

Growth and Properties of (001)-oriented Pb(Zr_{0.52}Ti_{0.48})O₃/LaNiO₃ Films on Si(001) Substrates with TiN Buffer Layers

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Abstract—Pulsed laser deposition has been used to grow Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT)/LaNiO₃ (LNO) heterostructures with restricted crystallographic orientations on bare Si(001) and SiO₂-coated Si(001) substrates, using TiN buffer layers. The effect of background gas pressure on orientation of the thin films was investigated in detail. XRD analyses showed that under optimized conditions, (001)-oriented PZT/LNO/TiN heterostructures could be grown on either Si(001) or SiO₂/Si substrates. The (001)-textured PZT films had remnant polarizations as high as 23μC/cm², and also had a low coercive field. Up to 10¹⁰ switching cycles have been achieved in these PZT films.

Keywords — Pulsed laser deposition; Ferroelectric thin films; PZT; Crystallographic orientation; Ferroelectric properties.

I. INTRODUCTION

IN recent years, perovskite oxide thin films have become one of the widely studied materials, due to their wide applications in microelectronic and optoelectronic devices, including non-volatile ferroelectric memories [1, 2], piezoelectric micro-actuators and sensor [3 - 5], superconducting quantum interference devices (SQUID), optical waveguides, and microwave devices [6, 7]. Among many types of perovskite thin films, lead zirconate titanate (PZT) is being intensively studied due to its large remnant polarization and relatively high Currie temperature. Typically, submicron films are deposited onto various oxide single crystal substrates, such as MgO [8], SrTiO₃ (STO) [9], LaAlO₃ (LAO) and yttria stabilized zirconia (YSZ) [10], over a wide range of deposition conditions. However, these substrates are not only expensive but also are limited to diameters less than 5 cm, and especially have unacceptably large losses. Much research has been carried out on the integration of high-quality ferroelectric thin films onto technically practical Si wafers, in hope of achieving compatibility with current Si integrated circuit (IC) processing. However, it is difficult to deposit perovskite

thin films directly on Si single crystal substrates due to inter-diffusion and high lattice mismatches.

Polycrystalline ferroelectric thin films are conventionally grown on Pt-coated Si substrates with Pt top contact electrodes to form metal-insulator-metal (MIM) capacitor structures, because Pt has low electrical resistance and a high oxidation resistance [11-13]. However, the high-angle grain boundaries in ferroelectric thin films and poor interfaces between the ferroelectric layer and metal electrode deteriorate device performance. Moreover the pyrochlore phase is frequently observed in PZT films even though PZT targets contain excess lead oxide to overcome the loss of Pb. Hence conducting oxide electrodes have been developed to surmount the above problems in PZT capacitors [14]. PZT films with superior properties have been successfully obtained with YBa₂Cu₃O₇ (YBCO), SrRuO₃ (SRO) and (La,Sr)CoO₃ (LSCO) as bottom electrodes [14]. However, YBCO superconductor layers have not been seriously considered as suitable electrodes for integrated ferroelectric capacitors because of its low chemical stability and poor surface roughness [15]. The presence of outgrowths in SRO films will also limit their application as electrodes [16]. LaNiO₃ (LNO) is an isotropic n-type metallic oxide with a low resistivity of about 150-210μΩ cm at 300K, comparable to that of LSCO but having a simpler composition than LSCO. Since LNO also has a perovskite structure with a lattice constant of 0.386nm that well matches that of PZT, it can promote oriented and even epitaxial growth of PZT thin films [17].

In order to integrate perovskite oxide films on Si substrates without inter-diffusion and reactions, an appropriate approach is the introduction of buffer layers which are lattice-matched with both perovskite thin films and silicon, that can be grown at relatively low temperatures, and can act as diffusion barriers. TiN thin films have attracted much attention for their potential application as a chemically stable buffer layer on Si. Epitaxial or oriented

TiN films are preferred for the deposition of ferroelectric thin films since epitaxial films demonstrate better properties than their polycrystalline counterparts.

In this study, we have grown (001)-textured PZT thin films with LNO bottom electrodes on TiN buffer layers on Si(001) and SiO₂/Si(001) substrates, using the pulsed laser deposition (PLD) technique. The structure, surface morphology and ferroelectric properties of the PZT films have also been investigated.

II. EXPERIMENTAL PROCEDURE

A pulsed KrF excimer laser beam ($\lambda = 248\text{nm}$, pulse width = 25ns, repetition rate = 1-50 Hz) is incident on the target at an angle close to 45° with a spot size around 1mm x 4mm. The chamber is evacuated to a base pressure less than 1×10^{-5} Torr. The Si and SiO₂/Si substrates were first cleaned in organic solvent baths in an ultrasonic container. The bare Si substrates were then dipped in 20% HF solution for 2 minutes to remove the surface native oxide prior to loading into the chamber. The Pb(Zr_{0.52}Ti_{0.48})O₃ target with 10wt.% PbO excess was fabricated by conventional solid state reaction processing. The commercial LNO and TiN targets were stoichiometric with purities of about 99%. The laser ablation was carried out at a laser fluence of 3J/cm² and a repetition rate of 10Hz for all the targets. The target-substrate distance was kept at 4cm. The films were deposited at the optimized substrate temperature of 600°C, whereas the ambient pressure was varied in the range 0.01 to 300 mTorr.

An X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu K_{α} radiation was used to characterize the crystallographic structure of the thin film samples. The microstructure and surface morphology of the thin films were characterized using scanning electron microscopy (SEM, JEOL JSM-5600LV) and a Seiko SPA400 atomic force microscopy (AFM). To measure the electrical properties of the PZT thin films, 200 μm -diameter Pt electrodes were sputter deposited through a shadow mask onto the top of PZT films to serve as the top electrodes. Ferroelectric hysteresis behavior and fatigue properties were measured using a Precision Workstation Materials Analyzer (Radiant Technologies, USA).

III. RESULTS AND DISCUSSION

Fig.1 shows XRD spectra for TiN thin films deposited on Si (001) and SiO₂/Si substrates at a substrate temperature of 600°C and with a laser fluence of 3J/cm², and with nitrogen pressures ranging from 0.01 to 100mTorr. It can be seen that the films deposited at the N₂ pressures 0.01, 50 and 100 mTorr show only (200) out of plane texture the (the

peak at about 32° is a Si(002) peak). No noticeable orientation variation is observed with the increase in nitrogen pressure. The difference in the intensity of (200) diffraction peaks resulted from the different deposition durations and hence different thickness of the TiN films.

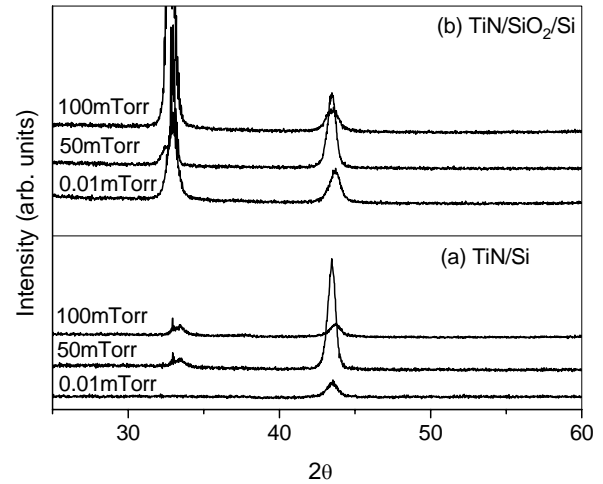


Fig.1. XRD spectra of TiN thin films deposited on (a) Si (001) and (b) SiO₂/Si substrates at a substrate temperature of 600°C and with a laser fluence of 3J/cm², with different nitrogen pressures. (The peaks at 32° are Si(002) peaks.)

It is also of interest to investigate the orientation of TiN thin films on SiO₂/Si substrates since amorphous SiO₂ insulator layers are often used in Si IC fabrication processing. The XRD spectra for TiN/SiO₂/Si structures are shown in Fig.1 (b). The deposition conditions are the same as those for TiN thin films on bare silicon substrates. It is evident that all the TiN films on SiO₂/Si also show (200) texture, even though the underlayers are amorphous.

TiN has a cubic crystal structure. In the absence of strain energy effects, (100) texture is thought to be due to surface energy minimization [18, 19].

Fig.2 shows XRD spectra of the PZT/LNO/TiN heterostructures on the Si(001) and SiO₂/Si substrates deposited at 600°C and under various background gas pressures. The TiN films which were deposited for 20min under a nitrogen pressure of 50mTorr have a (100) texture. When the LNO layers were deposited under a oxygen pressure of 50mTorr and the PZT layers under a 300mTorr oxygen pressure, all the peaks from PZT/LNO heterostructures corresponded to (00l) diffractions whether they were on Si(001) (Fig. 2(a)) or SiO₂/Si substrates (Fig. 2(b)), indicating that both the PZT and LNO films were (001) textured.

When the LNO film is deposited at the oxygen pressure 100mTorr, a mix of (001) and (110) textures are observed in the LNO and PZT films, as shown in Fig. 2(c) and (d) for Si(001) and SiO₂/Si substrates, respectively. These results

show that the oxygen pressure plays a key role in texture development in the LNO films, and that the orientation of the PZT films is strongly correlated with that of LNO underlayers.

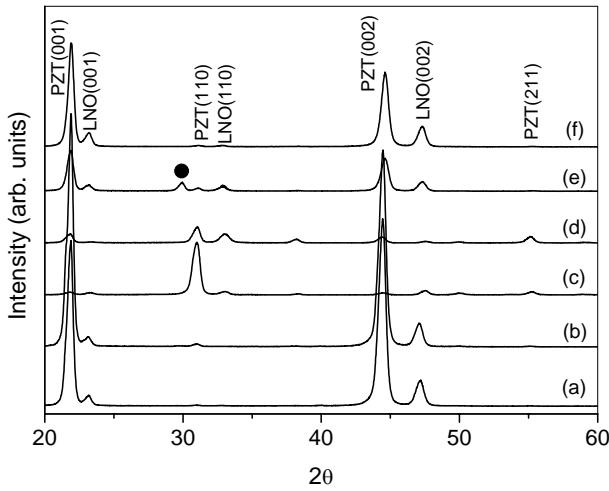


Fig.2. XRD spectra of PZT/LNO/TiN heterostructures deposited under different oxygen pressures. (a),(b): 50mTorr for LNO and 300mTorr for PZT; (c), (d): 100mTorr for LNO and 300mTorr for PZT; and (e), (f): 50mTorr for LNO and 100mTorr for PZT. (a), (c) and (d): on Si substrates; (b), (d) and (e): on SiO₂/Si substrates. (● pyrochlore phase)

To study the effect of oxygen pressure on the growth texture of PZT films, the PZT films were also deposited on (001)-oriented LNO/TiN coated Si and SiO₂/Si substrates under an oxygen pressure of 100mTorr. The corresponding XRD spectra are shown in Fig. 2 (e) and (f), respectively. It is clear that the preferred (001) texture could also be obtained in the PZT films deposited under 100mTorr of O₂ (Fig. 2(f)), but occasionally the pyrochlore phase forms due to insufficient reaction between the ambient oxygen and Pb ions in laser-induced plume, as shown in Fig. 2(e). Therefore, it is suggested that relatively high oxygen pressures favor the growth of completely perovskite PZT films.

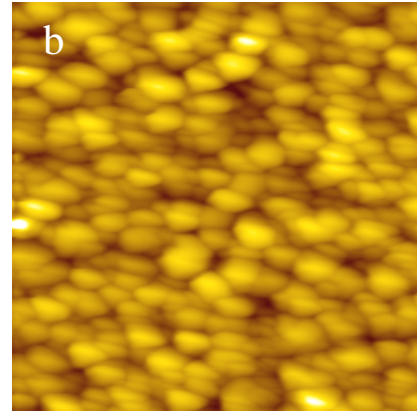
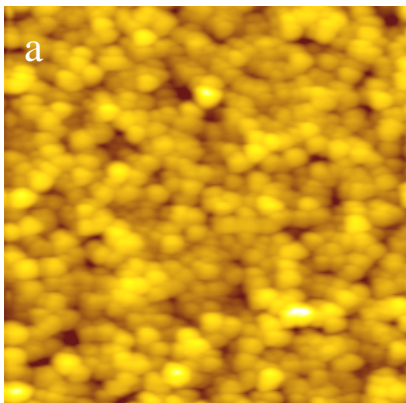


Fig.3. Typical AFM images of (a) (001)-textured PZT thin films on Si (001) substrates, and (b) PZT films with mixed (001) and (110) texture grown on SiO₂/Si substrates.

Fig. 3a shows an AFM image with a $2 \times 2 \mu\text{m}^2$ scan area of a (001)-textured PZT thin film with LNO/TiN underlayers grown on a Si(001) substrate, where the PZT, LNO and TiN layers were deposited under a background gas pressure of 300, 50 and 50mTorr, respectively. The film consists of close-packed round-shaped particles with a homogeneous size distribution. No cracks are observable and the surface is very smooth with root mean square (rms) roughness of 5nm. AFM images of (001)-textured PZT films on SiO₂/Si substrates show similar results. No significant difference in surface morphology can be found for the films deposited at other oxygen pressures in the range 200-400mTorr. An AFM image at $2 \times 2 \mu\text{m}^2$ scan scale of PZT film with mixed (001) and (110) texture on a SiO₂/Si substrate is shown in Fig. 3(b). The particles are a little large compared to the (001) textured PZT films, and the surface roughness is approximate 11nm.

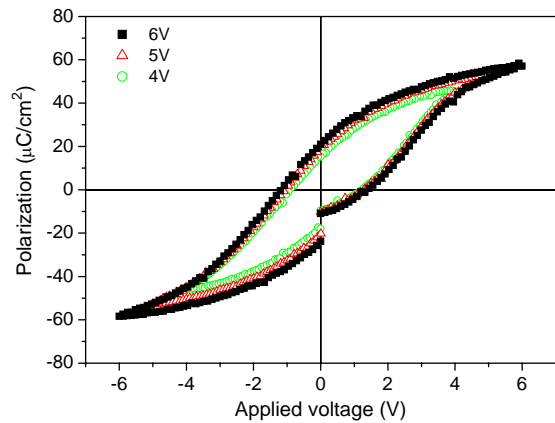


Fig.4. *P-E* hysteresis loops for a (001) textured PZT film on LNO and TiN underlayers and on SiO₂/Si substrate, at applied voltages of 4, 5 and 6V.

Fig. 4 shows typical hysteresis loops for the (001)-textured PZT films on LNO/TiN/SiO₂/Si, measured at a frequency of 1kHz and triangular pulses of ± 4 , ± 5 and ± 6 V. The PZT film was about 200nm thick. The loops are nearly saturated at the applied voltages. As can be seen, the

remnant polarization and coercive field at 6V of a (001)-textured PZT film on a LNO/TiN/SiO₂/Si substrate are 23.2 $\mu\text{C}/\text{cm}^2$ and 55kV/cm, respectively. They are about 22.7 $\mu\text{C}/\text{cm}^2$ and 45kV/cm respectively for the (001)-textured PZT film on a LNO/TiN/Si(001) substrate. These remnant polarization values are much higher than those of polycrystalline PZT films on Pt-coated Si substrates, which about 10 $\mu\text{C}/\text{cm}^2$ [20]. The coercive fields were also low enough that the polarization in these films can be switched using an applied voltage of 5V, which is standard for integrated circuits in Si.

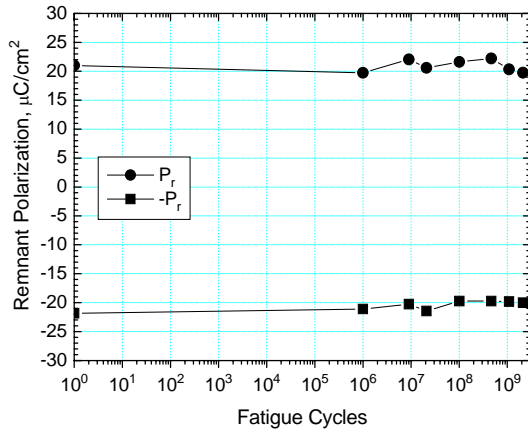


Fig. 5. Polarization fatigue of a PZT/LNO heterostructure grown on a SiO₂/Si substrate with a TiN buffer layer.

The film resistivity at 5V is typically in the range of 5×10^9 to $6.5 \times 10^{10} \Omega \text{ cm}$, which is a suitable value for electronic memory application [14] and can be attributed to better control over the deposition parameters, including the film thickness, lead deficiency, etc. The polarization fatigue of a (001)-textured PZT/LNO/TiN heterostructure grown on a SiO₂/Si substrate with a Pt top electrode is shown in Fig. 5. Approximately 97% of the remnant polarization can still be maintained after 10^{10} polarization switching cycles. The result is markedly better than observed for Pt/PZT/Pt capacitors in which the remnant polarization often significantly drops after only 10^6 switching cycles, indicating that LNO is a good oxide electrode candidate for the replacement of Pt.

IV. SUMMARY

(001)-textured PZT thin films have been successfully grown using the PLD technique on Si(001) and SiO₂/Si(001) substrates with LNO as bottom electrodes and TiN used in buffer layers. TiN films tend to form preferred (100) texture under a wide range of nitrogen pressures, while perovskite PZT and LNO films with a (110) naturally occurring texture are sensitive to oxygen pressure. (001) texture can be obtained only at optimized deposition parameters. The (001)-oriented PZT/LNO/TiN films on Si(001) and SiO₂/Si

show good ferroelectric properties. Fatigue-free characteristics can be observed in Pt/PZT/LNO capacitors, even up to 10^{10} polarization switching cycles. These results demonstrate that the PZT/LNO/TiN structure provides a suitable solution to integration of PZT films on Si substrates for microelectronic applications.

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