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Residual stresses in Pt bottom electrodes for sol-gel derived lead zirconate titanate thin films

Lulu Zhang, Masaaki Ichiki*, Ryutaro Maeda

National Institute of Advanced Industrial Science and Technology, 1-2-1 Namiki, Tsukuba 305-8564, Japan

Abstract

Residual stresses in Pt bottom electrodes for MEMS multilayer structures comprised of PZT thin films were investigated by measuring the changes in radius of wafer curvature. The Pt bottom electrodes were compressive under sputtering but changed to tension after the subsequent annealing of PZT film. This tension increased with the increase in the thickness of PZT film. Furthermore, when the PZT film was chemically etched the stresses in the Pt bottom electrodes decreased compared with after the first coating of PZT film. Therefore, the stresses in Pt bottom electrodes were changed due to the subsequent PZT coating. Thermal stress and other factors like lattice parameters, crystallite dimension and diffusion, are thought to contribute the change in the stresses.

Keywords: Mechanical properties; Pt; PZT; Sol-gel processes; X-ray methods

1. Introduction

Pt thin films are widely used as bottom electrodes for micro electro mechanical system (MEMS) multilayer structures comprised of piezoelectric lead zirconate titanate ($Pb(Zr,Ti)O_3$:PZT) thin films. However, there are some problems associated with Pt films. One of the problems is residual stress in the multilayer structure. Pt films have a larger thermal expansion coefficient than the PZT films and substrates. Therefore thermal stresses caused by the mismatch of thermal expansion coefficient between Pt bottom electrodes and the substrates occur during the sequent heat-treatment of PZT films. The properties of the PZT thin film such as dielectric permittivity and piezoelectric coefficients are influenced by the stresses.[1] Also, the stresses in the multilayers reduce the yield of the MEME devices by undesired buckling when released structures are required.[2]

This study reports the residual stress changes in the Pt bottom electrodes during the fabrication of multilayer structures. The residual stresses in each film were investigated by measuring the changes in the radius of wafer curvature before and after the deposition of each film. The interactions between the PZT films and the Pt bottom electrodes were also investigated by chemical etching of PZT films.

2. Experimental procedure

Oxides with the thickness of 0.5 μm on Si(100) substrates were grown by thermal oxidation. Then the bottom electrodes were prepared by sputtering titanium of 0.05 μm and platinum of 0.1 μm at 200 °C. The PZT thin films were fabricated by sol-gel technique. The detailed preparation procedure of $Pb_{1.2}(Zr_{0.52}Ti_{0.48})O_3$ solution was described in our previous work.[3] The PZT films were coated on the $Si/SiO_2/Ti/Pt$ substrates by using a spin coater. The coated films were then treated using a three-step heat-treatment process. They were first dried at 120 °C for 10 min to remove residual water and then heated at 300 °C for 30 min to pyrolysis, and finally annealed at 600 °C for 30 min to crystallize the film into a perovskite type structure. The coating and heat-treatment process were repeated several times until the preferred thicknesses of the PZT films were obtained. Furthermore, the PZT films were chemically wet-etched. The crystal orientations of the fabricated films were examined by an X-ray diffractometer (XRD) before and after each procedure.

* Corresponding author. Tel.: +81-298-61-7140; fax: +81-298-61-7129.

E-mail address: ichiki@mel.go.jp (M. Ichiki).

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The residual stresses in the films were calculated from the changes in the radius of the wafer curvature after each procedure. The curvatures were obtained from the parabolic shapes of the films, which were measured by an auto-leveling surface profiler. The total residual stress σ in the film can be calculated from the difference in the radii of the curvature by using the Stoney formula:

$$\sigma_{\mathrm{f}} = \frac{E_{\mathrm{S}}}{6(1-\upsilon_{\mathrm{s}})}\frac{t_{\mathrm{s}}^2}{t_{\mathrm{f}}}\left(\frac{1}{r}-\frac{1}{r_0}\right) \quad (1)$$

where r_0 is the initial and r is the final radius of wafer curvature, t_f is the thickness of the coated film, and t_s, E_s and υ_s are the thickness, Young's modulus (130 GPa) and Poisson ratio (0.28) of the Si substrate, respectively. The stress is defined as tension (positive) if the substrate bends in a way decreasing the film length, and compression (negative) if the film tends to expand. No curvature measurement was carried out on the Si substrate before oxidation. The data presented are averages of four measurements per wafer.

3. Results and discussion

3.1. Stresses in as-deposited and annealed Pt bottom electrodes

The stress in a sputtered Pt film varies due to sputtering conditions such as deposition temperature.[4] In this experiment, the Pt bottom electrodes were sputtered at 200 °C and were subjected to compressive stresses (100–300 MPa) under the sputtering conditions and immediately after film deposition. The Pt bottom electrodes were annealed (until 600 °C) prior to the coating of PZT film to investigate the influence of annealing of subsequent PZT coating on the Pt bottom electrodes. The stresses in the Pt films changed to tension (about 1150 MPa) after the annealing. In general the total stress determined by curvature measurements is comprised of an intrinsic (or growth) stress and a thermal stress. The intrinsic stress arises from film contamination and the incomplete structural-ordering processes occurring during film growth. Thermal stress resulted from the thermal expansion mismatch between the Pt film and the Si substrate is given by

$$\sigma_{\mathrm{th}} = \frac{E_{\mathrm{f}}}{1-\nu_{\mathrm{f}}}\int_{T_{\mathrm{anneal}}}^{T_0}(\alpha_{\mathrm{f}}-\alpha_{\mathrm{s}})\mathrm{d}T \quad (2)$$

E_f (170 GPa) and υ_f (0.39) are the Young's modulus and Poisson ratio of the Pt film. α_f (9.0×10^{-6} deg^{-1}) and α_s (2.5×10^{-6} deg^{-1}) are the thermal-expansion coefficients of the Pt film and the Si substrate, respectively. Using Eq. (2) the thermal stress was calculated as about 1050 MPa. Hence, the thermal stress is predominant in the measured total residual stress in the Pt bottom electrode.

Fig. 1 shows the XRD patterns for as-deposited and annealed Pt film. Table 1 shows the *d*-spacing (*d*), intensity (*I*) and full width at half-maximum of the rocking curves of the diffraction lines (Δ*W*) of Pt(111) and Pt(200) planes. The *d*-spacing of both (111) and (200) textures decreased after the annealing of the Pt film. This indicates that the Pt film contracted the film perpendicular to the substrate and enhanced tensile stress in the film due to the annealing. Moreover, the peaks of (111) and (200) textures showed stronger intensity and smaller full width at half-maximum on the annealed Pt film. In other words, crystallization progressed due to the annealing of the Pt bottom electrodes. Also, the decrease in the $\Delta W_{(111)}$ and $\Delta W_{(200)}$ of the annealed Pt bottom electrode means an increase in the crystallite dimension. The increase in crystallite size, however, leads to a decrease in stress because of the crystallite boundary relaxation effect. Therefore, factors such as the predominant one of thermal stress, and lattice parameters and crystallite dimension are thought to contribute the changes in stress in annealed Pt film complicatedly.

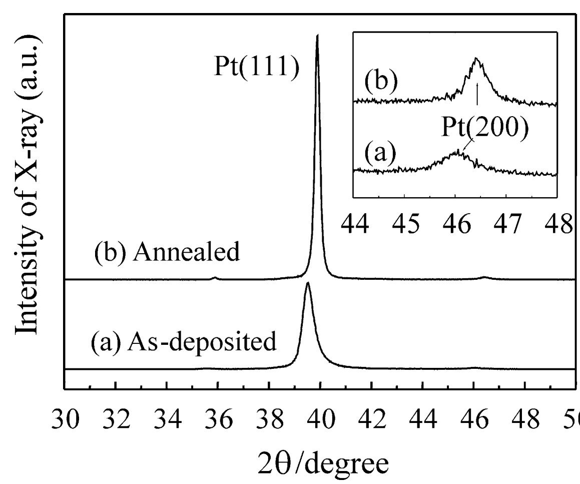

Fig. 1. XRD patterns for as-deposited and annealed Pt bottom electrodes.

Table 1
The *d*-spacing (*d*), intensity (*I*) and full width at half-maximum of the rocking curves of the diffraction lines (Δ*W*) of (111) and (200) planes of as-deposited and annealed Pt bottom electrodes

	As-deposited			Annealed		
	d (Å)	*I* (cps)	Δ*W* (°)	d (Å)	*I* (cps)	Δ*W* (°)
Pt(111)	2.2773	11 011	0.518	2.2576	42 289	0.247
Pt(200)	1.9690	225	0.502	1.9545	11 706	0.445

3.2. Stresses in the as-deposited and annealed Pt bottom electrodes after the coating of PZT films

Fig. 2 shows the changes of the stresses in the as-deposited and annealed Pt bottom electrodes and PZT film with the increase in the thickness of the PZT film. For the Pt bottom electrodes, the tensile stresses in both annealed and as-deposited electrodes increased with the increase in the thickness of PZT film. After the first coating of PZT, the stress in the annealed Pt bottom electrodes was smaller than the ones in the annealed Pt film without PZT coating as shown above. The Pt films were stretched during cooling process and the stress became smaller. This is because the thermal expansion coefficient of the PZT has large temperature dependence and is smaller compared with the Si substrate below the Curie temperature. However the stresses for the as-deposited Pt bottom electrodes were smaller compared with the annealed ones. Since the thermal coefficients of the multilayer has the relation of $\alpha_{Pt} > \alpha_{PZT} > \alpha_{Si}$ above the Curie temperature of PZT film, the shrinkage of the Pt bottom electrode was prevented by the PZT film and consequently Pt film showed a smaller stress compared with the annealed one.

For the PZT films, on the contrary, the stresses decreased with the increase in the thickness of PZT film. First coating of PZT film on the as-deposited Pt bottom electrode was under smaller tensile stress compared with the PZT film on the annealed one. Also, the PZT film showed only a slight decrease in the stress when the film thickness was more than 1 μm. In other words, the stress was hardly changed in a thick film.

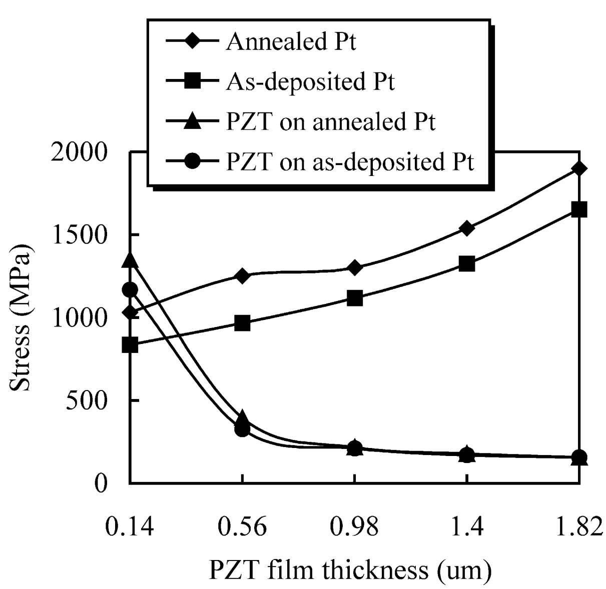

Fig. 2. Changes of the stresses in the as-deposited and annealed Pt bottom electrodes and PZT film with the increase in the thickness of the PZT film.

Fig. 3 shows the XRD patterns for PZT films (1.8 μm) coated on as-deposited and annealed Pt bottom electrodes. Since the annealed Pt film showed a stronger (200) texture as shown in Fig. 1, the peaks of (100) and (200) planes of the perovskite phase were stronger in the PZT film coated on the annealed bottom electrode compared with the ones coated on the as-deposited film. As reported by Spierings et al., annealing the Pt bottom electrode prior to the sol-gel deposition of PZT enhances the formation of a well-crystallized PZT.[5] Table 2 shows the full width at half-maximum of the rocking curves of the diffraction lines of perovskite phase (100), (110) and (111) of PZT film and (111) plane of Pt bottom electrodes. The values for the PZT film on the as-deposited Pt bottom electrode were smaller than that on the annealed Pt film, which means the grain size is larger and stress is smaller. Therefore, the intrinsic stress in the PZT film on the as-deposited Pt bottom electrode should be smaller than that on the annealed Pt film. However, the stresses in the PZT films measured from the wafer curvatures were almost the same as shown above because of the large thickness. Moreover, the ΔW value for as-deposited Pt(111) was also smaller. This means that the PZT coating on the as-deposited Pt electrode leads to a larger grain size in Pt film and consequently results in a smaller stress.

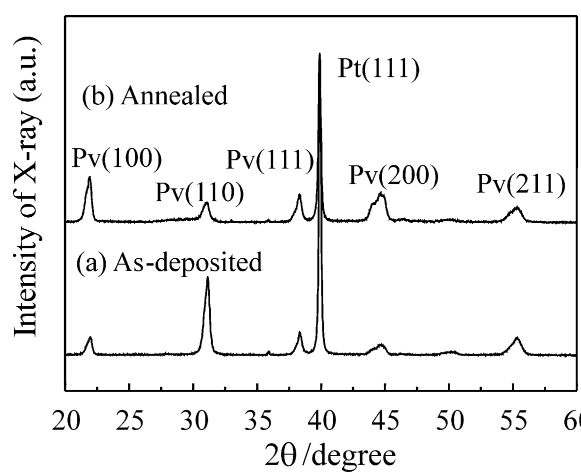

Fig. 3. XRD patterns for PZT films coated on as-deposited and annealed Pt bottom electrodes. Pv: perovskite phase of PZT film.

Table 2
The full width at half-maximum of the rocking curves of the diffraction lines of perovskite phase Pv (100), (110) and (111) of PZT film coated on as-deposited and annealed Pt bottom electrodes and (111) plane of Pt bottom electrodes

	As-deposited Pt	Annealed Pt
Pv(100)	0.415	0.450
Pv(110)	0.427	0.590
Pv(111)	0.382	0.426
Pt(111)	0.207	0.236

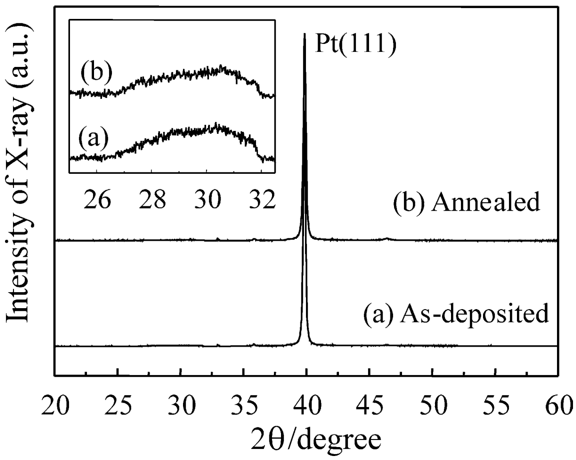

Fig. 4. XRD patterns for as-deposited and annealed Pt bottom electrodes after the etching of PZT films.

3.3. Stresses in the as-deposited and annealed Pt bottom electrodes after the etching of PZT films

The PZT films were wet-etched and the curvatures were measured to investigate the influence of the subsequent coating of PZT film on the bottom electrodes. The stresses in the as-deposited and annealed Pt films after the etching of PZT films were approximately 630 MPa and 860 MPa, respectively. Therefore, the stress in Pt bottom electrode was changed due to the subsequent PZT coating. The crystal orientations for as-deposited and annealed Pt bottom electrodes after the etching of PZT films were examined by XRD. As shown in Fig. 4, peaks from 26° to 32° of 2θ appeared, which did not exist in as-deposited and annealed Pt film before the PZT coating. Kim et al. reported that Ti diffused out along the Pt grain boundaries to form titanium oxide on the Pt surface as well as Pt–Ti alloy in the grain boundary region,[6] which were in the range of 2θ shown above. The diffusion of Ti likely contributes to the changes in the stresses in the Pt bottom electrodes due to the coating of the PZT film. Also, the full width at half-maximum of the rocking curves of the (111) diffraction line ($\Delta W_{(111)}$) of the as-deposited Pt bottom electrodes showed a smaller value and consequently resulted in a smaller tensile stress. Spierings et al. found that the stress in the Pt bottom electrode is hardly influenced by the subsequent deposition and annealing process.[5] In our results, however, the stress in Pt bottom electrode was changed by the subsequent PZT coating.

4. Conclusions

The residual stresses in the SiO_2/Ti/Pt/PZT multilayer structure were investigated by measuring the changes in the radius of the wafer curvatures. To study the influence of annealing on the Pt bottom electrodes, as-deposited and annealed Pt films were used.

The Pt bottom electrodes were under compression under the sputtering condition but changed to tension after the annealing of PZT film. The predominant factor of thermal stress and other contributions such as lattice parameters and crystallite dimension are thought to result in the change in stress after the annealing of Pt film.

After the subsequent coating of the PZT films, the tensile stresses in Pt bottom electrodes increased with the increase in the thickness of PZT film. Also, the PZT coating on the as-deposited Pt electrode leaded to a larger grain size in Pt film and consequently resulted in a smaller stress compared with the annealed ones.

After the etching of PZT film, the stresses in the Pt bottom electrode decreased. The diffusion of Ti likely contributes to the changes in the stresses in the Pt bottom electrodes due to the coating of the PZT film. A larger grain size and consequently smaller stress were found in the as-deposited Pt film also.

In conclusion, the stresses in Pt bottom electrodes were changed due to the subsequent PZT coating. Thermal stress and other factors like lattice parameters, crystallite dimension and diffusion, are thought to contribute the change in the stresses. Annealing of Pt bottom electrode prior to the sol-gel deposition of PZT film enhanced the formation of a well-crystallized PZT film and also increased the stress in Pt bottom electrode.

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