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# Characterization of PZT Ferroelectric Thin Films Prepared by A Modified Sol-Gel Method

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*Abstract*—**This paper presents the growth and characterization of PZT ferroelectric thin films by using the sol-gel technology. In this paper, we study the influences of annealing temperatures, different film thickness and different substrates, including titanium and platinum layers on silicon substrate, on the ferroelectric performance of PZT thin films by analyzing the polarization hysteresis. The polarization hysteresis of PZT thin films is measured by using a Sawyer Tower circuit. The results show that the remnant polarization of PZT thin films are higher with the increase of thickness, and the remnant polarization are 8.6μC/cm$^2$ and 11.0μC/cm$^2$ on Ti electrode and Pt/Ti electrode at the annealing temperature of 650℃, respectively. Thus the PZT thin films prepared by using the sol-gel method can be used for developing PZT-based ferroelectric MEMS devices.**

***Keywords-PZT thin films; Sol-gel method; ferroelectric***

## I. INTRODUCTION

Ferroelectric material has been much reported due to their potential applications such as non-volatile random access memories and micro-electromechanical systems. For example, J.F. Scott and L. Kammerdimer et al, Junhao Chu and Xiangjian Meng et al, H.S. Kang and W.J. Lee [1-3].

Lead zirconate titanate (PZT) is a piezoelectric material with high electromechanical coupling coefficient, high dielectric constant and large remnant polarization. It can be used for various applications [4], such as nonvolatile memory and dynamic random access memories (DRAM), piezoelectric actuators, pyroelectric infrared detectors, and ultrasonic devices, since PZT-based devices can own advantages of wide working bandwidth, fast response, and high sensitivity. With the rapid development of MEMS technologies during the past 20 years, many investigators are studying to develop PZT-based ferroelectric MEMS devices for new applications. This requires that PZT thin films can be prepared on the silicon substrate with an appropriate thickness and good performance.

Many techniques are being investigated for the growth of PZT thin films, including sputtering, electron beam or ion-beam deposition, PLD, MOCVD and the sol-gel method. Among these methods, the sol-gel process offers numerous advantages, including low processing temperature, excellent compositional control, uniform homogeneity, easy fabrication over large areas and low cost. In this paper, we present a method of precursor-monomer and a spinning coating method to grow PZT ferroelectric thin films by using the sol-gel technology, the ferroelectric properties of PZT thin films prepared by sol-gel are characterized, with a target of being used in MEMS and nano devices.

## II. PZT THIN FILMS PREPARED BY SOL-GEL METHOD

For the sol-gel method, solid powders of trihydrated lead acetate, zirconium nitrate and tetrabutyl titanate are prepared, and 2-methoxyethanol is used as solvent. Appropriate amount of acetylacetone, with a PZT/acetylacetone ratio of 0.03 mol/4mL, is added to stabilize the solution. The precursor solutions are prepared with a Zr/Ti ratio of 52/48, and 10 percent mole excess lead is added to the solution to compensate lead oxide loss in the annealing process and suppress the pyrochlore formation. The solution is filtered through a 0.2μm syringe filter to minimize the incorporation of particles and dust during solution preparation. After distillation, the solution is kept mixing for another 30 minutes in order to be cooled to room temperature. The concentration of the final solution is 0.3mol/L, and is aged more than 24 hours before used. In order to increase the thickness of PZT thin films, we also prepared the solution that poly(vinyl pyrrolidone) (PVP) is as additives.

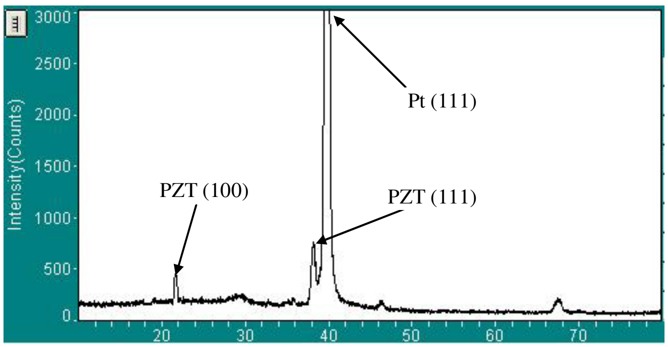
The PZT films are coated by spinning the precursor solution on Ti and Pt/Ti at 3000rpm for 30 seconds. The ferroelectric properties of PZT thin films with three different thicknesses, including 4 layers, 7 layers and 10 layers are studied. A thermal process is adopted for crystallization of each layer of PZT thin film, which is to dry each layer of PZT thin film at 400℃ for 120 seconds. The measured average thickness of an annealed PZT single layer is 200~300Å. The PZT thin films with desired thickness are achieved by repeating spin-coating and thermal treatment cycles. The samples are pre-fired for 120 seconds to remove the residual organics and then annealed at 550ºC, 600ºC, 650ºC, respectively, for 60 minutes under a flowing oxygen atmosphere for final crystallization.

## III. CHARACTERIZATION OF PZT THIN FILMS

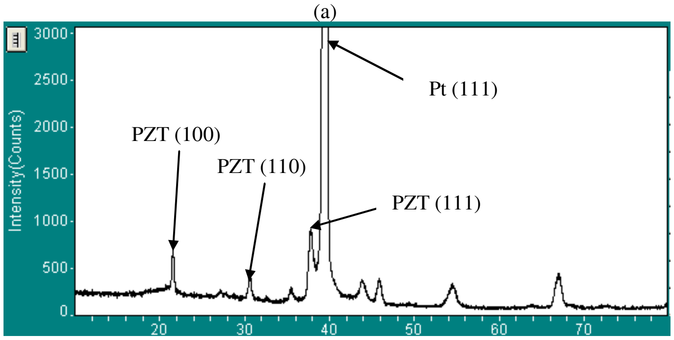
### A. *Crystallographic phases analysis by XRD method*

After the PZT thin films are coated and post-processed, their micro-structures are tested and analyzed by using X-ray diffraction (XRD) with a Ni-filtered Cu Kα radiation source (D5000, Siemens, Germany). The scan step is 0.067º.

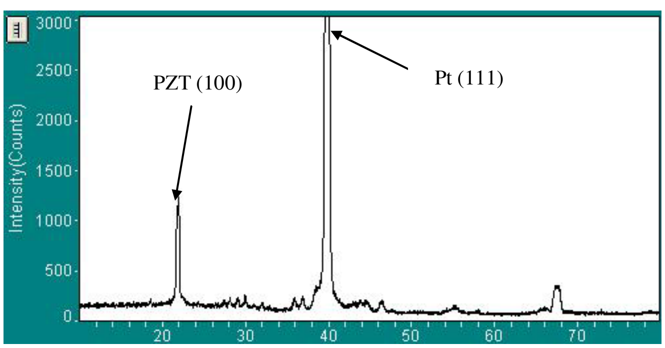
Figure 1 shows XRD patterns of PZT thin films on Pt/Ti layer of Silicon substrate with non-annealing, annealing on 550 ºC and Annealing on 650 ºC. We can see from Figure 1 (a) that the diffraction intensity of PZT (111) phase occurs, with the value a little stronger than another peak before annealing. After annealing, the PZT (111) phase dominates shown in Figure 1 (b), the value is higher than non-annealing, but there still have other phases. In Figure 1 (c), there is only one peak PZT (100), with the value increased from 465 to 1240. This result suggests that annealing on 650℃ is a preferred orientation in crystallization of PZT thin films than that on 550℃.




(a)




(b)



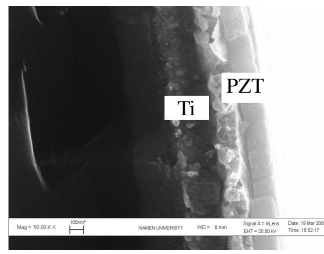

(c)

Figure 1. X-ray diffraction patterns of PZT thin films on Pt/Ti of Si substrate. (a)Non-annealing, (b) Annealing on 550 ºC, (c) Annealing on 650 ºC.

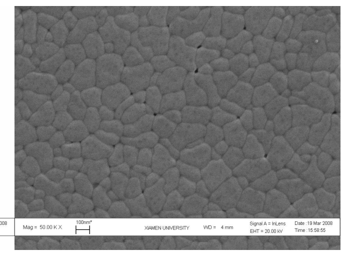
We can conclude from the XRD data that the PZT thin films prior to annealing present a poor crystalline quality, which consist of not only a phase with a perovskite structure, but also a pyrochlore phase. The reason for observed orientation may be speculated that some of the acetate content has been left in the dried films. The residue may affect the nucleation and the growth of the perovskite phase. For nucleation and orientation of PZT on Pt/Ti electrodes, the Pt surface may be partially covered with $TiO_2$ due to the diffusion of active titanium element, and a Ti-enriched layer near the bottom electrode interface is formed which easily nucleates and in-situ creates a perovskite-seeding layer for the rest of the film due to the chemical reaction [5-6].

## B. *Morphologies measurement by SEM*

The morphologies of PZT thin films on the Pt/Ti layer with the annealing at 550 ºC and 650 ºC are measured by using the SEM and shown in Figure 2 and 3. We can observe that PZT thin films annealed at 650 ºC have a more uniform structure than annealed at 550 ºC. TABLE I shows the thickness of different spinning layers.

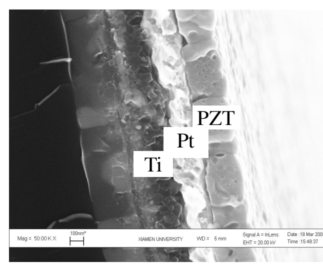



(a) cross section-view

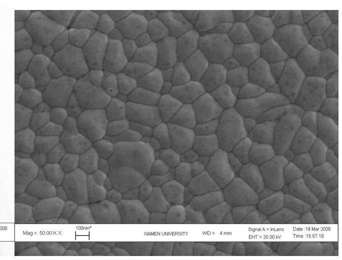


(b) plain-view

Figure 2. SEM micrograph of PZT thin films on Pt/Ti annealing at 550 ºC.




(a) cross section-view



(b) plain-view

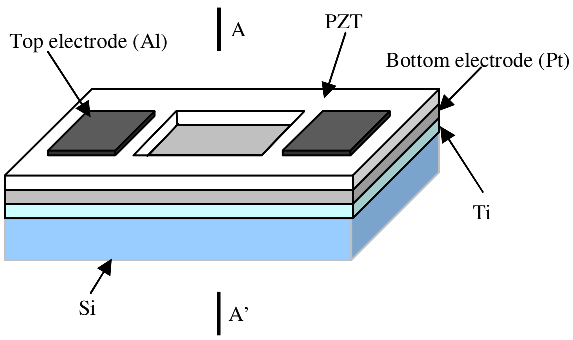
Figure 3. SEM micrograph of PZT thin films on Pt/Ti annealing at 650 ºC.

TABLE I. THE THICKNESS OF DIFFERENT SPINNING LAYERS

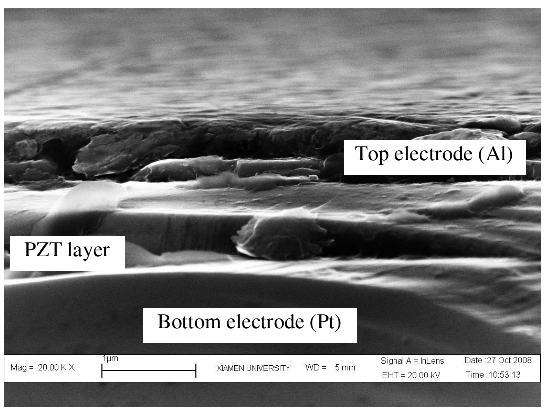
| Layers | | Thickness (nm) | |
|---|---|---|---|
| | | On the Pt electrode | On the Ti electrode |
| PZT sol-gel only | 4 | 80 | 74 |
| | 7 | 135 | 130 |
| | 10 | 203 | 195 |
| PZT sol-gel with PVP | 4 | 150 | 143 |
| | 7 | 250 | 244 |
| | 10 | 380 | 362 |

## C. *Ferroelectric properties measurement*

Before applied to practical applications in the MEMS and nano devices, PZT thin films should be characterized to get their electrical properties. Thus, we study their ferroelectric properties. The RT66A standardized ferroelectric tester (Radiant Technologies) is used for measurement of field induced polarization. With this tester, the polarization hysteresis loop can be obtained with the traditional sawyer-tower circuit mode or with a virtual ground circuit mode [7]. The testing signal is a triangular wave with a frequency of 1 kHz. Figure 4 shows the PZT microstructure for ferroelectric measurement by using MEMS process.




(a)




(b)

Figure 4. PZT microstructure for ferroelectric measurement by MEMS process. (a) Schematic structure. (b) SEM micrograph of A-A' cross section.

The PZT film with single-layer heating treatment at 400ºC and annealing treatment at 550ºC on the Ti electrode resulting in maximum polarization ($P_M$) of 2.9μC/cm$^2$, remanent polarization (Pr) of 1.95μC/cm$^2$ under an applied voltage of 3V in Figure 5. When the annealing temperature is raised to 650ºC, the maximum polarization increase to 13.0μC/cm$^2$ and the remanent polarization is to 8.6μC/cm$^2$ in Figure 7. Similarly, the PZT thin film with single-layer heating treatment at 400ºC and annealing treatment at 550ºC on the Pt/Ti electrode has the maximum polarization of 6.5μC/cm$^2$ and remanent polarization of 2μC/cm$^2$ in Figure 6, and Figure 8 shows the maximum polarization of 30.5μC/cm$^2$ and remanent polarization of 11.0μC/cm$^2$ at 650ºC. The results indicate that PZT thin films are not completely crystallized at 550ºC, but can be fully crystallized at 650ºC. So the ferroelectric properties of PZT thin films are better at 650ºC than 550ºC. Moreover, the PZT thin films on Pt/Ti electrode have better ferroelectric properties than on Ti electrode.

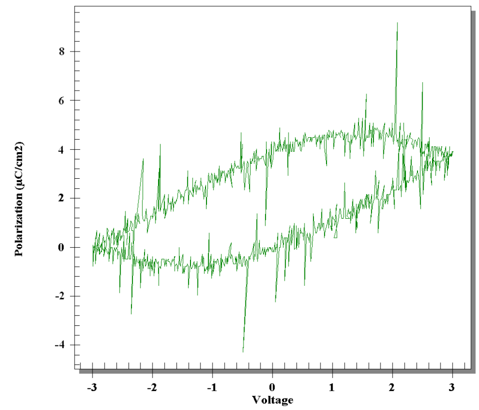



Figure 5. P-V hysteresis loops of PZT films which spinning 10 layers and annealing at 550℃ on Ti bottom electrode.

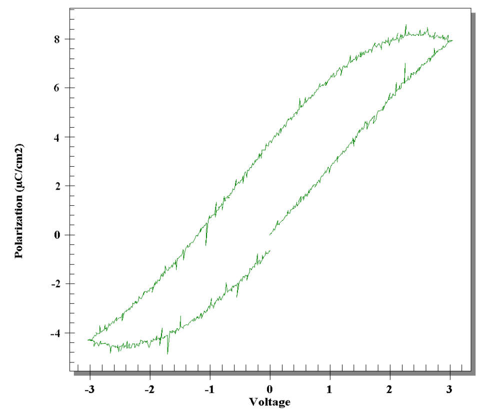



Figure 6. P-V hysteresis loops of PZT films which spinning 10 layers and annealing at 550℃ on Pt bottom electrode.

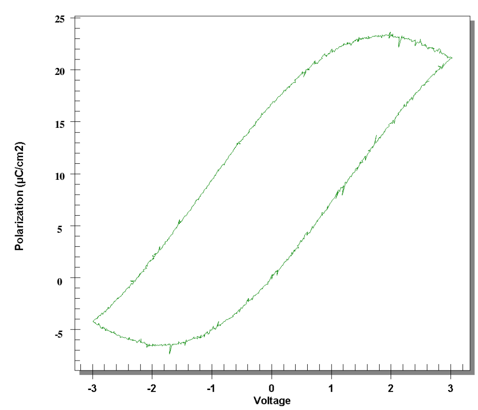



Figure 7. P-V hysteresis loops of PZT films which spinning 10 layers and annealing at 650℃ on Ti bottom electrode.

From Figure 8, 9 and 10, the remanent polarization of PZT films, which spinning with 4 layers, 7 layers and 10 layers, and annealing at 650℃ on Pt bottom electrode are 6.4μC/cm$^2$, 9.5μC/cm$^2$ and 11.0μC/cm$^2$, respectively. Obviously, the remanent polarization increases with the film thickness.

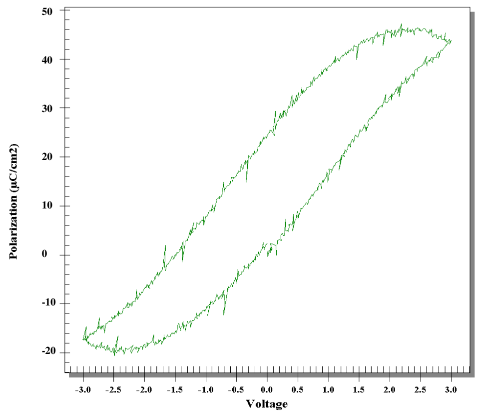



Figure 8. P-V hysteresis loops of PZT films which spinning 10 layers and annealing at 650℃ on Pt bottom electrode.

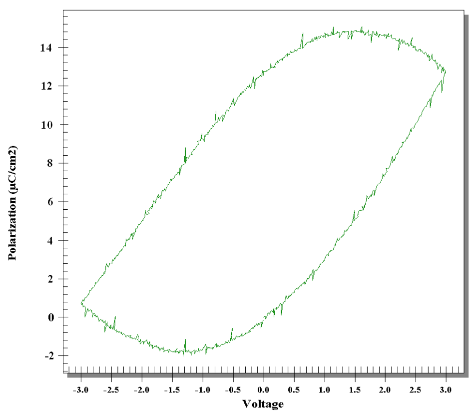



Figure 9. P-V hysteresis loops of PZT films which spinning 4 layers and annealing at 650℃ on Pt bottom electrode.

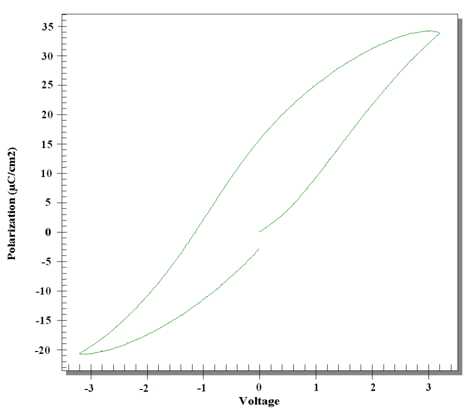



Figure 10. P-V hysteresis loops of PZT films which spinning 7 layers and annealing at 650℃ on Pt bottom electrode.

Dielectric properties are also studied. Capacitance-voltage measurements are performed at 100KHz by using the Agilent 4294A impedance analyzer. For the PZT thin film on the Ti electrode, spinning 10 layers, its dielectric constant is about 749, free dielectric constant is 695, and dielectric loss is about 0.3; for the PZT film on the Pt/Ti electrode, its dielectric constant is 876, free dielectric constant is 853, and a dielectric loss is about 0.25. The dielectric constants of the PZT (100) aligned film are higher than the PZT (110) aligned film in the measured frequency range. These results also illustrate that the PZT thin films have better ferroelectric property than that of the bulk material, which allows the development of many micro and nano devices, such as pyroelectric sensors, capacitors, transistors, and etc. Note that the dielectric constant of PZT films are different on the Ti and Pt/Ti electrodes, which may be used in some new applications, for example, tunable microwave devices by using different bottom electrodes.

## IV. CONCLUSIONS

In this paper the PZT thin films have been successfully coated on Ti and Pt/Ti electrodes of Silicon substrates by using the sol-gel method. Then, we study the influence of annealing temperatures and different film thickness.The XRD method is employed to characterize the preferential orientation of PZT thin films on Pt/Ti layer of Si substrate at different annealing temperature, and then the SEM is used to study the morphologies of PZT thin films. Measurement results show that the PZT film with single-layer heating treatment at 400ºC and annealing treatment at 650ºC on the Ti electrode, resulting in maximum polarization ($P_M$) of 13mC/cm2 and remanent polarization (Pr) of 8.6mC/cm2 under an applied voltage of 3V. The PZT thin film with single-layer heating treatment at 400ºC and annealing treatment at 650ºC on the Pt/Ti electrode has larger maximum polarization of 30.5mC/cm2 and remanent polarization of 11.0mC/cm2, owing to the preferential orientation of PZT (100). Based on these, PZT thin films prepared by using the sol-gel method in our study can be applied to developing PZT-based ferroelectric MEMS devices.

## ACKNOWLEDGMENT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