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The growth behavior and stress evolution of sputtering-deposited $LaNiO_3$ thin films

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Abstract

$LaNiO_3$ (LNO) thin films were deposited on Si(1 0 0) substrates by ratio frequency (RF) magnetron sputtering. It was found that the stress evolution was directly related to the film morphology. At the early growth stage, the grain size and the orientation factor T_{100} increased rapidly below a critical thickness (about 100 nm), meanwhile the residual stress shows a compressive-tensile-compressive transition behavior associated with Volmer–Weber growth mode. With the films thickening, the columnar structure was developed, and simultaneously the compressive stress decreased gradually as a consequence of the grain growth. Finally, an additional influence of the thermal stress and hygroscopic extrinsic stress has also been taken into consideration.

Keywords: $LaNiO_3$ thin films; Magnetron sputtering; Residual stress; Growth mode; Thickness effect

1. Introduction

Lanthanum nickel oxide, $LaNiO_3$ (LNO) is a pseudocubic perovskite metallic oxide with the lattice parameters matching well with most of the perovskite-type ferroelectric materials including $Pb(Zr, Ti)O_3$(PZT) and $(Ba, Sr)TiO_3$(BST). Moreover, it has good performances, such as low resistivity, excellent diffusion barriers properties and good thermal stability. Metallic LNO films with controlled crystalline orientation can be used not only as a promising bottom electrode material in various ferroelectric related devices [1–3], but also as a seed layer for the growth of highly textured ferroelectric thin films [4–6].

Several methods have been adopted to prepare LNO films, such as metalorganic decomposition technique (MOD) [7], pulsed laser deposition (PLD) [8] and RF magnetron sputtering [9–10]. RF sputtered LNO films begin to crystallize at an extraordinarily low temperature, about 150 °C, while it goes beyond 600 °C for MOD and PLD [11]. So, LNO thin films can be easily prepared by RF magnetron sputtering at a moderate temperature and then ferroelectric thin films can be coherently deposited on the LNO electrodes at a reduced process temperature.

The residual stress was suggested to be one of the key factors that determine the performance and reliability of thin films. For instances, the residual tensile stress can induce microcracks and lead to a broken circuit, while the residual compressive stress can lead to hillocks formation which may lead to a short circuit in interconnects [12]. In addition, the residual stress could considerably influence the ferroelectric and dielectric properties of ferroelectric thin films. Experimental investigations demonstrated an increase of Curie temperature and a broadening of the phase-transition temperature range with increasing compressive stress of $BaTiO_3$ thin films on a Si substrate [13,14]. Therefore, the study on residual stress has significance for the application of thin films. So far, although several studies have tried to explore the microstructure characters of LNO films, there is no systematic investigation on the evolution of residual stress in LNO thin films. Further, since the intrinsic stress is directly related to the film growth process, some important microstructural information can be extracted from the stress evolution [15]. In this work, we have carried out an investigation on the residual stress of LNO films grown on Si(1 0 0) by RF magnetron sputtering and tried to clarify the relation between the stress evolution and growth behavior.

2. Experimental

LNO thin films were prepared by sputtering on Si(1 0 0) substrates with native oxide layers. Sputtering targets (75 mm diameter) were prepared by sintering calcined La_2O_3 and Ni_2O_3

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powder (both 99.9% purity) in stoichiometric molar ratio at 1100 °C for 2 h. A radio frequency (13.6 MHz) sputtering system was employed, and the chamber was evacuated to 7.5×10^{-5} Pa before deposition. Optimal processing conditions were explored to obtain a highly (1 0 0) preferred orientation and good electrical properties of LNO films. Pre-sputtering was performed for 20 min, and the deposition was carried out at a substrate temperature of 230 °C. A mixture of Ar and O_2 gases ($Ar/O_2 = 9.0{:}1.0$, total flow rate 20 sccm) was introduced, while the sputtering pressure was kept at 0.2 Pa and the deposition was performed at a plasma power of 150 W. Various deposition times were applied to obtain different thicknesses of LNO films. Notably, in our experiments, the deposition condition was adopted to suppress the destructive effect of energetic particles on the preferred orientation.

The phase of the film was characterized using X-ray diffraction (XRD, Shimadzu-7000) with Cu Kα radiation. The morphology of the films was observed by high-resolution scanning electron microscopy (HRSEM, JSM-6700F), and the thickness was determined by means of cross-section image. The concentration profile and valence states of oxygen in the films were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB MK-II) performed directly on the surface of the films as well as after etching by the Ar ion beam. The residual stresses in the films were deduced from the curvature radius of substrate measured by BGS6341 Curvature Radius Measuring Instrument made by Beijing Institute of Opto-electro Technology. The instrument can directly determine the profile of a bended composite structure and the curvature radii is then obtained by the data of the profile with error less than 5%. The curvature measurements reflect the average biaxial stress in the film, $\langle\sigma\rangle$. Furthermore, as a full-field optical method it can map the stress within the film on whole surface through the profiles. And the difference between maximum and minimum stress values within the film can denote the uniformity of spatial distribution of stresses. The measurements were carried immediately after the deposition process. The residual stress σ in the film can be calculated using Stoney's formula [16]:

$$\sigma = \frac{E_s}{6(1-\nu_s)}\frac{t_s^2}{t_f}\left(\frac{1}{R_2}-\frac{1}{R_1}\right) \quad (1)$$

where $E_s/(1-\nu_s)$ is the substrate biaxial modulus, t_s and t_f are the thicknesses of substrate and film, respectively, R_1 and R_2 are the curvature radii of substrates measured before and after films deposition. It is obvious that the curvature evolution is directly proportional to the product of the film stress and the film thickness σt_f which represents the film force during the film growth. The slope coefficient at any point on the curve of film force against thickness exhibits an "incremental" stress associated with the instantaneous growth of new film [17]. Notably, a positive (negative) slope corresponds to a tensile (compressive) incremental stress, even in cases where the absolute stress–thickness product is negative (positive). Although the stress was *ex situ* measured in this experiment, it may bring us certain insights into the microstructural evolution of LNO thin film by additional consideration of the stress relaxation behavior, like water adsorption effect.

3. Results and discussion

3.1. Growth behavior and thickness effect

Fig. 1 presents a series of XRD patterns of LNO films in various thicknesses. The figure is divided into three parts to distinguish the weaker peaks of thinner films. All films are identified to be pseudocubic perovskite crystal structures whose strong (1 0 0) and (2 0 0) peaks can be observed. Weaker (1 1 0) diffraction peaks are present in thinner films. As shown in Fig. 2, the preferred orientation is enhanced with increasing the film thickness, which is demonstrated by the orientation factor T_{100} [7], *i.e.*,

$$T_{100} = \frac{I(1\,0\,0)}{I(1\,0\,0) + I(1\,1\,0)} \quad (2)$$

where I is the integrated intensity of a certain diffraction peak. It can be seen that T_{100} is close to 1 when the thickness exceeds

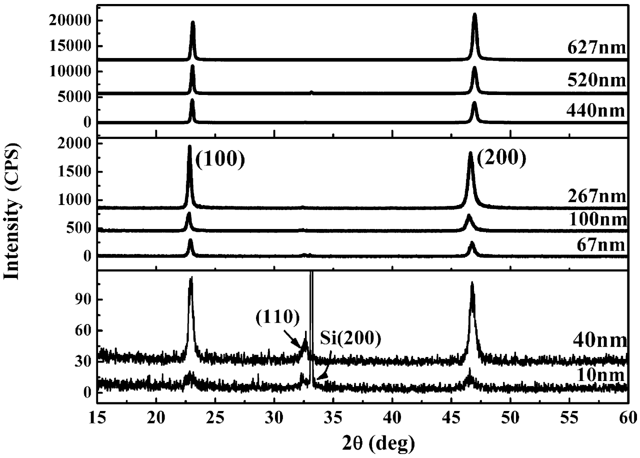

Fig. 1. XRD patterns of LNO films deposited on Si substrate with various thicknesses.

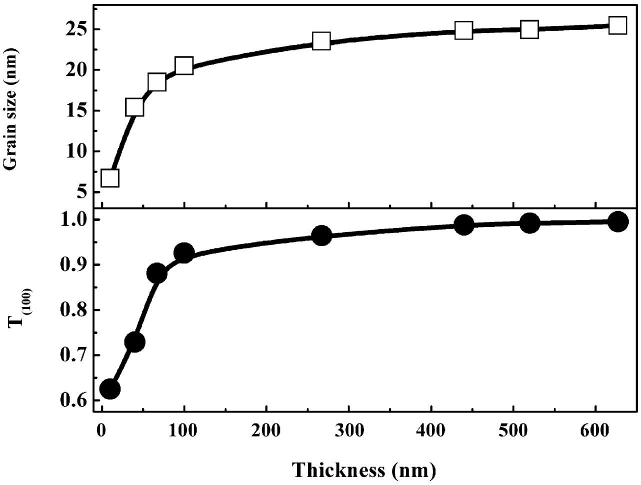

Fig. 2. The variations in grain size and orientation factor T_{100} for LNO films with various thicknesses.