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*

C. M. Foster, R. Csencsits, P. M. Baldo, G. R. Bai, Z. Li, and L. E. Rehn

Materials Science Division, Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

L. A. Wills and R. Hiskes

Hewlett Packard Laboratories, Hewlett-Packard Company
3500 Deer Creek Road, Palo Alto, CA 94304

D. Dimos and M. B. Sinclair

Sandia National Laboratories, Albuquerque, NM 87185

December 1994

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.


*This work was supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Science, under contract #W-31-109-ENG-38 under a joint CRADA with Hewlett-Packard Company #C9301701.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
EPITAXIAL Pb(Zr0.40Ti0.60)O3/SrRuO3 AND PbTiO3/SrRuO3 MULTILAYER THIN FILMS PREPARED BY MOCVD AND RF SPUTTERING

C. M. FOSTER, R. CSENCSITS, P. M. BALDO, G. R. BAI, Z. LI, AND L. E. REHN
Materials Science Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439

L. A. WILLS AND R. HISKES
Hewlett Packard Laboratories, Hewlett-Packard Company, 3500 Deer Creek Road, Palo Alto, CA 94304

D. DIMOS AND M. B. SINCLAIR
Sandia National Laboratories, Albuquerque, NM 87185

ABSTRACT

Epitaxial SrRuO3 thin films were deposited by RF sputtering on SrTiO3 or MgO substrates for use as underlying electrodes. On these conductive substrates, epitaxial Pb(Zr0.35Ti0.65)O3 (PZT) and PbTiO3 (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 channeling 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/cm2, a coercive field of 54.9 KV/cm, a dielectric constant of 410, a bipolar resistivity of ~5.8x109 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 ferroelectric materials [1]. The synthesis of thin films of the lead-based ferroelectrics, PbTiO3, Pb(Zr1-xTi1-x)O3 (PZT), (Pb1-xLa_x)(ZrTi1-y)O3 (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 PbTiO3 [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 PbTiO3 thin films [6-7]. In this paper, we report preliminary results on the growth, characterization and properties of Pb(Zr0.35Ti0.65)O3 and PbTiO3 thin films deposited on SrRuO3 buffered SrTiO3 and MgO substrates using MOCVD.

EXPERIMENTAL

Epitaxial SrRuO3 thin films were deposited on epitaxial-grade (001) SrTiO3 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 an Ar/O₂ flow rate of 120/80 sccm. The growth rate of the SrRuO₃ layers was estimated from RBS to be ~160Å per hour. For MgO (001) substrates, the same growth conditions were used, however, an additional BaTiO₃ (100) buffer layer was used between the SrRuO₃ and the MgO substrate to improve the crystallinity of the SrRuO₃.[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(C₂H₅)₄, zirconium t-butoxide, Zr(OC(CH₃)₃)₄, and titanium isopropoxide, Ti(OC₃H₇)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 PbTiO₃ have been previously reported [3-6] and those for growth of Pb(Zr₀.₃₅Ti₀.₆₅)O₃ are shown in Table I.

<table>
<thead>
<tr>
<th>Table I. Growth Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
</tr>
<tr>
<td>Reactor pressure</td>
</tr>
<tr>
<td>OM precursor temperature</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>OM precursor pressure</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Flow rate of reactant gas (O₂)</td>
</tr>
<tr>
<td>Flow rate of OM and carrier gas (N₂)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Flow rate of background gas (N₂)</td>
</tr>
<tr>
<td>Film thickness</td>
</tr>
<tr>
<td>Film growth rate</td>
</tr>
<tr>
<td>Substrates</td>
</tr>
</tbody>
</table>

X-ray θ-2θ diffraction and θ-rocking spectra of the films were obtained using a Rigaku diffractometer and a 10 kW CuKα 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 hysteresis, 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 SrRuO₃(001) buffered SrTiO₃(001) [Fig. 1a, θ-2θ; Fig. 1b, θ-rocking PZT(002); Fig. 1c, θ-rocking PZT(200)] and epitaxial SrRuO₃(001)/BaTiO₃(001) buffered SrTiO₃(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 SrTiO₃ and MgO substrates, respectively. The thickness of the SrRuO₃ and BaTiO₃ 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(Zr₀.₃₅Ti₀.₆₅)O₃; 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(Zr0.35Ti0.65)O3 thin films grown on epitaxial SrRuO3(001) buffered SrTiO3(001) pig. la, 8-2θ; Fig. 1b, θ-rocking PZT(002); Fig. 1c, θ-rocking PZT(200) and epitaxial SrRuO3(001)/BaTiO3(001) buffered SrTiO3(001) pig. 1d, 8-2θ; Fig. 1e, θ-rocking PZT(002); Fig. 1f, θ-rocking PZT(200)].

Figure 2. RBS channelling result for epitaxial Pb(Zr0.35Ti0.65)O3 thin films grown on epitaxial Pb(Zr0.35Ti0.65)O3 grown directly on SrTiO3(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 PbTiO3 (001) / SrRuO3 (001) / SrTiO3 (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 SrRuO3 layer is ~330Å. Note that the 90° domains visible in the image clearly nucleate at SrTiO3 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(Zr0.35Ti0.65)O3 grown directly on SrTiO3(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°.
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 are 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 of 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 $>5.8 \times 10^9$ $\Omega$-cm at 275 KV/cm. The dielectric breakdown strength was $>400$KV/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 $>5.8 \times 10^9$ $\Omega$-cm at 275 KV/cm. The dielectric breakdown strength was $>400$KV/cm; this was the limit of our instrument.
ACKNOWLEDGMENTS
This work was supported by the U. S. Department of Energy, Basic Energy Science-Materials Science under contract #W-31-109-ENG-38 under a joint CRADA with Hewlett-Packard Company #C9301701.

REFERENCES


