Research Article

Properties of RF-Sputtered PZT Thin Films with Ti/Pt Electrodes

Cui Yan, Yao Minglei, Zhang Qunying, Chen Xiaolong, Chu Jinkui, and Guan Le

Key Laboratory for Micro/Nano Technology and System of Liao-Ning Province, Dalian University of Technology, Dalian 116024, China

Correspondence should be addressed to Cui Yan; yancc@dlut.edu.cn

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Effect of annealing temperature and thin film thickness on properties of $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) thin film deposited via radiofrequency magnetron sputtering technique onto Pt/Ti/SiO₂/Si substrate was investigated. Average grain sizes of the PZT thin film were measured by atomic force microscope; their preferred orientation was studied through X-ray diffraction analysis. Average residual stress in the thin film was estimated according to the optimized Stoney formula, and impedance spectroscopy characterization was performed via an intelligent LCR measuring instrument. Average grain sizes of PZT thin films were 60 nm~90 nm and their average roughness was less than 2 nm. According to X-ray diffraction analysis, 600°C is the optimal annealing temperature to obtain the PZT thin film with better crystallization. Average residual stress showed that thermal mismatch was the decisive factor of residual stress in Pt/Ti/SiO₂/Si substrate; the residual stress in PZT thin film decreased as their thickness increased and increased with annealing temperature. The dielectric constant and loss angle tangent were extremely increased with the thickness of PZT thin films. The capacitance of the device can be adjusted according to the thickness of PZT thin films.

1. Introduction

PZT thin film has been broadly applied in various kinds of microelectromechanical system devices, such as ferroelectric random access memory [1], digital switch [2], vibration energy harvesting [3, 4], and piezoelectric proton exchange membrane fuel cells [5, 6]. PZT thin film could be utilized in these applications due to the fact that it possesses low leakage current density, large electromechanical coupling coefficient, and excellent dielectric properties.

Frunza et al. [7] have investigated the preparation and characterization of PZT thin films by RF-magnetron sputtering with Au electrodes and alumina substrate; energy dispersive X-ray spectroscopy analysis has shown that resulting PZT thin film had the right stoichiometry and no Pb loss was detected by comparison with the target ceramic composition. Lu et al. [8] experimentally have shown that Pt/Ti as bottom electrode is effective to reduce the curvature of the wafer after the PZT thin film deposition and prevent the PZT thin

film cracking while annealed by rapid thermal annealing. Furthermore, Zhou et al. [1] have shown that the structure with Pt top electrode displays stronger ferroelectric effect and lower leakage current density.

The functionality and reliability of devices based on PZT thin film are strongly affected by their residual stresses. Residual stresses are primarily generated due to (i) different thermal expansion coefficient of the substrate and film when environment temperature changes and (ii) growth stresses. Although residual stress analysis on PZT thin film deposited via sol-gel method has been paid great attention in recent years [8], investigation on reducing the residual stress in sputtered PZT thin film is rare.

PZT thin film was deposited via RF-sputtering technique onto Pt/Ti/SiO₂/Si substrate. Effect of annealing temperature and thin film thickness on preferred orientation, grain size, residual stress, and dielectric properties of the PZT thin film was investigated.

FIGURE 1: Atomic force microscope images of PZT thin films with thickness of about 150 nm annealed at various temperatures for 8 min: scan on a $3 \times 3 \mu\text{m}^2$ square area.

2. Materials and Methods

2.1. The Preparation of PZT Thin Films. 2 in. Si (100) wafer was oxidized in an oxygen environment and obtained SiO_2 insulation layer with thickness of $1.5 \mu\text{m}$. Then, Ti as adhesion layer with thickness of 90 nm and Pt as seed layer with 300 nm were deposited through RF-sputtering technique. The PZT thin film was deposited from a PZT ceramic target (Kurt J. Lesker) onto Pt/Ti/ SiO_2 /Si substrates. Thicknesses of PZT thin films were 150 nm, 300 nm, and 600 nm, respectively. In order to decrease volatilization of Pb and eliminate the formation of the pyrochlore phase in PZT thin films, the annealing treatment was implemented in the air with a rapid thermal process at 500°C , 600°C , and 700°C . After that, the PZT thin films were cooled down to room temperature naturally.

2.2. PZT Thin Film Performance Testing. Average grain sizes of the PZT thin film were measured by atomic force microscope; their preferred orientation was studied through X-ray diffraction analysis. Average residual stress in the thin film was estimated according to the optimized Stoney formula, and impedance spectroscopy characterization was performed via an intelligent LCR measuring instrument.

3. Results and Discussion

3.1. Surface Microstructure of PZT Thin Films. The surface structure characterization of PZT thin film influenced by annealing temperature was tested with atomic force microscope. Figures 1(a), 1(b), and 1(c) showed surface images of PZT thin films and their average roughness was less than 2 nm. Average grain sizes of PZT thin films were 78.91 nm, 68.08 nm, and 86.41 nm while annealed at 500°C , 600°C , and 700°C , respectively. Amplitude parameters of PZT thin films indicated that 600°C is the optimal temperature, at which PZT thin films with relatively smaller grain size and surface roughness can be obtained.

3.2. Crystallization of PZT Thin Films. The crystallization characterization of the PZT thin films deposited on Pt bottom electrode was measured with an X-ray diffractometer (D8 Discover, Bruker Co.) in geometry (θ - 2θ) using $\text{Cu K}\alpha$ radiation with a scan step of 0.02° . X-ray diffraction analysis results

FIGURE 2: X-ray diffraction results of PZT thin films annealed at different temperatures.

of the PZT thin films were illustrated in Figure 2. All peaks of perovskite phase appeared when annealing temperature was set at 500°C , enhanced when annealing temperature was elevated to 600°C , and degraded when annealing temperature was 700°C . 600°C is the optimal annealing temperature to obtain the PZT thin film with better crystallization.

3.3. Average Residual Stresses in PZT Thin Films. Residual stress in PZT thin film σ_f primarily includes thermal stress σ_{thermal} and growth stress σ_{growth} .

It is an extensively used technique for calculating film residual stress σ_f by testing the wafer curvature and exploiting the optimized Stoney equation [9]:

$$\sigma_f = \frac{E_s t_s^2}{6(1-\nu_f) t_f} \left(\frac{1}{R} - \frac{1}{R_0} \right), \quad (1)$$

where E is Young's modulus, ν is Poisson's ratio, and t is the thickness. The subscripts s and f denote the substrate and the film, respectively. R_0 and R are the radius of the wafer curvature before and after film fabrication.

Thermal stress due to thermal mismatch between substrate and film can be calculated by [10–12]

$$\sigma_{\text{thermal}} = E_f \times (\alpha_f - \alpha_s) \times \frac{\Delta T}{(1-\nu_f)}, \quad (2)$$

(a) Curvature radius curves of Pt/Ti layer

(b) Curvature radius curves of the PZT thin film with thickness of 150 nm

(c) Curvature radius curves of the PZT thin film with thickness of 300 nm

(d) Curvature radius curves of the PZT thin film with thickness of 600 nm

FIGURE 3: Curvature radius curves were tested via the step profiler after thin film deposition.

TABLE 1: Average residual stress and thermal stress in Pt/Ti layer annealed at different temperatures.

Annealing temperature	Without annealing	500°C	600°C	700°C
Radius of curvature: R (mm)	44035	5049	4169	4824
Average residual stress: σ_r (MPa)	85.6	747	904	781
Thermal stress: σ_{thermal} (MPa)	0	1320	1583	1874

where α is the coefficient of thermal expansion and ΔT is the cooling temperature range in environment.

In order to calculate average residual stress in Pt/Ti layer and PZT thin film itself, their curvatures were measured by the step profiler (Surfcorder ET4000M, Kosaka Laboratory Ltd., Japan). Moreover, thickness of the films was measured via ellipsometer (M-2000DI).

The Si wafer is much thicker than Pt/Ti layer or PZT thin film, so (1) is applicable in this case. The effect of SiO_2 on residual stress could be ignored, because both two sides of Si were oxidized and SiO_2 was symmetrical.

Figure 3(a) indicated radius of curvature of Pt/Ti/ SiO_2 /Si substrate. According to Table 1, radius of curvature of

Pt/Ti/ SiO_2 /Si substrate without annealing treatment was 44035 mm with average roughness of 3 nm. Average residual stress in Pt/Ti layer was compressive and 85.6 MPa according to (1). It is generally intrinsic stress generated during sputtering process which is associated with the pinning effect caused by the Ar gas bombardment. After annealing, average residual stress in Pt/Ti layer changed to be tensile. According to (1) and (2), average residual stresses and thermal stress in Pt/Ti layer annealed were summarized in Table 1. It indicated that thermal stress is a fundamental component of residual stress in Pt/Ti layer.

Curvature radius curves after the PZT thin film deposition were summarized in Figures 3(b), 3(c), and 3(d).

TABLE 2: Average residual stresses in PZT thin films with different thicknesses annealed at 500°C, 600°C, and 700°C for 8 min.

	500°C		600°C		700°C	
	R (mm) R_a (nm)	σ_r (MPa)	R (mm) R_a (nm)	σ_r (MPa)	R (mm) R_a (nm)	σ_r (MPa)
PZT ($T = 150$ nm)	8549/21	1150	4650/32	2115	4423/36	2223
PZT ($T = 300$ nm)	9558/16	514	7298/21	674	4059/27	1211
PZT ($T = 600$ nm)	14655/2	168	4528/4	543	3458/6	711

R_a denoted average roughness of curvature radius.

FIGURE 4: Dielectric constant and dielectric loss coefficient of PZT thin films with different thicknesses.

They showed that the average residual stress in samples was compressive before annealing treatment and turned out tensile after. Average residual stress in PZT thin films was calculated according to (1) and given in Table 2. It indicated that average residual stress in PZT thin films decreased as the thickness increased and it increased with annealing temperature.

3.4. Dielectric Property of Sputtered PZT Thin Films. The dielectric and leakage characterization of the PZT thin films at room temperature was performed in metal-ferroelectric-metal configurations. Impedance spectroscopy characterization was performed in the frequency with a range of 0.1 kHz to 100 kHz at 1 V via an intelligent LCR measuring instrument (ZL5, Shanghai Instrumentation Research Institute).

Dielectric constant and dielectric loss coefficient of sputtered PZT thin films were summarized in Figures 4(a) and 4(b). From the results, the dielectric constant was about 35000, 4000, and 400 in PZT thin films with thicknesses 600 nm, 300 nm, and 150 nm, respectively. Moreover, there is extraordinary stability as frequency varied in 0.1 kHz–100 kHz. Dielectric constant and dielectric loss coefficient were extremely increased with PZT thin film thickness.

4. Conclusions

PZT thin film was deposited via RF-sputtering method onto Pt/Ti/SiO₂/Si substrate. Moreover, roughness and residual stress were similar to the PZT thin film with the same thickness via sol-gel method. 600°C is optimal annealing temperature, at which we can obtain the PZT thin film with smaller roughness and better crystallization. Average residual stress in PZT thin films decreased as the thickness increased and increased with annealing temperature. The capacitance of the device can be adjusted according to change the thickness of PZT thin films.

Conflict of Interests

The authors declare that there is no conflict of interests.

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