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Orientation effects on polarization and pyroelectric properties of ferroelectric thin films on Si

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Abstract

Oriented ferroelectric thin films ($\leqslant$ 1 μm) of PZT (90/10), $Bi_4Ti_3O_{12}$, and La-modified $Bi_4Ti_3O_{12}$, on Pt(111)/Ti/SiO_2/Si(100) substrates were fabricated using (MOD) technique. Film orientation was controlled through heat treatment, composition and layer structure, and correlated to structural changes using XRD, SEM and RAMAN techniques. Measured properties included *P–E* hysteresis loop, static pyroelectric and fatigue behavior. Temperature stable (25–90°C) polarization with $2P_r$ values of 6–24 μC/cm^2 and low switching fields E_c = 10–40 kV/cm were determined. For L-BIT films, low E_c values are attributed to easier domain wall mobility with La ions on the different Bi sites, resulting in improved fatigue behavior, comparable to SBT films, at much lower switching fields (Scott, J. F., High-dielectric constant thin films for dynamic random access memories (DRAM). *Ann. Rev. Mater. Sci.*, 1998, **28**, 79–100; Joshi, P. C. and Krupanidhi, S. B., Switching, fatigue, and retention in ferroelectric $Bi_4Ti_3O_{12}$ thin films. *Appl. Phys. Lett.*, 1993, **62**, 1928–1930; Dimos, D., Al-Schareef, N. H., Warren, W. L. and Tuttle, B. A., Photoinduced changes in the fatigue behavior of $SrBi_2Ta_2O_9$ and Pb(Zr,Ti)O_3 thin films. *J. Appl. Phys.*, 1996, **80**, 1682–1687). High pyroelectric coefficients ~10–60 nC/cm^2 K were also determined for the different films, up to ~100°C.

Keywords: Sensors; Ferroelectric properties; Films; Pyroelectric properties; PZT

1. Introduction

Metallo-organic (MOD) solution processing of thin films has been demonstrated for: PZT, $BaTiO_3$, $Bi_4Ti_3O_{12}$ (BIT), high T_c superconductors, ZrO_2, YSZ, and Ni–ZrO_2, mainly on Si or Pt/Si substrates.[1–7] This technique allows for easy film fabrication, rapid densification (when combined with rapid thermal annealing), and preferred orientation, achieved through process control. With preferred orientation, key properties such as polarization, coercivity and dielectric constant in the polycrystalline films can approach those of single crystals, and even lower coercive fields are achievable with near epitaxial films.[8] The ferroelectric film systems investigated in this study were PZT (90/10), $Bi_4Ti_3O_{12}$ (BIT), La-doped BIT. These material systems exhibit polarization and switching characteristics, suitable for capacitive memory applications, and also high pyroelectric coefficients for heat, flow and IR sensing applications. Understanding of the orientation and growth mechanisms in the films, correlated to the structural and property changes, relevant to thermal sensing and capacitive memory applications, were the main goals of this work.

2. Experimental

For the PZT films, zirconyl trimethylacetate, lead acetate, and titanium sec-butoxide [$Ti(OC_4H_9)_4$], were used as precursor compounds. Excess Pb, up to 6 mol%, was added to reduce sintering loss and promote orientation on heat treatment.[2] Bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], lanthanum nitrate [$La(NO_3)_3$], and titanium sec-butoxide were used for the preparation of precursor LBIT solutions in the molar ratio of 0.6/3.4/3 Excess Bi (6 mol%) was also added to the solutions to compensate for Bi loss during film heat treatment. The starting precursors were dissolved in a propionic acid/amylamine solvent system, and then passed through a

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Teflon filter with a pore size of 0.2 μm yielding a clear, yellowish solution, which remained stable in sealed bottles for several months. The solution was next spin-coated onto (111)-Pt/Ti/SiO_2/Si (100) substrates at speeds of 3000–4000 rpm for 30 s. The wet films were dried on a hot plate at 350–425°C for 1–3 min in air. The spinning and drying steps were repeated several times until desired film thickness was achieved. Heat treatment was carried out in air environment in two steps, first at 500°C/30 min to reduce residual carbon, and finally at 550–850°C under slightly oxidizing condition for 5–30 min, depending on film composition, for densification and structure development. High heating rates ($\geqslant$100°C/min) were typically needed to achieve high structural orientation in the films. Sputtered Au or Pt top electrodes (~1–2 mm diameter), were applied to the films. For this study, characterization of film structure was carried out using primarily XRD, RAMAN and SEM techniques. Ferroelectric measurements were made using a modified Sawyer Tower circuit for hysteresis and HP4194 impedance analyzer for dielectric data. Static pyroelectric coefficients were determined from the measured pyroelectric current at a constant heating rate of ~2°C/min up to 100°C.

3. Results and discussion

3.1. Heat treatment effects on orientation

In the BIT and PZT systems, prior studies have shown that heat treatment and composition can significantly affect preferred orientation.[2–4] The degree of preferred orientation, as discussed here is defined by a Lotgering factor, determined from summation of the peaks from a given family of planes as follows:[9]

$$\alpha = \frac{\Sigma I_{001}/\Sigma I(\text{oriented pattern}) - \Sigma I_{001}/\Sigma I(\text{JCPDS})}{1 - \Sigma I_{001}/\Sigma I(\text{JCPDS})} \quad (1)$$

where ΣI_{001} is the summation of intensities of the family of planes of interest, and ΣI is the summation of all peak intensities in the pattern. The designation is made in each term showing use of oriented pattern or JCPDS peak intensities. The Lotgering factor approaches the value of $\alpha = 1$ for complete preferred orientation, as shown in Fig. 1.

The MOD derived films all receive an initial heat-treatment at 500°C/30 min to remove carbon and other decomposition products. Fig. 1a shows the effect of heating rate above 550°C on orientation in the PZT films. As shown, preference is for (111) orientation at high heating rates $\geqslant$100°C/min, which gives values of $\alpha \approx 1$. Fig. 1b shows the effects of sintering temperature

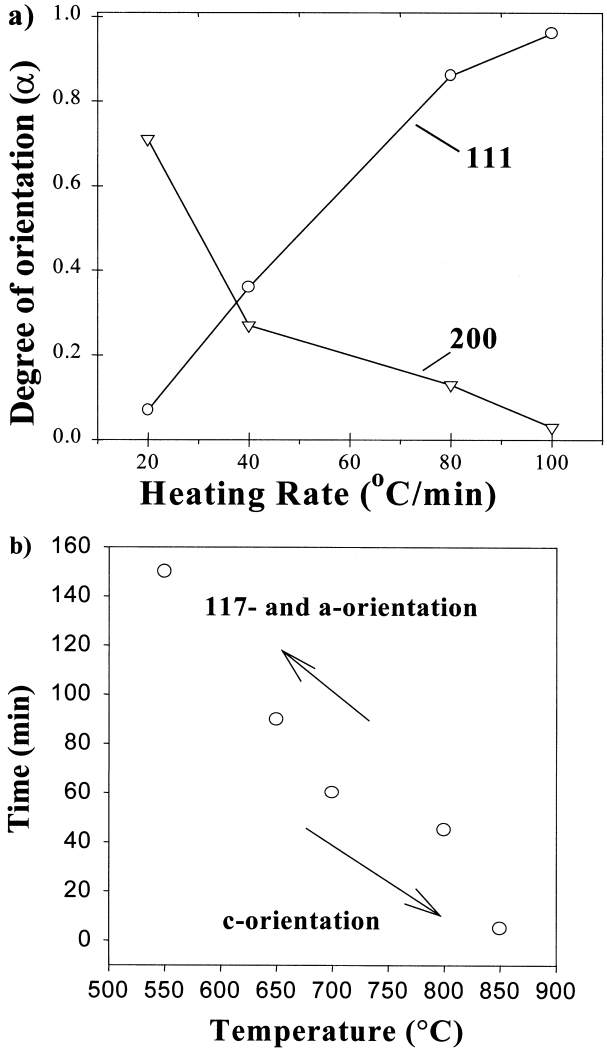

Fig. 1. Preferred orientation tendencies in (a) PZT for various heating rates, and (b) BIT as a function of heat treatment.

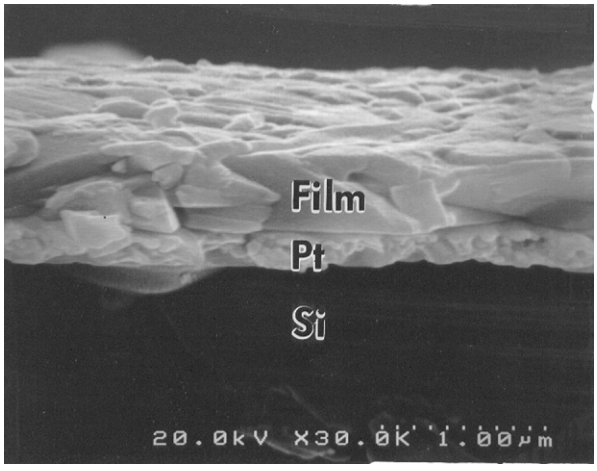

Fig. 2. Cross-sectional SEM micrograph of a highly c-oriented (α_{001} ~0.95) BIT film.

and time on orientation in BIT films. With long sintering times of 1.5–2.5 h at 550–650°C, the tendency is to form (100) or a-oriented films, which is the high polarization direction in the BIT structure. In contrast, heat treatment of 5–10 min at 750–850°C, produces strongly (001) or c-orientated films in BIT. Fig. 2 shows a cross-section of the BIT film, which is c-oriented, and exhibits plate like grains, normal to the substrate surface. Orientation in the films can be further enhanced by the solution incorporation of excess Pb or Bi, typically in amounts $\leqslant 6$ mol%, as liquid phase sintering aids.

3.2. Film structure effects on polarization and hysteresis

XRD of the highly oriented PZT (90/10) films showed a dominant (111) peak, with low intensity (100) and (200) peaks and no other peaks present. These films gave hysteresis loops with $P_r = 15$ μC/cm^2, and $E_c = 35$ kV/cm. With c-oriented BIT films, the XRD patterns showed primarily (001) peaks with the (117) peak, indicative of random orientation in this system, progressively depressed as α_{001} increases. For the films with ($\alpha = 0.95$), P_r is only ~3 μC/cm^2, with low E_c of ~15 kV/cm. In contrast, the BIT films of lower orientation ($\alpha = 0.7$) showed higher $P_r \sim 6$ μC/cm^2 and $E_c \sim 30$ kV/cm, indicating some (100) contribution to the polarization. For the oriented L-BIT films, the XRD pattern mainly revealed (00*l*) peaks, suppressed (117) peak and a (200) peak of higher intensity than in random BIT, reflecting the change towards tetragonal. For this film, the hysteresis loop is also more rectangular, with relatively high P_r ~13 μC/cm^2 and low E_c of ~10 kV/cm, all desirable characteristics for capacitive memory use.

Fig. 3 shows data on static pyroelectric coefficients as a function of temperature for oriented PZT, BIT and LBIT films. These high values are comparable to the best bulk ceramic pyroelectric materials such as lead titanate. The pyroelectric coefficient is seen to generally increase with temperature, polarization, and for the same composition films (e.g. BIT), with orientation, all as a result of the sharp changes in polarization observed with temperature. The highest observed pyroelectric figure of merit, p_i/ε_r, was achieved in the oriented BIT films. Table 1 summarizes and compares the relevant ferroelectric and pyroelectric data on the films studied for these dielectric systems.

Fig. 4 shows, for the oriented L-BIT film, hysteresis loop behavior at up to 4 V applied. Switching at 2 V was possible, but at lowered $P_r \sim 4.5$ μC/cm^2, while at a 3 V near maximum $P_r \sim 10$ μC/cm^2 was achieved, with saturation occurring at 4 V applied to the films. The L-BIT showed almost no aging up to 10^8 cycles, attributable to

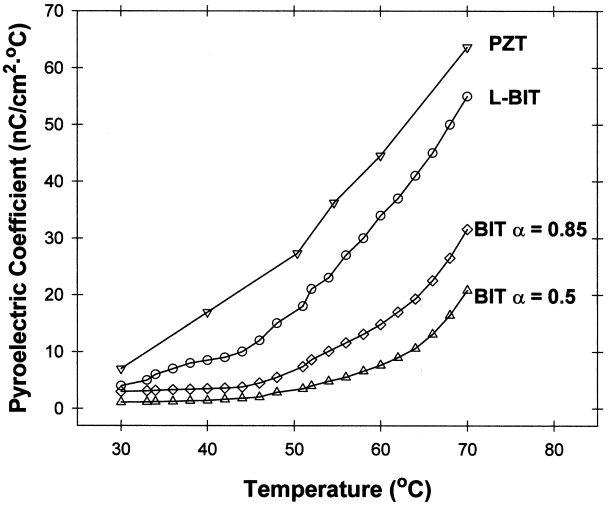

Fig. 3. Static pyroelectric coefficient as a function of temperature for oriented PZT, BIT and LBIT films.

Table 1
Properties of ferroelectric films on Pt/Ti/SiO_2/Si substrates

Film type	Orientation (fractional)	p_i[b] (25–100°C)	ε_r[a]	p_i/ε_r	P_s[c]	E_c[d]
BIT	(α- 001)					
	0.3	1–35	125	0.28	8	30
	0.5	1–60	110	0.55	6	28
	0.85	3–75	100	0.75	4.5	25
LBIT	0.85	5–95	240	0.40	16–20	8–10
PZT (90/10)	(α =111) 0.97	10–300	450	0.67	18–20	25–35

[a] ε_r = Dielectric constant.
[b] p_i = Pyroelectric coefficient (nC/cm^2°C).
[c] P_s = Saturation polarization (μC/cm^2).
[d] E_c = Coercive field (kV/cm).

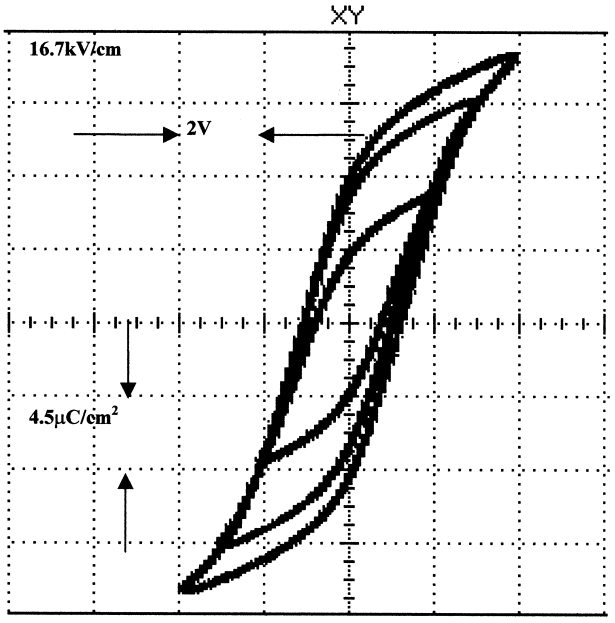

Fig. 4. Hysteresis in L-BIT film with 2, 3 or 4 V applied at 100 Hz showing near maximum P_r achieved at 3 V applied.

increased ordering in the lattice structure, from La substitution on both Bi sites, as determined by RAMAN and XRD analysis, leading to higher polarization and domain-wall mobility. This is in contrast to PZT films, where fatigue resistance, although improved with (111) orientation, still showed degradation with Pt electrodes. The coercive field E_c was lowered in all films with increased orientation. It is evident from these data, that sensor properties such as the pyroelectric coefficient p_i as well as the important capacitive memory storage properties of P_r, E_c and aging are related in a complex way to film composition, structure and orientation.

4. Conclusions

The study of PZT (90/10), BIT and L-BIT systems, has shown that good quality, thin films of these materials can be produced by the MOD process on Pt(111)/Ti/SiO_2/Si(100) substrates. High orientation and polarization, low coercive field and high pyroelectric coefficients were generally exhibited by these films. E_c values for the LBIT films were especially low, due to tetragonal modification of the orthorhombic BIT structure with La substitution, leading to enhanced polarization and domain wall motion. With ease of fabrication by the MOD process, and no poling treatment required, the highly oriented films can be advantageously used in thermal detection, sensing and in capacitive memory applications.

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