Growth and properties of (001) $BiScO_3-PbTiO_3$ epitaxial films

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The ferroelectric and piezoelectric properties of (001) $BiScO_3-PbTiO_3$ epitaxial films were investigated. Epitaxial films 1 μm thick were grown by pulsed laser deposition using ceramic targets of $(1-x)BiScO_3-xPbTiO_3$ $(x=0.5)$ at substrate temperatures of 700 °C on (100) $SrRuO_3$/(100)$LaAlO_3$ substrates. Well-saturated hysteresis loops with a remanent polarization of 36 $\mu C/cm^2$ were observed. The films had a room temperature dielectric constant of 800, $\tan\delta=0.09$ and a maximum permittivity of 3600 at 460 °C. The room temperature e_{31f} piezoelectric coefficient was -9 C/m^2. The piezoelectric properties obtained were comparable to those of $Pb(Zr,Ti)O_3$ or relaxor ferroelectric-$PbTiO_3$ films.
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Ferroelectric thin films have created considerable interest in recent years for a wide range of applications, such as microelectromechanical systems and nonvolatile memories. Since the temperature stability of the electrical properties, as well as good ferroelectric or piezoelectric activity, is important for device applications, ferroelectrics with high transition temperatures, T_c, are attractive.

Recently, $BiScO_3-PbTiO_3$ has been reported as a new piezoelectric with a high T_c.[1] At the morphotropic phase boundary (MPB) composition, T_c of $BiScO_3-PbTiO_3$ (64/36) is 450 °C, which is higher than that of $Pb(Zr,Ti)O_3$. A remanent polarization of ~32 $\mu C/cm^2$ and a d_{33} piezoelectric coefficient of ~465 pC/N were observed in bulk ceramics. In the present study, $BiScO_3-PbTiO_3$ epitaxial films were investigated in terms of their ferroelectric and piezoelectric properties. Since rhombohedrally distorted perovskite ferroelectrics show higher piezoelectric properties along the ⟨001⟩ direction,[2] (001) $BiScO_3-PbTiO_3$ epitaxial films in the rhombohedral phase were prepared.

$BiScO_3-PbTiO_3$ films and $SrRuO_3$ bottom electrodes were prepared by pulsed laser deposition (PLD) on (100) $LaAlO_3$ single crystal substrates (MTI Corporation). (Note that in this letter, the Miller indices 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) 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.). Details of the epitaxial growth of $SrRuO_3$ films are given elsewhere.[3,4]

$BiScO_3-PbTiO_3$ films were deposited using sintered ceramics of $(1-x)BiScO_3-xPbTiO_3$ $(x=0.5)$ 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.[5] Oxygen and ozone gases were introduced into the deposition chamber using a commercial ozone generator (PCI). The deposition ambient consisted of a mixture of 10% O_3/90% O_2. The crystalline structure of the films was characterized by x-ray diffraction (XRD) using Cu $K\alpha$ radiation. θ–2θ, ω, and ϕ scans were performed using a Scintag Pad V diffractometer and an X'pert Philips four circle diffractometer.

Figure 1 shows θ–2θ and ϕ XRD patterns of a 1 μm thick $BiScO_3-PbTiO_3$ film deposited at a substrate temperature of 700 °C, a deposition pressure of 200 mTorr, a laser repetition rate of 14 Hz, and a target to substrate distance of 40 mm. The deposition rate was 130 nm/min. The 101 diffraction peaks of $BiScO_3-PbTiO_3$ and $LaAlO_3$ were used in the ϕ scan. As can be seen, (001) $BiScO_3-PbTiO_3$ epitaxial films were obtained. Although small peaks corresponding to polycrystalline $BiScO_3-PbTiO_3$ were observed in the θ–2θ patterns, to the detection limits of our diffractometer, no second phase such as pyrochlore phase is present. The out-of-plane lattice constant determined by measuring the 2θ angles of the 00*l* type diffraction peaks and using the Nelson–Riley

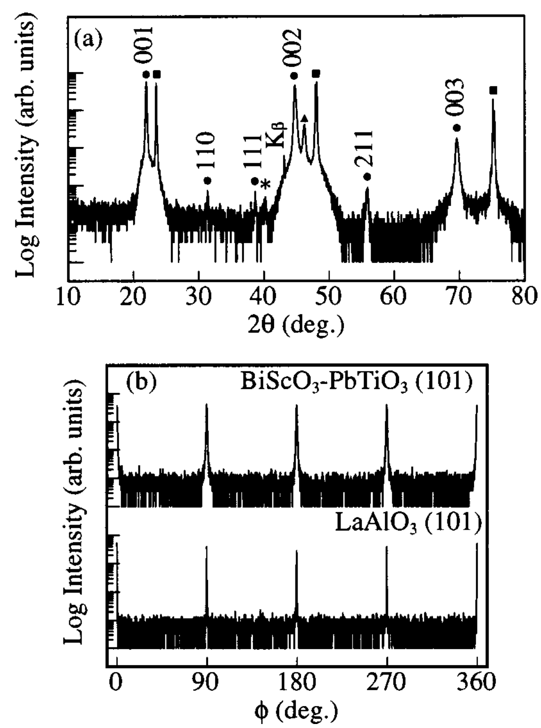

FIG. 1. (a) θ–2θ and (b) ϕ XRD patterns of a $BiScO_3-PbTiO_3$ film on a (100) $SrRuO_3$/(100) $LaAlO_3$ substrate. ● $BiScO_3-PbTiO_3$, * Pt 111, ▲$SrRuO_3$, and ■ $LaAlO_3$.

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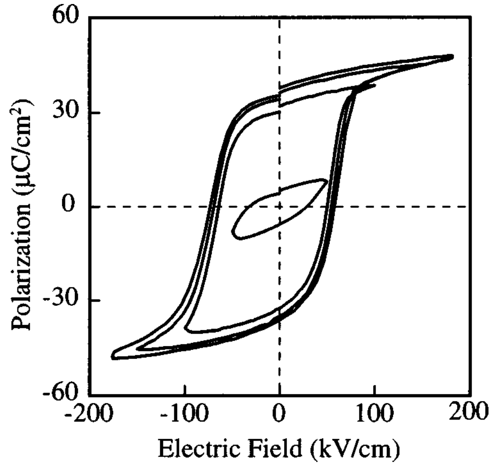

FIG. 2. Polarization hysteresis loop of the $BiScO_3-PbTiO_3$ film in Fig. 1.

method[6] was 4.051±0.005 Å. This value is consistent with the lattice constants reported in bulk ceramics of rhombohedral $BiScO_3-PbTiO_3$.[1] The full width at half maximum (FWHM) of the $BiScO_3-PbTiO_3$ 002 diffraction peaks in the θ–2θ and ω scans were 0.29° and 1.08°, respectively. Although perovskite (001) $BiScO_3-PbTiO_3$ films with no pyrochlore phase were obtained in a range of substrate temperatures (650–730 °C) and deposition rates (30–200 nm/min), the films deposited at 700 °C at relatively high deposition rates (130 nm/min) have the smallest FWHM values.

To characterize the electrical properties, Pt top electrodes (ϕ=0.44 mm) were sputtered through a shadow mask. Polarization hysteresis loops were measured by a Radiant Technologies RT66A standard ferroelectrics tester. The dielectric constant and loss were determined using an inductance-capacitance resistance meter (Hewlett Packard 4284A). Figure 2 shows the polarization hysteresis loops for the $BiScO_3-PbTiO_3$ film shown in Fig. 1. Well-saturated hysteresis loops were observed. The remanent polarization and coercive field were 36 $\mu C/cm^2$ and 65 kV/cm, respectively. The remanent polarization is comparable to that of bulk ceramics.[1] The temperature dependence of the dielectric constant and loss are given in Fig. 3. The dielectric constant was 800 at room temperature and exhibited a maximum near 460 °C. An inflection observed around 300 °C might correspond to the phase transition from rhombohedral to tetragonal distortions. It is encouraging that the dielectric loss remains below 0.1 up to 480 °C.

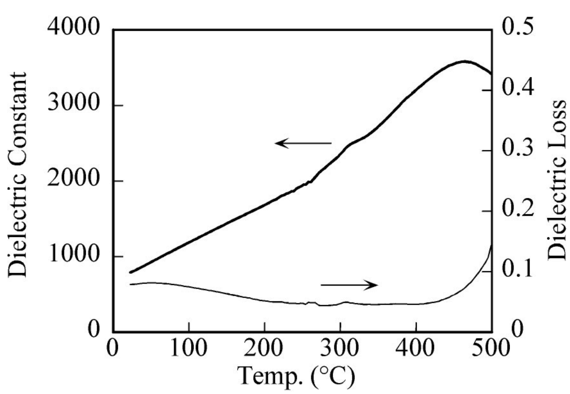

FIG. 3. Temperature dependence of the dielectric constant and loss for the $BiScO_3-PbTiO_3$ film.

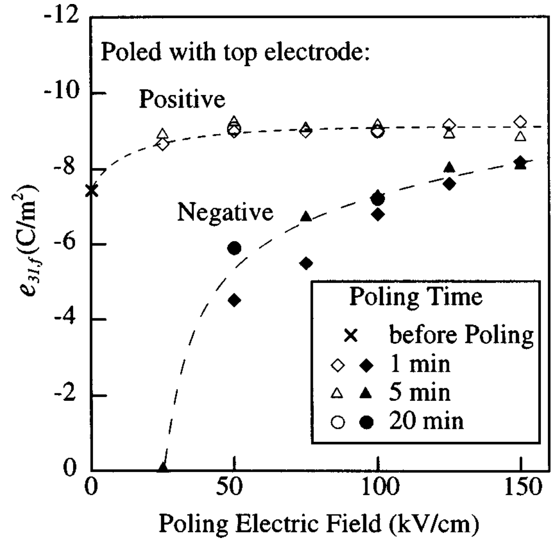

FIG. 4. e_{31f} coefficient as a function of the poling electric field and time.

The effective piezoelectric coefficients (e_{31f})[7,8] of the films was characterized. The e_{31f} coefficients were measured using a wafer flexure method described previously.[9,10] Prior to measurements of the e_{31f} coefficients, a dc electric field was applied to the top electrode of the $BiScO_3-PbTiO_3$ films at room temperature for poling. Figure 4 shows the e_{31f} coefficient as functions of the poling electric field and time. The e_{31f} coefficient after poling with a positive electric field was almost constant with the poling electric field and time. The value obtained (-9 C/m^2) was comparable to that of $Pb(Zr,Ti)O_3$ or relaxor ferroelectric-$PbTiO_3$ films.[4,7] This is very encouraging given the high transition temperature of the compound.

A relatively high deposition temperature (700 °C) was needed to deposit (001) $BiScO_3-PbTiO_3$ epitaxial films with good crystalline quality, and it was found that $BiScO_3-PbTiO_3$ had good perovskite stability. The remanent polarization of 36 $\mu C/cm^2$, e_{31f} piezoelectric coefficient of -9 C/m^2, and T_c of ~460 °C suggest that such $BiScO_3-PbTiO_3$ films are potentially interesting for micromechanical and semiconductor devices.

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[1] R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Rehrig, W. Hackenberger, and S. E. Park, Jpn. J. Appl. Phys., Part 1 **40**, 5999 (2001).
[2] S. E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[3] V. Bornand and S. Trolier-McKinstry, Thin Solid Films **370**, 70 (2000); J. Appl. Phys. **87**, 3958 (2000).
[4] T. Yoshimura and S. Trolier-McKinstry, J. Cryst. Growth **229**, 445 (2001); J. Appl. Phys. (in press).
[5] J. P. Maria, W. Hackenberger, and S. Trolier-McKinstry, J. Appl. Phys. **84**, 5147 (1998).
[6] B. D. Cullity, *Elements of X-ray Diffraction* (Addison–Wesley, Reading, MA, 1978).
[7] P. Muralt, J. Micromech. Microeng. **10**, 136 (2000).
[8] M.-A. Dubois and P. Muralt, Sens. Actuators A **77**, 106 (1999).
[9] J. F. Shepard, Jr., P. J. Moses, and S. Trolier-McKinstry, Sens. Actuators A **71**, 133 (1998).
[10] J. F. Shepard, Jr., F. Chu, I. Kanno, and S. Trolier-McKinstry, J. Appl. Phys. **85**, 6711 (1999).