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Pulsed Laser Deposition and Characterization of (001)-oriented $Pb(Zr_{0.52}Ti_{0.48})O_3/LaNiO_3$ Heterostructures

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Highly (001)-oriented ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3/LaNiO_3$ (PZT/LNO) heterostructures on $LaAlO_3$(001) (LAO) single crystal substrates have been grown using pulsed laser deposition technique. X-ray diffraction (XRD) analyses of θ–2θ, ω- and ϕ-scans indicate achievement of preferred orientation growth of PZT(001)//LNO(001)//LAO(001) and PZT<100>//LNO<100>//LAO<100>. Scanning electron and atomic force microscopic images reveal very smooth LNO surfaces with roughness of only about 0.4-0.6nm. Based on microstructural study of the LNO and PZT films, layer-by-layer growth mode for the LNO growth is proposed, while island growth is dominant for the PZT films. *P-E* measurements of the PZT films were carried out at an applied voltage of 5V. The best remnant polarization P_r and coercive field E_c were found to be 28μC/cm^2 and 74.5kV/cm, respectively.

Keywords: Thin films, lead zirconate titanate, ferroelectric properties, pulsed laser deposition

1. INTRODUCTION

Thin film ferroelectrics have attracted considerable attention for a variety of applications and in particular for ferroelectric memories, piezoelectric micro-actuators and sensors, electro-optic devices and pyroelectric detectors [1, 2]. Among many types of ferroelectric materials, the lead zirconate titanate (PZT) family of perovskites and its derivatives are being intensively investigated in recent years. They have been grown on various substrates, such as Si, $SrTiO_3$ (STO), MgO and $LaAlO_3$ (LAO), to study the role of crystalline quality on electrical properties [3-5]. Silicon substrates with Pt as the bottom electrodes ($Pt/Ti/SiO_2/Si$) have been commonly used because of its good metallic properties and high oxidation resistance [6-8]. However, PZT capacitors with Pt top and bottom electrodes tend to show a strong loss in switchable polarization. Hence conducting oxide electrodes have been developed to overcome the problem of fatigue in PZT capacitors. PZT films with superior properties have been successfully obtained with $SrRuO_3$ (SRO) and $(La,Sr)CoO_3$ (LSCO) as bottom electrodes [9, 10]. It is found that $LaNiO_3$ (LNO) is an isotropic n-type metallic oxide with low resistivity of about 150-210μΩ cm at 300K comparable to that of LSCO. Since it also has a perovskite structure with a lattice constant of 0.386nm well matching with that of PZT, it can promote the oriented and even epitaxial growth of PZT thin films [5]. However, PZT capacitors using LNO as bottom electrodes were rarely investigated.

It has been recognized that epitaxial films exhibit improved properties compared to their polycrystalline film counterparts [11]. To achieve growth of epitaxial PZT films, pulsed laser deposition (PLD) technique has been employed because of its unique advantages for the film growth of multi-component metallic oxides, such as high deposition rate, stoichiometric transfer and simple operation, and especially for research of muli-layers [12-15].

The present investigation focuses on the growth of highly (001)-oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ and $LaNiO_3$ thin films on $LaAlO_3$ (001) substrates using pulsed laser deposition technique. Structures and properties of the films are also investigated.

2. EXPERIMENT

Pulsed laser deposition method was employed to fabricate PZT/LNO/LAO(001) heterostructures. A Lambda Physik KrF excimer laser beam (λ = 248nm, pulse width = 25ns) was incident on the target at an angle close to 45°. The target-substrate distance was kept at 45mm. The chamber was evacuated to a base pressure less than 2×10^{-5} Torr.

The LAO substrates were cleaned in organic solvent baths in an ultrasonic container prior to load into the chamber. The commercial LNO target was stoichiometric with purity of about 99.9%. The PZT target was fabricated by conventional solid state reaction with a composition corresponding to Zr/Ti ratio of 0.52/0.48. The laser ablation was carried out at a laser fluence of 2-5 J/cm^2 and a repetition rate of 10Hz. The films were deposited at the optimized substrate temperature of 600°C, whereas the oxygen partial pressures varied in the range from 50 to 400 mTorr.

Structure and crystallinity of the thin film samples were measured by a Shimadzu XRD-6000 X-ray diffractometer with Cu K_α radiation. Surface morphology of the thin films was characterized using a JEOL JSM-5600LV scanning electron microscope (SEM) and a Digital Instrument Multimode atomic force microscopy (AFM) operating in the tapping mode. For the measurement of the electrical properties, gold electrodes of 500μm diameter were deposited through a contact metal mask onto the top of PZT films by sputtering to serve as the top electrodes. Ferroelectric hysteresis behavior was studied using a Precision Workstation Materials Analyzer (Radiant Technologies).

3. RESULTS AND DISCUSSION

The LNO film was first deposited on LAO substrate at 600°C and oxygen pressure of 50mTorr. The PZT films were subsequently deposited on LNO films of about 100nm thickness at oxygen pressure of 200-400mTorr and the optimized substrate temperature of 600°C. Fig.1 shows XRD θ-2θ scan of a PZT/LNO/LAO (001) stack in which the PZT layer was grown under oxygen pressure of 300mTorr. It is clear that all peaks corresponded to (00*l*) diffractions and the growth relationship of PZT(001)//LNO(001)//LAO(001) was achieved. No diffraction peaks from lead deficient pyrochlore phases can be observed in the spectrum, indicating good phase purity. The formation of the ferroelectric perovskite phase may be favored by the presence of a suitable structural and chemical template, i.e., the (001) surface of the LNO bottom electrode. To investigate the in-plane alignment of the (001)-oriented PZT film, XRD ϕ-scan was performed on PZT (113) diffractions, which is shown in the inset of Fig.1. Four strong peaks of the PZT (113) diffractions were obtained at every 90° with a tilt, α, about 25°. The results shown in Fig. 1 thus suggestes that the PZT film was epitaxially grown on the LAO (001) substrate with good in-plane alignment, that is, PZT<100>//LNO<100>//LAO<100>.

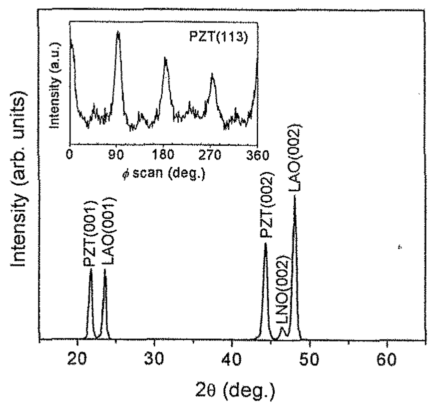

Fig.1. XRD spectra of the PZT/LNO heterostructure on the LAO (001) substrate. The inset shows ϕ–scan from 0°-360° on the PZT (113) reflection.

The ω-scan rocking curves on the PZT(002) and LNO(002) diffractions indicate that the full width at half maximum (FWHM) of each curve is 1.32° and 1.74°, respectively. The values of the FWHM of the rocking curves are relatively large. The structural disorder in LNO and PZT thin films may occur to certain extent. LAO has a rhombohedral structure. However, its interaxial angle is so close to 60° that LAO is often regarded as pseudocubic structure. LAO $(012)_r$ approximately corresponds to LAO $(001)_{p.c.}$. The unit cell parameter of the LAO pseudocubic cell is 0.379nm [16] and those of LNO and PZT (001) crystal plane are 0.386nm and 0.404nm respectively. The lattice-mismatch values can be calculated to be around 1.84% and 4.56% at room temperature for LNO/LAO and PZT/LNO interfaces respectively. The values are small enough and acceptable to obtain epitaxial growth. Thus the structural disorder was possibly by caused by the difference in the thermal expansion coefficients and non-optimum deposition conditions.

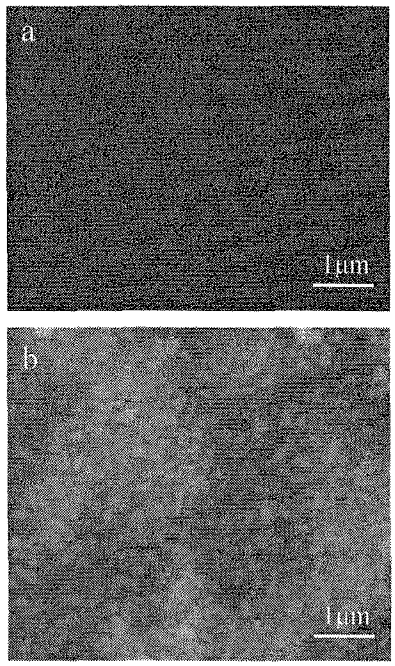

Fig.2. SEM images of two deposited thin films: (a) LNO and (b) PZT.

Typical SEM images of the surface morphology of the LNO and PZT films are shown in Fig. 2. From Fig. 2 (a), no grain boundaries and cracks can be observed on the surface of the LNO film. Hiratani et al. [17] noted that molecular-beam-epitaxy-like condition could be achieved in PLD for growth of STO on MgO(100). In the present work, it seems that the well-oriented LNO film has been obtained. Surface morphology of the epitaxial LNO film was investigated using an AFM. Typically, images at 2 × 2 μm^2 scale were captured, which is shown in Fig. 3 (a). It is clear that the film was very flat and smooth. Root-mean-square (rms) roughness of the randomly selected region was calculated to be 0.4-0.6nm, which is on the unit cell level. Thus layer-by-layer growth mode (Frank-Merwe mode) for the LNO films was suggested to produce the single crystal film, in which case the extension of the smallest stable nucleus occurred overwhelmingly in two dimensions resulting in the formation of planar sheets. In this growth mode the adatoms are more strongly bound to the substrate than to each other. The first complete monolayer is then covered with a somewhat less tightly bound second layer. Therefore a smooth surface can form [18]. Whereas as shown in Fig. 2 (b), the island formation during the deposition of the PZT thin film is obvious, which happens when atoms or molecules in the deposit are more strongly bound to each other than to the substrate and the smallest stable clusters grow in three dimensions to form islands. Wakiya et al. [19] proposed Stranski-Krastanov (S-K mode) growth mechanism for the PZT thin films on MgO(001) single crystal substrates prepared by MOCVD. They reported that the growth of layer-like PZT thin film could be observed up to thickness of 1.0-2.0nm and thereafter the formation of island structure began. The transition from two- to three-dimensional growth is not completely understood now, but film-substrate lattice mismatch, strain energy accumulates in the growing film will all disturb layer growth. When released, the high energy at the deposit-intermediate-layer interface may trigger island formation. AFM image with 1μm × 1μm scan area of the (001)-oriented PZT film is shown in Fig.3 (b). The surface was smooth and comprised densely packed round-shaped grains. The laser-induced droplets from the PZT target can also be observed, which are usual for a PLD process. The rms surface roughness was between 6-10nm.

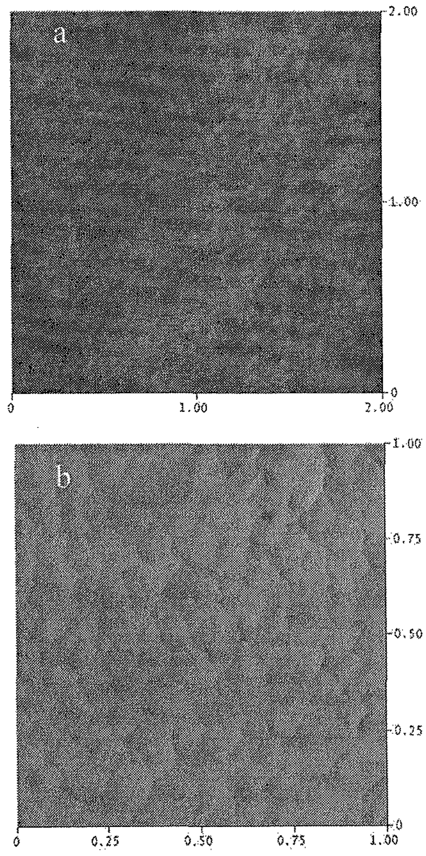

Fig.3. AFM images: (a) LNO and (b) PZT thin films on the LAO (001) substrates.

Fig. 4 shows the *P-E* hysteresis loop at a frequency of 1kHz and an alternating applied voltage of 5V for the PZT/LNO/LAO ferroelectric capacitor structure with Au as top electrode. The measurement configuration is schematically illustrated in the inset. The thickness of the PZT layer is about 200nm. The best value of saturation polarization at 5V is 58μC/cm^2, while the corresponding remnant polarization P_r and the coercive field E_c were found to be 28μC/cm^2 and 74.5kV/cm, respectively. These values are comparable to those obtained previously by others [3-5]. The high values obtained in this work are possibly due to the excellent epitaxial quality of the PZT films. It is noted that the hysteresis loop is a little asymmetric in shape along the abscissa, which means that an internal bias field has built up in the PZT film due to the inhomogeneous distribution of space charges. The shift towards the negative field direction (from the bottom electrode to the top electrode) indicates an internal field directed from the top electrode towards the bottom electrode.

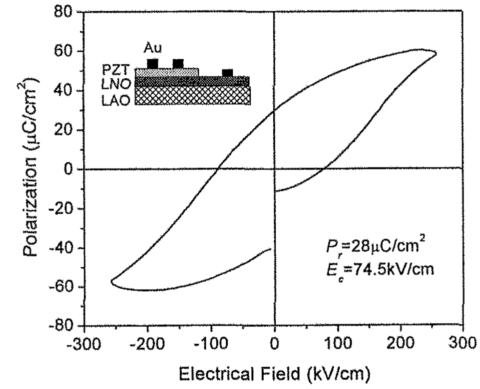

Fig.4. Ferroelectric hysteresis loop of the epitaxial PZT thin film on LAO (001) substrate where the inset shows the schematic illustration of measurement configuration.

4. CONCLUSIONS

Highly (001)-oriented PZT thin films with good in-plane alignment have been successfully synthesized on LAO (001) substrates with (001)-oriented LNO films as bottom electrodes by pulsed laser deposition method. It is observed that the LNO thin film is a good selection of template since it can promote the preferred growth of perovskite PZT thin films. The Au/PZT(001)/LNO(001) capacitor structure exhibits very good electrical properties, which is promising for the ferroelectric memory elements.

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