Journal of Physics: Conference Series

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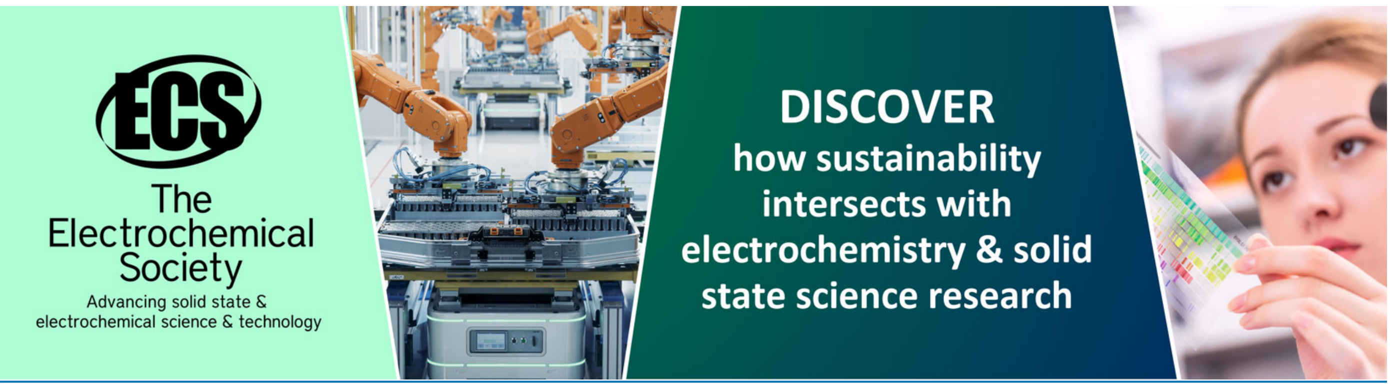
To cite this article: Zhenxing Bi *et al* 2007 *J. Phys.: Conf. Ser.* **61** 120



IOP Publishing Journal of Physics: Conference Series **61** (2007) 120–124
doi:10.1088/1742-6596/61/1/025 International Conference on Nanoscience and Technology (ICN&T 2006)

Characterization of PZT Ferroelectric Thin Films by RF-magnetron Sputtering

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Abstract. By using Radio Frequency (RF) magnetron sputtering method, $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) thin films were deposited on Pt/Ti/ SiO_2/Si substrates. Pt/Ti bottom electrode was fabricated on SiO_2/Si substrates by magnetron dual-facing-target sputtering system. Phase and crystalline structure analyses of the PZT films were performed on an X-ray diffraction(XRD), Surface morphology, roughness and particle size of the PZT films were observed with MMAFM/STM+D3100 atomic force microscopy (AFM). Experiment results show that after annealing at 700℃ for 20 min, the thickness of PZT films can get perovskite structure. The surface of PZT thin films was uniform and density. Raw mean, Root Mean Square roughness and Mean roughness of PZT thin films is 34.357nm, 2.479nm and 1.954nm respectively. As test frequency was 1kHz, dielectric constant (ε) of PZT thin films was 327.6, electric hysteresis loop showed that coercive field (Ec), remanent polarization (Pr) and spontaneous polarization(Ps) of PZT thin films were 79.14 kV/cm, 37.78μC/cm^2 and 19.10μC/cm^2, respectively.

1. Introduction

Thin films lead zirconate titanate (PZT) are widely studied because of their advanced ferroelectric and piezoelectric properties. Main applications are on one hand FeRAM using the high remanent polarization of the PZT and on the other hand sensors and actuators like micromotors or micropumps [1].PZT materials are suitable to memory devices due to their high dielectric constant and spontaneous polarization capability. This is mainly due to its properties such as high remanent polarization, fast switching speed, high Curie point, wear-proof, and radiation hardness. For this purpose, various thin film preparation techniques such as sol-gel process[2], pulsed laser deposition[3], sputtering[4], MOD [5] and chemical vapor deposition [6] in which the most used techniques are sol–gel and sputtering have been investigated in recent years.

A Pt/Ti bilayer has been widely studied as a bottom electrode for PZT films. Pt is primarily selected because of its high thermal conductivity, good stability in a high temperature oxygen environment, and its leakage current. Ti is introduced to promote the adhesion of Pt films to the substrate [7]. It has been reported that when a Pt/Ti bilayer is used as a bottom electrode for PZT films, Ti atoms diffuse out through the grain boundaries of the Pt layer onto the Pt surface, and the out-diffused Ti enhances the formation of a perovskite PZT film.

In this work, ferroelectric PZT thin films were sputter-deposited using a sputtering target containing excess Pb and O at various sputtering atmosphere, sputtering power and different anneal temperature. The effects of sputtering atmosphere, excess contents of Pb and anneal temperature on the formation of PZT films with perovskite phase were investigated.

2. Experimental

2.1. Experimental process

Lead zirconate titanate Pb $(Zr_{0.52}Ti_{0.48})O_3$ ceramic target were prepared by stoichiometric ratio analytically pure ZrO_2,TiO_2 and excessive 20% PbO as a result of Pb is easy to volatilize in sputtering and annealing. It will decrease ferroelectric quality evidently because of Pb's volatilization. Ball milling for 15h, washing, drying for 12h, sifting out, hydraulic pressing at $100kgf/cm^2$ and pressing at 180Mpa, a surface smooth and dense PZT target (Φ=70mm) was made by calcining in 1250℃ for 2h.

Pt/Ti bottom electrode was prepared on SiO_2/Si substrate with DPS-III high vacuum dual-facing-target magnetron sputtering system.150 nm Pt layer and 20 nm Ti layer were prepared at Ar,2.0 Pa,25 ℃ and 75 W for 7 min (Pt), and at 40 W for 15 min (Ti) respectively. PZT thin films were deposited on Pt/Ti/SiO_2/Si substrate in an off-axis RF-magnetron sputtering system. A uniform deposition of PZT films could be obtained by rotating the substrate during the deposition. The sputtering parameters are reported on Table 1.

Table 1. Sputtering parameters of PZT samples

No	Pressure (Pa)	RF power (W)	Sputtering atmosphere	Substrate temperature(℃)	Sputtering time(h)	Anneal temperature(℃)	Anneal time (min)
1	2	40	Ar	20	5	600	20
2	3	40	Ar	250	5	700	20
3	2.7	40	Ar/O_2 (9: 1)	250	5	700	20

For the annealing of the deposited films, a rapid thermal anneal (RTA) system was adopted. The films deposited in Ar and Ar/O_2 were annealed for 20 min in air at 600 and 700℃, respectively.

2.2. Characterization of PZT thin film

Phase and crystalline structure analyses of the PZT films were performed on an X-ray diffraction (XRD), Surface morphology, roughness and particle size of the PZT films were observed with MMAFM/STM+D3100 atomic force microscopy (AFM). The thickness of PZT thin film was measured with DEKTAK6M surface profiler. Hysteresis loops behaviour analyses were performed on TRC-2.

3. Results and discussion

3.1. XRD analyze

Pt bottom electrode is selected primarily because of its good stability in high temperature oxidizing environments, its high electrical conductivity, and its low leakage current. Ti is introduced to promote adhesion between Pt and silicon substrate. Crystal lattice constant of cube crystal lattice Pt (a=0.39nm) is close to lattice constant of perovskite PZT (a＝0.40nm).Thickness analyze indicate that the thickness of Pt and Ti layer are about 150nm and 20nm respectively.

Figure 1 illustrates the XRD patterns of the PZT thin films annealed at various temperatures (600 ℃, 700℃) and various sputtering gas (pure Ar or Ar/O_2).Thin film deposited in room temperature is amorphous. The patterns indicate that the PZT films deposited in Ar gas has pyrochlore structure (py) after being annealed at 600℃ for 20min. However, the pyrochlore phase is almost eliminated and dominant phase at 650℃ is perovskite phase. When the annealing temperature increases to 700℃ for 20min, no pyrochlore remains. Moreover, perovskite is the main factor to improve the residual polarization strength of PZT ferroelectric thin film. In order to prevent pyrochlore structure form, rapid thermal annealing (RTA) is used, which can shorten the residence time of amorphous PZT thin film in lower temperature. As a result, the pine pore, transition phase and Pb loss are prevented. Furthermore, RTA is crucial to lower leakage current density for PZT ferroelectric thin films [8].

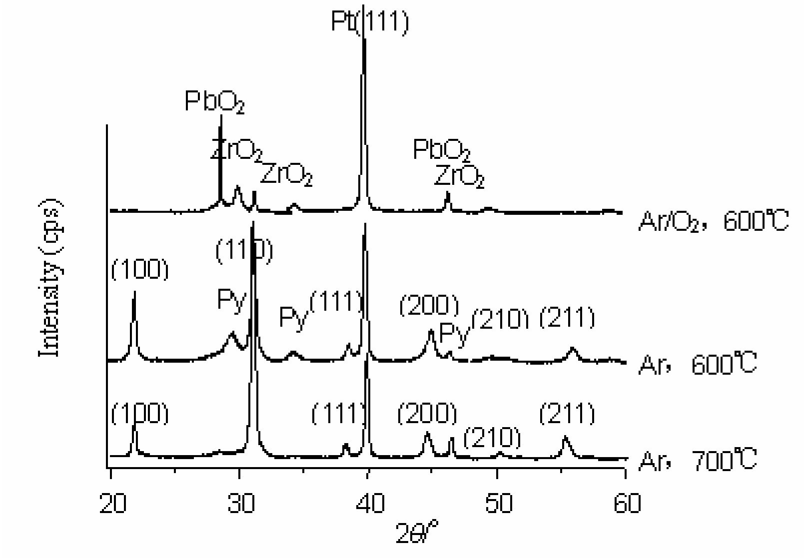

Fig 1. XRD spectra of PZT thin films

In addition to the diffraction lines corresponding to the titanium and platinum layers, the X-ray diagrams display the lines (1 0 0), (1 1 0), (1 1 1), and (2 0 0) characteristic of PZT. XRD pattern of PZT thin film deposited in Ar/O_2 and rapid-thermal-annealed at 600℃ shows that the diffraction peak of PbO_2 and ZrO_2 is notable. There is a weak perovskite (1 0 0) diffraction peak in 2θ= 31°.It is disadvantageous for PZT thin film to form the perovskite structure when O_2 is introduced into sputter system. XRD pattern of PZT thin film deposited in Ar and rapid-thermal-annealed at 600℃ for 20min shows that besides Pt in 2θ= 40°epitaxial diffraction peak, perovskite (1 0 0) diffraction peak in 2θ= 31° and pyrochlore diffraction peak in 2θ=29° is very strong. Under this condition, the perovskite structure and pyrochlore structure coexist. Fig 1 shows that crystal structure of thin film deposited in Ar ambience and rapid thermal annealed at 700℃ changes obviously. The diffract peak of perovskite phase (1 0 0) direction become stronger in evidence and the diffract peak of pyrochlore phase in 2θ=31° disappears, PZT thin film exhibits a single perovskite phase. XRD pattern indicate thin film that deposited in Ar ambience with the target of excessive 20% PbO and rapid-thermal-annealed at 700℃ for 20min exhibits a single perovskite phase.

3.2. AFM analysis

AFM analysis shows that the surface of PZT thin film deposited in Ar/O_2 and rapid thermal annealed at 600℃ for 20 min is homogeneous and dense (Figure 2a), the root-mean-square (rms) roughness and mean roughness is 67.70nm、51.01nm respectively. The mean surface grain size of thin film is 219nm, a litter bigger size of 200~470nm nm and a litter smaller size of 110~200nm.

Figure 2c is a plan-view AFM image of the PZT thin film. The surface of PZT thin film deposited in pure Ar and rapid-thermal-annealed at 700℃ for 20 min is extremely dense and smooth with Raw mean, root-mean-square (rms) roughness of 2.48nm over 1×1μm scan area. The AFM micrograph reveals that the PZT thin film is well crystallized and cracks free, and has nearly uniform grain distribution. The mean grain size of surface of thin film is 70nm, a litter bigger size of 100~120nm and a litter smaller size of 20~30nm. Compared with PZT thin film deposited in Ar/O_2, the PZT thin film deposited in pure Ar has better surface morphologies. The mean grain size and surface roughness of PZT thin film deposited in pure Ar is smaller than the thin film deposited in Ar/O_2.

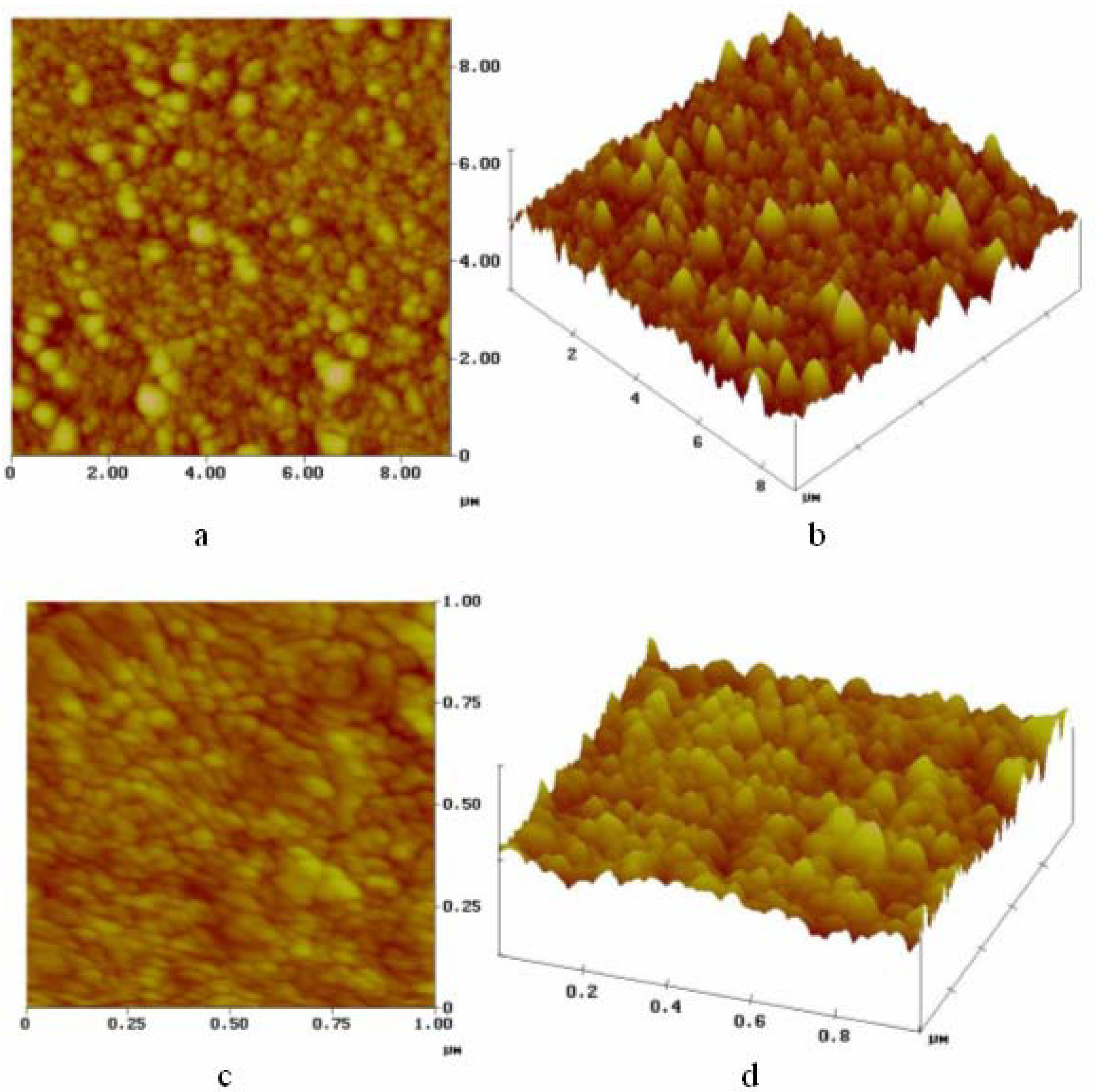

Fig 2. AFM micrographs of PZT thin film deposited in (a, b) Ar/O_2 and (c, d) pure Ar

3.3. P-E hysteresis loop of PZT thin films

Ferroelectrical hysteresis loops of PZT thin film capacitor annealed at 700℃ for 20min are shown in Figure 3. Dielectric constant (ε) of PZT thin film that deposited in Ar and RTA in 700℃for 20min is 327.6 as the test frequency is 1 kHz. The coercive field strength (Ec) of PZT thin film is 79.14 kV/cm; the residual polarization strength (Pr) and spontaneous polarization strength (Ps) are 37.78μC/cm^2 and 19.10μC/cm^2 respectively.

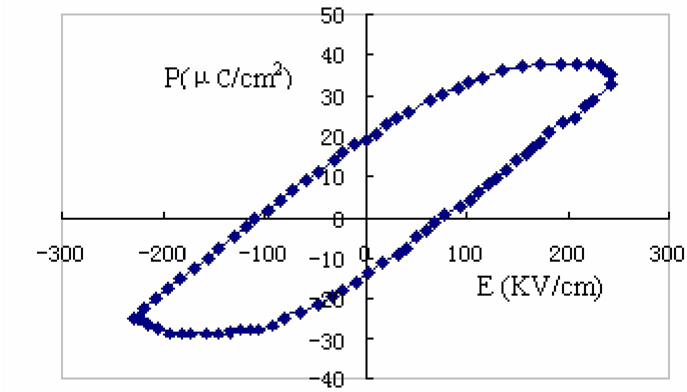

Fig 3. P-E hysteresis loop of PZT thin films deposited in Ar and RTA for 20 min at 700℃

4. Conclusion

Pt/Ti bottom electrode was prepared on SiO_2/Si underlay by DC dual-facing-target sputtering system. The Pt bottom electrode shows an obvious (111) epitaxial growth. XRD, SEM and AFM show that the PZT thin film deposited on Pt/Ti/SiO_2/Si underlay in Ar gas by Radio Frequency sputtering and RTA in 700℃ for 20min is a single perovskite structure and no pine pore and crack on the surface of thin film. Raw mean, Root Mean Square roughness and Mean roughness of PZT thin films are 34.357nm, 2.479nm and 1.954nm respectively. The thickness of the PZT thin film is about 800nm. Dielectric constant (ε) of the thin film is 327.6, The coercive field strength (Ec) of PZT thin film is 79.14 kV/cm, the residual polarization strength（Pr）and spontaneous polarization strength（Ps）are 37.78μC/cm^2 and 19.10μC/cm^2 respectively.

Acknowledgements
This work was supported by The National Science Foundation of Tianjin China (Grant No. 983601211)

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