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PROPERTIES AND ORIENTATION OF ANTIFERROELECTRIC LEAD ZIRCONATE THIN FILMS GROWN BY MOCVD*

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DISCLAIMER

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ABSTRACT

Single-phase polycrystalline $PbZrO_3$ (PZ) thin films, 3000–6000 Å thick, have been grown by metal-organic chemical vapor deposition (MOCVD) on (111)Pt/Ti/SiO_2/Si substrates at ≈525°C. X-ray diffraction analysis indicated that the PZ films grown on (111)Pt/Ti/SiO_2/Si (Pt/Ti/Si) showed preferred pseudocubic (110) orientation. In contrast, PZ films grown on 150 Å thick $PbTiO_3$ (PT) template layers exhibited a pseudocubic (100) preferred orientation, and PZ films deposited on TiO_2 template layers consisted of randomly oriented grains. The PZ films grown on Pt/Ti/Si with or without templates exhibited dielectric constants of 120–200 and loss tangents of 0.03–0.01. The PZ films with (110) orientation exhibited an electric-field-induced transformation from the antiferroelectric phase to the ferroelectric phase with a polarization of ≈34 $\mu C/cm^2$, and the energy that was stored during switching was 7.1 J/cm^3. The field needed to excite the ferroelectric state and that needed to revert to the antiferroelectric state were 350 and 250 kV/cm, respectively. Relationships between the MOCVD processing and the film microstructure and properties are discussed.

INTRODUCTION

$PbZrO_3$ (PZ) has been a subject of many studies in recent years. PZ is a well-known antiferroelectric (AFE) material at temperature below 230–236°C [1,2]. It has been demonstrated that PZ thin films [3-6] or doped PZT AFE ceramics exhibit an electric-field-induced transformation from the antiferroelectric phase to ferroelectric phase at room temperature. The energies stored during the switching can be as high as ≈50 J/cm^3. These characteristics would make PZ or doped PZT-based AFE ceramics good candidates for charge-storage applications.

Interest in preparing PZ thin films also arises from work on processing of $PbZr_xTi_{1-x}O_3$ (PZT) films, which are potential candidates for many microelectronic applications, especially for nonvolatile ferroelectric random assess memories (NVFRAMs). It has been observed that single-phase PZT in the Ti-rich region, especially at $x = 0$, can be readily prepared at relatively low temperatures. However, when preparing the PZT phase in the Zr-rich region, especially $x = 1$, processing conditions become more restricted and the desired single perovskite phase is not readily obtained. The difficulty in preparing single-phase PZ probably arises from the fact that the rate of formation of PZ is much lower than that of PT [7,8], and also that adhesion of ZrO_2 on the substrate during the growth would disrupt growth of PZT [4,9]. Studies of PZ formation, film microstructure, and grain orientation under different growth conditions would provide a better understanding of growth mechanisms in PZT system.

The goal of this study was to grow room-temperature-switchable PZ films by MOCVD, and to examine the relationships among growth conditions, structures, and properties.

EXPERIMENTAL DETAILS

PZ films, PT films, and TiO_2 template layers were all deposited in a low-pressure, horizontal-flow, cold-wall reactor that contained a resistive substrate heater. Tetraethyl lead

($Pb(C_2H_5)_4$), zirconium t-butoxide ($Zr[OC(CH_3)_3]_4$), and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) were used as the metal-ion precursors. The growth conditions for PZ films and PT templates are shown in Table I. It has been reported that the reaction rate of PbO with ZrO_2 is much slower than that of PbO with TiO_2. In order to obtain the desired single perovskite phase, the Pb partial pressure had to be increased to compensate for evaporation of Pb from substrates. The optimum growth conditions for PZ films deposited on PT templates included a 10% reduced flow rate of Pb precursor, compared with PZ films grown directly on Pt/Ti/Si substrates. PZ film growth conditions on TiO_2 templates were the same as on Pt/Ti/Si directly. When grown under optimal conditions, the PZ films exhibited a shiny, smooth surface.

X-ray θ and 2θ diffraction (XRD) scans were obtained with a Rigaku diffractometer and a 3 kW Cu Kα X-ray source. X-ray 2θ peaks were identified according JCPDS-ICDD index 35-0739. The film thickness was measured using Rutherford backscattering (RBS). The thickness measured using RBS were confirmed using an optical wave-guide method [10]. Film surface roughness, grain structure, and cross sections were characterized by scanning electron microscopy (SEM), and film compositions were determined by energy dispersive X-ray spectroscopy.

For electrical measurements, Ag top electrodes were produced on the surface of the PZ films, using electron-beam evaporation through a patterned mask to form capacitor structures with contact areas of $2 \times 10^{-3} - 1 \times 10^{-5}$ cm^2. Ferroelectric hysteresis loops were obtained with a Radiant Technologies RT6000HVS test system. Dielectric-breakdown strengths were measured with a Keithley 237 source measurement unit. Dielectric constants and loss tangents at 1 kHz were obtained with a Hewlett-Packard HP4192A impedance analyzer.

Table I. Growth conditions for PZ films on (111)Pt/Ti/SiO_2/Si.

Variable	Species	Value
Substrate temperature	—	525°C (PZ) 475°C (PT)
Reactor pressure	—	30 Torr
Organometallic (OM) precursor temperature	$Ti(OC_3H7)_4$ $Zr[OC(CH_3)_3]_4$ $Pb(C_2H_5)_4$	38°C (PT) 45°C (PZ) 28°C
OM precursor pressure	$Ti(OC_3H7)_4$ $Zr[OC(CH_3)_3]_4$ $Pb(C_2H_5)_4$	100 Torr (PT) 150 Torr (PZ) 300 Torr
Flow rate of reactant gas	O_2	400 sccm
Flow rate of OM precursor and carrier gas (N_2)	$Ti(OC_3H7)_4$ $Zr[OC(CH_3)_3]_4$ $Pb(C_2H_5)_4$	50 sccm (PT) 50 sccm (PZ) 20-30 sccm
Flow rate of background gas	N_2	600 sccm
Film thickness		0.2–0.7 μm
Film growth rate		50–70 Å/min

RESULTS AND DISCUSSION

PZ films grown directly on Pt/Ti/Si at 525°C exhibited (221) fiber texture, which corresponds to the pseudocubic (110) orientation (Fig. 1). However, the film reproducibility in terms of phase purity and morphology was poor, probably due to the reasons discussed in the introduction. The processing window in terms of gas-phase ratio of Pb/Zr was very narrow for the given temperature and substrate. Shiosaki et al. reported similar results for PZT films that were grown by MOCVD at low temperatures [11]; poor perovskite phase development and significant pyrochlore phase formation were observed for Zr-rich PZT compositions.

The PZ phase purity was improved by depositing PT and TiO_2 intermediate layers on Pt/Ti/Si, which was similar to previous results for PZT films [12]. The effect of PT and TiO_2 template layers on PZT film morphology has been observed for several deposition methods [13-16]. For ion-beam-sputtered PZT films, it was found that intermediate PT layers helped to eliminate the formation of undesirable second phases and improved electrical properties [13]. Thin TiO_2 template layers, intentionally deposited on Pt or as a result of Ti diffusion through Pt, significantly affected the PZT crystallization behavior of sol-gel-derived films. Aoki et al. found that PZT crystallization is initiated at 460°C when the PZT films are grown on a TiO_2 template layer. This crystallization temperature is 60°C lower than that for the case of PZT films grown without a template layer [14].

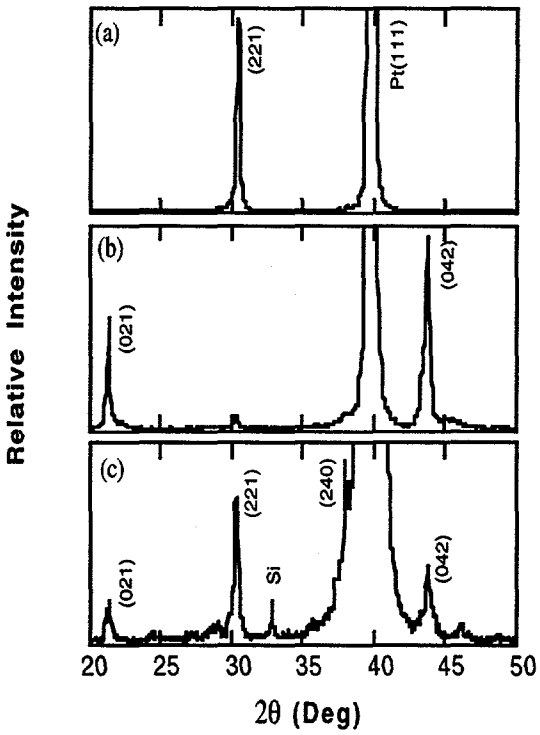

Figure 1. XRD 2θ scans of PZ films grown on (a) Pt/Ti/Si directly, (b) with a PT template, and (c) with a TiO_2 template at 525°C.

The effect of PT and TiO_2 seed layers on PZ film orientation was also investigated. As shown in Fig. 1, the PZ films on PT templates had preferred (021) grain orientation, which corresponds to the pseudocubic (100) orientation. Furthermore, PZ films grown on TiO_2 template layers showed randomly oriented grain structures. These results are compared with previous studies of PZT growth on PT and TiO_2 template layers. Earlier observations for MOCVD films showed that PZT grown on TiO_2 templates exhibited highly oriented grains [12]. Results for sputtered TiO_2 template layers show that oriented PZT could be obtained for an optimum TiO_2 thickness of 2 μm [16]. From the present results and those of other researchers, template layers have been found to favor grain orientation of both PZT and PZ; however, Pb activity, substrate temperature, Ti/Zr ratio, and template layer thickness also affect film growth and orientation.

SEM micrographs of top surfaces of PZ films revealed that PZ films grown on Pt/Ti/Si without templates exhibit a white surface layer. This phase is probably a byproduct that results from a gas-phase ratio of Pb/Zr that is higher in Pb content than needed for growth of PZ films. Both types of PZ films grown with PT and TiO_2 templates exhibited uniformly distributed fine-grain structures, regardless of differences in grain orientations.

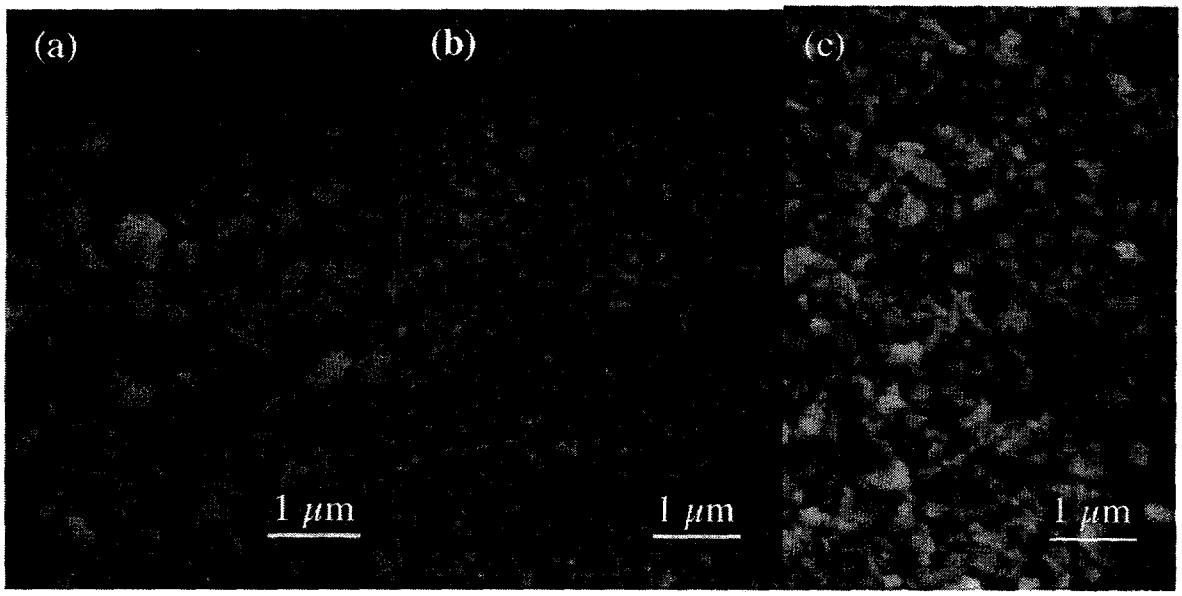

Figure 2. SEM photomicrographs of top surfaces of PZ films (a) grown without template, (b) grown on PT templates, and (c) grown on TiO_2 templates.

The relative dielectric constants estimated from capacitance measurements performed at 100 kHz were 150–200 for all PZ films. The measured loss tangents were 0.03–0.01. The dielectric breakdown fields were in the range of 2–7 x 10^7 V/m. There was no obvious dependence of dielectric-constant or breakdown-field values on growth conditions or grain orientation. The D-E hysteresis loops of PZ films grown on Pt/Ti/Si directly and on a PT template are shown in Fig. 3. The PZ film grown on Pt/Ti/Si directly with (221) preferred orientation exhibited an electric-field-induced AFE-to-FE phase transformation. The AFE-to-FE transition field was ≈350 kV/cm; the reverse FE-to-AFE was ≈250 kV/cm. The saturation polarization was ≈34 μC/cm^2, and the energy that was stored during switching was 7.1 J/cm^3. On the other hand, the PZ film grown on a PT template with (021) orientation exhibited no AFE-to-FE switching characteristics at fields up to 600 kV/cm. Figure 4 shows the dielectric constant as function of electric field derived from hysteresis loops for films grown on Pt/Ti/Si. The dielectric constant was as high as 1400 at peak value.

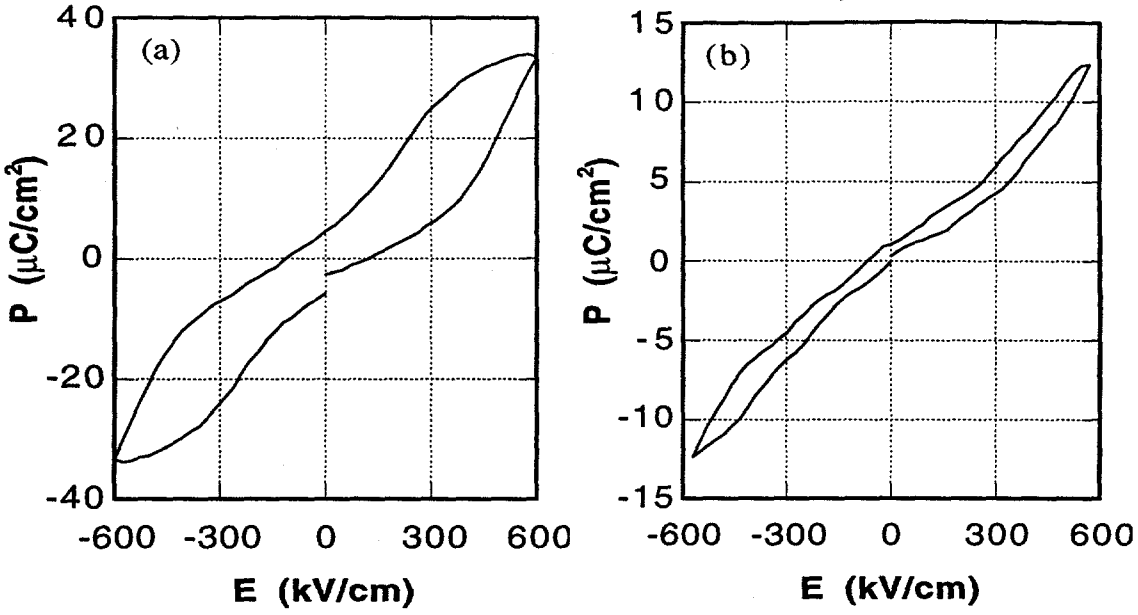

Figure 3. Hysteresis loops of PZ films grown on (a) Pt/Ti/Si and (b) PT templates.

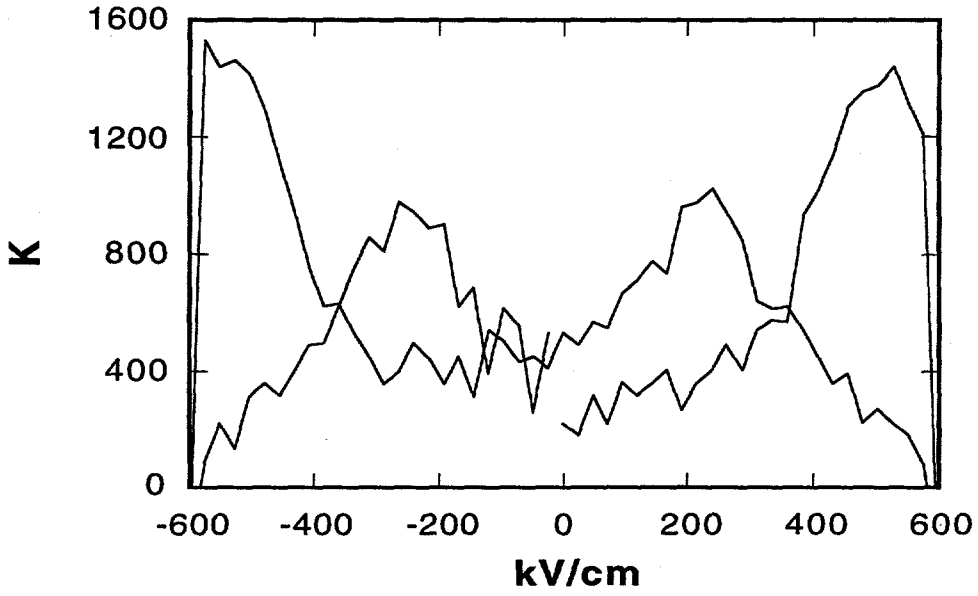

Figure 4. Dielectric constant as function of electrical field derived from hysteresis loops for a PT film grown on Pt/Ti/Si.

The saturation polarization for the PZ film grown directly on Pt is similar to values found for polycrystalline ceramics or films. Larger polarization values from the field-induced antiferroelectric-ferroelectric phase transition are expected for fiber-textured (120) PZ films because the rhombohedral ferroelectric phase develops polarization along the pseudocubic [111] direction [17].

SUMMARY

Single-phase PZ films with pseudocubic (110) preferred orientation were grown directly on Pt/Ti/Si substrates at 525°C. The PZ phase purity was improved by depositing PT and TiO_2 intermediate layers. PZ films with pseudocubic (100) preferred orientation were deposited on Pt/Ti/Si with 150–200 Å thick PT template layers. Randomly oriented PZ films were grown on Pt/Ti/Si substrates with 150–200 Å thick TiO_2 template layers. P-E hysteresis measurements showed that PZ films with (110) orientation exhibited an electric-field-induced phase transformation.

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