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SCIENCE DIRECT

Surface & Coatings Technology 198 (2005) 395–399

SURFACE & COATINGS TECHNOLOGY

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Effect of Tb^{3+} doping on the preferred orientation of lead titanate thin film prepared by sol–gel method on ITO/glass substrates

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Available online 2 December 2004

Abstract

Tb doped $PbTiO_3$ (PT) thin films were prepared on ITO/glass substrates by sol–gel method. XRD was used to investigate the phase status of the thin films. It is shown that through rapid thermal process, the perovskite phase $PbTiO_3$ thin films with highly (100) preferred orientation could be formed on the astatic ITO/glass substrates when Tb is doped into $PbTiO_3$ system. The (100) preferred orientation of Tb-doped $PbTiO_3$ films is attributed to the heterogeneous nucleation mechanism of the perovskite $PbTiO_3$ phase induced by Tb doping and rapid thermal preparation process. It is successfully explained according to this mechanism that the content of the (100) oriented Tb-doped perovskite phase in $PbTiO_3$ films varies with Tb doping concentration. An optimal doping concentration of Tb to achieve highly (100) oriented and well-crystallized $PbTiO_3$ films is discovered. And a theoretical equation of the perovskite phase content as a function of Tb doping concentration is deduced.

Keywords: Sol–gel process; Oriented thin film; Lead titanate; Tb doping

1. Introduction

Preparation of $PbTiO_3$ (PT) based ferroelectric thin films has attracted extra attention recently because of their excellent properties and large amount of potential applications such as memory devices, electro-optical devices, sensors and actuators [1–4]. As it is known, PT ferroelectric material has a polar axis, hence it shows various electric properties depending on the different phase orientation. Highly oriented ferroelectric films will help to further enhance desired electrical properties. For this reason, many ways to prepare highly oriented film have been attempted [5–7].

In this article, we report on the results of the preparation of highly (100)-oriented Tb-doped PT film deposited on astatic ITO substrate by sol–gel method via rapid thermal annealing. The reason for the orientation of Tb-doped PT film will be discussed.

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doi:10.1016/j.surfcoat.2004.10.035

2. Experimental

Tb-doped PT films were prepared by sol–gel method. Firstly, transparent Tb doped PT precursors were prepared using $Pb(CH_3COO)_2$, $Ti[(CH_3)_2CHO]_4$, and $Tb(NO_3)_3$ as starting materials and $CH_3OCH_2CH_2OH$ as solvent. Then the films were deposited on ITO/glass substrate by dip-coating method with a withdrawal speed of 0.067 cm/s. After that, the films were calcined via rapid thermal process and slow thermal process, respectively. During rapid thermal process, the films were directly put into furnace with 600 °C heat treatment temperature and calcined for 5 min, then removed from the furnace and cooled at room temperature. During slow thermal process, the films were heated to 600 °C at a heating speed of 20 °C/min and kept at 600 °C for 5 min, then they were cooled to room temperature at a cooling speed of 20 °C/min. Film thickness was increased by repeating many times dip coating and calcinating process.

The phase structures of Tb doped PT thin films were measured by X-ray diffraction (XRD) using CuKa radiation of 1.5418 A, sampling interval of 0.02° and scan speed of

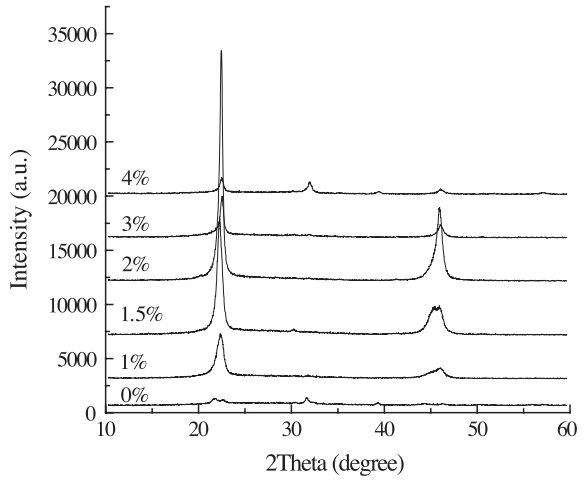

Fig. 1. XRD patterns of PT thin films with different Tb doping concentration prepared via rapid thermal process.

4°/min. The film thickness and morphology were observed by scanning electron microscopy (SEM) (Hitachi S-4100).

3. Results

Fig. 1 shows the XRD patterns of PT films with different Tb doping concentration prepared via rapid thermal process. Many weak diffraction peaks related to the perovskite phase appear in the PT thin film without doping Tb. The relative intensity between the peaks of the film is similar to those obtained from PT powder. For Tb doped PT thin films, strong (100) and (200) peaks of the perovskite phase appear in the pattern and other peaks disappear. Moreover, intensities of the two peaks increase with increasing Tb doping as Tb concentration is below 2% and decrease while the other peaks of the perovskite phase gradually reappear with increasing Tb doping as Tb concentration is above 2%.

Fig. 2 shows the XRD patterns of 2% Tb doped PT thin films prepared via rapid thermal process which are repeated for different times of coating-calcination process. Only (100) and (200) peaks of the perovskite phase can be seen in Fig. 2. And the peak intensities increase with increasing repeating layers.

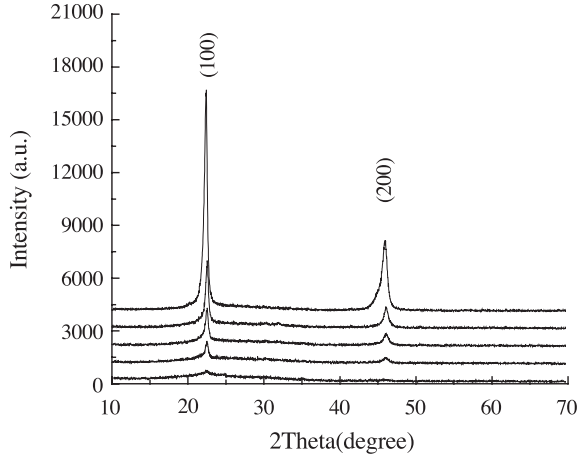

Fig. 2. XRD patterns of 2% Tb^{3+} doped PT thin films on ITO substrate with different thicknesses prepared via rapid thermal process.

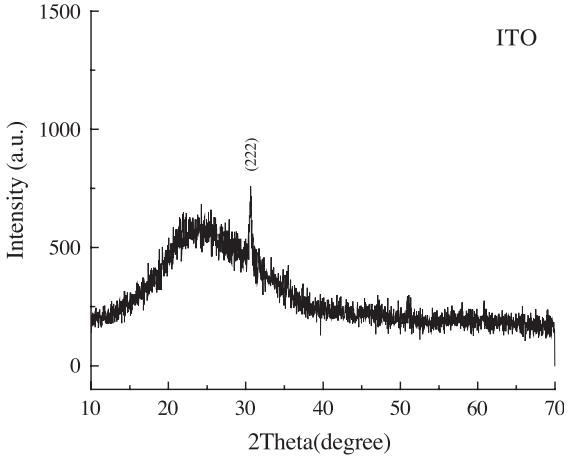

Fig. 3. XRD pattern of blank ITO/glass substrate.

Fig. 3 is the XRD pattern of blank ITO/glass substrate on which the thin films are prepared. The only observed (222) peak of ITO phase locates at around 30° in 2θ, which is much far away from the location of (100) and (200) peaks of the perovskite phase in Tb doped PT thin films.

Fig. 4 depicts the XRD pattern of 2% Tb doped PT thin films prepared via slow thermal process which are repeated for different times of coating-calcination process. Many weak diffraction peaks related to perovskite PT appear in the spectra. The relative intensity between the peaks of the film is similar to those obtained from PT powder.

4. Discussion

As it is shown in Fig. 1, the perovskite phase in PT thin film without Tb doping is non-orientated and randomly distributed when the thin film is prepared on ITO/glass substrate by sol–gel process via rapid thermal treatment.

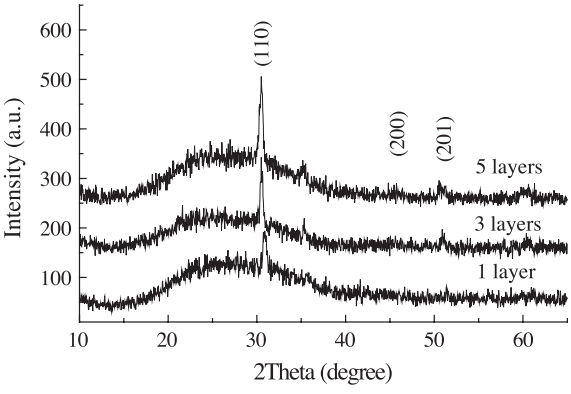

Fig. 4. XRD patterns of 2% Tb^{3+} doped PT thin films on ITO substrate with different thickness prepared via slow thermal process.