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# Analysis of Material Processing of Sol-Gel Derived PZT to the Performance of Microaccelerometer Applications

Jyh-Cheng YU and Jun-Xiang Wu
National Kaohsiung First University of Science and Technology
2 Jhuoyue Rd.,Nanzih , Kaohsiung City 811,Taiwan, R.O.C.

*Abstract-* **The processing conditions of the sol-gel derived lead zirconate titanate (PZT) thin films have significant influences on the piezoelectric characteristics and the interface quality, and affect the device performance of the following applications. High temperature annealing of sol-gel derived PZT is required to crystallize the spin-on precursors, but often cause cracking and diffusion of structure layers. The introduction of LSMO oxide electrode in this study not only improve the crystallization and fatigue resistance of PZT film, but also prevent possible cracking due to excessive thermal stress. Two types of annealing including furnace and rapid thermal annealing are investigated and the following poling conditions are presented. To assess the overall performance of the PZT films from various processing conditions, a single-axial piezoelectric accelerometer is fabricated. The initial result shows the feasibility of the experimental concept. Future experiments are pending to derive the optimum processing conditions for the accelerometer application.**

## I. INTRODUCTION

Piezoelectric thin films have the cost advantage over crystal materials. Many piezoelectric thin film devices employ zinc oxide (ZnO) [1][2] and aluminum nitride (AlN)[3]. The application of Lead Zirconate Titanates (PZT) thin films is very promising because the electromechanical coupling coefficient ($K^2$) of is three to nine times over AlN and ZnO, which can greatly improve the sensitivity of sensing devices.

Sol-gel derived PZT thin film is promising because the required coating facility is much less expensive than sputtering and chemical vapor deposition (CVD). Typical sol-gel processes include the preparation of precursor, spin coating and heat treatment. Furnace heating and rapid thermal annealing are often applied to transform the sol-gel thin film into perovskite. However, high temperature annealing process may cause the cracking and diffusion of structure layers. The deposition of perovskite buffer layers, such as $(La_xSr_{1-x})MnO_3$, between the PZT thin film and the structure layers can improve the piezoelectric characteristics, fatigue resistance and ferroelectricity, and reduce leaking current [4][5].

Because sole-gel derived PZT is polycrystalline, poling of thin film is required to enhance the piezoelectric characteristics. However, the study of thin film poling is very limited especially in the device application.

Sol-gel derived PZT based devices such as microaccelerometer often adopts a PZT transducer to convert mechanical deflection into electrical signal. Conventional material structure for PZT thin film based transducers use Pt/Ti as lower electrodes. Thin layer of Ti serves as an adhesion layer between Pt and the silicon based substrate. Platinum is selected because of the high conductivity and the superior oxidation resistance to high temperature. However, due to the lattices mismatch and the difference of thermal expansion coefficient, the PZT thin film is liable to cracking during the high temperature annealing of PZT thin films. Because perovskite buffer layers such as LSMO are conductive, the application of oxide buffer layer not only resolve the interface problem but also serve as a lower electrode to prevent thermal cracking of PZT films due to the use of metal electrodes.

This study will present the application of PZT thin film to the design and fabrication of a single-axial microaccelerometer. Two types of annealing, thermal heating and rapid thermal annealing, will be compared. Here, LSMO is used as lower electrode of the PZT transducer. The processing conditions and the critical thickness of LSMO for electrode application will be investigated. The microaccelerometer will then illustrate and determine the influence of thin film processing on the sensor performance.

## II. PREPARATION OF PZT AND LSMO THIN FILMS USING SOL-GEL

Both LSMO and PZT thin films are multiple-coated using sol-gel techniques. Heat treatment is required to transform the spin-on precursor thin films into polycrystalline layers. Two types of heat treatment, furnace heating and RTA, are used to compare the difference. If furnace annealing is used, the spin-on precursor is soft baked at 150°C for 5 minutes followed by a low temperature pyrolysis at 300°C for 30 minutes. According our study, with the introduction of LSMO buffer layer, the furnace annealing at 650°C for 30 minutes yields satisfactory perovskite structures without the pyrochlore phase. Rapid thermal annealing provides similar

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result at 650°C for merely one minute. There is no difference from the observation of the XRD of the thin films from different annealing methods.

Fig. 1 presents the X-ray diffraction (XRD) patterns of PZT/LSMO that were furnace annealed at 650°C for 30 minutes. The PZT on the LSMO annealed every layer and every three layers presents similar preferred orientation patterns. Also, the crystallization of PZT is not sensitive to the thickness of LSMO. However, if the LSMO layer also serves as a lower electrode, the critical thickness has to be determined for acceptable conductivity. The thickness of one sol-gel layer of LSMO is about 150 (nm). Therefore, multiple coating of LSMO is applied to achieve the required thickness. Two types of annealing strategy are used: (1) annealing every three layers and (2) annealing every layer. Fig. 2 shows that the LSMO from annealing every layer will provide better conductivity than annealing every three layer. Also, the thin film resistivity reduces as the increase of thickness, and saturates after thickness of 700 (nm). Therefore, this study suggests annealing every layer of sol-gel LSMO. The thickness of the LSMO electrode is selected as 700 (nm) and the corresponding resistivity is about $5.2\times10^{-4}(\Omega\cdot m)$.

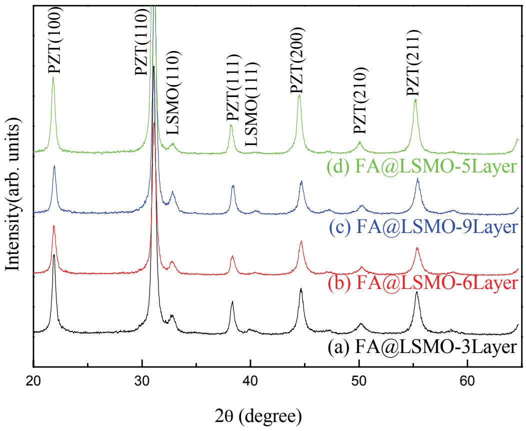


Fig. 1. XRD of PZT/LSMO/SiO$_2$/Si at various annealing conditions of LSMO (a)~(c) LSMO annealed every three layers, (d) LSMO annealed every layer

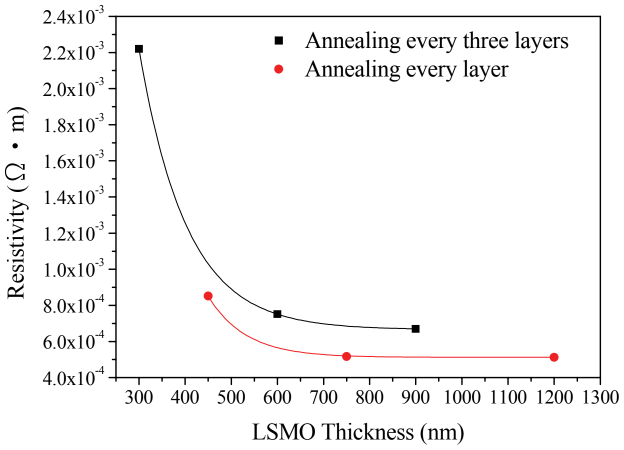
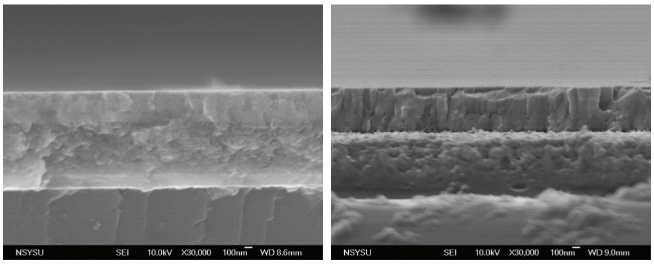


Fig. 2. Influences of the thickness and the annealing method of LSMO on the electric resistivity

Sol-gel PZT is multiple-coated on LSMO and annealed every layer. Fig. 3 shows the cross-section SEM photos of the PZT on LSMO structure. The PZT on LSMO annealed every layer shows a more noticeable column structure than the PZT on LSMO annealed every three layers. Also, the layer thickness for LSMO annealed every layer is averaged 130 (nm) that is thicker than the LSMO annealed every three layers which is 100 (nm). The column structure of the LSMO annealed every layer provides a thicker layer thickness, and promotes the following crystallization of sol-gel PZT.



(a) (b)

Fig. 3. SEM photos of the cross-section of sol-gel PZT/LSMO/Si$_3$N$_4$/Si (a) annealing every three layers (b) annealing every layer

## III. POLING OF PZT THIN FILMS

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. Trial and error suggests a poling field of 5 time's coercive field for 30 minutes without heating. The poling voltage is selected at 13.5V which is equivalent to polarization field of 450(KV/cm).

HP 4194A Impedance Gain-Phase Analyzer is used to measure the frequency response of the capacitance of PZT transducer. 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 $\varepsilon$ 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 $Q_{12}$ = $-3.1\times10^{-2}m^4/C^2$ [6] and $Q_{11}= 9.3512\times10^{-2}m^4/C^2$ [7].

Table 1 present the poling effect on remnant polarization $P_r$, relative dielectric constant $\varepsilon_r$, piezoelectric constants $d_{31}$ and $d_{33}$. The results show that the poling increases the remnant polarization $P_r$ by 26%, the relative dielectric constant $\varepsilon_r$ by 21%, and the piezoelectric constants $d_{31}$ by 53%, which will certainly improve the performance of PZT sensing devices. The piezoelectric characteristics of the sol-gel PZT film has shown three times as high as of the bulk PZT, and demonstrates application potential in piezoelectric devices.

**Table 1.** Poling Effect of sol-gel PZT thin films

| | $\varepsilon_\gamma$ | $d_{33}$ (pC/N) | $d_{31}$ (pC/N) |
|---|---|---|---|
| Before poling | 872 | 228.4 | -75.7 |
| After poling | 1059 | 350.5 | -116.2 |
| Improving % | 21% | 53% | 53% |
| Bulk PZT (48/52) | - | 110 | -43 |

## IV. DESIGN OF MICROACCELEROMETER

The testing microaccelerometer is designed to evaluate the performance of PZT thin film. A simple configuration is adopted to ensure fabrication consistence, which consists of a membrane suspension, a seismic mass, and four piezoelectric displacement transducers as shown in Fig. 4. To verify the accelerometer design, finite element analysis using ANSYS is applied to analyze the sensing linearity and the frequency response. The result demonstrates that the generated charge is in proportional to the out-of-plane acceleration and the transverse piezoelectric constant $d_{31}$. The resonant frequency of the accelerometer is 40 kHz and the sensor sensitivity is about 0.02 (mV/g).

## V. FABRICATION OF MICROACCELEROMETER

The schematic fabrication flowchart is shown in Fig. 6. A 3000×3000 μm supporting membrane of 30 μm with a 1500×1500 μm seismic mass is fabricated using anisotropic wet etching of <100> SOI silicon. Convex corner compensation of <100> extension is applied in the masking layer design. Four transducers are arranged symmetrically on the membrane between the seismic mass and the supporting rim. The PZT transducer is designed on a (100) silicon substrate with 3000 Å of oxide by sequential deposition of a multiple coated $(La_xSr_{1-x})MnO_3$ layers of 0.7 μm, and a multiple coated PZT films of 0.9 μm, another LSMO layer of 1000 Å and a Pt upper electrode of 1500 Å. The LSMO layer is served as the lower electrode and a buffer layer between the PZT thin film and silicon based substrate. PZT and LSMO layers are etched using diluted BOE (1:20) and $HNO_3$ (1:2) respectively. The upper electrode Pt is deposited using E-beam PVD and patterned with lift-off techniques. The relatively thick PZT film was prepared by a sol-gel method involved multiple deposition and annealing sequences. Furnace heating and RTA of thin film are used to prepare samples for performance comparison.

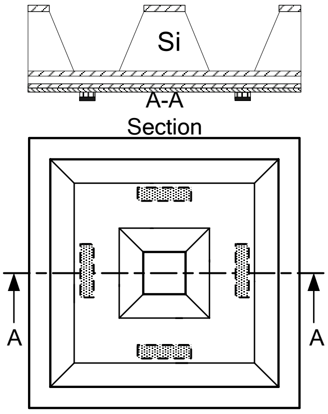


Fig. 4.Schematic presentation of the micro-accelerometer

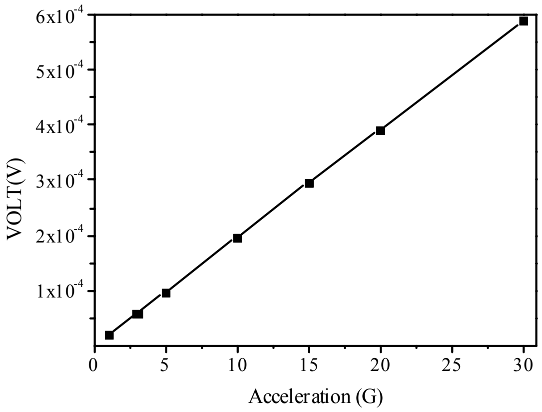


Fig. 5.Sensitivity of the micro-accelerometer

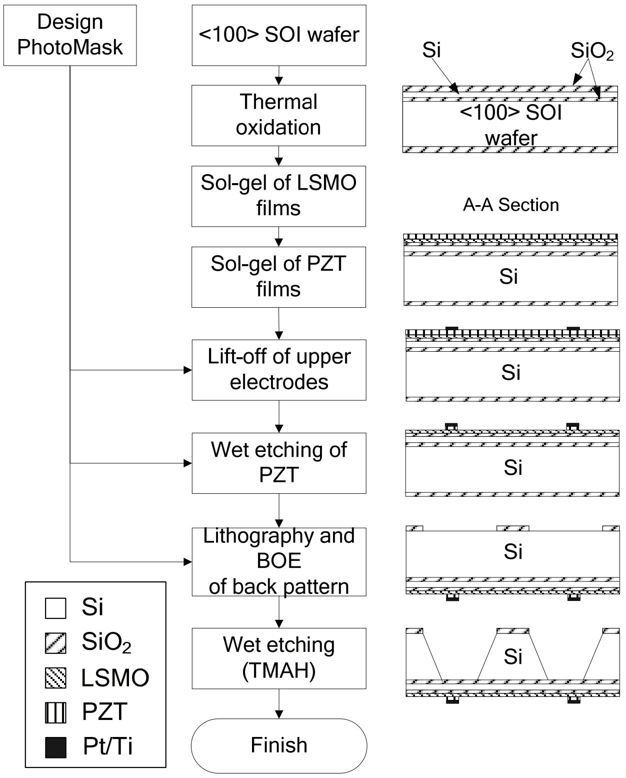


Fig. 6.Schematic fabrication flowchart of the micro-accelerometer

## VI. EXPERIMENTAL LAYOUT AND MEASUREMENT RESULT

The accelerometer is mounted on a piezoelectric shaker. The response of the PZT transducers via a charger amplifier is analyzed by an oscilloscope. The amplitude and the frequency of the shaker are controlled by a function generator and a power amplifier. For PZT prepared under various processing conditions will be measured to determine the influence on sensor performance. Fig. 8 shows a preliminary measurement result for the proposed microaccelerometer excited at a acceleration of 14.5g. The sensor sensitivity is about 0.007 (mV/g). Qualitative analysis for the influence of various material processing on the sensor performance will be conducted in the future.

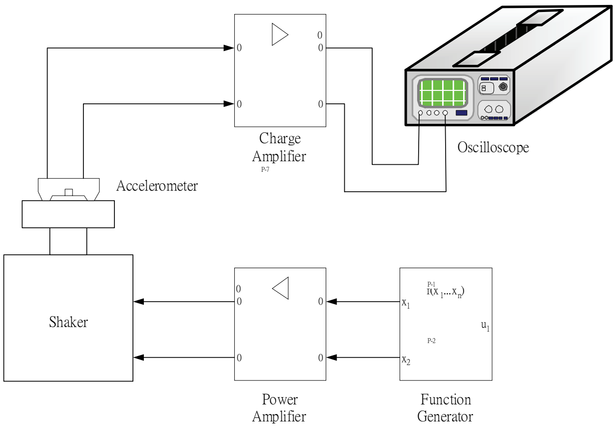


Fig. 7. Experimental layout for the measurement of micro-accelerometer

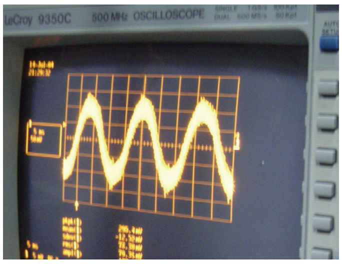


Fig. 8. Preliminary measurement of the proposed micro-accelerometer

## IV. CONCLUSION

This study has presented the influence of the material processing conditions on the quality of sol-gel derived PZT thin films. The introduction of LSMO as a buffer layer will improve the crystallization quality of sol-gel derived PZT. A less expansive annealing method using furnace heat treatment will provide the crystallization of PZT films as good as RTA due to the LSMO buffer layer. Also, cracking of PZT thin film during the annealing process can be prevented if LSMO instead of metal layer is used as a lower electrode. The critical thickness of LSMO is then determined for the electrode application. Also, the preliminary poling result of PZT thin film shows the importance of proper poling to the piezoelectricity. Parameter design of the poling conditions will be followed to optimize the performance. A single axial piezoelectric accelerometer is introduced and fabricated to assess the overall performance of the PZT films. The preliminary measurement has demonstrated the feasibility of the proposed concept. In the future, the PZT from various processing conditions will be introduced to the microaccelerometer to compare the influence on device applications.

## ACKNOWLEDGMENT

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