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The Effect of Deposition Temperature of $Pb(Zr,Ti)O_3$ (PZT) Thin Films with Thicknesses of around 100 nm on the Piezoelectric Response for Nano Storage Applications

Han Wook Song

Center for Mass and Related Quantities, Division of Physical Metrology, Korea Research Institute of Standards and Science, Daejeon, South Korea.
Email: hanugi16@kriss.re.kr

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ABSTRACT

We investigated the effect of the deposition temperature of PZT thin films with thicknesses of around 100 nm on the piezoelectric response using an atomic force microscope (AFM). The preferred orientation of the PZT thin film was changed from (001) to (110) as the deposition temperature increased. The surface roughness of PZT thin films decreased with the increase of deposition temperature. The maximum amplitude of the piezoelectric response of PZT thin films decreased till the deposition temperature increased to 350˚C. This tendency seems to be due to the change of the preferred orientation form (001) to (110). At over 450˚C, this maximum value decreased due to both the increase of the surface roughness and the degradation of the crystallinity.

Keywords: PZT; AFM; Deposition Temperature; Orientation; Piezoelectric Response

1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) is one of most promising ferroelectric materials for various devices because of their attractive properties (high dielectric constant, high remnant polarization, excellent piezoelectric properties, and so on). For better properties, a plethora of deposition techniques have been successfully used to synthesize PZT thin films, including sol-gel [1], metal-organic decomposition (MOD) processes [2], ion-beam sputtering [3], electron cyclotron resonance (ECR) plasma deposition [4], and radio frequency (rf) magnetron sputtering method [5].

It is well known that properties of PZT thin films depend on many parameters including composition, texture, substrate, film thickness, and microstructure. Piezoelectric properties are known to be mainly affected by the preferred orientation of film, and the preferred orientation of film is affected by the deposition temperature. In addition, along with the domain imaging technique [6,7], it was reported that if one manipulate domain structure by giving dc pulses through the nanometer-scale tip, a domain of less than 100 nm size could be artificially formed in two opposite directions. This domain could be labeled either "0" or "1" depending on its polarization direction, thereby acting as a bit in a memory device. This ability of manipulation of domains smaller than 100 nm showed its potential as a data-storage technique with a density of tens of Gbits/cm^2. Therefore, it is important to decrease the critical thickness over which the PZT showed piezoelectric properties to decrease the bit size and to investigate the reasons why the PZT did not show the piezoelectric properties below the critical thickness.

In this study, we investigated the relationship between the deposition temperature and the preferred orientation of PZT thin films with thicknesses of around 100 nm with the composition of 0.52 and 0.48 for Zr and Ti content at which PZT was known to show the maximum piezoelectric properties. The effects of the deposition temperature on the piezoelectric response were also presented and discussed. PZT thin films were grown on $Pt/TiO_2/SiO_2/Si$ substrate using rf magnetron sputtering. The piezoelectric response was measured using AFM.

2. Experimental Details

The PZT films were deposited on the $Pt/TiO_x/SiO_2/Si$ (100) substrates using rf magnetron sputtering. A hot-pressed sintered $Pb_{1.3}(Zr_{0.52}Ti_{0.48})O_3$ target of 99.9% purity was used. The experimental conditions are summarized in **Table 1**. The PZT thin films were deposited from 250˚C to 500˚C for 40 min at 25˚C intervals. The annealing was conducted in an O_2 atmosphere at 650˚C for 10 min using a furnace. The thickness of the samples was about 100 nm. The crystallinity and the orientation of the deposited films were analyzed using x-ray diffraction method (XRD) with Cu Kαradiation and the microstructure was observed using scanning electron microscope (SEM). The composition of as-deposited films was analyzed using wave dispersive x-ray spectroscopy (WDS). The surface roughness and piezoelectric response were measured using an atomic force microscope (AFM) (PSIA, Autoprobe M5). For the measurement of the piezoelectric response, DC voltage was applied to the tip, and the bottom electrode was grounded. The voltage sequence is shown in **Figure 1**. The applied AC voltage was 1 $V_{p\text{-}p}$ (peak to peak), and the modulation frequency was 17 kHz. The piezoelectric property was evaluated by the measurement of the phase difference between the amplitude of the tip vibration and the applied AC voltage.

3. Results and Discussion

Figures 2(a) and **(b)** show the XRD patterns of PZT thin films deposited at various temperatures but annealed at 650˚C, and **Figure 3** shows the relative intensity ratio between the PZT (001) peak (indicated as ▼ in **Figure 2** and the (110) peak (indicated as ● in **Figure 2**). In **Figure 3**, the relative intensity ratio (α) was defined in Equation (1):

$$\alpha = \frac{\dfrac{I_{(001)}}{I_{\text{sub}}}}{\dfrac{I_{(001)}}{I_{\text{sub}}} + \dfrac{I_{(110)}}{I_{\text{sub}}}} \quad (1)$$

Table 1. Experimental conditions for the deposition of PZT thin films.

Substrate	Pt(200 Å)/TiO(600 Å)/ SiO(600 Å)/Si
Target	$Pb_{1.3}(Zr_{0.52}Ti_{0.48})O_3$
Deposition temperature (˚C)	250 - 500
Atmosphere	Ar
Working pressure (Torr)	1×10^{-3}
Rf power (W)	50
Deposition time (min)	40

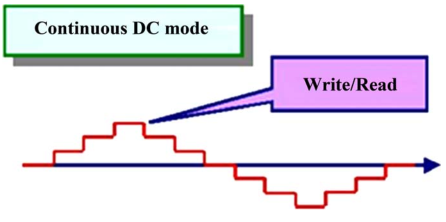
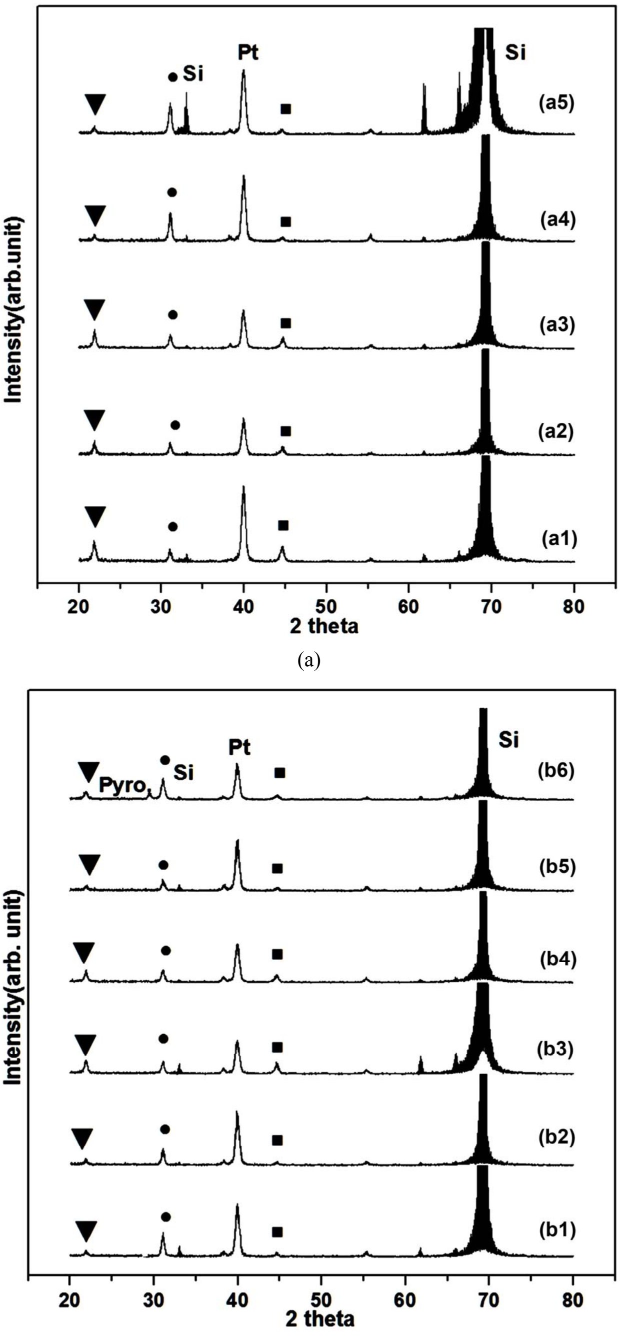


Figure 1. Sequence of applied voltage.

where Isub is the XRD intensity of the substrate, $I_{(001)}$ is the XRD intensity of the (001) peak at various deposition temperatures in **Figure 2**, and $I_{(110)}$) is the XRD intensity of the (110) peak and at various deposition temperatures in **Figure 2**.



(a)

(b)

Figure 2. (a) XRD patterns of PZT thin films deposited at (a1) 250˚C, (a2) 275˚C, (a3) 300˚C, (a4) 325˚C, and (a5) 350˚C, but annealed at 670˚C for 10 min. (▼: PZT (001); ●: PZT (110); ■: PZT (002)); (b) At (b1) 375˚C, (b2) 400˚C, (b3) 425˚C, (b4) 450˚C, (b5) 475˚C, and (b6) 500˚C.

The samples deposited to 300˚C show (001) preferred orientation because the intensity ratio values are high (1.66, 1.16, and 1.15, respectively) compared to the value of a randomly oriented PZT powder sample (0.08 [8]). This intensity ratio decreases from 250˚C to 325˚C and increases again as the deposition temperature increases. We speculate that there might be two possibilities for this tendency. One is due to the microstructure of the as-deposited PZT thin film, and the other is due to the amount of Pb in the as-deposited film. **Figures 4(a)** and **(b)** show the XRD patterns of PZT thin films deposited at various temperature (not heat-treated), and **Figure 5** shows the variation of the relative intensity of the (222) rochlore peak to the Si substrate with the deposition temperature. The formation energy of PZT (001) nucleation is lower than that of PZT (110) nucleation, and it is known that the nucleation of the perovskite phase in the pyrochlore matrix is easier than that from the amorphous matrix [9]. Relating **Figure 5** to **Figure 3**, we speculate that the de-

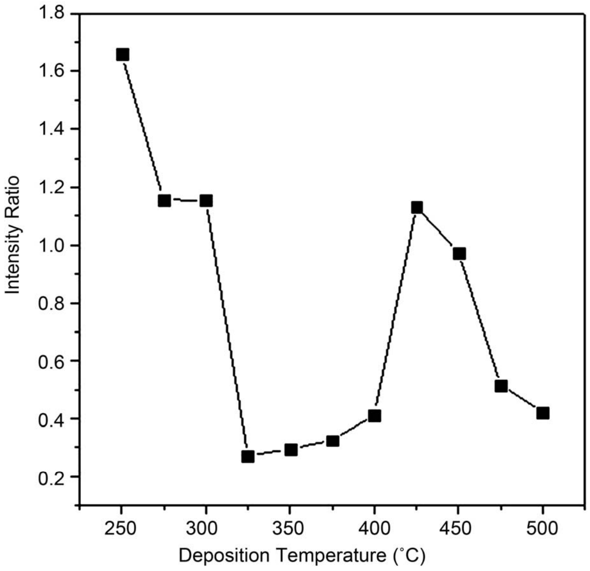
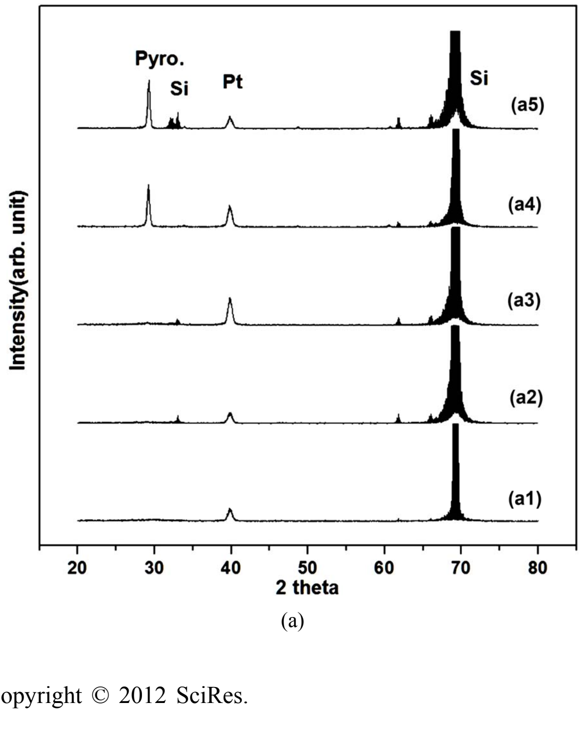
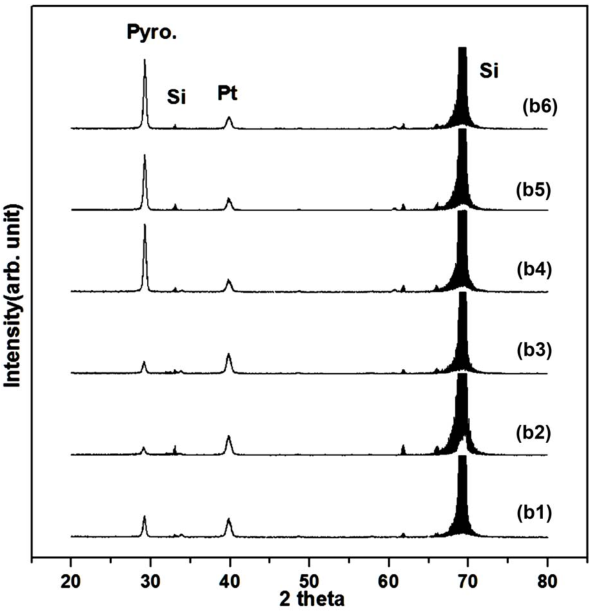


Figure 3. Variation of intensity ratio between PZT (001) and PZT (110) with deposition temperature.



(a)



(b)

Figure 4. (a) XRD patterns of PZT thin films deposited (a) at (a1) 250˚C, (a2) 275˚C, (a3) 300˚C, (a4) 325˚C, and (a5) 350˚C; (b) at (b1) 375˚C, (b2) 400˚C, (b3) 425˚C, (b4) 450˚C, (b5) 475˚C, and (b6) 500˚C.

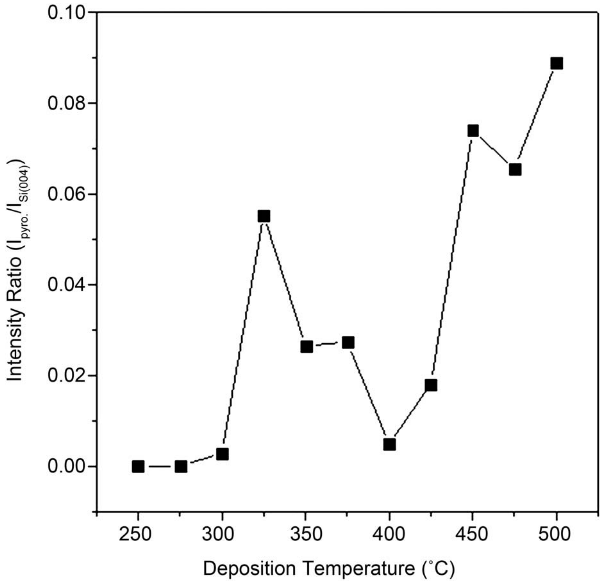


Figure 5. Variation of intensity ratio between pyrochlore and Si (004) with deposition temperature.

velopment of PZT (001) might be depend on the amount of pyrochlore phase, which was that the PZT nucleation with random orientation was much easier from the phyrochlore matrix than from the amorphous matrix. **Figure 6** endorses this assumption. As shown in **Figure 6**, the PZT thin film deposited at 325˚C completely consists of phychlore phase while the PZT thin film at 250˚C shows the amorphous phase. Therefore, the PZT film deposited at 250˚C showed (001) preferred orientation, while the PZT film deposited 325˚C showed the random orientation.

On the other hand, the amount of Pb with the various deposition temperatures affected the film orientation (**Figure 7**). Relating **Figure 7** to **Figure 3**, (001) preferred PZT thin films were grown sufficient Pb existed [10]. Yang *et al.* reported that excess Pb promoted the growth of (001) oriented PZT thin film with the formation of PbO (100) at the interface of the Pt bottom electrode when the relative amount of Pb in a PZT thin film exceeded one [11].

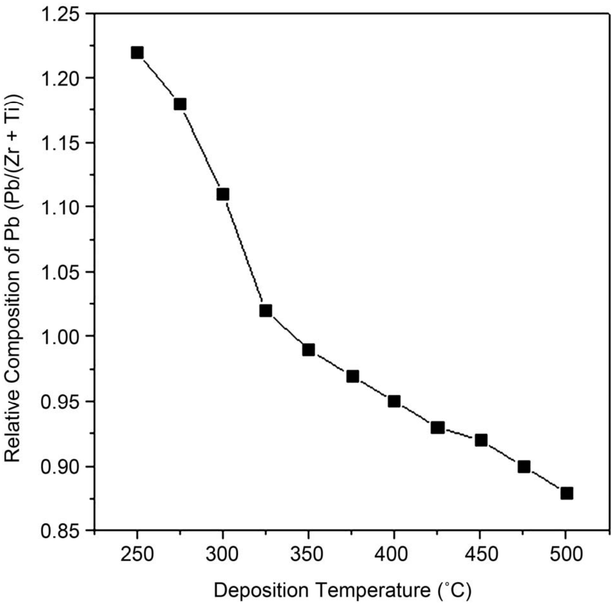
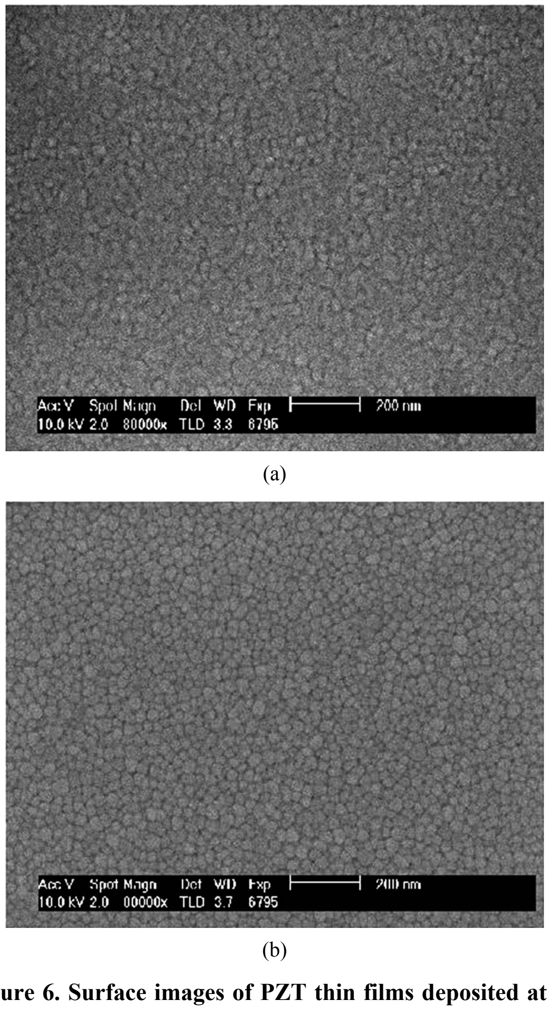


Figure 7. The amount of Pb with the various temperatures.



(a)

(b)

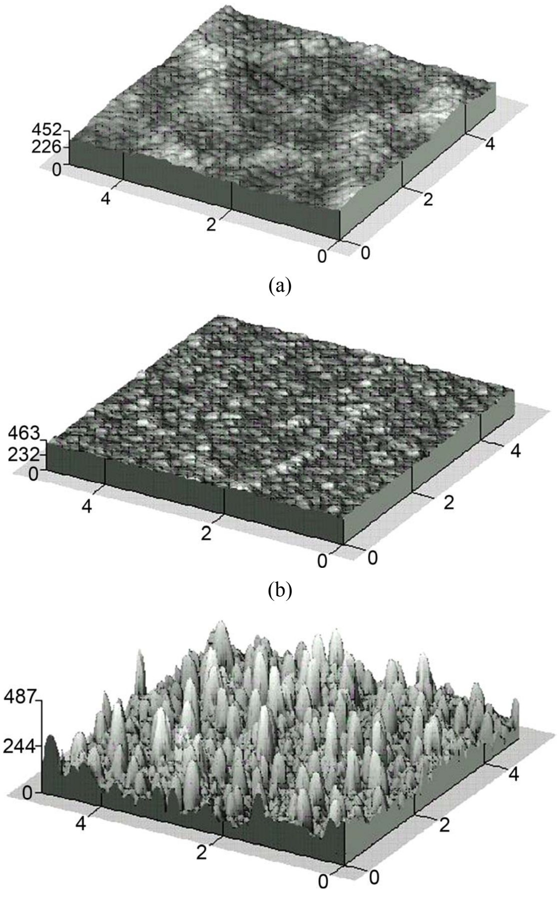
Figure 6. Surface images of PZT thin films deposited at (a) 250˚C and (b) 350˚C.

Between 350˚C and 450˚C, the films also show the (001) preferred orientation even though there is not sufficient Pb. We speculate that this phenomena is due to the fact that the attached molecular had sufficient energy to move to form the (001), which had the lowest surface energy in PZT. Over 450˚C, the films has (110) preferred orientation, and this phenomena seems to be due to the increase of surface roughness [12], which will be discussed later in this article.

We measured the surface topology of PZT thin films deposited at various temperatures but annealed at the same temperature (**Figure 8**). The surface roughness of PZT thin films decreased until the deposition temperature increased to 400˚C. **Figure 9** shows this relationship.

We speculate that this decrease was due to the increase of the mobility of the atoms with the increase in the deposition temperature. The attached atom gained increased mobility with the increase in the deposition temperature; therefore, the atoms could move to the open space between particles and these movements decreased the surface roughness. At over 400˚C, the surface roughness increased. We speculate that this increase was due to both the Ti diffusion to the PZT surface during PZT deposition and the evaporation of Pb.

Figure 10 shows the amplitude and phase of the tip vibration signal from PZT thin films deposited at 250˚C, 350˚C, 450˚C, and 500˚C, but annealed at the same temperature, and **Figure 11** shows the variation of the maximum value of the amplitude and the coercive field with the deposition temperature. As shown in **Figure 9**, the maximum value of the amplitude decreased until the deposition temperature increased to 350˚C. Over 350˚C, this value increased. With regards to **Figure 3**, we inves-



(a)

(b)

(c)

Figure 8. Topological image of PZT thin films deposited at (a) 250˚C, (b) 350˚C, and (c) 450˚C, but annealed at 670˚C for 10 min.

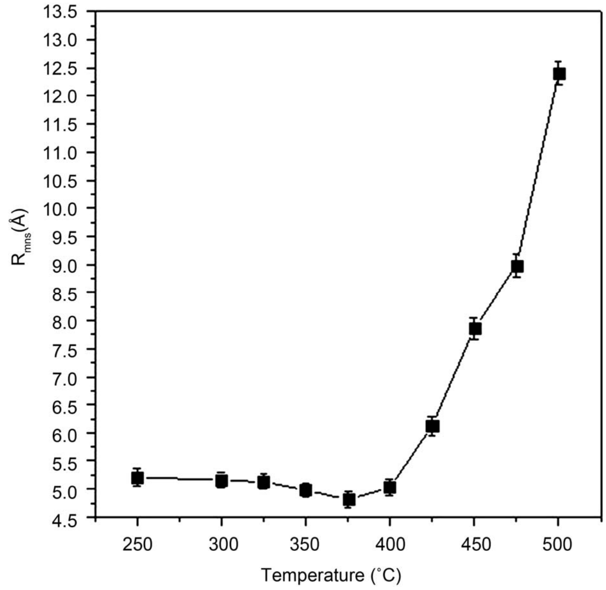
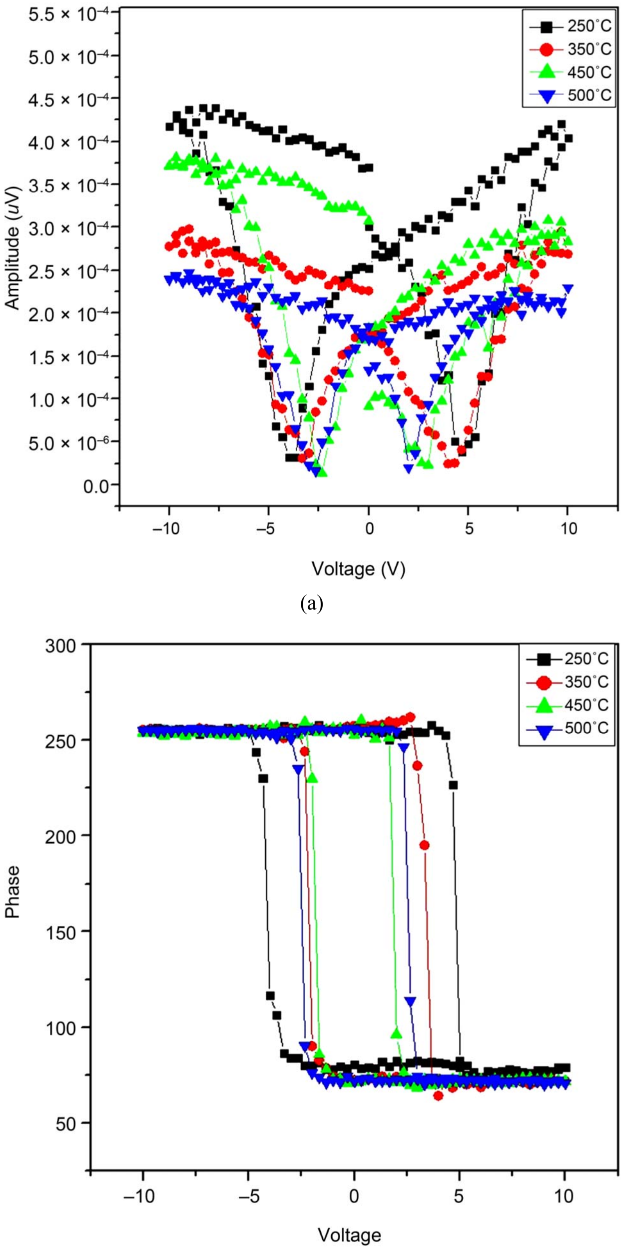


Figure 9. Surface roughness variation of PZT thin films with deposition temperature.



(a)

(b)

Figure 10. The (a) amplitude and (b) phase of the tip vibration signal as a function of the DC bias voltage applied to the tip.

tigated whether this decrease might be due to both the change of film orientation, because it was reported that the largest piezoelectric coefficient lies along the (100) crystallographic direction [13], and the decrease of damping at the grain boundary with the increase of the grain size. At over 450˚C, this value decreased again. It seems that this decrease might be due to both the increase of the surface roughness and the degradation of crystallinity. On the other hand the coercive field de-

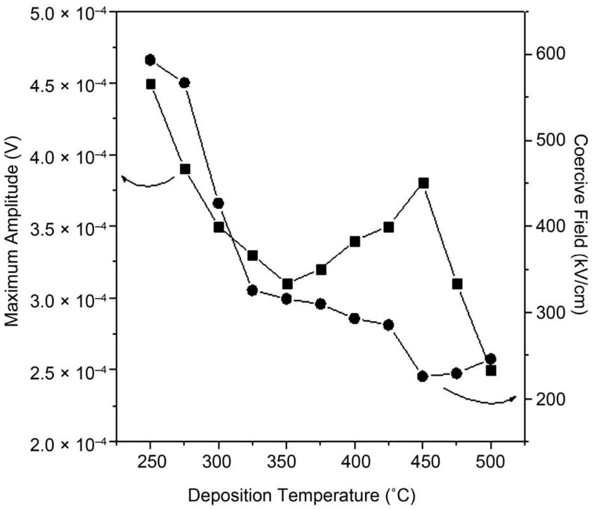


Figure 11. Variation of the maximum amplitude value and coercive field with the deposition temperature.

creased till the deposition temperature increased to 450°C. We speculated that this decrease of the coercive field was due to the increase of grain size with deposition temperature. At over 450°C, the coercive field increased slightly. Relating to **Figure 2(b)**, this increase seems to be due to the degradation of crystallinity.

4. Conclusions

The preferred orientation of PZT thin films depends on the as-deposited status. (001) preferred PZT thin films were grown from the amorphous phase, and (110) preferred PZT thin films from the pyrochlore phase. The surface roughness decreased with the increase of the deposition temperature. At over 400°C, the surface roughness increased because of the diffusion of Ti to the PZT surface during film deposition.

The deposition temperature affected the piezoelectric response of PZT thin films by changing both the film orientation and the surface roughness.

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