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Compatibility of Material Processing and Fabrication of Sol-Gel Derived PZT Based Devices

JYH-CHENG YU,[1*] JUN-XIANG WU,[1] TSUNG HER YEH,[2] and CHEN-CHIA CHOU[2]

[1]Department of Mechanical and Automation Engineering
National Kaohsiung First University of Science and Technology
2, Juoyue Rd., Nantz, Kaohsiung 811, Taiwan, R.O.C.

[2]Department of Mechanical Engineering
National Taiwan University of Science and Technology
43 Keelung Rd., Sec. 4, Taipei 106, Taiwan, R.O.C.

This study investigates the compatibility of material processing and fabrication of micro devices based on sol-gel derived lead zirconate titanate (PZT) thin films. High temperature annealing of sol-gel derived PZT may cause cracking and diffusion of structure layers. The introduction of a buffer layer, $(La_xSr_{1-x})MnO_3$, between PZT thin film and metal electrodes improves PZT crystallization and ferroelectricity. Annealing temperature of PZT/LSMO structure using furnace heating is investigated and compared with CO_2 laser annealing. A parameter study of PZT poling shows the improvement of film properties. The fabrication procedures of two exemplar devices, a micro accelerometer and a FPW acoustic sensor illustrate the interaction issues among material structures and processes.

Keywords: Flexural Plate Wave, Sol-gel PZT, PZT device, Poling, PZT annealing

Introduction

Piezoelectric thin films are less expensive than crystalline materials, explaining the considerable interest owing to the possible applications. The electromechanical coupling effect and the dielectric constant of PZT noticeably surpass other piezoelectric films such as AlN and ZnO, making PZT films attractive for sensor applications. Piezoelectric sensors such as accelerometers and acoustic sensors are widely used in automotive, interactive entertainment electronics, biomechanics and aerospace technology.

Sol-gel deposition [1] is promising because its need for a deposition facility is much less expensive than sputtering and chemical vapor deposition. Typical material structure in these PZT sensors is $Pt/PZT/Pt/Ti/SiO_2/Si$. A thin layer of Ti is used to increase the adhesion of Pt to silicon. However, Ti will diffuse to PZT layer during high temperature annealing and degrade the piezoelectricity of PZT films. Also high temperature annealing during the treatment PZT may cause cracking and diffusion of structure layers.

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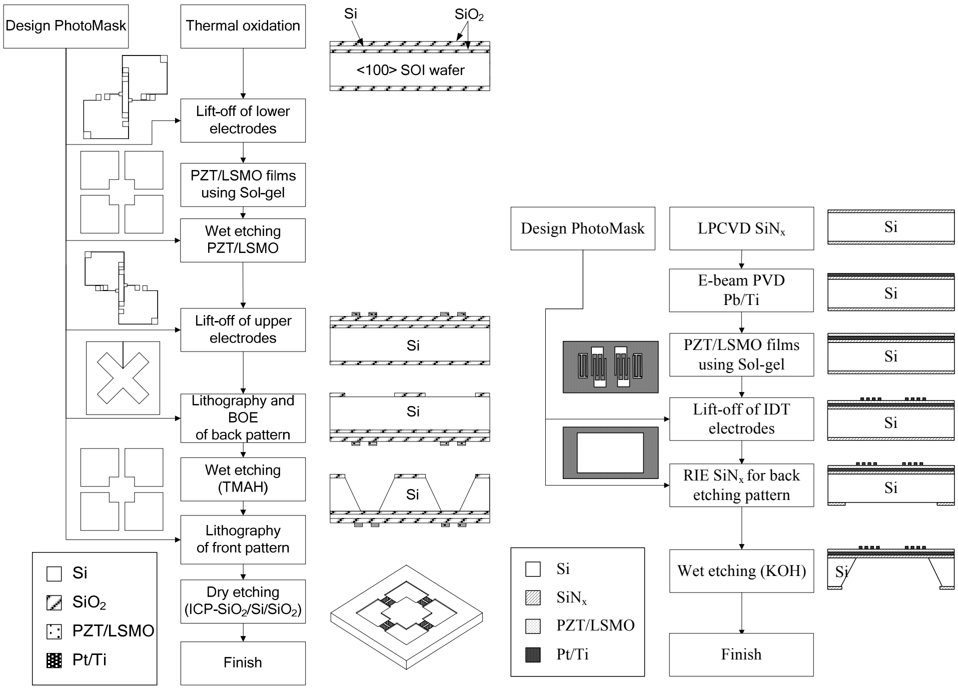
[*] Corresponding author. E-mail: jcyu@ccms.nkfust.edu.tw

Several solutions were reported to resolve the problems: (1) Introduction of a buffer layer between Pt and PZT as a diffusion barrier layer to improve the interface problem due to lattice mismatch between PZT and metal electrodes [2][3][4]. (2) Applications of lower temperature heat treatment such as laser annealing [5]. The study introduces a buffer layer, $(La_xSr_{1-x})MnO_3$, LSMO, between the PZT thin film and electrode layers to improve interface behavior. The fabrication of two exemplar devices, a micro accelerometer and a Flexural Plate Wave (FPW) acoustic sensor are presented to illustrate the compatibility of material processing and critical fabrication issues including the introduction a buffer layer to PZT and metal electrodes, annealing processes of PZT film, and thin film poling.

Design and Fabrication PZT microsensors



(a) Piezoelectric micro-accelerometer (b) Acoustic sensors

Figure 1. Typical fabrication procedures of PZT based micro sensors

Fabrication Procedure of Piezoelectric Micro-accelerometer

Figure 1(a) presents the fabrication procedure of a piezoelectric micro-accelerometer. A seismic mass is supported by four symmetric beam suspensions [6]. The piezoelectric transducers are arranged on the suspension beams as shown in Figure 1(a). A silicon oxide layer of 3000 Å is first deposited on a <100> SOI wafer by thermal oxidation. The lower electrodes Pt/Ti are deposited using E-beam PVD and patterned with lift-off. The electrodes consist of 400 Å of titanium and 1500 Å of platinum. The Ti layer serves as an adhesive layer between silicon and Pt. A thin LSMO layer of 3000Å serves as a buffer layer between the PZT thin film and the metal electrodes. A relatively thick layer PZT of 1.0 μm is then prepared by multiple sol-gel coating and annealing. Upper electrodes are again patterned using lift-off. The seismic mass is wet etched using TMAH etching (25%, 85°C). A Teflon chuck is used in backside etching to protect piezoelectric transducers on the front. The introduction of ultrasonic agitation in etching increases etching rate and improves etching uniformity. Etching stops at the insulator layer to form a supporting membrane for the seismic mass. ICP-RIE is finally applied on the front side to machine four suspension beams.

Fabrication Procedure of Flexural Plate Wave Device

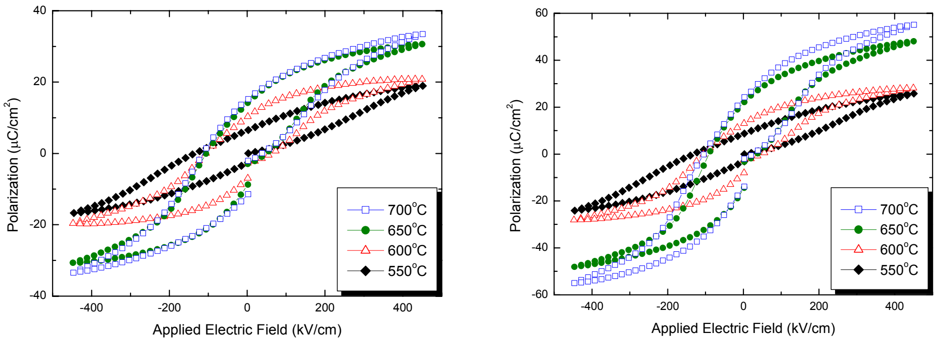
A similar yet simpler fabrication procedure for a FPW sensor [7] is shown in Figure 1(b). The composite membranes were first formed on a on a <100> silicon by sequential deposition of a silicon nitride layer of 1.2µm, Pb/Ti ground layers, LSMO buffer layer, and multiple coated PZT films. The interdigital electrodes Pt/Ti are then deposited and patterned on the PZT surface using lift-off. The SiN_x mask for the backside etching is patterned using Reactive Ion Etching (RIE), and a composite membrane of 2~3µm is fabricated after KOH wet etching.

Sol-gel Coating of PZT

Heat Treatment of sol-gel PZT

Heat treatment is essential to crystallize sol-gel PZT film. The ferroelectric hysteresis loops of the furnace annealed PZT films coated on $Pt/Ti/SiO_2$ at temperature 550~700°C are shown in Figure 2(a) measured using Precision Workstation 2000. Though higher annealing temperature produces a higher remnant polarization, severe thermal stress will become a problem in the composite films of various materials.

It has been reported that the structural quality of PZT films deposited on conducting oxide electrodes is better than that on Pt electrodes by optimizing the interfacial conditions, and therefore greatly enhances specimen ferroelectric properties and fatigue resistance. LSMO has the same perovskite structure and close lattice parameters that match fairly well with the PZT thin films and thus it is investigated as a buffer layer between PZT and Pt electrodes. Figure 2(b) shows that the introduction of LSMO can greatly increase the remnant polarization and decrease the coercive field. Furnace annealing at 650°C for 30 minutes provides satisfactory result with the addition of LSMO. Table 1 shows that LSMO also increases the fatigue resistance of PZT which is very important in high frequency devices such as acoustic sensors.



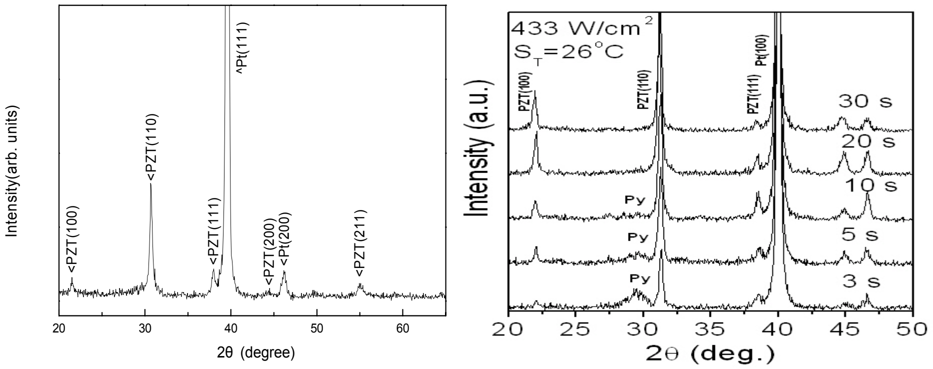
(a) Au/PZT（4L）/Pt/Ti/SiO2/Si (b) Au/PZT/LSMO /Pt/Ti/SiO2/Si

Figure 2. Comparison of P-E curves of PZT at various furnace hardening temperatures

Table 1. The degrading percentage after cyclic loads for PZT on Pt and LSMO/Pt

Switching Cycles	10^5	10^6	10^7	10^8
Degrading percentage for PZT/Pt	29.5	37.1	38.0	43.8
Degrading percentage for PZT/LSMO/Pt	16.1	28.8	31.7	36.3

The high temperature in furnace annealing is still a threat to PZT based device fabrication and often results in cracking of PZT film especially with patterned lower electrodes. PZT films are also annealed at a relatively low temperature using CO_2 laser at this study. A continuous wave annealing at a fluence of 433 W/cm^2 is shown in Figure 3(b). The substrate was kept in room temperature. The results revealed that the laser anneal PZT films of 30 seconds exhibited well-crystallized features with polycrystalline perovskite structures, suggesting an attractive alternative of PZT crystallization in device fabrication.



(a) Furnace annealing at 650 for 30 minutes (b) CO_2 laser annealing at 433 W/cm^2

Figure 3. XRD of sol-gel PZT using furnace annealing and laser annealing

Poling of sol-gel PZT films

Poling Effect on PZT transducer capacitance due to parallel poling

Because PZT is polycrystalline, DC poling is required to produce a net polarization of the transducer. There are three main factors influencing the poling result including poling time, poling voltage, and substrate temperature. The selection of applied poling field is very important in the poling of PZT thin film. The poling field has to be larger than the coercive field of the piezoelectric thin film. The electrode area of the test piece is 0.004cm^2, and the PZT thickness is 0.3μm at this study. Previous experiments show that a poling field of 3 time's coercive field at 120°C for one minute had led to breakdown of thin film. Trial and error suggests a poling field of 5 time's coercive field for 30 minutes without heating.

HP 4194A Impedance Gain-Phase Analyzer is used to measure the frequency response of the capacitance of PZT transducer. The P-E curve is determined by Precision Workstation 2000. The poling voltage is selected at 13.5V which is equivalent to polarization field of 450(KV/cm) for 30 minutes. Since the capacitance is in proportional to dielectric constant, the change of capacitance implies a change of dielectric constant. And the transverse piezoelectric constant d_{31} and the longitudinal piezoelectric constant d_{33} can be estimated as follows:

$$\varepsilon_r = C \frac{d}{A\varepsilon_0} \tag{1}$$

where ε is dielectric constants, d is the thickness of PZT film, A is the electrode area, and C is the measured capacitance.

$$d_{31} = 2Q_{12}P_r\varepsilon_0\varepsilon_r \tag{2}$$

$$d_{33} = 2Q_{11}P_r\varepsilon_0\varepsilon_r \tag{3}$$

where Q are electrostriction constants Q_{12} = $-3.1\times10^{-2}\mathrm{m}^4/\mathrm{C}^2$ [8] and Q_{11}= $9.3512\times10^{-2}\mathrm{m}^4/\mathrm{C}^2$ [9].

Table 2 presents the poling effect on remnant polarization P_r, relative dielectric constant ε_r , piezoelectric constants d_{31} and d_{33}. The results show a significant improvement of the piezoelectricity due to proper poling of sol-gel thin film, which will certainly improve the performance of PZT sensing devices. The piezoelectric constants of the sol-gel PZT film are as high as twice the constants of bulk PZT, which leads to a higher sensitivity of PZT thin film sensors and demonstrates application potential to other piezoelectric devices.

Table 2. Poling Effect of sol-gel PZT thin films

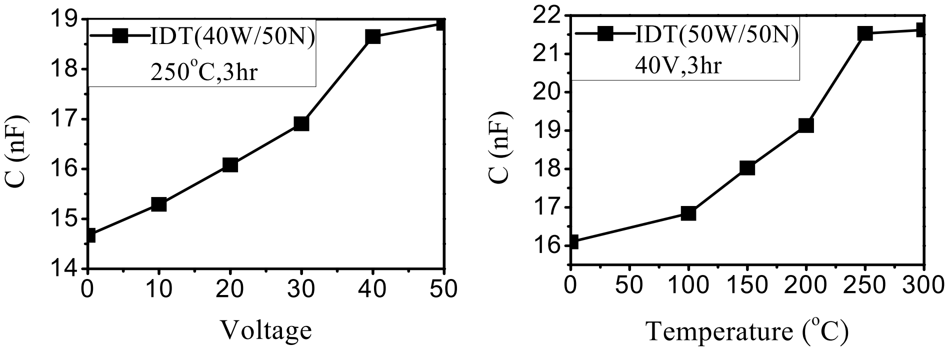
	P_r (μC/cm^2)	C (nF)	ε_γ	d_{33} (pC/N)	d_{31} (pC/N)
Before poling	15.82	10.30	872	228.4	-75.7
After poling	19.99	12.51	1059	350.5	-116.2
Improving %	26%	21%	21%	53%	53%
Bulk PZT (48/52)	-	-	-	110	-43

Poling Effect on PZT IDT capacitance due to in-plane poling

For an acoustic device, interdigital transducers (IDTs) are used to drive elastic waves. Therefore in-plane poling is attempted by applying poling voltage across pairing IDT. The period of the test IDT is 80 μm with gap-to-finger width ratio = 1/2. Figure 4(a) shows the measured capacitance of IDT using the poling voltage from 10(V) to 50(V) at substrate temperature of 250(°C) for three hours. The capacitance increases significantly with the applied poling voltage. When the applied voltage exceeds 40(V), the increase of the capacitance becomes saturate. Figure 4(b) shows that the effect of the heating temperature in the poling process. The poling voltage is set as 40 V for 3 hr as suggested from the previous experiment. Again, the capacitance increase saturates when the poling temperature reaches 250(°C). The final poling condition is selected as 40(V), 250(°C) for 3 hours. The capacitance increases 47% compared with thin film before poling.

Conclusions

This study investigates the material processing in sol-gel PZT that will greatly influence the fabrication quality of PZT devices. Several fabrication issues are raised through the fabrication of two exemplar PZT devices. The LSMO buffer layer improves material interface, crystallization of PZT film, and fatigue resistance. Cracking of PZT will be prevented even a patterned lower electrodes is presented. A poling of PZT at 5 time's coercive field for 30 minutes will promote piezoelectric properties that increase sensor and actuator performance.



(a) poling at 250 °C for 3 hr (b) poling at 40 V for 3 hr.

Figure 4. The effect of the poling voltage and temperature on the IDT capacitance

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