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Determination of residual stress in PZT films produced by laser ablation with X-ray diffraction and Raman spectroscopy

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Abstract

The stresses in lead zirconate titanate (PZT) films, produced by pulsed laser deposition with different ratios Zr/Ti, 92/8, 65/35 and 55/45, was studied using Raman spectra and X-ray diffraction techniques. Based on lattice parameters and the elastic constants of PZT the films stresses were estimated from XRD measurements using the calculated d-spacing in the stressed and unstressed states. The results revealed the presence of compressive stress in PZT with composition 55/45 and tensile stress in the others. On the other hand, analysing the Raman phonon frequency in the $A_1(TO_3)$ and $E(LO_3)$ vibration modes and taking into account the phonon frequency under zero stress and the stress under which the phonon frequency becomes zero the stress in these films was estimated. The residual stresses extracted from the $A_1(TO_3)$ mode are consistent with those extracted from the $E(LO_3)$ mode and with those measured by X-ray diffraction technique.

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Keywords: X-ray diffraction; Raman spectroscopy; Residual stress; PZT films

1. Introduction

Because of its excellent properties PZT films has been widely used for preparing ferroelectric, piezoelectric and pyroelectric devices, such as non-volatile memories, infrared sensors, optical shutters, and modulators. Residual stress in ferroelectric thin films is inevitably induced upon cooling due to structural and thermal mismatch between the film and substrate.

Film stresses are usually divided into two broad categories. One category is growth stresses, which are those stress distributions present in films following growth on substrates or on adjacent layers. Growth stresses, also commonly called intrinsic stresses, are strongly dependent on the materials involved, as well as on the substrate temperature during deposition, the growth flux and growth chamber conditions.

A second category of film stress represents those stress conditions arising from changes in the physical environment of the film material following its growth. Such externally induced stresses are commonly called extrinsic stresses. In many cases, these stresses arise only when the film is bonded to a substrate, and the distinction between growth stresses and induced stresses becomes hazy at times [1]. Internal stress or strain in films deposited on thick substrates has two major sources. The first is due to differences in thermal expansion coefficients for films deposited at elevated temperatures and measured at room temperature. The second is caused by a high growth rate and low surface mobility of added material which prevents the atoms from reaching low energy states [2].

Many researches have shown that the excessive residual compressive or tensile stress may cause film delamination from the substrate, surface crack in films, splintering and adhesion problems of the film to the substrate [3,4]. The residual stress in films has important effects on the properties, performance and long term stability of the films [5], leading for a need for better understanding of mechanical properties of films. A range of methods is currently available to estimate residual stresses such as neutron diffraction [6], nano-indentation [7], X-ray diffraction [8] and Raman spectroscopy [9].

In this work the stress in lead zirconate titanate (PZT) films, that are produced by pulsed laser deposition, with different ratios Zr/Ti, 92/8, 65/35 and 55/45, was studied using X-ray diffraction

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and Raman spectroscopy, which are two nondestructive methods used to measure residual stresses in PZT films.

2. Experimental details

Lead Zirconate Titanate (PZT) films were deposited on Pt/TiO_2/SiO_2/Si substrates by Pulsed Laser Deposition (PLD) technique, using a Nd:YAG laser (Surelite) with a source pulse wavelength of 1064 nm and duration of 5–7 ns delivering an energy of 320 mJ per pulse and a laser fluence energy about 20 J/cm^2. Film growth was performed in O_2 atmosphere (0.40 mbar) while the substrate was heated at 600 °C by a quartz lamp. Starting from ceramic targets based on PZT compositions and containing 5 mol.% of excess of PbO to compensate for lead evaporation during heat treatment, three films with different compositions Zr/Ti 55/45, 65/35 and 92/8 were produced.

The crystalline structure of PZT films was studied by X-ray diffraction technique. The XRD patterns were recorded by a Philips X'Pert X-ray diffractometer, using Ni filtered CuKα radiation. Raman scattering measurements were carried out on a Jobin-Yvon T64000 spectrometer equipped with liquid nitrogen cooled CCD detector, in a Stokes frequency range, 25–1200 cm^{-1}, using the 514.5 nm excitation line from an Ar^+ laser in the back scattering geometry.

3. Results and discussion

The perovskite phase was formed in all these films, but the selected annealing conditions were not sufficient to eliminate secondary phases like pyrochlore in case of PZT with composition 55/45 and 65/35. In all the films a preferential orientation along the (1 1 0) (highest peak) are show.

3.1. Stress calculation from X-ray diffraction

The lattice parameters of each homogeneous films produced by pulsed laser deposition with different Zr/Ti ratios, have been calculated from XRD patterns considering that the diffracting planes are due to the rhombohedral structure of the perovskite phase (JCPDS card no 29-775). Comparing the lattice parameters of the films with the lattice parameters of the targets that originated them, we can see a little difference between them as Fig. 1 show. These differences showed the existence of strains in these films, tensile strain for composition 55/45 and compressive strain for composition Zr/Ti 65/35 and 92/8.

This change in the interplanar spacing Δd will produce a corresponding change in the Bragg angle, such that lattice strain normal to the plane of the film can be expressed from:

$$\varepsilon_{33} = \frac{d_{1\,1\,0} - d_0}{d_0} \tag{2}$$

where $d_{1\,1\,0}$ is the lattice spacing for the plane with Miller index (1 1 0) and d_0 is the unstrained lattice spacing. The nonzero components of stress in the film, with reference to the orthogonal co-ordinate system X, where x_3 is perpendicular to the plane of the film, are $\sigma_{11} = \sigma_{22} = \sigma_m$. The corresponding nonzero strain

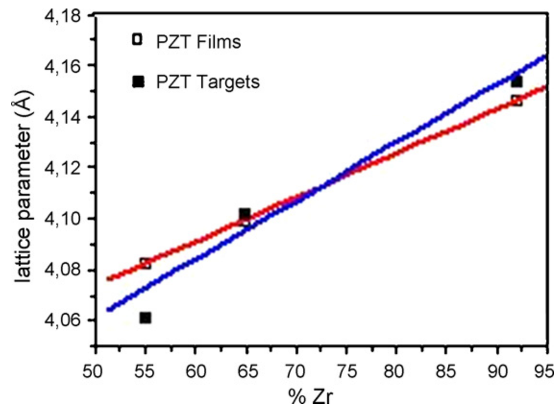

Fig. 1. Relation between lattice parameters of films and targets for the three different films compositions.

components are $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_m$ and is given by Eq. (3), taking into account the elastic constants of PZT:

$$\varepsilon_{33} = -\frac{2(c_{11} + 2c_{12} - 2c_{44})}{c_{11} + 2c_{12} + 4c_{44}} \varepsilon_m \tag{3}$$

After that, the equi-biaxial mismatch stress is given by the relation:

$$\sigma_m = \varepsilon_m \times M_f \tag{4}$$

where ε_m is the mismatch strain and M_f is the biaxial modulus, which is related to the elastic modulus and the Poisson ratio for PZT films, as represented in Eq. (5):

$$\sigma_m = \varepsilon_m \times \frac{E}{1 - \nu} \tag{5}$$

The elastic constants for PZT films are estimated as [10]:

$$E = 71\,\text{GPa}$$

$$\upsilon = 0.3$$

$$c_{11} = 1.53 \times 10^3\,\text{GPa}$$

$$c_{12} = -2.73 \times 10^3\,\text{GPa}$$

$$c_{44} = 2.13 \times 10^3\,\text{GPa}$$

The stress in PZT films was calculated from the equations presented before and the results are given in Table 1.

3.2. Stress calculation from Raman spectroscopy

From Fig. 2 is possible to see that the silent mode (B_1 + E) appears to be indifferent to the PZT composition.

Table 1
The stress of PZT films after annealing.

PZT films	Stress (MPa)
$PZT_{55/45}$	137.1
$PZT_{65/35}$	−14.6
$PZT_{92/8}$	−44.5

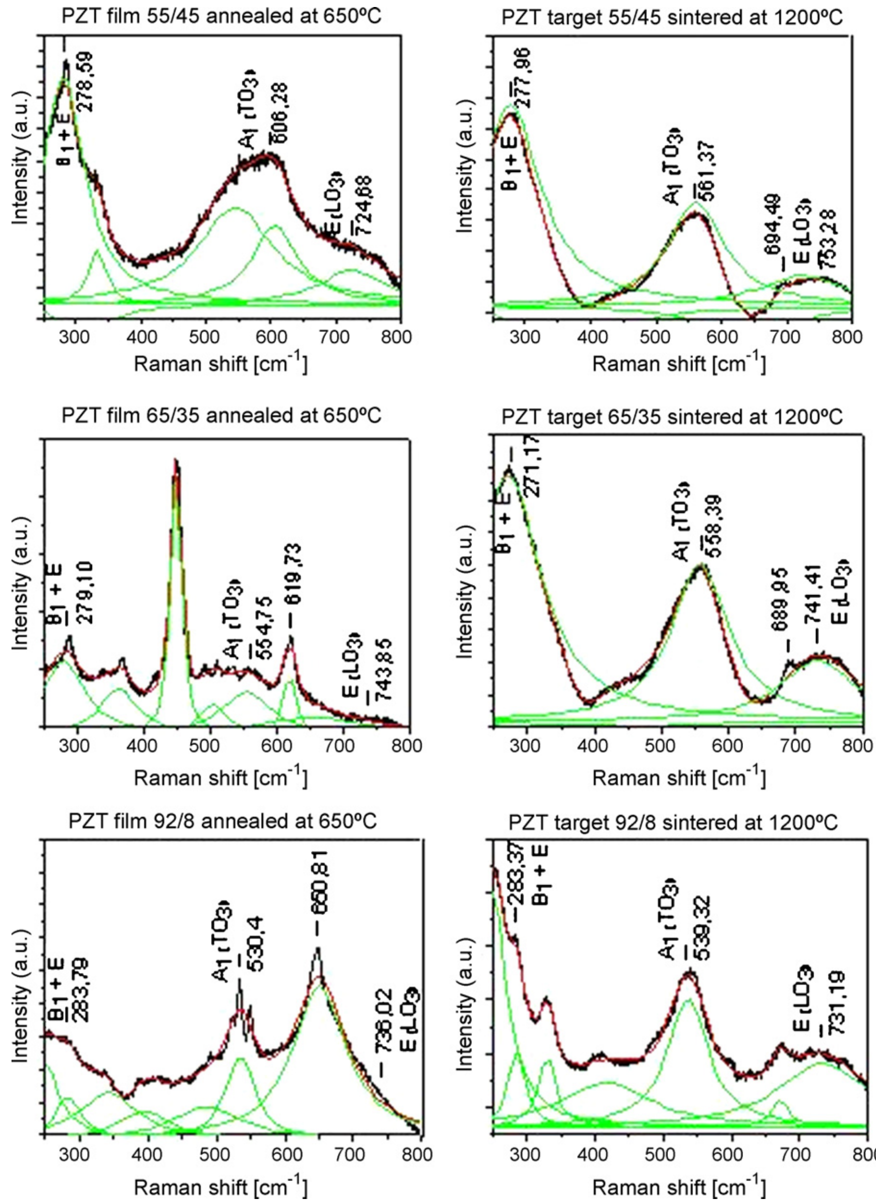

Fig. 2. Raman spectra of PZT films (left) and targets (right) for the different compositions Zr/Ti 55/45, 65/35 and 92/8.

Experiments have shown that the wave number shift of the $A_1(TO_3)$ and $E(LO_3)$ vibration modes must be caused principally by stress. From the Raman spectra of bulk samples and films, with different Zr/Ti ratios, shown in Fig. 2, it is possible to know the frequency of Raman modes $B_1 + E$, $A_1(TO_3)$ and $E(LO_3)$. Several spectra recorded from each PZT film were found to be similar. So, the phonon frequencies showed in Tables 2 and 3 were just related to one typical spectrum. From Fig. 2, it is possible to see that the silent mode ($B_1 + E$) (at $\approx 280\,\text{cm}^{-1}$) appears to be independent of the applied stress for each PZT composition [12]:

The relationship between Raman spectra and films stress is expressed by equation:

$$\omega^2 = \omega_0^2 \left(1 - \frac{\sigma}{\sigma_1}\right) \quad (6)$$

where ω is the phonon frequency measured under stress, σ_1 is the stress under which the phonon frequency becomes zero and ω_0 is the phonon frequency under zero stress [11]. The residual stress, for PZT films, evaluated from the phonon frequency shift are tabulated in Tables 2 and 3, extracted from the $A_1(TO_3)$ and $E(LO_3)$, respectively.

Table 2
The stress of PZT films measured from the Raman vibration mode $A_1(TO_3)$.

PZT film	ω (cm^{-1})	ω_0 (cm^{-1})	σ_1 (MPa)	σ (MPa)
55/45	606.28	561.37	−22.0	120.14
65/35	554.45	558.39	−714.4	−9.28
92/8	530.4	539.3	−666.3	−21.81

Table 3
The stress of PZT films measured from the Raman vibration mode $E(LO_3)$.

PZT film	ω (cm^{-1})	ω_0 (cm^{-1})	σ_1 (MPa)	σ (MPa)
55/45	724.6	753.28	1668.1	124.26
65/35	743.85	741.41	1615.9	−10.65
92/8	736.02	731.19	1571.7	−20.83

4. Conclusion

Residual stress in films has important effects on the films life and for that reason it is very important to estimate it. In this work the residual stress in PZT films, produced by pulsed laser deposition technique, was studied with help of X-ray diffraction and Raman spectroscopy. The residual stress estimated from X-ray diffraction is in agreement with the relation between the lattice parameters of films and their respective targets. Analysing the results of stress estimated for each samples, we can see that for PZT film with composition Zr/Ti 55/45 the stress is in tension while in PZT films with ratio Zr/Ti 65/35 and 92/8 we have a compressive stress. It is well known that shortly after it first arises during growth of a polycrystalline film, the tensile stress is observed to decrease in magnitude, implying a negative or compressive incremental stress [1]. For a residual stress in tension, a large grain size, excess of oxygen vacancies in the lattice sites and lower intensity of the rhombohedral phase leads to a high residual stress in tension. Other possible origins of tensile stress are related to the phase transition and to difference in film and substrate thermal expansion coefficients [11]. The film with composition Zr/Ti being 55/45 is under tensile stress might be due to the fact it is near of the morphotropic phase boundary, were the dielectric constant is higher and the value of stress increases and could change from compressive to tensile stress as observed. Further, films with higher Ti content exhibit low intensity of the rhombohedral phase when compared with those with low Ti content (PZT with ratio Zr/Ti 65/35 and 92/8) which allows to an increase of tensile stress [13].

The fact that the residual stress extracted from the $A_1(TO_3)$, $E(LO_3)$ Raman modes are consistent one with other and with those calculated from X-ray diffraction leads to a credible value of PZT stress.

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