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Dependence of Crystalline, Ferroelectric and Fracture Toughness on Annealing in Pb($Zr_{0.52}Ti_{0.48}$)O_3 Thin Films Deposited by Metal Organic Decomposition

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Crystalline, electric and fracture properties of Pb($Zr_{0.52}Ti_{0.48}$)O_3 (PZT) thin films are strongly affected by annealing temperatures in rapid treatment annealing (RTA) of metal organic decomposition (MOD). X-ray diffraction (XRD), RT66A standard ferroelectric analyzer and Vickers indentation method were used to investigate the crystalline, ferroelectric and mechanical properties, respectively. PZT thin film with complete perovskite structure and best ferroelectric property can be obtained at 750 °C, however the fracture toughness was weaker than the thin films annealed at 600 °C and 650 °C. With the increase of annealing temperature from 600 °C to 750 °C, the remanent polarization and coercive field increased in the ranges 13.8~25.2 ($\mu C/cm^2$) and 7.2~8.3 (kV/cm) respectively, while the fracture toughness of PZT thin films decreased from 0.49 $MPam^{1/2}$ to 0.47 $MPam^{1/2}$.

Keywords: *PZT thin film, Annealing procedure, X-ray diffraction, ferroelectric property, Fracture toughness*

1. Introduction

Ferroelectrics thin films are today widely used in many fields, such as nonvolatile memories, thermal or ultrasonic image sensors, and surface acoustic wave filters, since they are better distinct properties than those of bulk materials[1]. Many methods such as pulsed laser ablation (PLD), rf sputtering, chemical vapor deposition (CVD), metal organic decomposition (MOD), sol-gel process and multiple electrophoretic deposition are used to prepare ferroelectric thin films[2-7]. MOD is one of the considerable deposition methods, since it is a non-gelling chemical process in which molecular homogeneity is attained in the liquid phase, and the solutions can be produced without solution gelling and at a lower processing temperature[5]. Few reports have shown that the microstructural charactheristics and electrical properties of PZT thin films depend greatly on the annealing temperature[8] and film thickness[9-11], however little has been done in regard to the dependence of ferroelectric properties and fracture toughness on annealing procedure. It is known that ferroelectric and mechanical properties of thin film including remanent polarization, coercive field, fracture toughness, residual stress and hardness are very important parameters, which will be used to the design of the film/substrate system. In addition, the origin of the changes in crystalline, ferroelectric and mechanical properties with annealing procedures have not been clearly understood. It is obvious that research effort in this aspect should be directed to crystalline microstructure, ferroelectric property and fracture toughness.

In this paper, the dependence of crystalline microstructure, ferroelectric property and fracture toughness on annealing temperature for PZT thin films grown on the multilayer composite substrate Pt/Ti/SiO_2/Si (001) by MOD technique were investigated. For achieving perovskite structure, PZT thin films deposited by RTA at different temperatures were analyzed by X-ray diffraction. The variation of remanent polarization and coercive field with annealing temperature was analyzed in P-V hysteresis loops obtained by RT66A standard ferroelectric analyzer. The crack patterns of PZT thin films in indentation in relation to annealing

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temperature and the indentation load were examined and the fracture toughness of PZT thin film was measured by the indentation model proposed by Lawn *et al.*[12-13]. The fracture pattern diagram is described as a function of the indentation load and the annealing temperature. It is expected that the present research may offer useful guidelines to the design of film/substrate systems.

2. Experimental Procedure

2.1. Samples preparation

In the preparation of metal organic decomposition, the precursor compounds used for $Pb(Zr_{0.52}Ti_{0.48})O_3$ were $Zr(OCH_2CH_2CH_3)_4$, $Ti(OCH_2CH_2CH_3)_4$ and $Pb(CH_3COO)_2{\cdot}3H_2O$, all in CH_3COOH,$CH_3CH_2CH_2OH$ solution. The ratio Zr/Ti = 52/48 was propitious to form ferroelectric phase, because it was locate in the morphotropic phase boundary. The spin coating speed was 3000 rpm, and the wet films were roasted for 3 to 5 min on a hot desk at 260 °C every time. In this case, the dissolvent with a low boiling point could be volatilized and thus dry films could be obtained. Ti transition-layer, Pt bottom electrode and PZT thin film were prefabricated on the Si(001) substrate in sequence, and the aptitude thickness of PZT thin film 2.5 µm was controlled by the spin coating time to obtain good perovskite crystalline. The different temperatures in furnace for the annealing duration of 3 min were respectively taken as 600, 650, 750 and 850 °C. A set of Pt electrode dots was made on the surface of PZT thin films using the shadow mask method to measure hysteresis loops.

2.2. Measurement of properties

A D500 X-ray diffractometer with the Cu-Ka radiation was used to analyze the crystalline phases in the PZT thin films. The virtual ground mode of RT66A standard ferroelectric analyzer made in Radiant Technologies Corporation of America was used to measure the ferroelectric property. Hysteresis loops were directly obtained by RT66A manual procedure in which five pulses were used and each alternation was 1 s. The indentation test was carried out using MIERO-DURC MET 4000 ultramicroscopic sclerometer attached to a POLYVAR-MET4000 metallographic microscope. Indentations were made on PZT ferroelectric thin films using a Vickers diamond pyramid. In the experiment, the indentation load varied from 60 to 180 g and the increment of load was 20 g per step. The duration for every indentation load was 10 s and the experiment was conducted at ambient conditions. Within 10 s after indentation, the contact surfaces were observed by a POLYVAR-MET4000 metallographic microscope.

2.3. Indentation method

In order to describe qualitatively the effect of annealing temperature on fracture toughness of PZT thin film itself, the indentation method was used to evaluate fracture toughness of PZT thin film. Using the equation given by Lawn *et al.*[12] for the fracture toughness of brittle materials, the fracture toughness of the ceramic thin film/coating investigated in the present study may be given as follows:

$$K_{IC,f} = 0.13 \cdot \left(\frac{E_f}{H_f}\right)^{\frac{1}{2}} \cdot W \cdot C_r^{-\frac{3}{2}} \tag{1}$$

where E_f is the elastic modulus of the thin film, H_f hardness of the thin film, W the normal load and C_r the radial crack length on the surface of thin film. Generally, electric charges are produced during the indentation of ferroelectric thin film and consequently the fracture toughness of PZT thin film is affected. In the investigation, piezoelectric effect is negligible and Eq. 1 is assumed to be valid for PZT thin film. Substituting the experimental values for the indentation load W and the radial crack length C_r and the material properties such as the hardness 6 GPa[14] and elastic modulus 85 GPa[15] into Eq. (1), the fracture toughness of PZT thin film prepared by different annealing temperatures is determined.

3. Experimental results and discussions

3.1. Annealing effect on crystalline and ferroelectric property

The XRD patterns of PZT thin film deposited on $Pt/Ti/SiO_2/Si(001)$ substrates at the different annealing temperature are given in Fig.1. It is evident that a lot of complete perovskite crystals are formed in PZT thin film within the annealing temperature range of 600 to 750 °C. The higher annealing temperature is, the better the crystalline quality. However, when the annealing temperature is as high as 850 °C, pyrochlore phase arises.

P-V hysteresis loops of PZT thin films annealed at the different temperature are shown in Fig. 2. According to the P-V hysteresis loops, the remanent polarizations and coercive fields can be calculated, and the variations of the remnant polarization P_r and coercive field E_c with annealing temperature are described as Fig. 3 and Fig. 4, respectively. It is seen that the remanent polarization and coercive field increase in the ranges 13.8~25.2 µC/cm^2 and 7.2~8.5 kV/cm, respectively, with the increase of annealing temperature from 600 °C to 750 °C. However, the remanent polarization and coercive field decrease respectively to 16.6 µC/cm^2 and 8.1 kV/cm, when annealing temperature is as high as 850 °C.

3.2. Annealing effect on fracture pattern and toughness

Figure 5 shows a typical effect of the annealing temperature on fracture pattern after indentation with Vickers

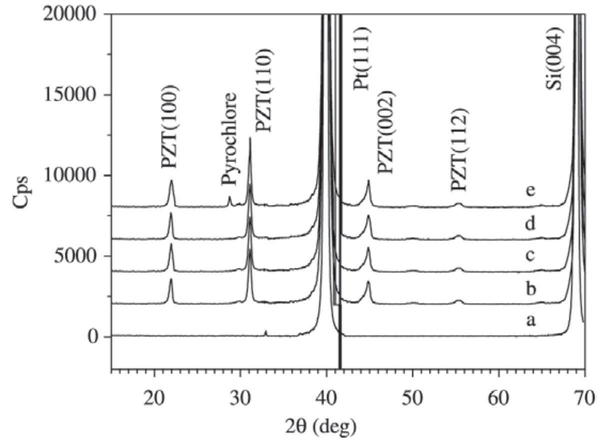


Figure 1. The XRD patterns of PZT/Pt/Ti/SiO$_2$/Si(001) thin films annealed at different temperatures: a) *in situ* plating; b) 600 °C ; c) 650 °C; d) 750 °C; e) 850 °C.

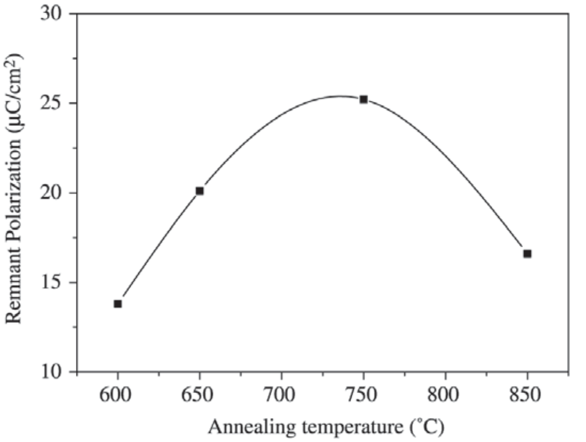


Figure 3. Remnant polarization as a function of the PZT thin film annealing temperature.

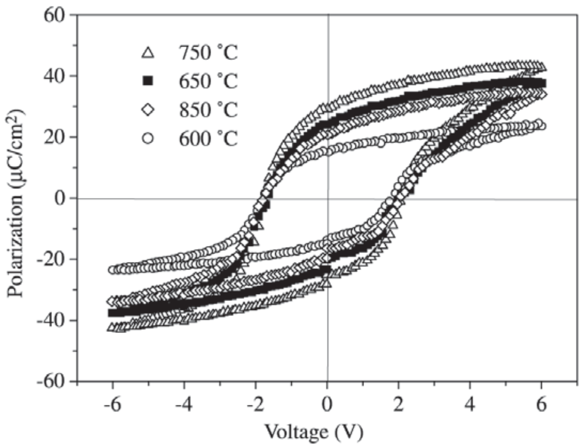


Figure 2. P-V hysteresis loops of the PZT thin films annealed at different temperatures.

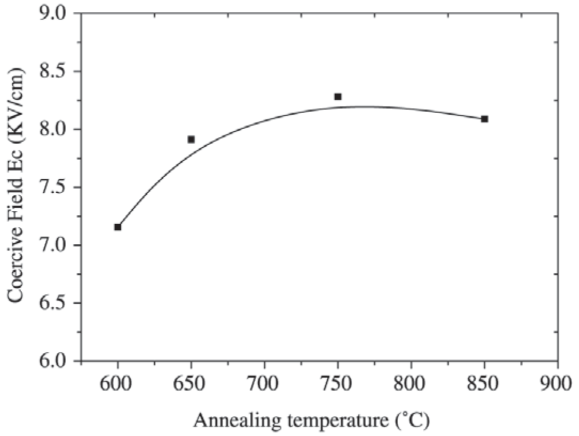
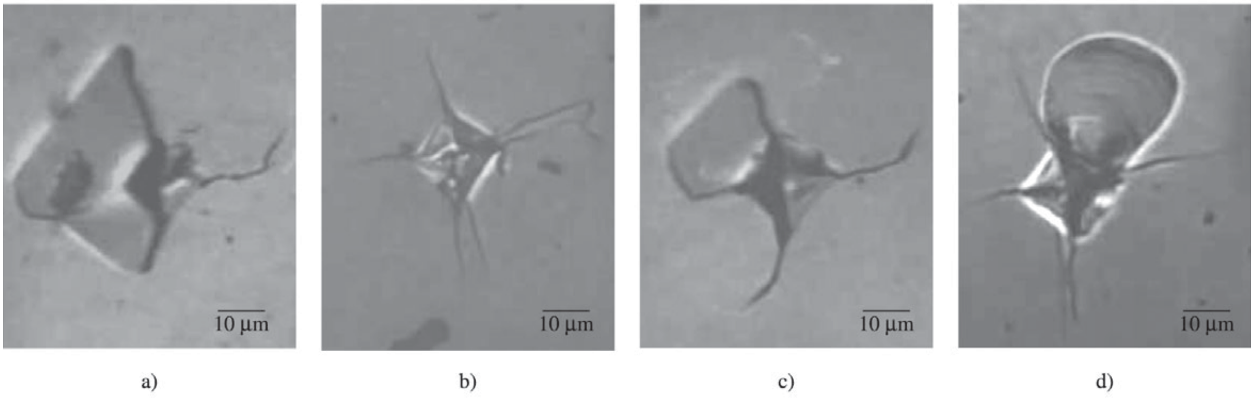


Figure 4. Coercive field as a function of the PZT thin film annealing temperature.

diamond indenter at a load of 180 g. At 600 °C annealing temperature, a part of PZT thin film outside the contact area is spalled due to the extensive propagation of lateral cracks (see Fig. 5a). When annealing at 650 °C, only radial cracks were observed (see Fig. 5b). Radial cracks and some bulging are observed at annealing 750 °C (see Fig. 5c). Figure 5d displays the interfacial delamination of PZT thin films annealed at 850 °C. The mean crack in each indentation picture was measured 5 to 6 times and the average value was adopted to minimize the error. The radial crack length and indentation load are listed in Table 1. It is found that there are two fracture patterns as follow: one only with radial cracks and another with both, radial and lateral cracks. It is obvious that only the experimental data of the former condition can be used to evaluate the fracture toughness of thin film itself by the formula given as Eq. 1. In the latter condition, fracture phenomena of the thin film such as bulging, spallation and delamination can be observed. Generally, the bulging should be due to a lateral crack meanwhile the spallation or delamination is the result of interface crack propagation. All experimental observations of the crack patterns are summarized as a fracture pattern diagram in Fig. 6 in relation to indentation load and annealing temperature. In the figure, the critical indentation load for generation of lateral cracks and partial spalling is strongly affected by the annealing temperature, and there are two regions partitioned by the curve of critical indentation load. The upper region denotes that there are only radial cracks and no lateral crack



a) b) c) d)

Figure 5. Fracture patterns at a normal load of 180 g for the annealing temperature: a) 600 °C; b) 650 °C; c) 750 °C; d) 850 °C.

Table 1. Radial crack lengths (μm) in Vickers indentation test.

Annealing temperature	Indentation loads						
	60g	80g	100g	120g	140g	160g	180g
600 °C	$15.18^{\oplus}$	$18.33^{\oplus}$	21.34^{Δ}	$24.15^{\oplus}$	$26.82^{\oplus}$	29.36^{Δ}	31.80^{Δ}
650 °C	$15.32^{\oplus}$	$18.64^{\oplus}$	21.67^{Δ}	24.50^{Δ}	27.19^{Δ}	29.75^{Δ}	32.20^{Δ}
750 °C	$15.45^{\oplus}$	$18.78^{\oplus}$	21.83^{Δ}	24.67^{Δ}	27.37^{Δ}	29.94^{Δ}	32.40^{Δ}
850 °C	$15.33^{\oplus}$	18.81^{Δ}	22.23^{Δ}	24.95^{Δ}	27.81^{Δ}	31.33^{Δ}	32.88^{Δ}

Note: The superscript "⊕"denotes that there were only radial cracks, while the superscript "Δ" denotes that both radial cracks and lateral cracks were observed and as well as the phenomenon of bulging or spallations.

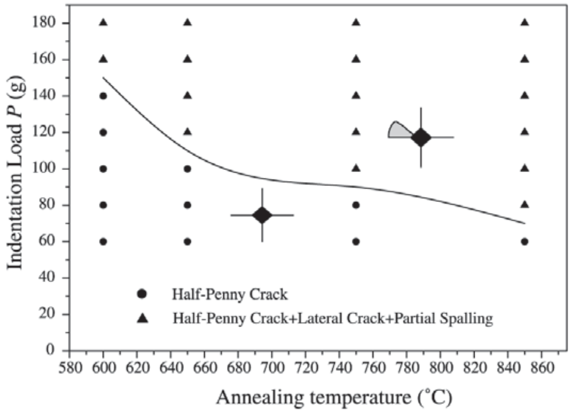


Figure 6. Fracture pattern diagram of PZT thin film as a function of indentation load and annealing temperature.

or interfacial crack. The above region indicates that there are both of radial and lateral cracks and the bulging and the partial spalling is the result of interface crack propagation.

In Table 1, only the radial crack lengths with the superscript "⊕" are available to assess the fracture toughness of PZT thin films. Substituting them into Eq. 1, the fracture toughness of PZT thin film at different annealing temperature is obtained and the results are shown in Fig.7, where the average values of the fracture toughness are adopted for each annealing temperature. It is obvious that the fracture toughness decreases from 0.49 to 0.47 $\mathrm{MPam}^{1/2}$ with the increase of annealing temperature from 600 to 850 °C.

3.3. Relationships between crystalline, ferroelectric and fracture properties

In the investigation, the higher annealing temperature within the range of 600 to 750 °C is, the stronger the perovskite phase peaks. It is inevitable to result in the high remanent polarization and coercive field. It is primarily considered that the contact between thin film and substrate is not perfect due to the roughness of thin film surface in the preparation. The higher annealing temperature is, the smoother the surface of PZT thin film. At the same time, the remnant polarization and coercive field increase with the annealing temperature because PZT thin films can grow rapidly at high temperature by diffusing mechanism, increasing the perovskite phase portion. As stated in the aforementioned analysis, ferroelectric properties are degraded at high annealing temperatures, such as 850 °C and higher, because

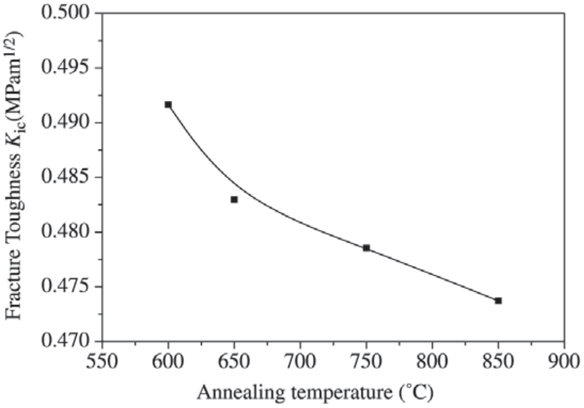


Figure 7. Fracture toughness as a function of the PZT thin film annealing temperature.

perovskite phase in PZT thin films decrease due to the loss of PbO and the emergence of a pyrochlore phase.

The annealing temperature will change the residual compressive stresses and different oriented domains in PZT ferroelectric thin films, both of the variations effect on the fracture toughness of PZT thin film. Using multi-domains model[16], with the increase of grain size the residual compressive stresses among different oriented domains partly eliminate each other and the deviation degree of ferroelectric cubic lattice will be restrained diminishingly[17]. Generally, the higher the annealing temperature is, the larger the crystal grain is[8]. This indicates that the compressive stress in PZT thin film annealed at high annealing temperature is weaker than that for low annealing temperature. The variation of residual stress in PZT thin films against annealing temperature has been investigated and the increase of annealing temperature results in the residual compressive stresses decrease[18]. The lower residual compressive stresses for high annealing temperature will lead to the closure effect, and consequently, the fracture toughness of ferroelectric thin film decreases with the increase of the annealing temperature.

4. Conclusions

The annealing effects on the crystalline microstructure, remanent polarization, coercive field and fracture toughness are respectively investigated by X-ray diffraction scan profiles, RT66A standard ferroelectrics analyzer and Vickers indentation method, respectively. The conclusions can be summarized as followed: (1) Using a multilayer composite substrate Pt/Ti/SiO_2/Si(001), 2.5 μm PZT thin film with only perovskite structure phase can be obtained at the annealing temperature of 750 °C for 3 min. (2) In the range of 600 to 750 °C, the higher the annealing temperature is, the better the film crystallinity. (3) When the annealing temperature increases from 600 to 750 °C, the remnant polarization increases from 13.8 to 25.2 μC/cm^2 and the coercive field increases from 7.2 to 8.5 kV/cm. (4) The fracture patterns and fracture toughness of PZT thin film are all strongly affected by the annealing temperature, and the fracture toughness decreases from 0.49 to 0.47 MPa.m$^{1/2}$ with the increasing of the annealing temperature from 600 to 850 °C.

Acknowledgments

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