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Hybrid influences of defect dipole and intrinsic inducing field on orientation of $PbTiO_3$ thin film deposited on Indium Tin Oxide/glass substrate

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ABSTRACT

(001)/(100) oriented $PbTiO_3$ (PT) thin film is prepared on a non single crystal Indium Tin Oxide (ITO)/glass substrate by sol–gel method. The mechanism of orientation is investigated via dopant element, dopant amount, oxygen pressure of atmosphere, different type of substrate, different thickness of substrate, different sol concentration and blocking layer. By substituting 2% Zn^{2+}, or 2% Fe^{3+}, or 2% Co^{2+} ions in the Ti site of PT perovskite phase and heating at the oxygen-poor atmosphere, the PT thin film grown on the ITO(260 nm)/glass substrate forms well with (001)/(100) orientation. Moreover, this orientation phenomenon only appears when the solution concentration is below 0.1 mol/L. The orientation of PT which is attributed to the hybrid influences of defect dipole from the PT and the intrinsic electrostatic field from the ITO substrate is revealed. This work represents an important step toward controllable formation of oriented thin film on a non single crystal substrate.

1. Introduction

Epitaxial or oriented $PbTiO_3$ (PT) thin films have attracted extensive interest [1] for the excellent properties which are from the preservation of anisotropy by single crystal substrates [2–4]. However, the high cost of single crystal substrates limits the application of the oriented thin films in micro-electronics. Generally, high quality of orientation of thin film is dependent on the lattice match between single crystal substrate and thin film [5–10], the lattice-matched single crystal substrates are thus dominantly necessary. If orientation growth can be achieved without lattice match, the single crystal substrates might be replaced by other low cost substrates, which may be of great attraction. In recent years, PT thin films with doping rare earth such as Ce, Sm, Dy, Er, Yb [11] and Tb [12] grown on Indium Tin Oxide/glass (ITO/glass) substrate by sol–gel method exhibit their highly (100) orientation in nature. However, the mechanism of the orientation growth is still unclear.

It has been reported that there are $(Fe'_{Ti}-V_O^{\bullet\bullet})^{\bullet}$ defect dipoles in the Fe doped PT thin films and the defect dipoles are always along <001> or <100> direction [13]. If an electrostatic field is applied, would the PT thin film grow with (001)/(100) orientation?

Herein sol–gel PT thin films with (001)/(100) orientation were deposited on the Indium Tin Oxide (ITO/glass) substrate by doping different ions, or by controlling oxygen pressure. It is worth noting that ITO/glass is a low cost and an industrialized substrate, and PT is a universal dielectric thin film used in micro-electronics. In this work, PT thin films with and without doping were prepared on ITO/glass substrate. The correlations between orientation and dopant element, dopant amount, oxygen pressure of atmosphere, different types of substrate, different thickness of ITO, different sol concentration, as well as the TiO_2 blocking layer (to block the PT from the ITO substrate) were studied. The hybrid influences of defect dipole and intrinsic inducing field are exhibited in PT thin film with (001)/(100) orientation. This (001)/(100) oriented PT thin film can be used as inducing layer for depositing oriented (Pb,Sr)TiO_3 (PST) thin film and thus improve its tunable dielectric property evidently.

2. Experimental details

$PbTiO_3$ (PT) sol were prepared using $Pb(CH_3COO)_2$, Ti $[(CH_3)_2CHO]_4$ as starting materials and $CH_3OCH_2CH_2OH$, CH_3COOH as solvent [12], in which the volume ratio of $CH_3OCH_2CH_2OH$ and CH_3COOH was 2:3. The sol with the concentration of 0.1 mol/L contained Ti of 0.1 mol/L, Pb of 0.1 mol/L. Zn^{2+}, Fe^{3+}, Co^{2+} or Zr^{4+} was added in the PT solution respectively by dissolving powder $Zn(C_2H_3O_2)_2{\bullet}4H_2O$, $Fe(NO_3)_3{\bullet}9H_2O$, $CoCl_2$ or $ZrOCl_2{\bullet}8H_2O$. Before coating, the ITO coated glass substrate (25 mm × 50 mm) was washed by HNO_3 of 0.15 mol/L, or NaOH of 0.25 mol/L to remove the adsorbates on the surface of ITO. The PT wet film was prepared by dip-coating the PT sol on the washed ITO/glass substrate at room temperature, with the withdrawal speed of 4 cm/min. After that the wet thin film was dried by an infrared lamp and then heat treated using two

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kinds of processing. 1. The Rapid Thermal Processing (RTP) was carried out by putting the dried thin films directly into the 600 °C furnace (Naberthem, L5-11, air) for rapid heating, holding for 5 min, and taking out directly for rapid cooling in air. 2. The Slow Thermal Processing (STP) was carried out by putting the dried thin films into a tube furnace (Naberthem, R/50) at different atmosphere (O_2 flow, 10 L/min; N_2 flow, 10 L/min; Fe_2O_3 powder; Fe powder), 30 min rising from room temperature to 600 °C, holding at 600 °C for 60 min and finally cooling down to room temperature slowly in the same atmosphere. TiO_2 blocking layer was prepared by the same sol–gel method with its precursor concentration of 0.3 mol/L. The thickness of the PT thin film was 20–30 nm. TiO_2 blocking layer was prepared by the same sol–gel method with its thickness of 35 nm or 130 nm. X-ray diffraction (XRD, Rigaku-MAX-C, Cu K_α $\lambda = 0.154$ nm) was used to measure the crystal direction of PT thin film by $\theta - 2\theta$ scans, during XRD measuring the surface of the middle part of the PT thin film (about 10 mm × 10 mm) was exposed to the X-ray. Sample for Transmission Electron Microscope (TEM, CM200UT, 160 kV) measurement was the powder shaved from the PT thin films.

3. Results and discussion

Fig. 1a shows the XRD pattern of $PbTiO_3$ (PT) thin films grown on ITO/glass substrate. The 1%–5% Zn doped PT thin films are (001)/(100) oriented with only the (001)/(100) and (002)/(200) peaks observed, while the pristine PT thin film is randomly oriented with all the perovskite peaks observed. The 10% Zn doped PT shows almost no diffraction peak of perovskite phase. Here Zn doped PT thin films are heat treated by RTP with 5 min at 600 °C which is suitable for depositing oriented $PbTiO_3$ (PT) thin films [14]. Fig. 1b shows the XRD patterns of 2%Zn–PT thin films prepared from two solutions, sol-A of 0.3 M and sol-B of 0.1 M. It shows clearly that the PT thin film fabricated from the solution of low concentration (sol-B, 0.1 mol/L) is well (001)/(100) oriented, while that with high concentration (sol-A, 0.3 mol/L) is only partly oriented, not only the (001)/(100) peaks but also the (011)/(110) peaks observed. By diluting, sol-A (0.3 mol/L) became sol-A1 (0.07 mol/L), sol-B became sol-B1 (0.063 mol/L) and sol-B2 (0.037 mol/L). Using these diluted solutions, Zn–PT thin films grow in well (001)/(100) orientation as shown in Fig. 1b. Therefore, to achieve the optimal oriented PT thin films, the doping concentration of Zn should be 2% and the solution concentration should not be higher than 0.1 M.

Fig. 2 shows the TEM images and selected area electron diffraction (SAED) patterns of randomly oriented PT thin film and the (001)/(100) oriented 2%Zn–PT thin film. The SAED pattern of the PT thin film shown in the inset of Fig. 2a exhibits ruleless diffraction pattern, suggesting the randomly orientation of PT thin film, which is consistent with the XRD result (Fig. 1a 0%Zn–PT). And the SAED pattern of the Zn–PT thin film shown in the inset of Fig. 2b exhibits several sets of single-crystal-like patterns, implying that this sample (2%Zn PT) consists of crystal particles which are arranged in a certain extent rather than randomly oriented polycrystalline phase, which is consistent with the XRD result of (001)/(100) orientation (Fig. 1a 2%Zn–PT).

Fig. 3 shows the lattice parameters *a* and *c* of Zn–PT thin films calculated from the XRD patterns shown in Fig. 1a. The lattice parameter *a* increases gradually and *c* decreases with content of Zn. It proves the change in tetragonality and the distortion in perovskite structure in doped PT thin films.

Fig. 4a shows the XRD patterns of pristine and doped $PbTiO_3$ (PT) thin films grown on ITO/glass substrates. PT thin films doped with Zn^{2+}, Fe^{3+} or Co^{2+} are (001)/(100) oriented with only the (001)/(100) and (002)/(200) peaks observed, while pristine PT thin film is randomly oriented with all the perovskite peaks observed. However, the XRD pattern of Zr^{4+} doped thin film shows that the diffraction

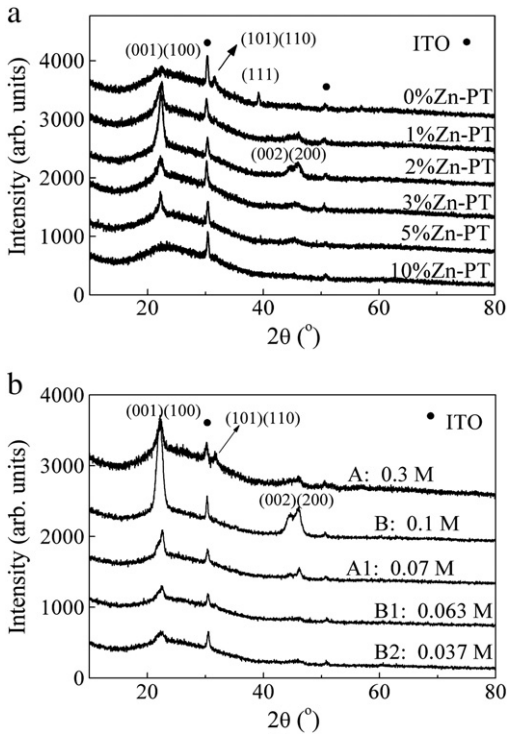

Fig. 1. XRD patterns of Zn–$PbTiO_3$ thin films with (a) different doping concentration and (b) different solution concentration.

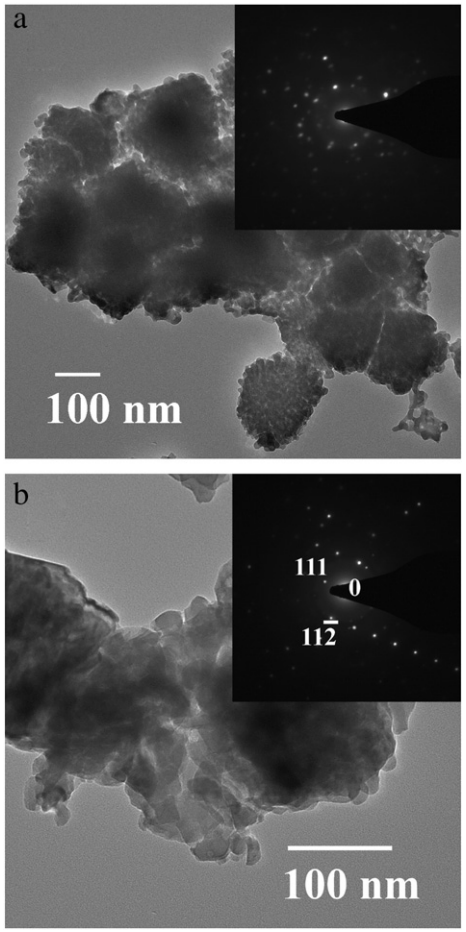

Fig. 2. TEM images and SAED of (a) randomly oriented PT thin film and (b) (001)/(100) oriented 2%Zn–PT thin film.