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Size effects of $0.8SrBi_2Ta_2O_9-0.2Bi_3TiNbO_9$ thin films

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The size effects of $0.8SrBi_2Ta_2O_9-0.2Bi_3TiNbO_9$ thin films, prepared by metalorganic deposition technique, were studied by determining how the ferroelectric properties vary with film thickness and grain size. It was found that the ferroelectric properties were determined by the grain size, and not by the thickness of the film in our studied thickness range of 80–500 nm. A 80 nm thick film showed good ferroelectric properties similar to the 500 nm thick film. The possible mechanisms for the size effects in SBT–BTN films are discussed. © *1998 American Institute of Physics.* [S0021-8979(98)06502-5]

I. INTRODUCTION

The size effects of ferroelectric bulk materials have been investigated for several decades.[1,2] There has been strong interest in the size effects of ferroelectric thin films in recent year, because of their promising nonvolatile memory applications.[3–5] So far, most studies of the size effects in ferroelectric thin films have focused on ABO_3 type materials such as $Pb(Zr,Ti)O_3$, $PbTiO_3$, and $BaTiO_3$. It has been found that the thickness and grain size of the thin film strongly effect the ferroelectric and optical properties, phase transitions, lattice structure, and stress distribution in ABO_3 type materials.[6–18] Generally speaking, a reduction in film thickness or grain size leads to a decrease in dielectric constant, remanent polarization, dielectric breakdown field, and the tetragonal distortion c/a, and leads to an increase in loss tangent, coercive field, band-gap energy, and diffuseness of the phase transitions.[7,10]

Several mechanisms for size effects in ferroelectric thin films have been postulated based on the effects of electrodes/film interfacial layers,[12–14] stresses,[17] defects,[18] and domain structure transitions.[19] The following two models may be the most probable mechanisms for size effects. One is the electrodes/film interfacial layers model.[12–14] The model assumes that an electrodes/film interfacial layers with low dielectric constant is formed at the interface between the electrode and ferroelectric film by the intrinsic stress during the synthesis process of the film. The low dielectric constant interfacial layers results in a decrease in the effective dielectric constant and remanent polarization, and increase in loss tangent and coercive field of the entire film.[12–14] The other model is based on the domain structure transition from multidomain predominance to single domain predominance at a critical grain size in the thin film.[19] The lack of the domain walls and the low domain wall mobility in the single domain predominated film, usually associated with small grains, may induce the size effects.

Recently, layered structure ferroelectric thin films, represented by $SrBi_2Ta_2O_9$ (SBT), have been intensively studied for their outstanding fatigue free property in nonvolatile memory applications. However, only a little work has been done on the size effects of layered structure ferroelectric thin films.[13] In this article, $0.8SrBi_2Ta_2O_9-0.2Bi_3TiNbO_9$ film was chosen to study the size effects of the film by determining how ferroelectric properties vary with the film thickness and grain size. Our previous articles[20] showed excellent ferroelectric properties for 0.8SBT–0.2BTN films at a low process temperature of 650 °C, which is about 100 °C lower than usual SBT process temperatures.

II. EXPERIMENT

In this study, the SBT–BTN thin films were prepared by our modified metalorganic solution deposition (MOD) technique, using an alkoxide–carboxylate precursor solution.[20] Strontium acetate, bismuth 2-ethylhexanoate, titanium isopropoxide, and tantalum ethoxide were selected as the precursors, and acetic acid, 2-ethylhexanoic acid, and 2-methoxyethanol were selected as the solvents. At room temperature, bismuth 2-ethylhexanoate and strontium acetate were initially dissolved in 2-ethylhaxanoic acid and acetic acid, respectively. These solutions were then added to the solution of tantalum ethoxide and titanium isopropoxide in 2-methoxyethanol to form a stoichiometric, clear, and stable SBT–BTN precursor solution. The films were coated on $Pt/Ti/SiO_2/Si$ substrates by spin coating. Then the films were kept on a hot plate (at 350 °C) in air for 10 min. The thickness of each coating layer was controlled by adjusting the viscosity of the solution and the spin speed. This step was repeated after each coating to obtain the desired final film thickness of 50, 80, 150, 200, and 500 nm. The films were annealed in a tube furnace at temperature of 650 °C for 1 h in an oxygen atmosphere to crystallize the films.

The ferroelectric properties were measured by a RT-66 (Radiant Technologies Inc.) test system. The dielectric measurements were also conducted by a HP4192A impedance analyzer. Their microstructure was observed by a D3000 atomic force microscope (AFM) (Digital Instrument, Inc.), and a Scintag XDS-2000 x-ray diffractometer (XRD) using Cu $K\alpha$ radiation at 40 kV.

III. RESULTS AND DISCUSSION

The films with thickness from 80 to 500 nm showed similar well saturated hysteresis loops the 50 nm film was electrically shorted. Figure 1 shows the hysteresis loop of the

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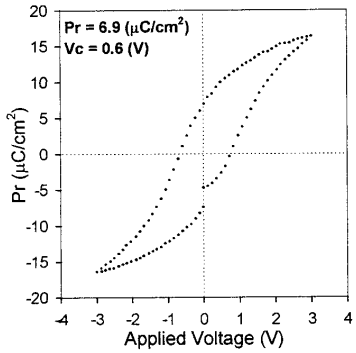

FIG. 1. Hysteresis loop of 0.8SBT–0.2BTN film with thickness of 80 nm at 3 V.

film with a thickness of 80 nm. The permanent polarization (P_r) of the 80 nm film has 6.8 μC/cm^2 and the coercive field (E_c) has 70 kV/cm at 3 V and 100 kHz. All the films in the thickness range from 50 to 500 nm showed similar XRD pattern. The XRD pattern indicated that the films were well crystallized. Table I shows the properties of permanent polarization, coercive field, dielectric constant, and dielectric loss (measured at 100 kHz) as a function of film thickness. The data in Table I indicates that the electrical properties of the SBT–BTN films are independent of film thickness in our studied thickness range. This results are contrary to the reports of piezoelectric (PZT) films, where the electrical properties of PZT films strongly depend on thickness in the thickness range from 25 to 300 nm.[6–8,11,12]

The films with thickness of 50–500 nm showed similar AFM microstructure. Figure 2 shows the AFM microstructure of the 80 nm film. It can been seen in Fig. 2 that the film was composed of large stripe shaped grains (about 200 $\times$60 nm) and small grains (about 20$\times$20 nm). The large stripe shaped grains result in the good ferroelectric properties, and the small grains reduces leakage current to avoid electrical breakdown even in such very thin 80 nm film. A SBT–BTN film with a thickness of 500 nm was annealed at temperature of 575 °C to obtain grain size of about 50 nm to confirm the role of the grain size in the size effects of the ferroelectric thin films. No ferroelectric properties were obtained in this film. It may be concluded that the grain size rather than the film thickness is the main factor for the size effects in these layered structure SBT–BTN films.

As we know, the ferroelectric properties are determined mainly by the ferroelectric domain structure, domain nucleation, and the domain mobility. In transmission electron microscopy (TEM) observation of $PbTiO_3$ film, Ren *et al.*[19] found that domain structures and the domain wall mobility were related to the grain size. The domain structure transition from multidomained predominance to single-domain predominance in $PbTiO_3$ films occurs when the grain size was below a critical grain size. The single-domain predominated grain is very stable under an external field, so that domain nucleation very difficult. Therefore, no good ferroelectric properties can been obtained in a single-domain predominated film, which usually has small grain. A similar dependence of ferroelectric properties on grain size has been found in SBT thin films by M. Nagata and S. B. Desu.[21] But the difference is that the grain size of SBT-based film is mainly determined by process temperature and not by the film thickness. However the grain size of ABO_3 materials is controlled not only by process temperature but also by the film thickness.

TABLE I. Electrical properties of 0.8SBT–0.2BTN thin films with different thickness.

Film thickness (nm)	P_r[a] (μC/cm^2)	E_c[a] (kV/cm)	Dielectric constant	Dielectric loss
80	6.9	71	213	0.028
100	6.9	74	204	0.027
150	7.3	76	214	0.025
200	6.8	75	199	0.024
250	6.6	75	211	0.027

[a]At an applied field of 300 kV/cm.

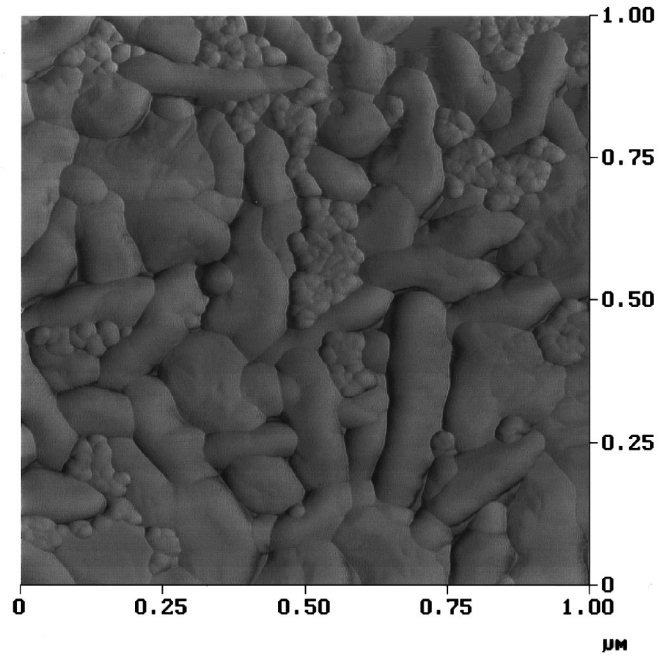

FIG. 2. The AFM picture of 0.8SBT–0.2BTN film with thickness of 80 nm.

Several researchers have reported a linear relationship between the grain size and the film thickness in the film thickness from 25 to 300 nm in ABO_3 type ferroelectric films, such as PZT[6,8] and $PbTiO_3$,[11] but this relationship was not observed in layered SBT-based thin films. We think that a small tetragonal distortion in ABO_3 type ferroelectric films makes the formation of spherically shaped grains much easier, and causes the grain size to be limited by the film thickness. However, the large difference between the lattice constants of *a* and *c* in the layered structure thin films causes anisotropic grain growth. Anisotropic grain growth is not limited by the film thickness, and causes the stripe shaped grains (as seen in this article).

IV. CONCLUSION

A series of $0.8SrBi_2Ta_2O_9$–$0.2Bi_3TiNbO_9$ thin films with thickness from 50 to 500 nm were fabricated by the

MOD method. The size effects of SBT–BTN thin films have been studied by comparing ferroelectric properties with film thickness and grain size. It has been found that the ferroelectric properties were determined by the grain size, and not by the thickness of the film in our studied thickness range of 80–500 nm. In contrast with ABO_3 type materials, the grain size is independent of the film thickness in layered ferroelectric materials. A 80 nm thick SBT–BTN film showed good ferroelectric properties similar to the 500 nm thick film. We believe that the large difference between the lattice constants of *a* and *c* in the layered ferroelectric materials causes anisotropic grain growth. Anisotropic grain growth results in grain size that is not limited by the film thickness.

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