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Intrinsic Stress Control of Sol-Gel Derived PZT Films for Buckled Diaphragm Structures of Highly Sensitive Ultrasonic Microsensors

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Abstract

Intrinsic stress of sol-gel derived lead-zirconate-titanate (PZT) films has been investigated from the viewpoint of diaphragm buckling behavior for highly sensitive structures of piezoelectric ultrasonic microsensors. Since upward-buckled diaphragms of the sensors yield higher sensitivity than flat or downward ones, a fabrication process which enables the diaphragms to buckle spontaneously upward was developed owning to intrinsic tensile stress of the PZT films. To control the intrinsic stress as adequate for the upward buckling, calcination temperature in the sol-gel deposition process has been modified in the range from 300°C to 400°C. The stress has decreased with increasing the temperature in the range and the 400°C-calcined PZT films have shown a suitable stress for the buckling deflection and probability of upward buckling for the sensor diaphragms.

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Keywords: sol-gel PZT; stress; diaphragm; buckling; sensitivity; ultrasonic sensor

1. Introduction

Piezoelectric ultrasonic microsensors have been developed for applications to underwater inspection, medical diagnosis and gesture recognition [1–5]. The authors have been developing ultrasonic microsensors with sol-gel derived PZT ($Pb(Zr,Ti)O_3$) thin films on silicon dioxide (SiO_2) thin diaphragm structures as illustrated in Fig. 1. The SiO_2 layer has a large compressive residual stress caused in its formation process during thermal oxidation of the silicon substrate, and the diaphragm with the SiO_2 layer buckles to show a static deflection if the total in-plane expansion force in the diaphragm exceeds its buckling limit when the diaphragm is released from the substrate. The static deflection of the piezoelectric sensor diaphragms strongly affects their sensitivity through linear and nonlinear components of in-plane strain on the vibrating diaphragm [6]. Figure 2 shows the output signals of the sensors versus center deflection of the diaphragms [7]. Here the upward buckling is defined as the buckling direction such that the buckled

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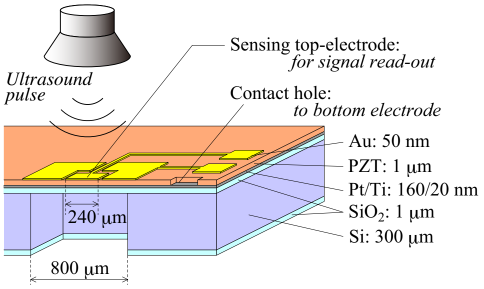

Fig. 1. A schematic illustration of the completed sensor structure. Although the diaphragm part is illustrated to be flat in this figure, fabricated diaphragm structures tend to show a static deflection due to the residual stress of the SiO_2 layer.

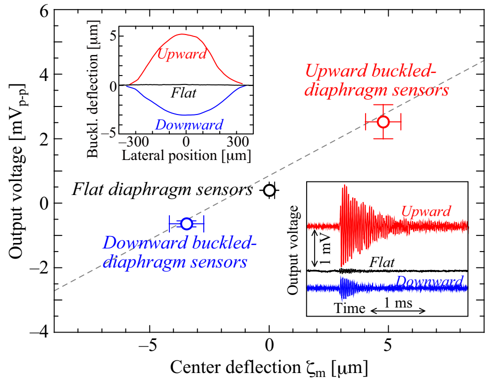

Fig. 2. Output voltage versus the center deflection of the sensor diaphragm. The dashed curve shows a calculation result of the sensitivity dependence for the structure shown in Fig. 1. The insets show typical buckling profiles of the diaphragms and examples of the response waveforms from the sensors.

diaphragm makes the PZT side convex and the SiO_2 side concave. The nonlinear component is negligible if the static deflection is small enough but the component rapidly increases in proportion to square of the deflection. These two components of the strain are summed up in the upward buckling region but cancel each other in the downward buckling region. The sensors with 5 μm upward buckled diaphragms show three or five times higher sensitivity compared to flat or downward ones.

The authors recently found that the buckling direction is controlled through the stress combination of the stacked layers of the diaphragm at the buckling limit during the silicon backside etching, and a tensile-stressed layer on the front side of the diaphragm causes upward buckling moment [8]. A sol-gel PZT film has tensile residual stress due to volume shrinkage during crystallization annealing and it is suitable for the front-side-tensile structure. The sol-gel PZT film for the ultrasonic microsensors needs to be deposited up to 1 μm for its piezoelectric performance, however, the full-thick, 1 μm PZT does not allow the diaphragm to buckle due to its too strong tension [9]. Previously the authors reported two-step deposition of the sol-gel PZT; half-thick PZT deposition before the silicon bulk etching to allow the diaphragms to buckle, then additional deposition of the PZT up to the full-thickness afterwards [8]. Although this technique enables the diaphragms to buckle upward even with the full-thick PZT of 1 μm, the two-step deposition is troublesome, especially in the second step: the diaphragms are easily broken during the spin-coating process of the sol-gel solution on the thin, fragile and curved diaphragm structures. The difficulty will be overcome if the tensile stress of the PZT film is reduced and the full-thick PZT allows the diaphragm to buckle. In this work the authors tried to reduce the intrinsic stress of the PZT films by modifying the calcination temperature in the sol-gel deposition process, expecting that volatile components remaining in the films affect the residual stress after the crystallization.

2. Experimental

A thermally oxidized 2 in-Si(100) wafer was used as a substrate and the bottom electrode of Pt(160 nm)/Ti(20 nm) was deposited on it by using rf magnetron sputtering at room temperature. A sol-gel solution (E1 type, Mitsubishi Materials Corp.) with the composition Pb/Zr/Ti = 115/52/48 at 15%wt in 1-butanol solvent was used to form the PZT thin films. The sol-gel preparation parameters are shown in Table 1. The solution was spin-coated on the substrate in 4,000 rpm for 20 s and calcined on a hot plate for 10 minutes to obtain a gel film. The calcination temperature T was selected as T = 300, 350 or 400°C. The gel film was annealed in a conventional tube furnace at 650°C in O_2 ambient to obtain a crystallized film. The PZT film formed through one set of the spin-coating, calcination and annealing has the thickness around 63 nm. To obtain thicker films up to near the full-thickness of 1 μm, the set of the spin-coating and calcination was repeated five times before the annealing, and 315, 630 and 945 nm-thick PZT samples were fabricated repeating the set until the annealing in one, two and three times. The annealing time is 10 minutes except for the final annealing for 30 minutes. After completed the PZT film deposition, the SiO_2 film on the

Table 1. Variations of sol-gel deposition parameters and thickness of the PZT samples.

(a) Sol-gel PZT formation process parameters.

Process	Condition	Time	Repetition
Spin-coating	4,000 rpm	20 s	m times be-
Calcination	T [°C], air	10 min.	fore annealing
Annealing	650 °C, O_2	t_i [min.]	k times

(b) Calcination temperatues.

T = 300, 350, 400 [°C]

(c) Thickness variation and process repetition.

63 nm	315 nm	630 nm	945 nm
$m = 1$	$m = 5$	$m = 5$	$m = 5$
$k = 1$	$k = 1$	$k = 2$	$k = 3$
$t_1 = 30$	$t_1 = 30$	$t_1 = 10$	$t_1 = 10$
		$t_2 = 30$	$t_2 = 10$
			$t_3 = 30$

backside were etched to make windows for the mask pattern to define the diaphragms in size $800 \times 800\,\mu m^2$, and the silicon was etched from the backside through the windows with an inductively coupled plasma-reactive ion etching (ICP-RIE) apparatus (RIE-400iPB, Samco Inc.) through a typical silicon deep etching technique (Bosch process) with the combination of SF_6-etching and C_4F_8-deposition. The diaphragm arrangement pattern on a wafer was the same as that for the ultrasonic array sensors; 7×7 diaphragms in a chip and 2×2 chips on a wafer, total 196 diaphragms on a wafer. All samples were evaluated without the top electrode in order to prevent the stress effect of the gold films.

The buckling direction of all diaphragms on a wafer were evaluated with an optical microscope. Upward buckling probability is defined as the ratio of the number of the upward-buckled diaphragms to that of the total number of diaphragms. Buckling profiles were measured with a surface scanning laser confocal displacement meter (LT-9000, Keyence Corp.) on ten diaphragms randomly selected form each wafer and an average buckling deflection was determined for each PZT deposition condition.

3. Results and Discussion

Figure 3 shows typical examples of three-dimensional profiles of diaphragms with the 945 nm-thick PZT. Figure 3 (a) shows almost flat profile with the maximum deflection less than $0.5\,\mu$m, which is near the noise level of the displacement meter. On the other hand, the diaphragm shown in Fig. 3 (b) exhibits a smooth buckling surface with maximum deflection up to $7\,\mu$m. The difference of the buckling behavior corresponds to the calcination temperature difference. Figures 4 and 5 show the buckling behavior of the fabricated diaphragms.

The probability of the upward buckling versus PZT thickness for the variety of the calcination temperatures is shown in Fig. 4. Larger tension is generated in the diaphragms with thicker PZT films and the probability of the spontaneous upward buckling increases. For the samples with the same PZT thickness, lower calcination temperatures enable the diaphragms to more easily buckle upward owing to larger tension, which means that the PZT calcined at a lower temperature causes a larger tensile stress. For the upward buckling, the 300°C-calcination case is an exception; these diaphragms were flattened or broken due to too strong diaphragm tension caused by a too strong tensile stress of the PZT film. Figure 5 shows the buckling deflection versus the PZT thickness for the variety of the calcination

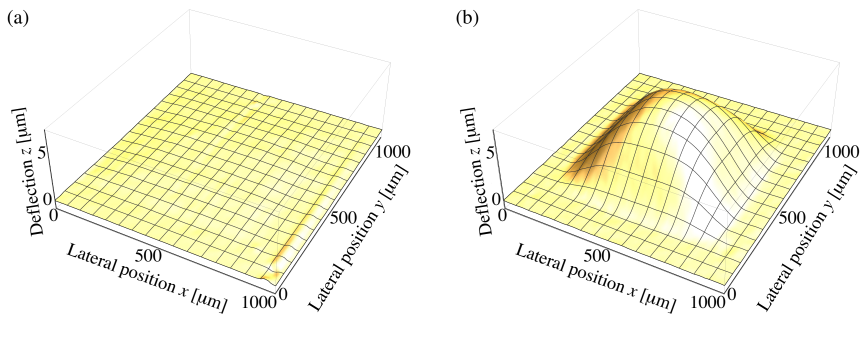

Fig. 3. Typical examples of 3D profiles of (a) flat and (b) upward-buckled diaphragms with full-thick PZT.

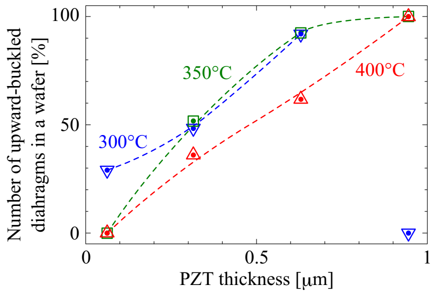

Fig. 4. The number of upward-buckling diaphragms in percentage versus PZT thickness.

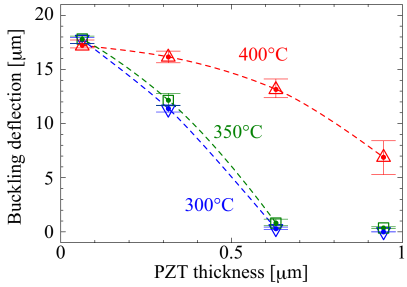

Fig. 5. Buckling deflection versus PZT thickness. The error bars indicate scattering of the deflection of ten diaphragms randomly selected from each wafer.

temperatures. The lower calcination temperatures generate the larger tensile stress, and the PZT films thicker than 600 μm calcined at 300 or 350°C cause too strong tension in the diaphragms resulting in small buckling deflections less than 1 μm. The upward buckling deflection over 6 μm, which is large enough for the highly sensitive structures as shown in Fig. 2, is obtained even on the full-thick PZT calcined at 400°C. These results indicate that the stress of the sol-gel derived PZT films were successfully controlled through the calcination temperature, and 400°C-calcination is adequate for the highly sensitive buckled diaphragm structures.

4. Conclusions

Buckling behavior of silicon-micromachined piezoelectric diaphragms was investigated for highly sensitive structures of ultrasonic microsensors. Although upward-buckled diaphragms yield higher sensitivity than flat or downward ones and tension of PZT films on the front side of the diaphragms cause upward buckling moment, too strong tension in the diaphragms does not allow them to buckle, and the tension should be controlled adequately. To control the intrinsic stress of sol-gel derived PZT films as suitable for the upward buckling, calcination temperature in sol-gel deposition process was varied from 300°C to 400°C. The 400°C-calcined PZT films showed suitable stress for the buckling deflection and probability of upward buckling for the sensor diaphragms. In this work, the authors focused on the buckling behavior with the calcination temperature. The quality of the PZT films in crystallographic, electrical and piezoelectric property will be next examined for the variety of the calcination temperatures, and actual sensitivity will be evaluated using full structured sensors with the PZT films.

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