High Curie temperature BiInO₃-PbTiO₃ films

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High Curie temperature piezoelectric thin films of $x\text{BiInO}_3-(1-x)\text{PbTiO}_3$ ($x = 0.10, 0.15, 0.20$, and 0.25) were prepared by pulsed laser deposition. It was found that the tetragonality of films decreased with increasing BI content. The dielectric constant and transverse piezoelectric coefficient (e_{31f}) exhibit the highest values of 665 and -13.6 C/m^2 at $x = 0.20$. Rayleigh analyses were performed to identify the extrinsic contributions to dielectric nonlinearity with different x . The composition with $x = 0.20$ also exhibits the largest extrinsic contributions to dielectric nonlinearity. The Curie temperature (T_C) is increased with increasing x content from 558 to 633 °C; T_C at $x = 0.20$ is about 584 °C. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4881797>]

I. INTRODUCTION

Actuation and sensing at higher temperatures than are available with current piezoelectric films is needed for automotive, aerospace and related industrial applications.¹ The operating temperature is usually limited to one half of the Curie temperature (T_C). As a result, commercial lead zirconate titanate (PZT) materials cannot be used in some applications due to their relatively low T_C ($\sim 386^\circ\text{C}$). In the $\text{Bi}(\text{Me})\text{O}_3\text{-PbTiO}_3$ ($\text{Me} = \text{Sc}, \text{In}, \text{Y}, \text{Yb}$, etc.) systems, $\text{Bi}(\text{Me})\text{O}_3$ end member with lower perovskite tolerance factors (t) yield higher T_C .²

The $x\text{BiInO}_3-(1-x)\text{PbTiO}_3$ ($x\text{BI}-(1-x)\text{PT}$) solid solution is attracting increasing attention not only because indium is less expensive than Sc but also because BiInO_3 boasts a smaller $t = 0.884$.² Zhang *et al.* reported the dielectric and piezoelectric properties of niobium-modified 0.15BI-0.85PT and 0.20BI-0.80PT ceramics, showing that 1.5 mol. % niobium doped 0.15BI-0.85PT possesses good piezoelectric coefficients with d_{33} around 60 pC/N and d_{15} of 85 pC/N.³ Ko *et al.* reported that the transverse piezoelectric coefficient e_{31f} of a chemical solution deposited 0.15BI-0.85PT film was -2.7 C/m^2 .⁴ Recently, Lee *et al.* reported improved e_{31f} up to -7.1 C/m^2 for 0.5 mol. % Mn doped 0.15BI-0.85PT in pulsed laser deposited films.⁵

However, information about the ferroelectric, dielectric and piezoelectric properties above $x = 0.15$ is still lacking both in bulk and thin film forms. In this paper, $\{100\}$ -textured $x\text{BI}-(1-x)\text{PT}$ thin films ($x = 0.10 \sim 0.25$) were grown by pulsed laser deposition and their crystal structure, ferroelectric properties, transverse piezoelectric response, and dielectric nonlinearity are reported. The nonlinear dielectric responses of the films are described by Rayleigh analyses to indicate extrinsic contributions from phase boundaries and/or domain walls.^{6,7} The temperature dependence of the dielectric constant was measured to confirm the Curie temperatures of the films.

II. EXPERIMENTAL PROCEDURE

Pt/Ti/SiO₂/Si substrates were used for the $x\text{BI}-(1-x)\text{PT}$ films. As reported previously, a PbTiO_3 seed layer was first deposited on the substrate to provide a perovskite template, as well as to increase the degree of $\{100\}$ orientation. For this purpose, a 0.15 M PbTiO_3 solution with 40 mol. % PbO excess was spin coated on the substrate and then pyrolyzed at 250 °C for 1 min and 400 °C for 1 min on a hot plate. The PbTiO_3 layer was crystallized at 580 °C for 1 min with oxygen flow in a rapid thermal annealer. The thickness of the PbTiO_3 layer was about 20 nm. Thin films over the composition range of $x\text{BI}-(1-x)\text{PT}$ ($x = 0.10, 0.15, 0.20$, and 0.25) were then deposited onto the coated substrates by pulsed laser deposition from ceramic targets. The targets were prepared by solid state reaction with 10 wt. % excess PbO to compensate for the volatilization during high temperature processing. In all cases, the targets were modified with 0.5 mol. % Mn additives to facilitate poling and decrease the leakage current.⁵ For deposition, the chamber was first pumped down to $\sim 10^{-7}$ Torr. Then a mixture of 10% ozone and 90% oxygen was introduced into the chamber to reach a working pressure of 100 mTorr. A KrF excimer laser (with 248 nm wavelength; Lambda Physik Compex 102, Fort Lauderdale, FL) with an energy density of $1.0 \sim 1.2 \text{ J/cm}^2$ was used. All of the films were deposited at a substrate temperature of 585 °C, a deposition time of 20 min, and a repetition rate of 10 Hz. The films were annealed at 600 °C for 5 min in an O₂ atmosphere by RTA. The thickness of the films was measured to be $520 \pm 3.2\%$, $560 \pm 3.9\%$, $660 \pm 1.1\%$, $650 \pm 0.7\%$ nm by an alpha step profilometer, corresponding to $x = 0.10, 0.15, 0.20$, and 0.25 , respectively.

The crystalline structures of the films were characterized using a Philips X'Pert MPD X-ray diffractometer with CuK α radiation. Rocking curves (ω scans) for 002 and 200 peaks were measured using a Philips X'Pert MRD 4-circle X-ray diffractometer. Rocking curves scans were collected using a step scan mode, $0.02^\circ/\text{step}$ and 1 s/step.

For electrical characterization of the films, platinum top electrodes (100 nm thick) were dc magnetron sputtered in a Lesker sputtering system at an Ar pressure of 2.5 mTorr and

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were patterned (dots with areas of $1.767 \times 10^{-4} \text{ cm}^2$) using a lift-off process. To improve the top electrode/film interface, film with top electrodes were rapid thermally annealed at 500°C for 1 min prior to electrical characterization. A Radiant Precision tester was used to evaluate the ferroelectric properties. Polarization-electric field (P - E) hysteresis loops were measured at 100 Hz. Dielectric properties were measured over the frequency range of 1 kHz~1 MHz and at an oscillation level of 30 mV by using an LCR meter (HP 4274 A) combined with a temperature control system. The transverse piezoelectric coefficient ($e_{31,f}$) was measured using the wafer flexure method.⁸ Prior to measurements of $e_{31,f}$, films were poled for 30 min at a dc voltage which is close to 3 times the coercive field.

III. RESULTS AND DISCUSSION

Figure 1(a) shows X-ray θ - 2θ diffraction profiles of $x\text{BI}-(1-x)\text{PT}$ thin films ($x = 0.10, 0.15, 0.20$, and 0.25) grown on the $\text{PbTiO}_3/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate. All XRD patterns exhibited a pure perovskite structure and strong 100 and 200 peaks, indicating that the films are {100}-textured. Compared to Ref. 5, the 0.15BI-0.85PT film reported here have stronger {100}-texture. With increasing x , it is seen that the diffraction angles of 100 and 200 shift downwards, indicating that the lattice parameter a is increasing with increasing BiInO_3 concentration. In order to distinguish the 002 and 200 peaks and calculate the lattice parameters, rocking curves were measured as shown in Fig. 1(b). The $x\text{BI}-(1-x)\text{PT}$ films at $x = 0.10$ has a tetragonal symmetry, as evidenced by the splitting of 002/200 peaks at a ω of around 22° . With increasing BI content, the tetragonality was reduced. The

FIG. 1. (a) X-ray diffraction θ - 2θ scan profiles and (b) rocking curves of $x\text{BI}-(1-x)\text{PT}$ films grown on a PbTiO_3 seed layer as a function of BiInO_3 . (c) Lattice parameters and tetragonality of $x\text{BI}-(1-x)\text{PT}$ films as a function of BiInO_3 content. Rocking curves (black) were fitted with pseudo-Voigt profiles (red).

TABLE I. Lattice parameters, tetragonality (c/a) and remanent polarization (P_r) for $x\text{BI}-(1-x)\text{PT}$ thin films.

x	Lattice parameters (Å)		Tetragonality c/a	P_r ($\mu\text{C}/\text{cm}^2$)
	c	a		
0.10	4.115 ± 0.007	3.950 ± 0.005	1.042	44
0.15	4.110 ± 0.006	3.968 ± 0.004	1.036	38
0.20	4.106 ± 0.005	3.991 ± 0.003	1.029	33
0.25	4.101 ± 0.007	4.002 ± 0.005	1.025	25

lattice parameters, a and c , calculated from the diffraction measurements are shown in Fig. 1(c) as a function of the BiInO_3 content along with the tetragonality (c/a). The data are also shown in Table I. It is evident that the tetragonality significantly decreases with increasing BI content. This trend is similar to that reported by Qi *et al.* based on first principles calculations in the $x\text{BiInO}_3-(1-x)\text{PbTiO}_3$ system.⁹ However the measured tetragonality here are smaller than the calculated values. Finally decreasing tetragonality with BiScO_3 additions is observed over most of the $x\text{BiScO}_3-(1-x)\text{PbTiO}_3$ phase diagram.^{2,10}

Figure 2 shows the polarization hysteresis loops of the $x\text{BI}-(1-x)\text{PT}$ films with $x = 0.10, 0.15, 0.20$, and 0.25 . It is seen that all the hysteresis loops have good shapes with little evidence for a strong leakage component at room temperature. The variation of remanent polarization (P_r) and coercive field (E_c) are shown in Table II. The polarization hysteresis loop of the $x\text{BI}-(1-x)\text{PT}$ films with $x = 0.10$ exhibits typical ferroelectric behavior, having a remanent polarization (P_r) of $44 \mu\text{C}/\text{cm}^2$, and a coercive field (E_c) of $100 \text{ kV}/\text{cm}$, respectively. As the BI content increases, the tetragonal distortion gradually decreases, resulting in a slightly decreased P_r . It is noted that the P_r of the textured 0.15BI-0.85PT films reported here is $38 \mu\text{C}/\text{cm}^2$; this value is significantly higher than that of 0.15BI-0.85PT film ($P_r = 29 \mu\text{C}/\text{cm}^2$) reported in Ref. 5.

The low and high field dielectric response was characterized using top and bottom electrodes on the films. The

FIG. 2. Polarization-electric field hysteresis loops of $x\text{BI}-(1-x)\text{PT}$ films at 100 Hz as a function of BiInO_3 concentration.

TABLE II. Summary of remanent polarization (P_r), dielectric constant (ϵ_r) and loss ($\tan \delta$) (measured at 10 kHz, 30 mV), transverse piezoelectric coefficient ($e_{31,f}$), dielectric nonlinearity characterization at 10 kHz, and Curie temperature (T_C) at 100 kHz for x BI-(1- x)PT films. The error of Curie temperature includes the fitting errors for individual data sets and the thermocouple error.

x	ϵ_r	$\tan \delta$	$e_{31,f}$ (C/m ²)	α' (cm/kV)	ϵ'_{init}	T_C (°C)
0.10	429 ± 24	0.009	-5.6 ± 0.9	2.26 ± 0.01	399 ± 0.7	558 ± 3
0.15	570 ± 27	0.011	-7.1 ± 0.6	3.92 ± 0.08	529 ± 0.7	570 ± 3
0.20	665 ± 33	0.014	-13.6 ± 1	5.06 ± 0.05	586 ± 0.7	584 ± 3
0.25	534 ± 21	0.091	-3.5 ± 0.4	4.28 ± 0.04	461 ± 1.0	633 ± 3

Rayleigh relations can be used to quantify the irreversible extrinsic contributions to the dielectric properties of ferroelectrics¹³

$$\epsilon_r = \epsilon'_{\text{init}} + \alpha' E_{\text{ac}},$$

where ϵ_r is the real component of the relative dielectric permittivity, ϵ'_{init} is reversible Rayleigh coefficient; it is the dielectric constant at the limit of zero applied field amplitude. α' and E_{ac} are the irreversible Rayleigh coefficient and field amplitude, respectively. The α' term is related to contributions to the dielectric response from irreversible domain wall or phase boundary displacements. The measured dielectric and piezoelectric response are usually due to the average response of single domains (e.g., the intrinsic behavior), and contributions due to the motion of the domain walls and phase boundaries and displacement of defects.^{13,14} For example, Ghosh *et al.* demonstrated enhancements in both the dielectric and piezoelectric properties in BaTiO₃ due to the displacement of domain walls,¹⁵ consistent with previous observations of Rayleigh behavior in PZT ceramics at low field levels.¹⁶ The AC field dependence of the dielectric constant in x BI-(1- x)PT films is reported in Fig. 3(a); the Rayleigh coefficients (α' and ϵ'_{init}) and variation are given in Fig. 3(b). The reported errors were determined from least squares analysis of the Rayleigh plots.

The Rayleigh parameters revealed a significant change in the nonlinear response with increasing BI content. Maximum α' coefficients value with 5.06 ± 0.05 cm/kV were observed at $x=0.20$. In BiScO₃-PbTiO₃ ceramics, the α' coefficients peaks at the MPB.⁶

The relative dielectric constant (ϵ_r) is shown as a function of BI content in Fig. 3(c) and Table II; it was found to be highest at $x=0.20$ (665 ± 33 at 10 kHz). The piezoelectric properties of the films were characterized in terms of the effective transverse piezoelectric coefficient ($e_{31,f}$). The maximum $e_{31,f}$ value of -13.6 ± 1 C/m² was at $x=0.20$, as shown in Fig. 3(c). This value is higher than those of randomly oriented PbZr_{0.52}Ti_{0.48}O₃ films ($e_{31,f} = -7$ C/m²) and 0.50BiScO₃-0.50PbTiO₃ epitaxial films ($e_{31,f} = -9$ C/m²) and comparable with {001} oriented PbZr_(1-x)Ti_xO₃ ($e_{31,f} = -12 \sim -27$ C/m²) and oriented 0.40BiScO₃-0.60PbTiO₃ epitaxial films ($e_{31,f} = -12$ C/m²).^{11,12}

Figure 4 shows the temperature dependence of the dielectric constant and dielectric loss of x BI-(1- x)PT films with $x=0.10, 0.15, 0.20$, and 0.25 at frequencies of 1 kHz,

FIG. 3. (a) The nonlinear behavior of dielectric constant with applied AC field and (b) variation of irreversible coefficient (α') and reversible coefficient (ϵ'_{init}) for x BI-(1- x)PT films at 10 kHz. (c) Dielectric constant (ϵ_r) at 10 kHz and (b) the average transverse piezoelectric coefficient, $e_{31,f}$, (shown with error bars for the standard deviation) of x BI-(1- x)PT films as a function of BiInO₃ content showing enhanced properties near $x=0.20$ for x BI-(1- x)PT films.

10 kHz, 100 kHz, and 1 MHz. It can be seen that the Curie temperature (T_C), corresponding to the maximum in the dielectric constant, increases with increasing BI concentration. The measured transition temperatures at 100 kHz are approximately 558, 570, 584, and 633 °C corresponding to $x=0.10, 0.15, 0.20$, and 0.25 as tabulated in Table II. The Curie temperature increase should be attributed to the high Curie temperature (>600 °C) of BiInO₃.¹⁷ The dielectric loss is large at high temperatures below 100 kHz; in the future doping studies to control the high temperature loss should be undertaken. In spite of this loss, it was possible to measure switchable polarization to temperatures of ~ 325 °C (data not shown).

To confirm the Curie temperatures of the 0.20BI-0.80PT film, temperature dependence of the X-ray diffraction pattern was measured at temperatures of 25 °C, 400 °C, 500 °C, 550 °C, 575 °C, and 600 °C. To align the sample and determine the sample surface temperatures, the sample was aligned

FIG. 4. Temperature dependence of dielectric constant (symbols) and dielectric loss (lines) for $x\text{BI}-(1-x)\text{PT}$ films at frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

to the Si peak, and $2\theta-\omega$ scan was collected for each temperature. After that, the 001, 100, 111, 002, and 200 peaks of the BI-PT film were collected as shown Figs. 5(a)–5(c). The 001 and 002 peaks appear on the left shoulder of the 100 and 200 peaks at room temperature, indicating that the 0.20BI-0.80PT is tetragonal. The splitting of 001/100 and 002/200 tetragonal reflection decreases with increasing temperature, and the 100, 111, and 200 peaks shifted to lower angles with increasing temperature. The a lattice parameter was calculated using the Nelson-Riley extrapolation function from the 100, 200, and 400 reflections.¹⁸ The c was determined from a and the

111 reflection. The variation of calculated lattice parameters a and c as a function of temperature is shown in Fig. 5(d). It is apparent that the film remains tetragonal until temperatures between 575 and 600 °C, where the ferroelectric-tetragonal to paraelectric-cubic phase transition occurs. This temperature range is in good agreement with that determined from the anomaly in the dielectric constant (~ 584 °C). It is noteworthy that the T_C of 584 °C for $x=0.20$ is significantly higher than that of PZT ($T_C=386$ °C) and PbTiO_3 ($T_C=490$ °C) as projected from the tolerance factor relationship presented in Ref. 2.

FIG. 5. The 2θ - ω scans of (a) the 001 and 100 peaks, (b) the 111 peak, (c) the 002 and 200 peaks for a 0.20BI-0.80PT film at temperature of 25 °C, 400 °C, 500 °C, 575 °C, and 600 °C. (d) The a and c lattice parameters as a function of temperature.

IV. SUMMARY

$x\text{BiInO}_3$ -(1- x) PbTiO_3 ($x\text{BI}$ -(1- x) PT , $x = 0.10, 0.15, 0.20$, and 0.25) films were deposited by using pulsed laser deposition. It was confirmed the maximum properties were observed near $x = 0.20$ as is evidenced by a peak in the permittivity ($\epsilon_r = 665$) and transverse piezoelectric coefficient ($e_{31f} = -13.6 \text{ C/m}^2$). Rayleigh analyses were performed to identify the extrinsic contributions to dielectric nonlinearity with different x . The magnitude of the irreversible Rayleigh coefficient, was found to be highest at $x = 0.20$; the corresponding Curie temperature was 584°C . These results are encouraging for sensor and actuator device development because the observed e_{31f} at $x = 0.20$ is as high as that of $\{001\}$ oriented $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ($e_{31f} = -12 \sim 20 \text{ C/m}^2$) and their T_C is higher than those of PZT films.

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