MASS-PRODUCTION OF PZT FILMS USING AUTOMATED SOL-GEL DEPOSITION SYSTEM FOR 8 INCH WAFER

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Abstract: In this work it has been investigated the suitability of piezoelectric PZT films using automated sol-gel deposition system for 8-inch wafer as an actuating element in MEMS devices. It has been confirmed that the defects on PZT films and PZT orientation were influenced by pyrolysis temperature. As the result of the optimization, the number of defects on the 8-inch wafer was decreased up to less than 10 pieces by the coating condition with the pyrolysis temperature of 250 degree C for the seed layer and 300 degree C for the following layers. The piezoelectric quality of the PZT films on the condition was measured that the PZT(100)(001)-oriented was strong up to 87 %, the remnant polarization was 27 μC/cm^2 , the piezoelectric constant d_{33} was 173 pm/V and uniformity of properties was at most 13 percent.

Keywords: PZT, Sol-gel, Pyrolysis, Mass-production

INTRODUCTION

The piezoelectric material of PZT has been used for various MEMS devices such as physical sensors, ink-jet heads, silicon micro-phones, micro-scanners [1], and so on. In these various MEMS devices, piezoelectric vibration energy harvesters (PVEH) has widespread attention with its practical value. The advantage of PZT over other piezoelectric materials is a high value of piezoelectric constant, d_{31} and d_{33}. The market scale for piezoelectric devices is expected to grow into a few billion US$ in 2012. Mass-production for PZT MEMS are needed Large Scale Wafer Fabrications.

The deposition methods for PZT can be categorized into four types, Sol-Gel, sputtering, MO-CVD and PLD. PZT deposition system currently sold to the world for 8-inch wafer is shown in *Table 1*[2-3]. Although PLD and Sputter have a high piezoelectric constant, uniformity of this property for 8-inch wafer is not clear. The sol-gel process is the most promising way for a large area deposition due to better uniformity of the thickness and the piezoelectric constant than the other methods. In addition, the equipment price for sol-gel process is inexpensive and the maintenance of the equipment is easy.

In this study, we designed automated sol-gel deposition system for 8-inch wafer and developed fabrication processes of PZT films for a PVEH. As the result, we confirmed the fabricated PZT films for a PVEH.

Table 1: PZT deposition system for 8 inch wafer.

Maker	SolmateS	ULVAC	SOKUDO
Deposition method	PLD 	Sputter 	Sol-gel 
Piezoelectric constant	180(d_{33})	12($e_{31\cdot f}$)	---
TAT/μm	60 min	20 min	60 min
Price	$2.56M	$1.9M	$1.5M

THEORETICAL CALCULATION

We set up the condition for the PVEH which we achieved the generated power more than 100 μW. Qiang Zou et al.,[4] and T.Yoshimura et al.,[5] reported the power delivered by a PVEH. The simple PVEH model for simulated power is shown in *Fig. 1*. The simple equivalent circuit of PVEH is a parallel connection of the PZT films and load resistor as shown in *Fig. 2*. The power P [4-5] is given by

$$\boldsymbol{P} = \frac{1}{R} \times \left(\frac{Q\cdot acc}{C_p}\right)^2$$

$$= \frac{acc^2}{R\cdot {C_p}^2} \times \left(\frac{d_{33}/3\cdot E_{\mathrm{p}}\cdot Z_{\mathrm{p}}\cdot m\cdot L^2}{E_S\cdot\left(\frac{1}{12}\cdot h_S{}^3 + h_S\cdot Z_S{}^2\right) + E_p\cdot\left(\frac{1}{12}\cdot h_{\mathrm{p}}{}^3 + h_{\mathrm{p}}\cdot Z_{\mathrm{p}}{}^2\right)}\right)^2 \quad (1)$$

$$C_{\mathrm{p}} = \varepsilon_0\cdot\varepsilon_{\mathrm{r}}\cdot\frac{L^2}{h_{\mathrm{p}}} \quad (2)$$

where Q is the induced charge, R is the resistance of the load resistor, acc is Z-axis acceleration, C_{p} is the capacitance of the PZT films, d_{33} is the piezoelectric constant, E_p and E_S are Young's modulus of PZT films and Si, Z_p is distance of between the center of the PZT films and bending neutral plane, Z_S is the distance of between the center of Si and bending neutral plane, h_p and h_s are the thickness of the PZT films and Si, m is the mass, L is the length of the PZT films, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of PZT films. Each parameter of equation (1-2) is shown in *Table 2* and simulated power is shown in *Fig. 3*. More than 100 μW is generated by the PVEH, Si beam thickness (h_s) of which is less than 10 μm. In the case of h_s: 7.5 μm, the generated power is saturated at more than 4 μm of PZT films thickness.

In the previous study, the piezoelectric properties for the PZT films using manual sol-gel deposition system on 4-inch wafer were shown by Kobayashi et al., [6]. From the view-point of mass-production, the research using 8-inch wafer was started to develop PZT films with the reference of the film quality, shown in *Table 3*. The target for uniformity and yield rate was set up for mass-production.

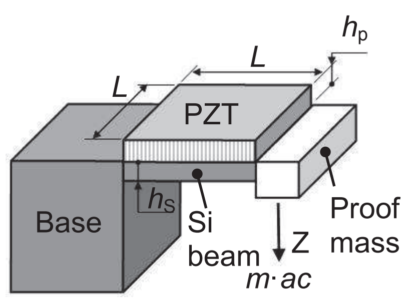

Fig. 1: The simple PVEH model.

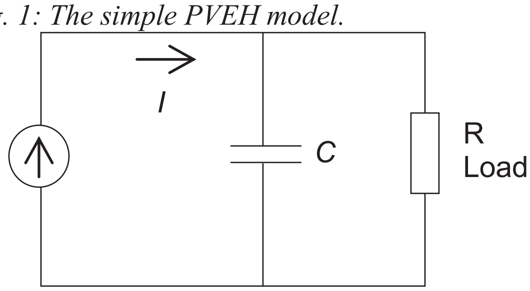

Fig. 2: The simple equivalent circuit of PVEH.

Table 2: Each parameter of equation (1-2).

Item	Value	Unite
Acceleration: *acc*	10	m/s^2
Mass : *m*	1	g
PZT Length: *L*	1	mm
Piezoelectric constant d_{33}	150	pm/V
Resistance: *R*	100	kΩ
Permittivity of vacuum: ε_0	8.85	pF/m
Relative permittivity: ε_r	1000	---

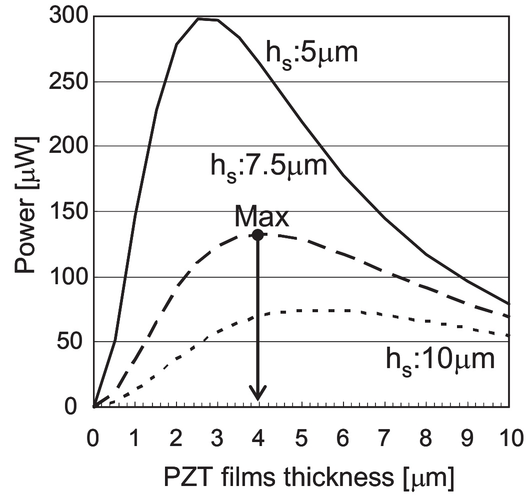

Fig. 3: Simulated power as a function of PZT films thickness and Si beam thickness h_s.

Table 3: Target.

Item	Value	Unite
PZT(100)(001)-oriented ratio	80	%
Maximum polarization	30	$\mu C/cm^2$
Remnant polarization	20	$\mu C/cm^2$
Relative permittivity: ε_r	1000	---
Piezoelectric constant d_{33}	150	pm/V
Thickness of PZT films	4	μm
Uniformity of properties/1σ	10	%
Yield rate	80	%
Number of defects/8" wafer (The height of defect > 1μm)	60	pieces

EXPERIMENT AND RESULTS

Automated sol-gel deposition system of PZT films for 8-inch wafer is shown in *Fig. 4*. This system has 1 cassette, 1 coater, 2 hot plates, 1 ramp anneal system and 1 robot.

Commercially available PZT solution (PZT-20, MPB, Kojundo Chemical Co., Saitama, Japan) was deposited by sol-gel methods on Pt/Ti/SiO2/Si substrates. After cycling these processes (1st Coating, 2nd Solvent evaporation, 3rd Pyrolysis, 4th Crystallization), 8 times or 16 times, we could fabricated the PZT films. And then we checked several properties using the wafer surface inspector (WM-7,TOPCON Co., Tokyo, Japan), SEM-EDS, XRD, Piezoelectric evaluation system (aixDBLI,aixACCT Systems GmbH, Aachen, Germany) and so on.

At first, we fabricated the PZT films under condition as shown in *Table 4*. The results of PZT films (a) PZT orientation and (b) Cross sectional SEM image and number of defects is shown in *Fig. 5*. In this condition, PZT(100)/(001)-oriented was strong and PZT films had columnar structure. But in the case of 16 layers, number of defects was more than 1000 pieces over 8-inch wafer.

We analyzed the element of defect. The results of a microscope and SEM-EDS is shown in *Fig. 6*. The defect had same elements as PZT solution and bottom electrode. And then we guessed the reason why a defect was generated. We had a reason that it was not enough to pyrolysis temperature.

In the case of pyrolysis temperature at 250, 275 and 300 degree C, number of defects is shown in *Fig. 7* and PZT orientation is shown in *Fig. 8*. In the case of pyrolysis temperature at 275 and 300 degree C, PZT orientation was at random. In the case of pyrolysis temperature at 300 degree C and 16 layers, number of defects on 8-inch wafer was less than 10 pieces.

And then we decided the optimize condition with the pyrolysis temperature of 250 degree C for the seed layer and 300 degree C for the following layers, PZT(100)(001)-oriented was strong up to 87%, PZT films had columnar structure and number of defects was 6 pieces. PZT orientation and cross sectional SEM image are shown in *Fig. 9*. And the result of piezoelectric constant d_{33} is shown in *Fig. 10*.

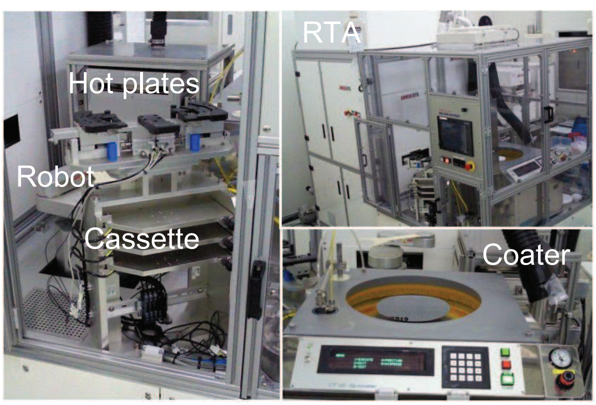

Fig. 4: Automated sol-gel deposition system.

Table 4: PZT films condition.

Item	Temperature	Time
Solvent evaporation	120 deg.C	2 min
Pyrolysis	250 deg.C	5 min
Crystallization	650 deg.C	2 min

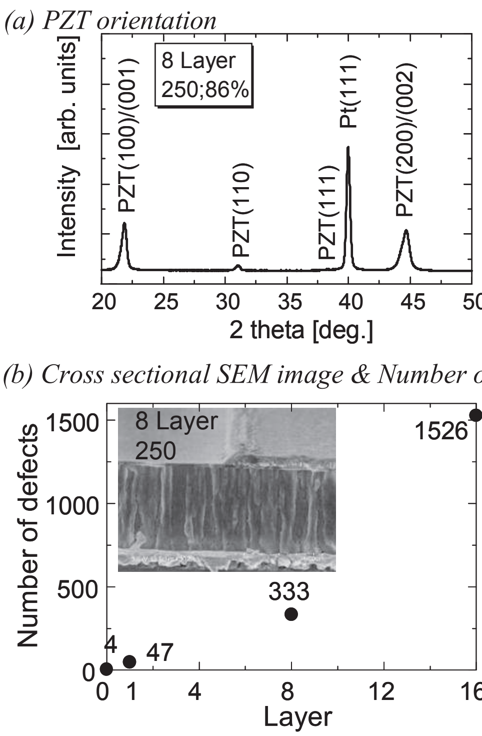

Fig. 5: The results of PZT films for 8-inch wafer. (a) PZT orientation; (b) Cross sectional SEM image & Number of defects

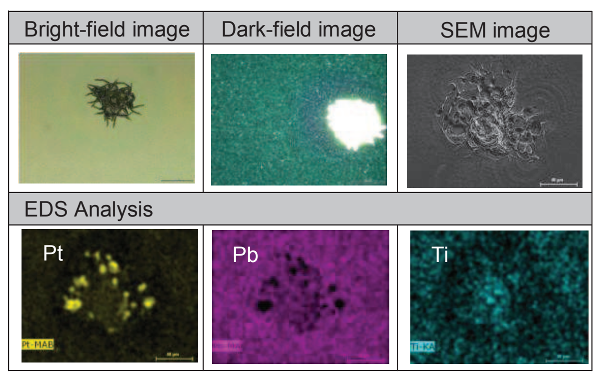

Fig. 6: The results of a microscope and SEM-EDS..

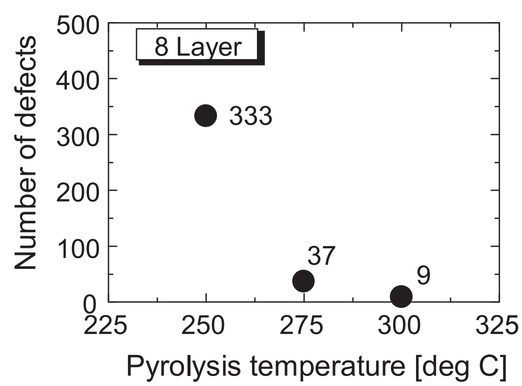

Fig. 7: Number of defects as pyrolysis temperature at 250, 275 and 300 degree C.

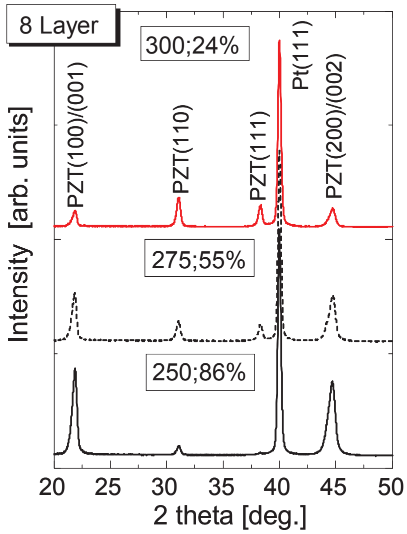

Fig. 8: PZT orientation as pyrolysis temperature at 250, 275 and 300 degree C.

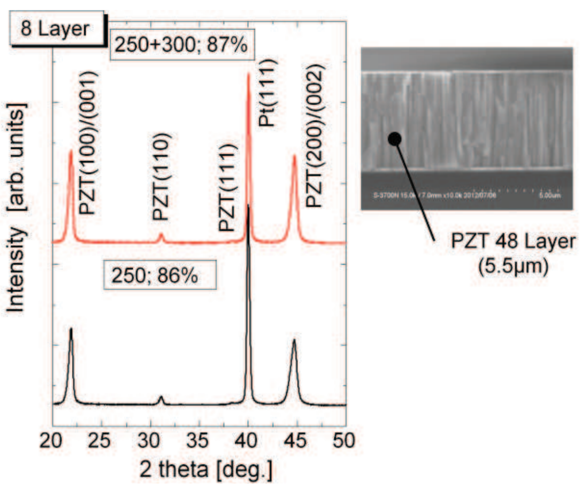

Fig. 9: PZT orientation of optimized PZT films and cross sectional SEM image.

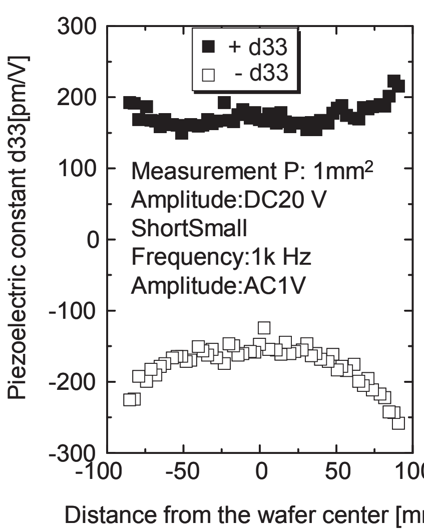

Fig. 10: The result of piezoelectric constant d_{33}..

Table 5: The characteristic result of optimized PZT films

Item	Value	Unite
PZT(100)(001)-oriented ratio	87	%
Maximum polarization	41	$\mu C/cm^2$
Remnant polarization	27	$\mu C/cm^2$
Relative permittivity: ε_r	---	---
Piezoelectric constant d_{33}	173	pm/V
Thickness of PZT films	5.5	μm
Uniformity of properties/1σ	13	%
Yield rate	---	%
Number of defects/8” wafer (The height of defect > 1μm)	<10	pieces

DISCUSSION

We designed automated sol-gel deposition system of PZT films for 8-inch wafer and fabricated the optimize condition with the pyrolysis temperature of 250 degree C for the seed layer and 300 degree C for the following layers. The characteristic result of optimized PZT films is shown in *Table 5*. It was confirmed that the defects on PZT films and PZT orientation were influenced by pyrolysis temperature. And then we guessed that remnant organic element stopped PZT crystallization.

CONCLUSION

We could obtain enough value of properties (Piezoelectric constant, thickness and number of defects and so on) for a PVEH. We found the fabrication processes of PZT films for mass-production.

ACHNOWLEDGMENTS

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