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RESIDUAL STRESS IN PIEZOELECTRIC THIN FILM PREPARED BY PULSE LASER BEAM ABLATION

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ABSTRACT

In the investigation, the piezoelectric thin film $Pb(Zr_xTi_{1-x})O_3$(PZT) was prepared by a pulse laser deposition method. The residual stress in piezoelectric thin film was tested by x-ray diffractometer (XRD). The relation of properties such as microstructures, piezoelectric response with residual stress was investigated. A theoretical model for residual stress formed mechanism is proposed. The model is based on the combined effects of the difference of thermal mismatch between substrate and thin film, the phase transformation and the different of lattice constant between thin film and substrate.

KEYWORDS

Piezoelectric thin film, Pulse laser ablation method, Residual stress

INTRODUCTION

Piezoelectric thin films are currently attention due to the potential application in MEMS (micro-electro-mechanical systems), information storage, et al[1]. Many methods are used to prepare piezoelectric thin films. Pulsed laser deposition (PLD) is one of the considerable deposition methods. In the investigation, the prepared lead zirconate titanate ($Pb(Zr_{0.52}Ti_{0.48})O_3$;PZT) piezoelectric ceramics were used as a target, Nd:YAG pulse laser as an evaporate source, Si(100) crystal slice as a substrate, oxygen as ambient gas. Residual stresses will be produced inevitably between thin film and substrate due to the structural misfit and thermal misfit of the thin films/substrate and the process from high temperature to low temperature during the preparation process of the thin films. The structure and properties of thin films have relation with residual stress in some degree. In the present paper, the residual stress in PZT thin film was tested by x-ray diffractometer (XRD) and a theoretical model was proposed to predict the residual stress. The effect of residual stress on piezoelectric property is also discussed.

EXPERIMENTAL PROCEDURE

Samples Preparation

PZT thin films were deposited on single crystalline silicon (100) by pulsed laser deposition (PLD). The substrates were coated beforehand with an 0.2μm-thick platinum film as a sub-electrode. A pulsed KrF laser beam with a wavelength of 248nm was focused on a $Pb(Zr_{0.52}Ti_{0.48})O_3$ target with an angle of 45^0. The frequency and pulse duration of the laser beam were, respectively, 5Hz and 30ns. The target was rotated with 5r/min in order to prepare a uniform thickness film. The target-substrate spacing was 60mm, and the incident energy density of laser beam was $1.5J/cm^2$. The substrate temperature and oxygen pressure in the chamber were 650^0C and 30Pa, respectively. When the target material was deposited on the substrate, the substrate was slowly cooled to ambient temperature. After PZT thin film was deposited, an 0.2μm-thick platinum film as a super-electrode was coated on the surface of film by pulse laser deposition. The ferroelectric hysteresis was measured by normal pulse measure system RT66A.

X-ray Diffraction and c-axis Orientation Ratio

The structure and residual stress of the samples were investigated with X-ray diffraction D500 and texture goniometer. The x-ray radiation source was Cu K_α with wavelength of 1.5406nm. The scanning angle was in the region of 20^0-70^0, scanning velocity was 4 degree/min and degree increment was 0.02^0. The diffractometer was operated at 36kV and 30mA. The c-axis orientation ratio is an important parameter which is defined as,

$$\alpha = \frac{I(002)}{I(110) + I(002)} \tag{1}$$

where I(002) and I(110) are the x-ray diffraction intensities of (002) and (100) reflection, respectively. It is considered that the orientation represents the volume ratio of a and c domains in the film.

Test Principle

Residual stress determination by means of X-ray diffraction is based on measurements of changes in crystal lattice spacing, which manifest themselves as shifts in angular positions of respective diffraction peaks [2]. From a set of lattice spacing in different orientations and a stress-free lattice spacing, an elastic strain tensor is constructed, which is then converted to stress tensor using Hooke's law [2]. When a beam of X ray with the wavelength of λ and is impinged to the surface of the samples with an incident angle Ψ, the diffraction of the X ray will occur with Bragg's diffraction equation,

$$n\lambda = 2d\sin\theta \tag{2}$$

where n is an integral, d is the crystal plane distance, θ is Bragg's diffraction angle. When there is a residual stress in the samples, the crystal plane distance d is different from that of the samples without residual stress, thereby the diffraction angle is different. The strain in thin film is related with the difference of crystal plane distance d,

$$\varepsilon_\psi = \frac{\Delta d}{d} = \frac{d_\psi - d_0}{d_0} = -\cot(\theta_\psi - \theta_0) \tag{3}$$

where θ_0 is the Bragg's angle at diffraction peak in the samples without residual stress, θ_ψ is the Bragg's angle at diffraction peak in the samples with residual stress. Generally, thin film is so thin that the residual stress in the thin film can be regarded as in plane stress. In this case, the residual stress σ_ϕ in the thin film along ϕ direction can be given

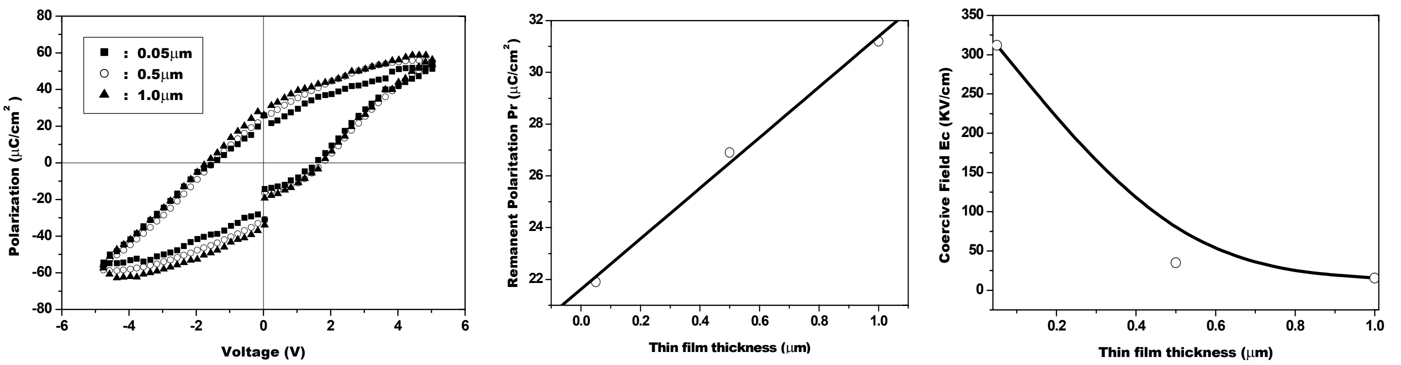
$$\sigma_\phi = -\frac{E}{2(1+\nu)}\cot\theta_o \frac{\pi}{180}\frac{\partial(2\theta)}{\partial(\sin^2\psi)} \tag{4}$$

where the unit of 2θ is degree, and E is Young's modulus, ν is Poisson's ratio of the thin film. Much research has shown that the relationship between 2θ and $\sin^2\psi$ is linear. In experiment, the slope of straight line on the plane of $2\theta_\psi$- $\sin^2\psi$can easily obtained by measuring different diffraction peak displacement under different ψ. Finally, the residual stress σ_ϕ in the thin films can be measured by using expression (4).

EXPERIMENTAL RESULTS

c-axis Orientation Ratio and Ferroelectric Properties

The structure of the ferroelectric thin films is sensitive to substrate temperature and oxygen pressure in the chamber during deposition. The dependence of micro-structure on substrate temperature and oxygen pressure was discussed by Luo, et al. [3]. $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin film, having a perovskite structure, was successfully deposited on single crystalline silicon (100) by pulsed laser deposition (PLD) at substrate temperature of 650^0C and oxygen pressure in the chamber of 30Pa. Figure 1 shows the ferroelectric properties with hysteresis, remnant polarization and coercive field for different film thickness. One can see that remnant polarization P_r increases linearly with increasing film thickness when the electric field is at a constant. However, the coercive decreases with increasing film thickness when the electric field is at a constant. When the film is thinner than 0.5μm, the coercive field decreases fast with increasing film thickness. When the film is thicker than 0.5μm, the coercive field decreases slowly with increasing film thickness. Figure 2 shows the c-axis orientation ratio for different thickness film. It is shown that the c-axis orientation ratio increases with increasing film thickness.



(a) (b) (c)

Figure 1: Ferroelectric properties: (a) hysteresis, (b) remnant polarization, (c) coercive field.

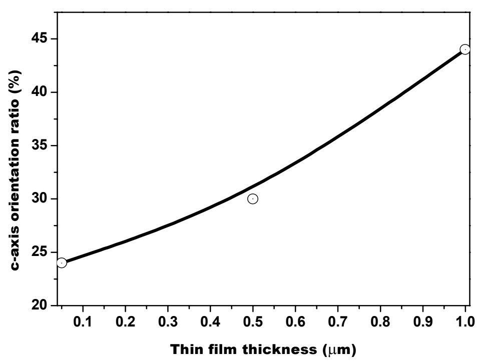
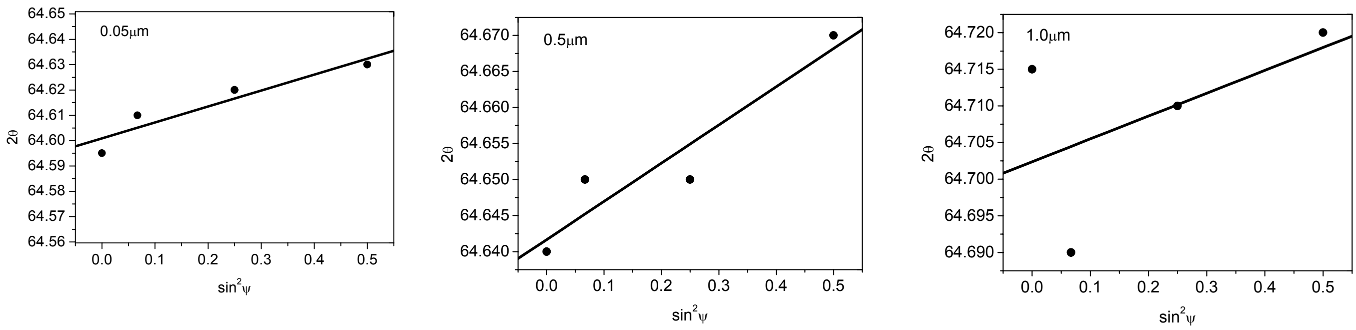


Figure 2: Relationship between film thickness and c-axis orientation ratio

Residual Stress

The incident angle ψ was adopted as three values which were $\psi=0^0$, 15^0, 30^0 and 45^0 in the residual stress test by X-ray diffraction. The diffraction peak displacement could easily be measured for different incident angle ψ. The results of $2\theta_\psi$ with $\sin^2\psi$ for different film thickness are listed in table 1 and shown in figure 3. One can easily obtained the slope of straight line from the figures. Based on formula (4) and the slope of $2\theta_\psi$ with $\sin^2\psi$, the residual stress in PZT thin film can be obtained. In the experiment, the mechanical parameters E and ν for PZT thin film were taken as 85Gpa and 0.28, respectively, and 2θ was taken as 64.68^{o}. Figure 4 shows the relationship between residual stress and film thickness. One can see that the residual stress is compressive stress. It gradually decreases with increasing film thickness.



(a) (b) (c)

Figure 3: The linear relationship of $2\theta_{\psi}$ with $\sin^2\psi$ for different film thickness: (a) 0.05μm, (b) 0.5μm, (c) 1.0μm

DISCUSSIONS

In the PZT thin film preparation by laser beam ablation, the PZT target materials were melted and vaporized. The melting and vaporous materials were deposited on the substrate by reverse impulse. During the film deposition at elevated temperature, strain due to misfit between the film and substrate would be developed. During cooling from the deposition temperature, thermal and transformation strains are developed in the film. The combination of these strains, lattice misfit, thermal misfit, and transformational, together with the effects of any structural relaxation processes, such as interfacial dislocation formation, leads to a net stress condition whin the film which affects the configuration of 90^0 domain structures in the film below the ferroelectric phase transition. Therefore, during the preparation of PZT thin film, there should have are four stress in the thin film which are epitaxial stress σ_{ep}, intrinsic stress σ_{in}, thermal stress σ_{th} and transformation stress σ_t[3]. The epitaxial stress is caused by the mismatch of the lattice parameter between thin films and substrate. The thermal stress is caused by the differences of the thermal expansion coefficients between thin film and substrate material. The intrinsic stress is generally caused by a collision of paraelectric particles which have kinetic energy to the deposited film. The phase transformation stress is the results from the change in lattice parameters of the PZT thin film during the process of ferroelectric phase transition at T_c. When the cubic PZT structure with a single lattice parameter a_o transforms to the tetragonal structure, there are two modes. One is the phase transition to a domains, and another is transition to c domains. Therefore, the phase transformation stress is caused by the mismatch between a or c and a_0. These four stresses all contribute to the change of the free energy during the forming process of PZT piezoelectric thin film.

$$F_{tot} = F_{ep} + F_{in} + F_{th} + F_{tr} + F_{sub} \tag{5}$$

where F_{tot} is total free energy of the film/substrate system, F_{ep}, F_{in}, F_{th}, F_{tr}, F_{sub} are , respectively, the contribution of epitaxial stress σ_{ep}, intrinsic stress σ_{in}, thermal stress σ_{th}, transformation stress σ_t and substrate to the total free energy. During the PZT film deposition process, the total energy will have a potential of system at minimum free energy. The free energy was discussed in the literature. Therefore, the residual stress in thin film should be written as,

$$\sigma_{res} = \sigma_{ep} + \sigma_{in} + \sigma_{th} + \sigma_{tr} \tag{6}$$

Epitaxial stress results from the lattice mismatch at the growth temperature between the film a_0 and the substrate a_s and can be written as,

$$\sigma_{ep} = \frac{E_f}{1-\nu_f}\frac{a_s - a_0}{a_s} \tag{7}$$

where a_0 is the lattice parameters of the PZT(0.58/0.42) thin film in the cubic phase before phase transition at the deposition temperature T_s=650°C. a_f and a_s are the lattice parameters of the film and the substrate in the cubic phase. E_f and ν_f are, respectively, Young's modulus and Poisson's ratio of the thin film and they are, respectively, 85GPa and 0.28. Since the substrate thickness is much greater than that of the film, the resulting epitaxial stress during growth in the film is tensile for a_s>a_0 and compressive for a_s<a_0 if we assume the absence of structural relaxation. However, since epitaxial strain develops at the growth temperature, it is reasonable that structural relaxation mechanisms (i.e., the formation of misfit dislocations at film/substrate interfaces) should be active to relieve this stress. Therefore, epitaxial stress has not contribute to residual stress[4].

The intrinsic stress can be relaxed by the orientation change. The difference of the c-axis lattice parameter before and after the annealing process was used to calculate the stored intrinsic stress as follows,

$$\sigma_{in} = -\frac{E_f}{2\nu_f}\frac{[A(c)_f - B(c)_f]}{A(c)_f} \tag{8}$$

where $A(c)_f$ and $B(c)_f$ are c-axis lattice parameters of PZT thin film in tetragonal phase at room temperature before and after annealing, respectively. The lattice parameters were calculated with the (002) peak position in the XRD patterns. In the investigation the c-axis lattice parameters $A(c)_f$ are, respectively, 4.0958 A^0,4.0861 A^0 and 4.0817 A^0 for the thickness of 0.05μm,0.5μm and 1.0μm PZT thin film. The c-axis lattice parameters $B(c)_f$ are, respectively, 4.0958 A^0,4.0861 A^0 and 4.0817 A^0 for the thickness of 0.05μm,0.5μm and 1.0μm. The intrinsic stresses for different film thickness are shown in figure 4. One finds that the intrinsic stress has the same profile as the total stress. Therefore, it is obvious the intrinsic stress greatly contributes to the total stress.

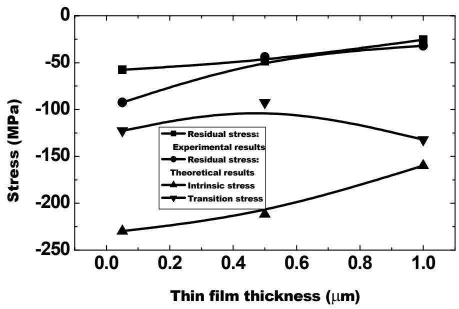


Figure 4: The contributions of intrinsic stress and transition stress to residual stress in PZT thin film

The thermal stress develops from thermal expansion mismatch between the film and substrate during cooling from the processing temperature to room temperature. The thermal stress can be written as,

$$\sigma_{th} = \frac{E_f}{(1-\nu_f)}\{[(\alpha(c)_f - \alpha_s)](T_s - T_{tr}) + [(\alpha(T)_f - \alpha_s)](T_{tr} - T_0)\} \tag{9}$$

where $\alpha(c)_f$ and $\alpha(T)_f$ are the thermal expansion coefficients of PZT (0.58/0.42) thin film in the basal plane for the cubic and tetragonal phases, respectively and they are assumed to be same and are taken as 7.0×10^{-6}/K. α_s is the thermal expansion coefficients of the substrate is taken as 3.5×10^{-6}/K. The thermal stress is about 0.26GPa and it is not dependent on film thickness. Since it is difficult for structural relaxation to occur at low temperature, thermal stresses are stored in the film. For many materials, the resultant residual stress often result in microcracking of the film.

During the cooling from the growth temperature, the PZT thin film undergoes a ferroelectric phase transition from a cubic phase to a tetragonal phase at 490^{0}C. Consequently, a high stress field is induced in the film. The stress in the film can be relieved by a domain formation. The phenomenon is similar to the formation of coherent alternating twins in martensities. The phase transition stress can be expressed as,

$$\sigma_{tr} = (1-P)\frac{E_f}{1-\nu_f}\frac{[a(T)-a_0]}{a_0} + \alpha\frac{E_f}{1-\nu_f}\frac{[c(T)-a_0]}{a_0} \qquad (10)$$

where a(T) and c(T) are a-axis and c-axis lattice parameters of tetragonal PZT at transition temperature and a_0 is the lattice parameter of cubic phase. the a-axis and c-axis lattice parameters of tetragonal structure (before annealing). The a-axis lattice parameters are, respectively, $4.030A^0$, $4.030A^0$ and 4.017 A^0 for the film thickness of 0.05μm,0.5μm and 1.0μm. The c-axis lattice parameters are, respectively, $4.0958A^0$, $4.0861A^0$ and $4.0817A^0$ for the film thickness of 0.05μm,0.5μm and 1.0μm. The contribution of phase transition stress to residual stress is shown in figure 4. It is obvious the phase transition stress has greatly contribution to the total residual stress. It is shown that the theoretical results and the experimental results for residual stress in PZT thin film are relatively consistent.

Observing the results for ferroelectric properties shown in figure 1, c-axis orientation ratio shown in figure 2 and residual stress shown in figure 4, one can see that there is a relationship of ferroelectric properties with residual stress. When the film is thin, the compressive residual stress is high and in this case, remnant polarization P_r and c-axis orientation ratio are both low. When the film is thick, the compressive residual stress is low and in this case, remnant polarization P_r and c-axis orientation ratio are both high. One can have the conclusion that the high compressive residual stress will result in the low values of remnant polarization P_r and c-axis orientation ratio. During the PZT thin film deposition, when the residual stress was gradually eliminated, crystal particles were ease to grow and the spontaneity polarization would be easy to progress.

CONCLUSIONS

In the investigation, the piezoelectric thin film $Pb(Zr_xTi_{1-x})O_3$(PZT) was prepared by a pulse laser deposition method. The residual stress in piezoelectric thin film was tested by x-ray diffractometer (XRD). The relation of properties such as microstructures, piezoelectric response with residual stress was investigated. A theoretical model for residual stress formed mechanism is proposed. The model is based on the combined effects of the difference of thermal mismatch between substrate and thin film, the phase transformation and the different of lattice constant between thin film and substrate. Remnant polarization P_r linearly increases with increasing film thickness and the coercive field gradually decreases with increasing film thickness at the same electric field. The residual stress has a great effect on ferroelectric properties of PZT thin films. Remnant polarization P_r decreases with increasing residual stress. The coercive field gradually increases with increasing residual stress.

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