EPITAXIAL $Pb(Zr_{0.40}Ti_{0.60})O_3/SrRuO_3$ AND $PbTiO_3/SrRuO_3$ MULTILAYER THIN FILMS PREPARED BY MOCVD AND RF SPUTTERING*

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ABSTRACT

Epitaxial $SrRuO_3$ thin films were deposited by RF sputtering on $SrTiO_3$ or MgO substrates for use as underlying electrodes. On these conductive substrates, epitaxial $Pb(Zr_{0.35}Ti_{0.65})O_3$ (PZT) and $PbTiO_3$ (PT) thin films were deposited by metalorganic chemical vapor deposition (MOCVD). X-ray diffraction (XRD), RBS channeling (RBS), transmission electron microscopy (TEM) and optical waveguiding were used to characterize the phase, microstructure, defect structure, refractive index, and film thickness of the deposited films. The PZT and PT films were epitaxial and c-axis oriented. 90° domains, interfacial misfit dislocations and threading dislocations were the primary structural defects, and the films showed a 70% RBS channelling reduction. Hysteresis and dielectric measurements of epitaxial PZT ferroelectric capacitor structures formed using evaporated Ag or ITO glass top electrode showed: a remanent polarization of 46.2 mC/cm^2, a coercive field of 54.9 KV/cm, a dielectric constant of 410, a bipolar resistivity of ~5.8×10^9 Ω-cm at a field of 275 KV/cm, and a breakdown strength of >400 KV/cm.

INTRODUCTION

Current interest in ferroelectric thin films results from the numerous potential applications for these materials which utilize the unique dielectric, pyroelectric, electro-optic, acousto-optic, and piezo-electric properties of ferroelectrics materials[1]. The synthesis of thin films of the lead-based ferroelectrics, $PbTiO_3$, $Pb(Zr_xTi_{1-x})O_3$ (PZT), $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$ (PLZT), etc., using a variety of techniques (e. g., sol-gel, sputtering, laser ablation, MOCVD) and the resulting properties of the films have been studied extensively [1]. For many applications, such as non-volatile dynamic random access memory (DRAM) or electro-optic waveguide modulators, a highly textured microstructure is preferable or essential. Ferroelectric film deposition using MOCVD has been widely reported and has been shown to be able to produce film microstructures from random polycrystalline to highly epitaxial [2].

We have systematically studied the effects of gas phase composition, substrate materials, substrate orientation, and deposition temperature on the phase, composition, crystallinity, morphology and domain structure of epitaxial thin films of $PbTiO_3$ [3-5]. We have also discussed the effects of the choice of substrate material on the crystallinity, microstructure, domain formation, defect structure and optical properties of $PbTiO_3$ thin films [6-7]. In this paper, we report preliminary results on the growth, characterization and properties of $Pb(Zr_{0.35}Ti_{0.65})O_3$ and $PbTiO_3$ thin films deposited on $SrRuO_3$ buffered $SrTiO_3$ and MgO substrates using MOCVD.

EXPERIMENTAL

Epitaxial $SrRuO_3$ thin films were deposited on epitaxial-grade (001) $SrTiO_3$ substrates by 90° off-axis, RF magnetron sputtering at a growth pressure of 15 Pa and deposition temperature of 650°C.

Sputter deposition commenced at a power of 60W and a Ar/O_2 flow rate of 120/80 sccm. The growth rate of the $SrRuO_3$ layers was estimated from RBS to be ~160Å per hour. For MgO (001) substrates, the same growth conditions were used, however, an additional $BaTiO_3$ (100) buffer layer was used between the $SrRuO_3$ and the MgO substrate to improve the crystallinity of the $SrRuO_3$[8].

PZT and PT thin film depositions were carried out in a low pressure, horizontal, cold wall reactor with a resistive substrate heater. Tetraethyl lead, $Pb(C_2H_5)_4$, zirconium t-butoxide, $Zr(OC(CH_3)_3)_4$, and titanium isopropoxide, $Ti(OC_3H_7)_4$, (Morton International, Advanced Materials, Danvers, MA) were chosen as the metal ion precursors. Details of the reactor design and deposition methods have been previously reported[3-7,9]. The growth conditions for deposition of $PbTiO_3$ have been previously reported [3-6] and those for growth of $Pb(Zr_{0.35}Ti_{0.65})O_3$ are shown in Table I.

Table I. Growth Conditions

Substrate temperature	700°C	
Reactor pressure	8 torr	
OM precursor temperature	$Ti(OC_3H_7)_4$	- 39-40 °C
	$Pb(C_2H_5)_4$	- 27-28 °C
	$Zr(OCH_3)_4$	- 29-30 °C
OM precursor pressure	$Ti(OC_3H_7)_4$	- 37 torr
	$Pb(C_2H_5)_4$	- 150 torr
	$Zr(OC(CH_3)_3)_4$	- 400 torr
Flow rate of reactant gas (O_2)	200 sccm	
Flow rate of OM and carrier gas (N_2)	$Ti(OC_3H_7)_4$	- 35 sccm
	$Pb(C_2H_5)_4$	- 50 sccm
	$Zr(OC(CH_3)_3)_4$	- 25 sccm
Flow rate of background gas (N_2)	600 sccm	
Film thickness	0.2-1.0 μm	
Film growth rate	40 Å/min.	
Substrates	MgO(001), $SrRuO_3/SrTiO_3$ (001)	
	$SrRuO_3/SrTiO_3$ (001)	

X-ray θ-2θ diffraction and θ-rocking spectra of the films were obtained using a Rigaku diffractometer and a 10 kW $Cu_{K\alpha}$ rotating anode x-ray source. Descriptions of the TEM sample preparation and methods have been previously reported[3-4]. The RBS and channeling methods as well as details of the ion-channeling apparatus have been described previously [10]. Prism-coupling waveguide experiments were performed with a Metricon 2010 Prism-Film coupler using a HeNe laser (632.8 nm); this system has been described elsewhere [9]. Ferroelectric hysterisis, bipolar resistance, and dielectric breakdown measurement were obtained using a Radiant Technologies RT66A tester, and the dielectric constant (1 MHz) was obtained using a HP4192A impedance analyzer.

RESULTS AND DISCUSSION

Using the growth conditions specified previously for PT [3-6] and in Table I for PZT, the films produced were pure perovskite phase with a single-crystalline structure. Shown in Fig. 1 are the two-circle XRD result for two epitaxial PZT films grown on epitaxial $SrRuO_3$(001) buffered $SrTiO_3$(001) [Fig. 1a, θ–2θ; Fig. 1b, θ-rocking PZT(002); Fig. 1c, θ-rocking PZT(200)] and epitaxial $SrRuO_3$(001)/$BaTiO_3$(001) buffered $SrTiO_3$(001)) [Fig. 1d, θ–2θ; Fig. 1e, θ-rocking PZT(002); Fig. 1f, θ-rocking PZT(200)]. The full width at half maximum for the PZT(200) peaks in the rocking curves were 0.75° and 0.93° for the $SrTiO_3$ and MgO substrates, respectively. The thickness of the $SrRuO_3$ and $BaTiO_3$ buffer layers were ~330Å determined by RBS and TEM measurements. From the XRD data, we determine that the films have a nominal composition of $Pb(Zr_{0.35}Ti_{0.65})O_3$; are *c*-axis oriented with the presence of the PZT(100) reflections resulting from 90° domain formation [6], and are epitaxial grown on both substrates. From the integrated intensity ratio of the PZT(002) and PZT(200) reflections, we determine that the films grown on

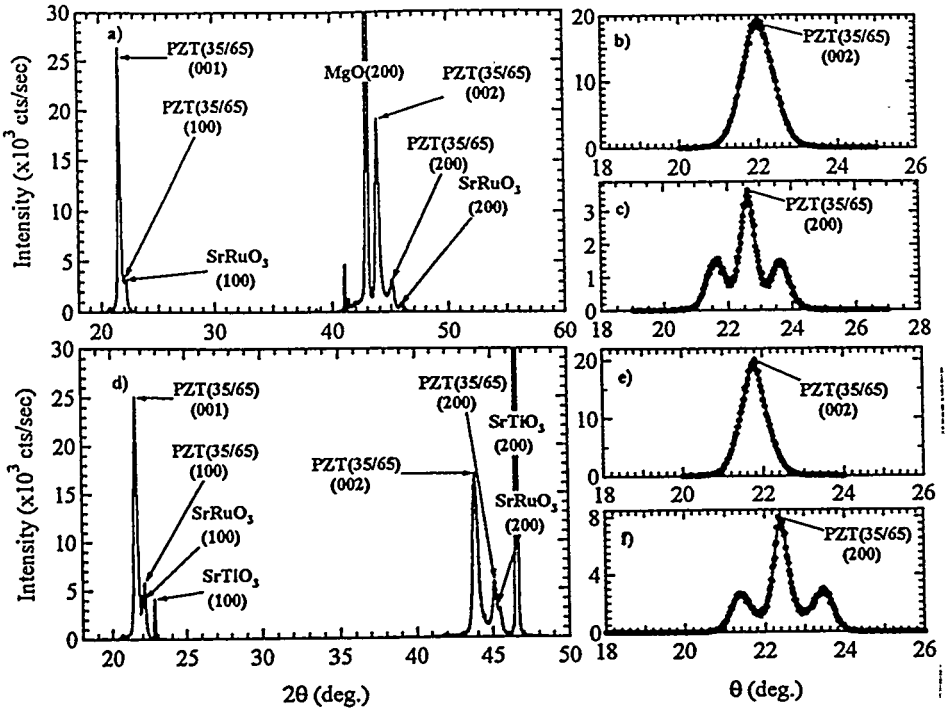

Figure 1. XRD result for $Pb(Zr_{0.35}Ti_{0.65})O_3$ thin films grown on epitaxial $SrRuO_3(001)$ buffered $SrTiO_3(001)$ [Fig. 1a, θ–2θ; Fig. 1b, θ-rocking PZT(002); Fig. 1c, θ-rocking PZT(200)] and epitaxial $SrRuO_3(001)/BaTiO_3(001)$ buffered $SrTiO_3(001)$) [Fig. 1d, θ–2θ; Fig. 1e, θ-rocking PZT(002); Fig. 1f, θ-rocking PZT(200)].

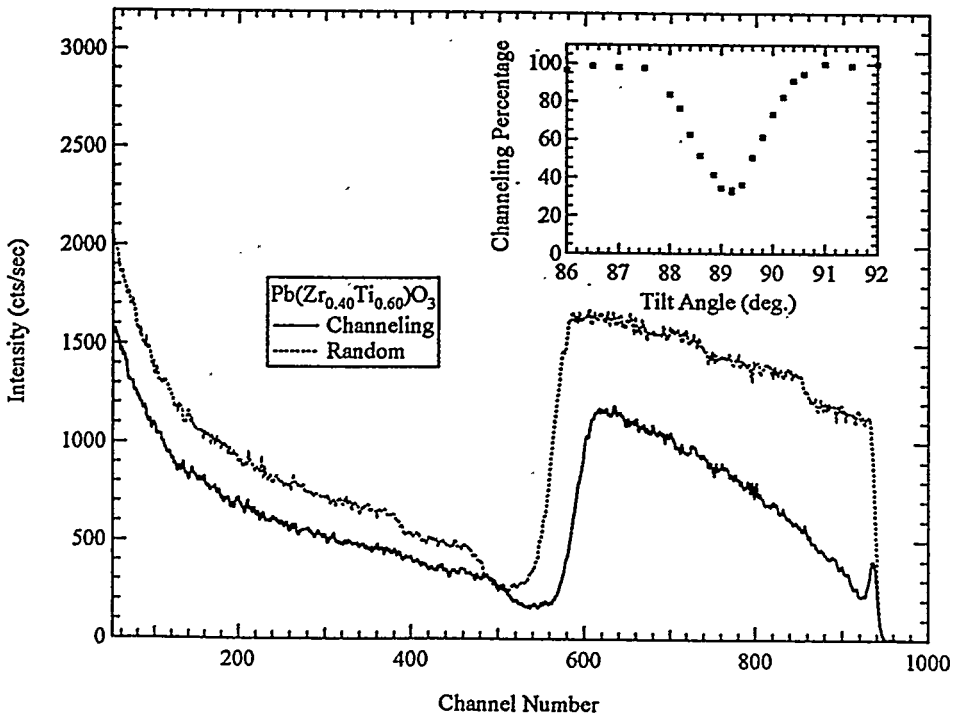

Figure 2. RBS channelling result for epitaxial $Pb(Zr_{0.35}Ti_{0.65})O_3$ thin films grown on $SrTiO_3(001)$. The inset shows the angular channelling width.

$SrTiO_3$ and MgO contain a volume fraction of 90° domain of ~32% and ~29%, respectively.

The epitaxial nature of the films implies that outside of twinned, *c*-axis oriented regions, there are no other orientations of PZT grains of any significant volume fraction within the film.

In Fig. 2, we show the results of RBS channelling measurements on the $Pb(Zr_{0.35}Ti_{0.65})O_3$ grown directly on $SrTiO_3(001)$, the maximum channelling yield reduction at the Pb signal is ~71%. The inset of Fig. 2 shows the angular channelling width; the full width at half minimum is ~1.6°.

In Fig. 3, we show the cross-section TEM image of a $PbTiO_3$ (001) / $SrRuO_3$ (001) / $SrTiO_3$ (001) epitaxial film. The image shows the films is epitaxial *c*-axis oriented, with 90° domains and threading dislocations being the primary structural defects. The thickness of the $SrRuO_3$ layer is ~330Å. Note that the 90° domains visible in the image clearly nucleate at

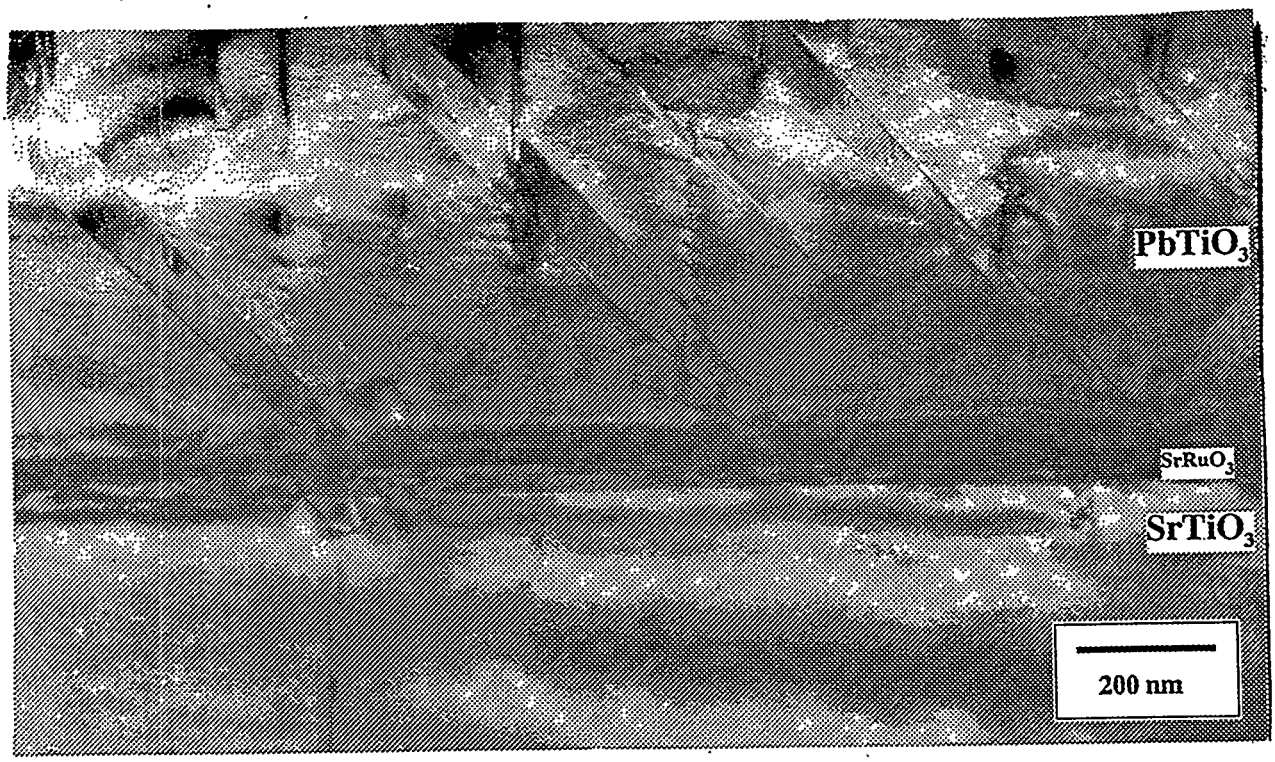

Figure 3. Cross-sectional TEM image of a $PbTiO_3(001)$ film deposited on a $SrTiO_3(001)$ substrate with a $SrRuO_3(001)$ epitaxial electrode buffer layer. The image shows that dominate defects in the film a 90° domains and threading dislocations

structural defects in the substrate. The strain contrast associated with the substrate defects sites appears to propagate directly through the $SrRuO_3$ layer into to the $PbTiO_3$ layer. In addition, the threading dislocations appear to be normal to the substrate/film interface and to propagate through the 90° domains. This would indicate that these dislocations form prior to the ferroelectric phase transition while the films is in the cubic state. In Fig. 4, we show the high-resolution cross-sectional TEM image of the $PbTiO_3(001)/SrRuO_3(001)/SrTiO_3(001)$ interfaces. The image shows that the interfaces a atomically sharp; note that the $PbTiO_3(001)/SrRuO_3(001)$ interface appears to be cleaner that the $SrRuO_3(001)/SrTiO_3(001)$ interface indicating that the deposition of the buffer layer appears to improve the quality of the substrate surface resulting in an improved ferroelectric film. Optical waveguiding experiments showed that the $Pb(Zr_{0.35}Ti_{0.65})O_3(001)$ film had high ordinary refractive index of 2.5811 at 632.8 nm.

Shown in Fig. 5 is the polarization hysteresis P-E curve of a $Ag/Pb(Zr_{0.35}Ti_{0.65})O_3(001)/SrRuO_3(001)/SrTiO_3(001)$ capacitor. The results of the measurement were: a remanent polarization if 46.2 $\mu C/cm^2$, the saturation polarization was 55.1 $\mu C/cm^2$, a coercive field of 54.9 KV/cm^2, and a bipolar resistivity of $>5.8x10^9$ Ω-cm at 275 KV/cm. The dielectric breakdown strength was >400KV/cm (this field strength was the limit of our instrument). The dielectric constant at 1 Mhz was 410. These electrical measurements indicate that the film properties are a significant fraction of those of bulk material (e. g., ~70% of the single crystal remanent polarization). However, we measured a volume fraction of 90° domains of ~30%. If we assume that only a small portion of this twin volume undergoes 90° switching, then this volume fraction of the film will not contribute to the measured remanent polarization; consequently, the true remanent polarization could be as high as ~60 $\mu C/cm^2$, very close to that of the bulk material at this composition. In addition, we note that the growth conditions for these PZT films have not been optimized and, in principle, improvements in the films crystallinity and properties could be achieved. These results indicate that through the use of epitaxial buffer layers and electrode materials, the very high structural perfection can be achieved with commensurate bulk-like properties in epitaxial ferroelectric films.

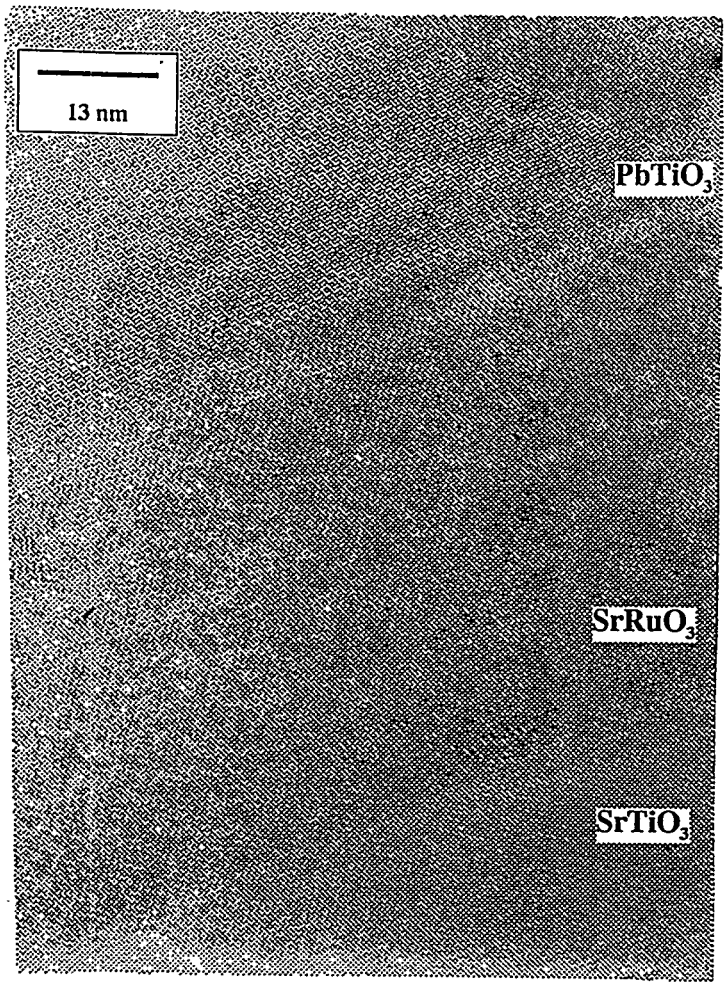

Figure 4. High resolution transmission electron microscope image of the $PbTiO_3(001)$ / $SrRuO_3(001)$ / $SrTiO_3(001)$ interfaces showing that the individual layer interfaces are atomically sharp.

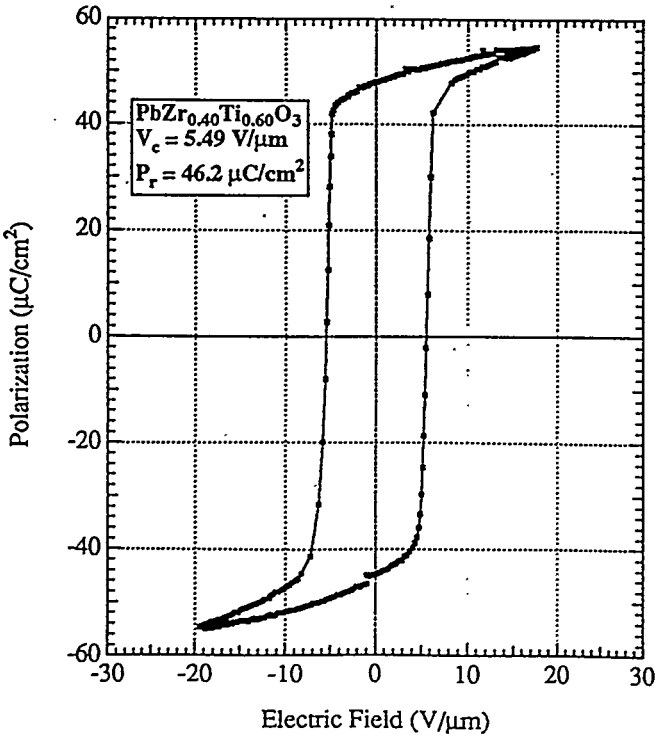

Figure 5. The ferroelectric polarization P-E hysteresis curve for a Ag / $Pb(Zr_{0.35}Ti_{0.65})O_3(001)$ /$SrRuO_3(001)$ / $SrTiO_3(001)$ capacitor: the remanent polarization was 46.2 $\mu C/cm^2$, the saturation polarization was 55.1 $\mu C/cm^2$, a coercive field of 54.9 KV/cm^2, and a bipolar resistivity of $>5.8x10^9$ Ω-cm at 275 KV/cm. The dielectric breakdown strength was >400KV/cm; this was the limit of our instrument.

ACKNOWLEDGMENTS

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