Dielectric, ferroelectric, and piezoelectric properties of (001) $BiScO_3$–$PbTiO_3$ epitaxial films near the morphotropic phase boundary

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The dielectric, ferroelectric, and piezoelectric properties of (001) $BiScO_3$–$PbTiO_3$ epitaxial films near the morphotropic phase boundary were investigated. Epitaxial films, 1-μm thick, were grown on (100) $SrRuO_3$/(100) $LaAlO_3$ substrates by pulsed laser deposition from a $BiScO_3$–$PbTiO_3$ (40/60) ceramic target. The films had room temperature dielectric constant of 850, $\tan\delta = 0.08$, and maximum dielectric constant of 5530 at 455 °C. Well-saturated hysteresis loops with a remanent polarization of 42 $\mu C/cm^2$ and a coercive field of 75 kV/cm were observed. The effective transverse piezoelectric coefficient $e_{31,f}$ was −12 C/m^2. This result is quite encouraging for sensor and actuator device development because the observed piezoelectric properties are as good as (001) oriented $Pb(Zr,Ti)O_3$ films ($e_{31,f} \sim -12$ C/m^2) while the transition temperature is 100 °C higher.

I. INTRODUCTION

In recent years, ferroelectric thin films have received considerable attention for their potential use in a wide range of applications such as microelectromechanical systems (MEM) and nonvolatile memory.[1,2] In addition to high ferroelectric or piezoelectric activity, temperature stability of the electrical properties is a critical design requirement for such devices. It has been found that in thin films, the temperature stability of the piezoelectric response is strongly dependent on the ferroelectric transition temperature (T_c).[3] A higher T_c results in more temperature-stable responses and enables expanded temperature operating range (typical use ranges in bulk ceramics are limited to approximately half of T_c).[4] Additional advantages of utilizing high-T_c thin films are protection against thermal depolarization and higher strain; therefore, development of new ferroelectric materials in thin film form with high transition temperatures is extremely attractive.

Eitel et al.[5] have recently investigated ceramics in the $BiScO_3$–$PbTiO_3$ solid-solution system as promising piezoelectrics exhibiting high T_c. At the morphotropic phase boundary (MPB) composition, T_c of $BiScO_3$–$PbTiO_3$ (36/64) is 450 °C, which is roughly 100 °C higher than that of $Pb(Zr_{0.52}Ti_{0.48})O_3$. A remanent polarization of approximately 32 $\mu C/cm^2$ and a d_{33} piezoelectric coefficient of approximately 465 pC/N were observed in the bulk ceramics.

Based on the fact that rhombohedrally distorted perovskite ferroelectrics show higher piezoelectric properties along the [001] direction,[6] (001) $BiScO_3$–$PbTiO_3$ epitaxial films in the rhombohedral phase were recently investigated by Yoshimura et al.[7] The films were grown by pulsed laser ablation from a ceramic target with composition $BiScO_3$–$PbTiO_3$ (50/50), which is far from the MPB. The films had a room temperature dielectric constant of 800, $\tan\delta = 0.09$, a maximum dielectric constant of 3600 at 460 °C, and a hysteresis loop with a remanent polarization of 36 $\mu C/cm^2$. The room temperature $e_{31,f}$ piezoelectric coefficient was −9 C/m^2.

While these reported properties are quite promising, it can be expected that thin films with nominal compositions closer to the MPB should exhibit enhanced properties as a result of higher polarizability. Higher piezoelectric response would enable lower voltage operation as well as enhanced speed in devices such as rf switches. It is not obvious, however, that the morphotropic phase boundary composition should be stress independent. Thus, while lead zirconate titanate (PZT) films typically show maximized piezoelectric properties near the bulk MPB composition,[3,8–11] other researchers have shown maximized responses with significantly different Zr:Ti ratios.[12,13] It has been reported that in the related system of $BiFeO_3$–$PbTiO_3$, the stress state can move the MPB, so that sintered ceramics and powdered samples showed different phase assemblages for the same composition.[14] Consequently, it becomes interesting to determine for one of the Bi-based perovskite piezoelectrics whether or not the stress state associated with the thin film geometry shifts the MPB.

In addition, while initial investigation on the $BiScO_3$–$PbTiO_3$ solid-solution system in bulk ceramics revealed close resemblance with the $PbZrO_3$–$PbTiO_3$ solid-solution system, recent transmission electron microscopy

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investigations have identified a ferroelectric rhombohedral (R3c phase, tilted) to ferroelectric rhombohedral (R3m, untilted) phase transition.[15] In particular, the R3c (tilted) rhombohedral phase was observed in $BiScO_3$–$PbTiO_3$ (50/50) compositions whereas the untilted phase (R3m) was observed in compositions close to the morphotropic phase boundary. The tilted phase has been associated with a significant decrease in the piezoelectric response of PZT-based ceramics.[16] Therefore, it is of interest to investigate if this ferroelectric–ferroelectric transition has any effect on the electrical properties observed in $BiScO_3$–$PbTiO_3$ thin films.

Based on these two main motivations, this article reports the growth and electrical characterization of (001) $BiScO_3$–$PbTiO_3$ epitaxial films near the bulk morphotropic phase boundary.

II. EXPERIMENTAL

$BiScO_3$–$PbTiO_3$ films and $SrRuO_3$ bottom electrodes were prepared by pulsed laser deposition (PLD) on (100) $LaAlO_3$ single-crystal substrates (MTI Corporation, Richmond, CA). (Throughout this paper, the Miller indexes of $LaAlO_3$, $SrRuO_3$, and $BiScO_3$–$PbTiO_3$ are given in terms of a pseudocubic unit cell.) A KrF excimer laser (Lambda Physik Compex 102, Fort Lauderdale, FL) with a 248-nm wavelength was used to ablate the target materials. The laser energy density was 1.5–2 J/cm^2. $SrRuO_3$ bottom electrodes were deposited using stoichiometric $SrRuO_3$ ceramic targets (Target Materials Inc., Columbus, OH). Details on the epitaxial growth of $SrRuO_3$ films are given elsewhere.[17,18]

$BiScO_3$–$PbTiO_3$ films were deposited using sintered ceramics of $(1 - x)BiScO_3$–$xPbTiO_3$ (x = 0.6, close to MPB) which were batched with 20 mol% excess PbO and 10 mol% excess Bi_2O_3 to compensate for the loss of lead and bismuth during growth.[19] Oxygen and ozone gases were introduced to the deposition chamber using a commercial ozone generator (PCI). The deposition ambient consisted in a mixture of 10% O_3/90% O_2. The crystalline structure of the films was characterized by x-ray diffraction (XRD) using Cu Kα radiation. θ–2θ, ω, and ϕ scans were performed using an X'PERT Philips (The Netherlands) four circle diffractometer. The stoichiometric composition of the films and ceramic targets was analyzed by electron probe microanalysis (EPMA) using a Cameca SX-50 (Trumbull, CT) electron microprobe operated at 10 kV and 20 nA. The surface microstructure was examined with an atomic force microscope (Multimode, Digital Instruments, Woodburg, NY) using contact mode. To characterize the electrical properties, Pt top electrodes (0.12 mm in diameter) were sputtered through a shadow mask. The temperature dependence of the dielectric constant and loss was determined using an Impedance analyzer meter (Hewlett Packard 4284A, Palo Alto, CA) in combination with a hot stage sample fixture. Polarization hysteresis loops were measured by a Radiant Technologies RT66A (Albuquerque, NM) standard ferroelectrics tester. The $e_{31,f}$ coefficients were measured using the wafer flexure method.[20,21] Prior to measurements of the $e_{31,f}$ coefficients, a dc voltage was applied to the top electrode of the $BiScO_3$–$PbTiO_3$ films at room temperature for poling.

III. RESULTS AND DISCUSSION

Figure 1 shows θ–2θ, ω, and ϕ XRD patterns of a 1-μm $BiScO_3$-$PbTiO_3$ film deposited at a substrate temperature of 730 °C, a deposition pressure of 26.67 Pa (200 mTorr), a laser repetition frequency of 14 Hz, and a target to substrate distance of 40 mm. The deposition rate was 1.67 nm/s (1000 Å/min). The 101 diffraction peaks of $BiScO_3$–$PbTiO_3$ and $LaAlO_3$ were used in the ϕ scan. It can be seen that (001) $BiScO_3$–$PbTiO_3$ epitaxial films were obtained. To the detection limits of our diffractometer, no secondary phases (such as a pyrochlore phase) were observed. In addition, there was no evidence for tetragonal splitting of the diffraction peaks in the films grown. The out-of-plane lattice constant determined by measuring the 2θ angles of the 00l type diffraction peaks and using the Nelson–Riley method[22] was 4.0422 ± 0.0004 Å. Although somewhat high for a composition close to the MPB, this value is consistent with the lattice constants reported in bulk ceramics of rhombohedral $BiScO_3$–$PbTiO_3$ (a ~4.021).[5] Increase in the out-of-plane lattice parameter of thin films is not uncommon and has been found to be dependent on the energetic bombardment during growth, among other factors.[23] The full width at half-maximum (FWHM) of the $BiScO_3$–$PbTiO_3$ 002 diffraction peaks in the θ–2θ and ω scans was 0.48° and 1.05°, respectively. The FWHM of the $BiScO_3$–$PbTiO_3$ 101 diffraction in the ϕ scan was 1.72°.

Figure 2 shows an atomic force microscopy (AFM) image of the microstructure of as-deposited $BiScO_3$–$PbTiO_3$ (40/60) thin films. The surface morphology of the films was granular with measured roughness (rms) approximately 8 nm and an average grain size of approximately 250 nm. The observed values are consistent with characteristic microstructures of PLD ceramic thin films grown at high deposition rates.[24]

Table I summarizes the stoichiometric composition analysis of the films using EPMA. Data for 1-, 2-, and 2.5-μm-thick films are included. When these values are compared with the expected stoichiometry ($0.4BiScO_3$–$0.6PbTiO_3$), various trends are clear: first, the Sc/Ti (B-site) composition is identical to the ideal 40/60 stoichiometry within the experimental error; second, the films are Bi excess and Pb deficient. The A-site/B-site ratio is one, within experimental error. It is unclear what compensation mechanism is operating in the films. One way to compensate for the presence of Bi^{3+} on the Pb^{2+} site would be by reduction of Ti^{4+} to Ti^{3+}, but this in turn

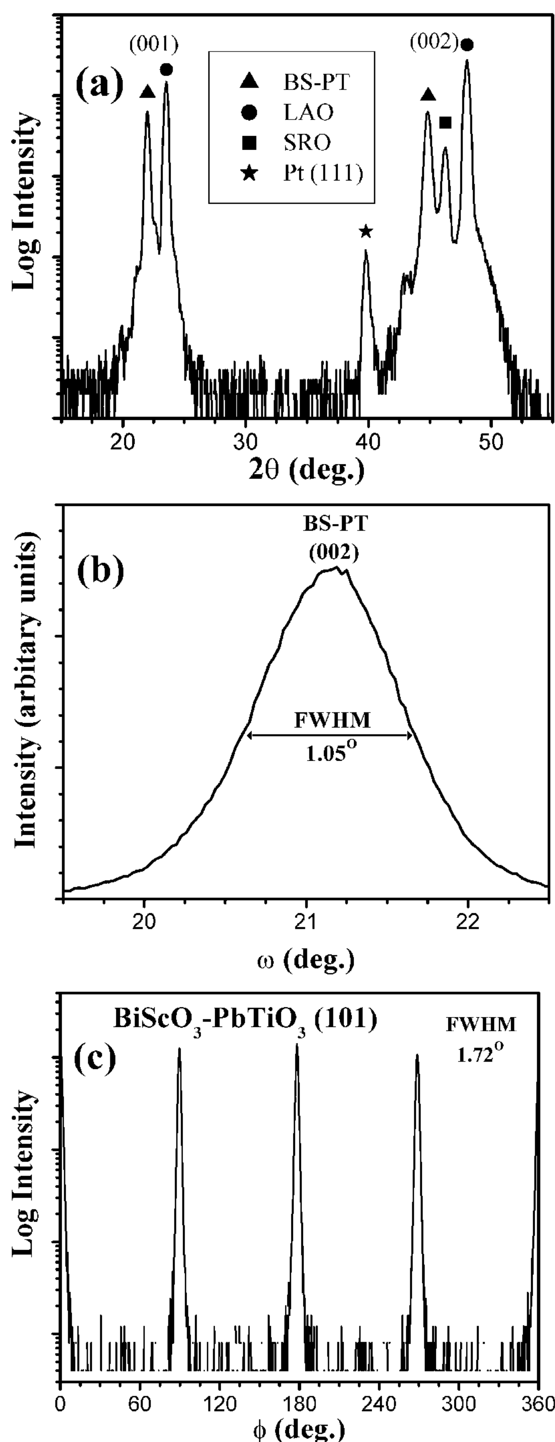

FIG. 1. (a) θ–2θ, (b) ω, and (c) ϕ XRD patterns of a $BiScO_3$–$PbTiO_3$ film on a (100) $SrRuO_3$/(100) $LaAlO_3$ substrate. (▲) $BiScO_3$–$PbTiO_3$, (★) Pt (111), (■) $SrRuO_3$, and (●) $LaAlO_3$. The full width at half-maximum (FWHM) is indicated for curves (b) and (c).

should make the films electrically leaky. However, as presented in Figs. 3 and 4, this was not the case. Furthermore, the fact that the films are insulating even at elevated temperatures suggests that the compensation is not electronic but rather ionic (defects, vacancies, and so

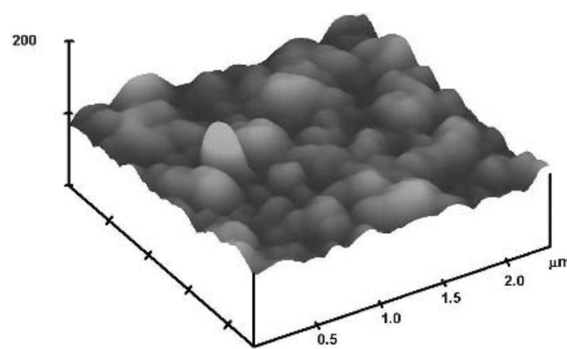

FIG. 2. Atomic force microscope image for the (001) $BiScO_3$–$PbTiO_3$ (40/60) thin film in Fig. 1.

forth). If this is the case, then it would suggest that the oxygen vacancy concentration should be suppressed while metal vacancies would be favored. Another possibility is the presence of secondary phases. Such phases were not detected by XRD analysis, and it is clear that the perovskite material is epitaxial. Therefore, it is possible that if secondary phases are present, their morphology is columnar, thus minimizing the effects on the structural and electrical properties observed in these films. This is an interesting area of future research requiring systematic investigation complemented by additional characterization techniques such as transmission electron microscopy and electron energy loss spectroscopy.

The temperature dependence of the dielectric constant and loss at 100 kHz is given in Fig. 3. The dielectric constant was 850 at room temperature and exhibited a maximum of 5530 near 455 °C. This is nearly identical to that observed in bulk ceramics at the same Sc/Ti ratio.[5] It is of interest to note that the dielectric constant at the transition temperature is ~6.5 times that at room temperature; this is higher than the typical ratio observed in ferroelectric thin films.[25,26]

In addition, two anomalies can be seen in the dielectric loss curve. First, at low temperature (<200 °C), a low temperature relaxation is observed. This phenomenon has been observed in $BiScO_3$–$PbTiO_3$ bulk ceramics and has been identified as a dielectric relaxation related to the Bi ions.[27] The second anomaly is a local increase in the dielectric loss observed around 375 °C, which was attributed in bulk samples to curvature in the MPB and the appearance of a tetragonally distorted phase. To investigate this, following the initial dielectric property measurement (Fig. 3), the sample was poled at 150 kV/cm and high temperature (400 °C), cooled under field, and then the measurement was repeated. In bulk samples, this type of poling treatment often sharpens the dielectric anomaly associated with a rhombohedral to tetragonal transformation. However, no difference between the two runs was observed. Therefore, it is not possible to conclude at this point whether this second anomaly is associated with a rhombohedral ferroelectric to a tetragonal ferroelectric

TABLE I. EPMA results on the stoichiometry of (001) $BiScO_3$–$PbTiO_3$ thin films as a function of thickness. General error ±5%. The oxygen content is calculated assuming typical valences for each cation.

Film (expected stoichiometry)	Pb (mol) (0.600)	Ti (mol) (0.600)	Bi (mol) (0.400)	Sc (mol) (0.400)	O (mol, calc) (3.000)
1 μm film composition	0.491	0.588	0.497	0.405	3.019
Difference (%)	−18.2	−2.0	24.4	1.2	⋯
2 μm film composition	0.520	0.576	0.483	0.409	3.011
Difference (%)	−13.3	−4.0	20.8	2.3	⋯
2.5 μm film composition	0.515	0.590	0.491	0.389	3.015
Difference (%)	−14.2	−1.6	22.7	−2.8	⋯

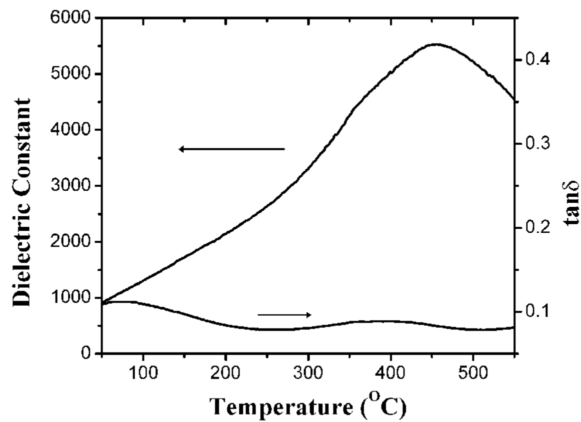

FIG. 3. The temperature dependence of the dielectric constant and loss for the $BiScO_3$–$PbTiO_3$ film measured at 100 kHz.

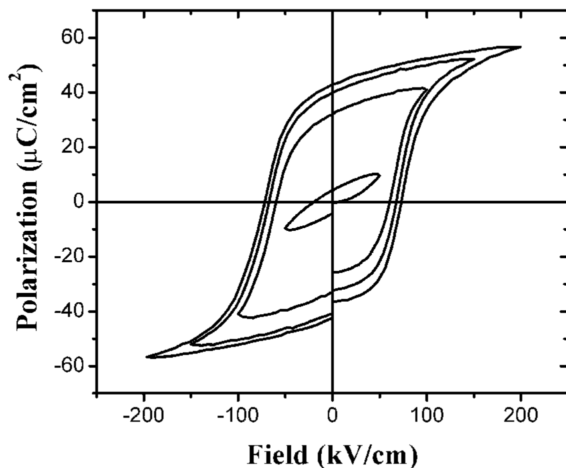

FIG. 4. Polarization versus electric field hysteresis loops for the $BiScO_3$–$PbTiO_3$ film.

transition in the film or some other factor. Nonetheless, it is important to point out that despite the anomalies observed at both low and high temperatures, the dielectric loss remains below 0.1 up to 550 °C which confirms that any defects associated with the Bi:Pb ratio do not introduce large electronic carrier concentrations. This should facilitate utilization of these films in high-temperature applications.

Figure 4 depicts the low-frequency (100 Hz) polarization hysteresis loops for the $BiScO_3$–$PbTiO_3$ film

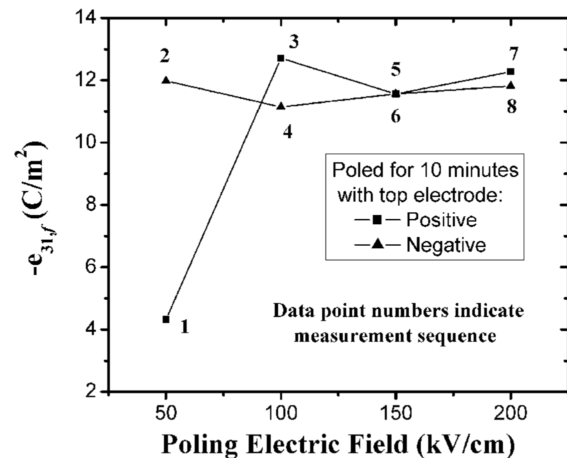

FIG. 5. The $e_{31,f}$ coefficient as a function of the poling electric field and polarity for the $BiScO_3$–$PbTiO_3$ film. Numbers next to data points indicate the measurement sequence.

shown in Fig. 1. Well saturated and centered hysteresis loops were observed and are indicative of high dc resistivity. The remanent polarization and coercive field were 42 $\mu C/cm^2$ and 75 kV/cm, respectively. The remanent polarization is 30% higher than that observed in bulk ceramics.[5] This suggests either the presence of some tetragonal phase or that the variation in the Pb/Bi stoichiometry increased the remanent polarization (P_r).

The piezoelectric properties of the films were characterized in terms of the effective piezoelectric transverse coefficients ($e_{31,f}$). Because piezoelectric thin films are clamped on a substrate, the directly measured piezoelectric coefficient of the thin films is not the free piezoelectric coefficient but an effective coefficient.[1,28] Figure 5 shows the $e_{31,f}$ coefficient as a function of the poling electric field and polarity. The alternating poling polarity sequence of measurements is indicated in Fig. 5. The $e_{31,f}$ coefficient after poling was almost constant and independent of the electric field polarity. The obtained value (−12 C/m^2) is comparable to the best of $Pb(Zr,Ti)O_3$ oriented films.[1,18] This is very encouraging given the high transition temperature of $BiScO_3$–$PbTiO_3$ that would enable expanded temperature operating range and enhanced thermal stability for micromechanical and semiconductor devices.

As a final comment, it is worth mentioning that the overall electrical and electromechanical properties of the $BiScO_3$–$PbTiO_3$ (40/60) thin films presented here are significantly better than those previously reported for the $BiScO_3$–$PbTiO_3$ (50/50) films.[7] This would be consistent with the MPB being close to the $BiScO_3$–$PbTiO_3$ ratio observed in polycrystalline samples, despite the difference in inherent stress state associated with the thin film geometry. It is also interesting that neither the MPB nor the phase-transition temperatures in the 40/60 films appeared to be significantly changed by the relatively high Bi/Pb ratio in the films. Based on the available data on bulk samples, and presuming the B-site ratio was maintained during the PLD process, the films reported in Ref. 7 ($e_{31,f}$ = −9 C/m^2) should be in the R3c space group whereas those in the current study should be R3m ($e_{31,f}$ = −12 C/m^2). This drop in properties in the 50/50 composition is smaller than that observed in bulk PZT ceramics due to the octahedral tilt transition (where d_{33} was observed to drop by a factor of 2)[16] suggesting that $e_{31,f}$ may be inherently less sensitive to tilt transitions than the d_{33} coefficient itself may be.

IV. CONCLUSIONS

One-micrometer-thick epitaxial films were grown by pulsed laser deposition of $BiScO_3$–$PbTiO_3$ (40/60) on (100) $SrRuO_3$/(100) $LaAlO_3$ substrates. The dielectric, ferroelectric, and piezoelectric properties of the (001) $BiScO_3$–$PbTiO_3$ films were investigated. The films had a room-temperature dielectric constant of 850, $\tan\delta$ = 0.08, and a maximum dielectric constant of 5530 at 455 °C. Well-saturated hysteresis loops with a remanent polarization of 42 μC/cm^2 and a coercive field of 75 kV/cm were observed. The effective transverse piezoelectric coefficient $e_{31,f}$ was −12 C/m^2. Additionally, the dielectric loss of the films remained below 0.1 up to 550 °C. These results are quite promising for sensor and actuator device development when compared with the best $Pb(Zr,T)O_3$ films reported.

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