other buckled ones. This high sensitivity can not be explained from the conventional relation between the buckling deflection and the sensitivity. Further examinations are necessary for the films including dielectric, ferroelectric and piezoelectric properties, and the relation to the buckling-limit stress might be also needed to be investigated.

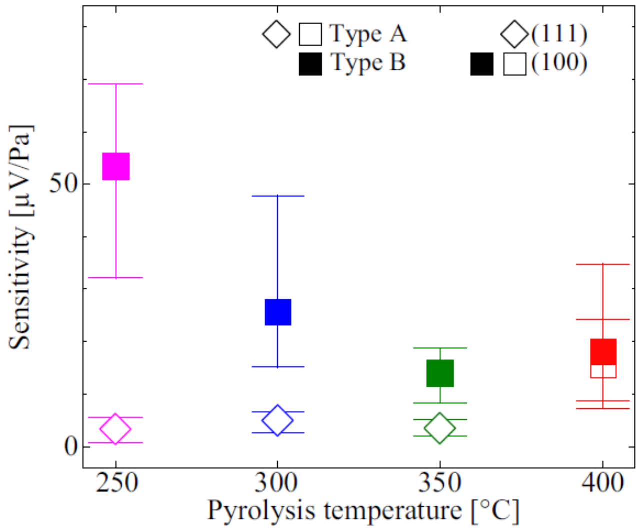

Figure 5. Sensitivity of the sensors having PZT films pyrolyzed at various temperatures.

4. Conclusions

Residual stress of sol-gel derived PZT films were investigated from the viewpoint of sensitivity of micromachined ultrasonic sensors with buckled diaphragm structures. Pyrolysis temperature in the sol-gel process were varied from 250 °C to 400 °C and the thickness of initial annealed layer was controlled to have a preferred orientation to (111) or (100). The PZT stress decreased with increasing the pyrolysis temperature, and the (111)-oriented films showed higher stress than (100)-oriented ones. The PZT stress corresponds to the buckling limit of the diaphragm was estimated around 150 MPa. Although most sensors with the buckled diaphragms showed higher sensitivity than those with no buckled diaphragms, the sensors with the 250 °C-pyrolyzed and (100)-oriented films showed exceptionally high sensitivity. The reason of the high sensitivity can not be explained from the conventional deflection-sensitivity relation. Further investigation is necessary to reveal the origin of the high sensitivity of the films including electrical property and relation to the buckling limit.

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Author Contributions: K.Y. conceived and designed the experiments; S.N. and J.S. performed the experiments; K.Y., S.N., J.S. and M.N. analyzed the data; K.Y. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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