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Study on PSZT Thin Films for Microforce Sensors

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Abstract — **$Pb_{1-x}Sr_x$ ($Zr_{0.53}Ti_{0.47}$) O_3 (PSZT) thin films have been fabricated on Pt/Ti/SiO_2/Si substrates by a sol–gel method combined with a rapid thermal annealing process. It is shown that the introduction of Sr^{2+} into the PZT thin films favors the growth of (111) orientation. The orientation ratio of (111) is increased from 0.304, 0.475 to 0.849 with the increase of the x value. The dielectric measurement results indicates that the addition of Sr^{2+} in the PZT thin films greatly improves the dielectric properties of the PZT thin films. Two kinds of the PSZT0.03 thin films with thickness of 1.68um and 2.19um were fabricated and tested for the same structure size, and the spring constant of 11.72N/m and 4.87N/m is obtained, respectively. The PSZT thin films with x=0, 0.03, 0.08 have an spring constant of 13.73N/m, 11.72N/m and 8.16N/m, respectively. Three kinds of the PSZT thin films for the microforce sensors were tested in quasi static state, the sensing sensitivity of the three kinds of microforce sensors are 0.017pc/uN, 0.033pc/uN, and 0.011pc/uN, respectively. The sensing sensitivity of the microforce sensors is 0.033pc/uN and 0.077pc/uN while thickness of PSZT0.03 thin films is 1.68um and 2.19um.**

Keywords — Dielectric losses, Force, Microsesnsors, PZT thin films

I. INTRODUCTION

Piezoelectric materials play an important role in the conversion between electrical and mechanical energy. $Pb(Zr_{0.53}Ti_{0.47})$ O_3(PZT) thin films are considered to be the most promising materials in microsensors and microactuators when the current signal and the force outputs are demanded. Microforce sensors with PZT thin films and PT/PZT/PT thin films have been fabricated and tested[1-3] before. Shao et al.[4] have studied the property of PZT thin films doped with Eu, and found that its remanent polarization increased. R.S. Nasaret al. [5] have reported that Sr^{2+} addition in PZT ceramics increased the remnant polarization. Kulcsar[6] considered that Pb^{2+} replaced by Sr^{2+} in the lattice increased the value of electromechanical coupling coefficient. Abhishek Dalakoti et al.[7] found that Sr^{2+} addition in PZT ceramics improved dielectric constant and polarization values. Y. Wang et al.[8]have done research on the polarization fatigue behaviors of $Pb_{1-x}Sr_x(Zr_{0.52}Ti_{0.48})O_3$ thin films as x=0-0.2 and came to the conclusion that Sr doping improved fatigue endurance. Qiyue Shao et al.[9] prepared $Pb_{1-x}Sr_x(Zr_{0.52}Ti_{0.48})O_3$(x=0.2-0.8) thin films and thought that Sr content over 0.4 would decrease the dielectric constant of PZT thin films. However, there is little research of Sr doped PZT thin films with Sr content below 0.1 and its application to a microforce sensor. This paper presents the fabrication and sensing properties of microforce sensor with PSZT thin films.

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II. EXPERIMENTS

A. Preparation of PSZT Thin Films

The content of each source material used in the preparation of PSZTx precursor solution was according to the molar ratio of Pb/Sr/Zr/Ti =1-x/x/53/47, with x=0, 0.03, 0.08 respectively. To compensate for the loss of lead during the annealing process, 15% excess lead was added. Dehydrated lead acetate trihydrate [$Pb(CH_3COO)_2{\cdot}3H_2O$], zirconium nitrate pentahydrate [$Zr(NO_3)_4{\cdot}5H_2O$] and titanium tetrobutoxide [$Ti(OC_4H_9)_4$] were used as the source materials, strontium acetate [$Sr(CH_3COO)_2{\cdot}1/2H_2O$] was selected as the dopant. Dehydrated $Pb(CH_3COO)_2.3H_2O$ and $Zr(NO_3)_4{\cdot}5H_2O$ were dissolved in 2-methoxyethanol at 97℃ with constant stirring. After a transparent solution was obtained, $Ti(OC_4H_9)_4$ and $Sr(CH_3COO)_2{\cdot}1/2H_2O$ were added successively. Stirring was kept on for several hours at 80℃, and then further heating was carried out to obtain the suitable concentration. After stabilizing for 24h at room temperature, the solution was filtered for spin coating.

The PSZT thin films were fabricated on Pt (111)/Ti/SiO_2/Si (100) substrates. Each layer was spin coated at 4000 rpm for 30 s and baked at 180℃ for 5 min on a hotplate to remove the residual solvents. Then the heat treatment was performed with a rapid thermal process (RTP) at 400℃ for 5 min to pyrolyze the organic materials. The processes above were repeated twice and then annealed at 600℃ for 8 min to induce complete crystallization. These processes were repeated several times to obtain the desired film thickness.

X-ray diffraction (XRD-6000) was used to measure structures and the crystallinity of the deposited films. The surface morphology of PSZT films was observed by atomic force microscope (CSPM4000). The dielectric property was measured using an intelligent LCR measuring instrument (ZL5) .

B. Fabrication of Microforce Sensors with PSZT Thin Films

We have fabricated the microforce sensors with three kinds of the PSZT thin films. The fabrication process was described below:

(a)A piece of 2inch double-side-polished silicon wafer was selected as the substrate. A 1.4μm thermal oxide was grown on both sides. Then the back-side bulk silicon was anisotropically etched using the back patterned SiO_2 as a mask layer.

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(b)The front-side SiO_2 layer was patterned by U shapes that would be used to free the microcantilevers.

(c)A Pt/Ti bottom electrode was sputtered and then wet etched by aqua-regia and diluted HF.

(d)The PSZT thin films were prepared by spin coating.

(e)The Pt/Ti top electrodes were sputtered and patterned by the lift-off technology.

(f)The baked PSZT thin films (approximately 260 nm) without post-annealing were deposited for electrical isolation.

(g)The PSZT thin films in the contact holes and U shapes at front-side were patterned.

(h)An Al layer (approximately 280 nm) was sputtered and patterned to form the bonding pads using the lift-off process.

(i)Finally, the silicon in the U shapes was dry etched by ICP to free the cantilever.

The thin film thickness of all the samples used in this work was measured by surface profiler (ET4000). The fabrication procedure of the microforce sensors with the PSZT thin films was shown in Fig. 1.

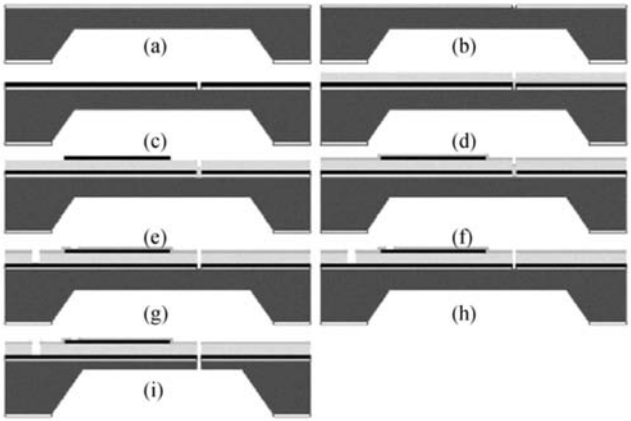

Figure 1. Fabrication process of the microforce sensor with the PSZT thin films

The micrograph of the microcantilever was shown in Fig. 2. The dimension of the microcantilever was 840μm×280μm×18μm.

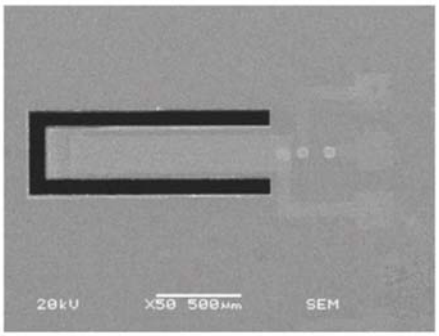

Figure 2. Micrograph of the microcantilever

III. RESULTS AND DISCUSSION

A. Structures of PSZT Thin Films

Fig. 3 displays the XRD results of PSZT thin films grown at 600℃ with a RTP method. We have gained a single perovskite phase in all the PSZT thin films. The (111) orientation parameter α_{111} calculated from the relative heights of the (100), (110), (111) reflection, i.e. $\alpha_{111}=I_{111}/(I_{100}+I_{110}+I_{111})$. The (111) orientation parameter α_{111} of the PSZT thin films is 0.304, 0.475 and 0.849 with x=0, 0.03, 0.08, respectively. It indicates that the introduction of Sr^{2+} into the PZT thin films favors the growth of (111) orientation.

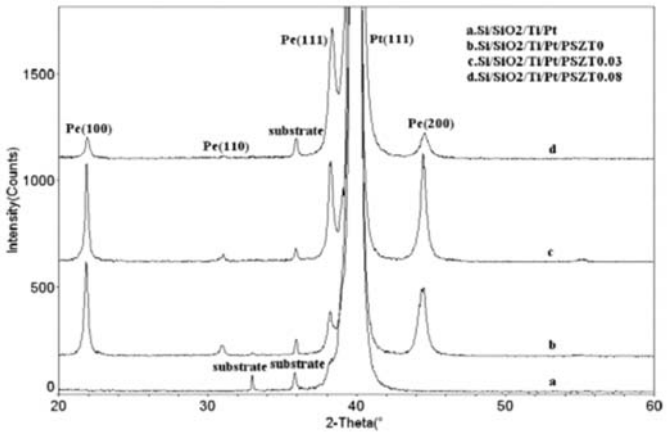

Figure 3. XRD spectra of the PSZT thin films with different x value (Pe denotes perovskite phase)

B. AFM Micrograph of PSZT Thin Films

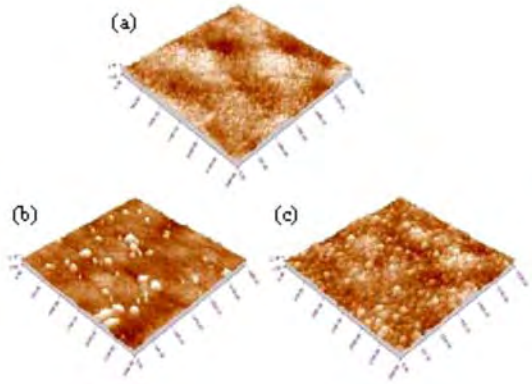

Figure 4. AFM image of the PSZT thin films with different x : (a) x=0, (b) x=0.03, (c) x=0.08

Fig. 4 shows AFM images of the surface morphology of the PSZT thin films. As shown in Fig. 4(a) , Fig. 4(b) and Fig. 4(c), the surface morphology is represented by a granular-shaped surface with average grain sizes of 25.39nm, 28.52nm and 26.51nm, respectively. The average roughnesses (Ra) are 1.11nm, 0.812nm and 1.33nm correspondently. It indicates that the substitution of Pb^{2+} in PZT by Sr^{2+} influences the grain size and morphology of PSZT thin films. To some extent, it reflects that the Sr migration into PZT thin films promote the crystallization.

C. Dielectric Properties of PSZT Thin Films

The dielectric constant and dissipation factor were measured as functions of frequency, and the results are shown in Fig. 5 and Fig. 6. The values of dielectric constant at a frequency of 2 kHz are 648, 1239 and 1136 for three kinds of PSZT thin films, respectively. Dissipation factors at a frequency of 2 kHz are 0.02, 0.03 and 0.07 for three kinds of PSZT thin films, respectively. PSZT0.03 thin films have better dielectric property than other two kinds of the thin films.

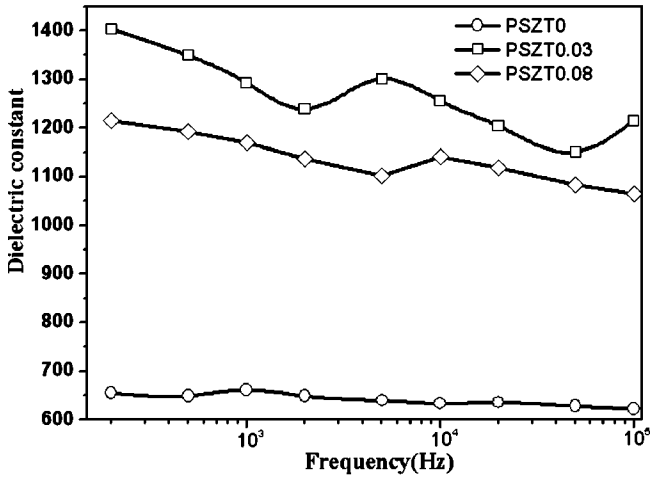

Figure 5. Variation of dielectric constant as functions of frequency for PSZT thin films with different x

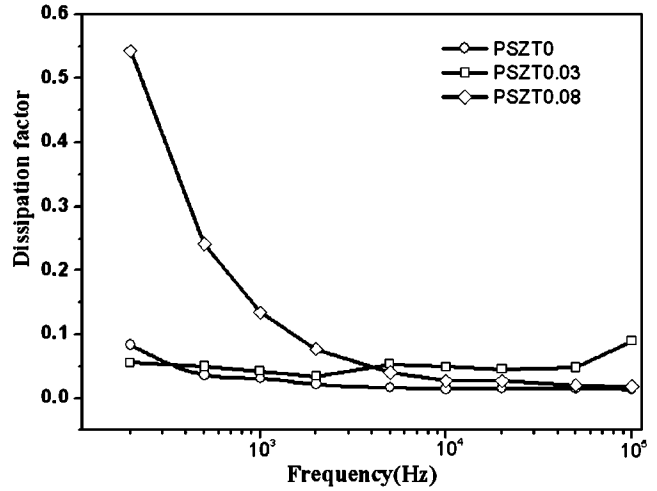

Figure 6. Variation of dissipation factor as functions of frequency for PSZT thin films with different x

Since the radius of Sr^{2+} ($r_{Sr^{2+}}$ =1.27Å) is almost as big as that of Pb^{2+} ($r_{Pb^{2+}}$ =1.32Å), Sr^{2+} can enter the crystal lattice by replacing for Pb^{2+}(A site). It was reported[5] that A site substitution could reduce oxygen vacancies by forming A site vacancy–oxygen vacancy defect dipoles and increased electric displacements could be expected. It is one of the reasons that the dielectric constants are increased with the entry of Sr^{2+} in the PZT thin films. Meanwhile, Pb volatilization from the PZT thin film through annealing process in the form of PbO is reduced with the substitution Pb^{2+} in PZT by Sr^{2+}. It is considered that PZT thin films would transfer from perovskite phase to pyrochlore phase with the volatilization of Pb. Accordingly, the dielectric properties are deteriorated. Sr^{2+} doping is the very method of alleviating this problem and improving the dielectric properties.

As to the slightly decrease effect of PSZT0.08 thin films compare to PSZT0.03 thin films, it can be speculated that with the increase of Sr dopant, some of them accumulate on the grain boundary which hinder the motion of domains and result in the degradation of dielectric properties of PZT thin films.

Ⅳ. Measurement of Sensing Properties of the Microforce Sensors

The measurement set-up included the driving system and the testing system which were described before[2].

A. The Test in the Static State

The ratio of the displacement of the bimorph probe and drive voltage was 0.522 μ m/V. As one end fixed to the XYZ micropositioner, the bimorph probe was statically driven by a dc voltage, whereupon an actuation force from the bimorph probe was loaded on the free end of the microforce sensors. The probing force was determined by the electronic balance (resolution of 0.1 μ N); the spring constant of the microforce sensors was calculated by Hooke's law as

$$F = k \cdot d \qquad (1)$$

Where F was the force; d was the displacement; k was the spring constant. For the experimental system, the bimorph probe was considered rigid relative to the microforce sensors. DC voltage was brought from 0 V to 30 V in step of 2 V. In order to illustrate the effect of the thin film thickness, two kinds of PSZT0.03 thin films with thickness of 1.68um and 2.19um were fabricated in the same structure size, both microforce sensors were tested in static state. The results were shown in Fig. 7 and the spring constant of 11.72N/m and 4.87N/m was obtained.

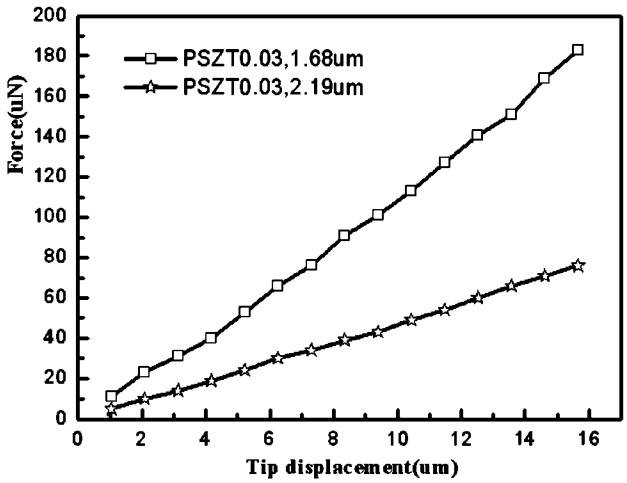

Figure 7. Spring constants of the microforce sensors with the PSZT0.03 thin films for different thickness

The three kinds of PSZT thin films with different x value in static state were tested. The results were shown in Fig. 8 and the spring constant of the three kinds of microforce sensors

was 13.73N/m, 11.72N/m and 8.16N/m.

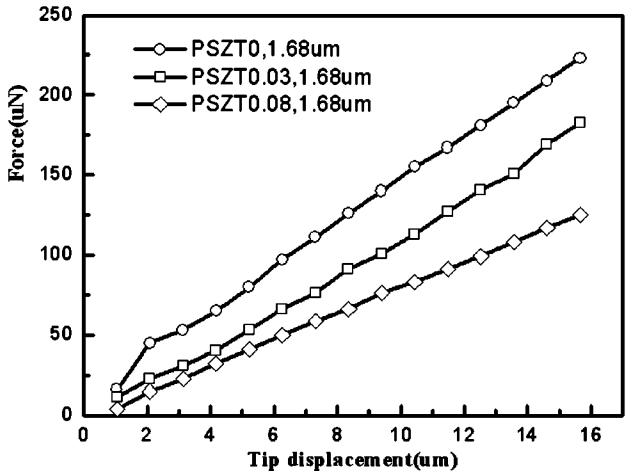

Figure 8. Spring constants of the microforce sensors with the PSZT thin films for different x

B. The Test in the Quasi Static State

The principle of the testing system in the quasi static state was based on Smits modes[10], the relationship between Q and F was

$$Q=\frac{-3d_{31}s_{11}^{Si}s_{11}^{P}h_{Si}(h_{Si}+h_P)L^2}{K}F \tag{2}$$

Where,

$$K = 4s_{11}^{Si}s_{11}^{P}h_{Si}(h_P)^3 + 4s_{11}^{Si}s_{11}^{P}(h_{Si})^3 h_P + (s_{11}^{P})^2(h_{Si})^4 + (s_{11}^{Si})^2(h_P)^4 + 6s_{11}^{Si}s_{11}^{P}(h_{Si})^2(h_P)^2 \tag{3}$$

Q was the charge produced by the PSZT thin film; F was the vertical force received by the PSZT microcantilever free end; s_{11}^{Si} and s_{11}^{P} was the coefficient of flexibility of Si and the PSZT thin film respectively; h_{Si} and h_P was the thickness of Si and the PSZT thin films respectively; L was the length of the PSZT thin films; d_{31} was the piezoelectric coefficient of the PSZT thin films. By simplifying (2) and (3), we got the following formulas:

$$S_q = \frac{Q}{F} = \frac{Q}{kV_{AC}K_{\delta-V}} \tag{4}$$

Where, S_q was the sensitivity of the piezoelectric microforce sensor, Q was the charge output, k was the spring constant, V_{AC} was the applied alternating current (AC) voltage, $K_{\delta-V}$ was 0.522um/V which was mentioned before.

AC voltage was applied to the bimorph to vibrate the microcantilever through the microprobe and the voltage amplitude was changed from 0V to 22.5V in step of 1.5V. The performance of the microforce sensors with the two kinds of PSZT0.03 thin films with different thicknesses were tested in quasi static state. The sensing curves of the two kinds of microforce sensors were shown in Fig. 9, the sensitivity of the microforce sensors with thickness of 2.19um and 1.68um was 0.033pc/uN and 0.077pc/uN.

Three kinds of PSZT thin films with different x value were tested in quasi static state. The sensitivity curves were shown in Fig. 10. The sensitivities of the microforce sensors were respectively 0.017pc/uN, 0.033pc/uN, and 0.011pc/uN as x=0, 0.03, 0.08, the sensitivities of the microforce sensors gained very good linearity behavior. The sensitivity of microforce sensor based on PSZT0.03 thin films was higher than the others which had the same trend with the dielectric property of the PSZT0.03 thin films.

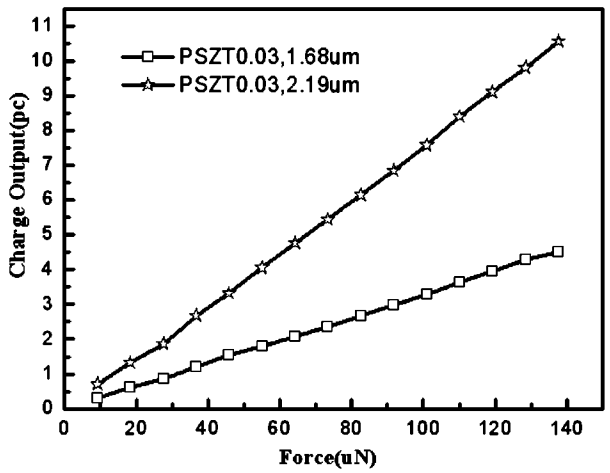

Figure 9. Sensitivities of the microforce sensors with the PSZT0.03 thin films for different thickness

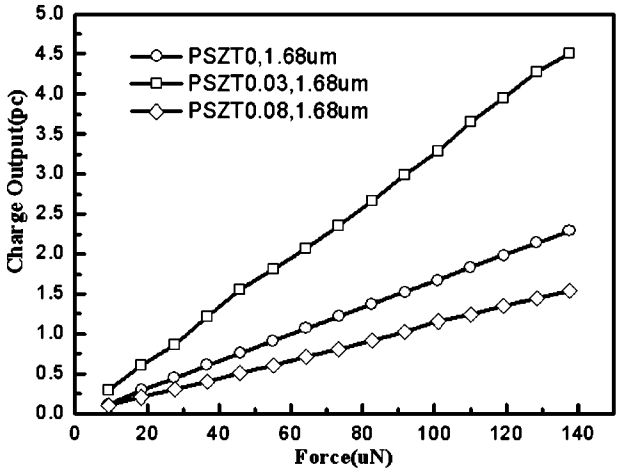

Figure 10. Sensitivities of the microforce sensors with the PSZT thin films for different x

V. CONCLUSIONS

The PSZT thin films were fabricated by the sol–gel process to improve the performance of the PZT thin films. Dielectric constant of Sr doped PZT thin films increased significantly while dissipation factor increased a little than undoped PZT thin films. The PSZT0.03 thin film showed the best results comparing with the PSZT thin film and the PSZT0.08 thin film. Microforce sensors with different PSZT thin films had been

fabricated and tested. The sensing properties indicated that Sr doped PZT thin films improved the sensing property of microforce sensors, and the PSZT0.03 thin film microforce sensor had the best effect comparing with the others, which showed the same tendency as the dielectric property of the PSZT0.03 thin film. The sensitivities for the three microforce sensors were 0.017pc/uN, 0.033pc/uN, and 0.011pc/uN as x=0, 0.03, 0.08, respectively. Combined with the micromachining processes, the PSZT thin films were shown to be good candidate materials for developing the application of micro sensors.

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