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Structural and electro-optic properties of laser ablated $Bi_4Ti_3O_{12}$ thin films on $SrTiO_3(100)$ and $SrTiO_3(110)$

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$Bi_4Ti_3O_{12}$ thin films have been grown by laser ablation on $SrTiO_3(100)$ and $SrTiO_3(110)$ substrates. Substrate surface orientation is found to be an important growth parameter which determines crystal axis orientation, grain growth behavior, and electro-optic properties of the $Bi_4Ti_3O_{12}$ thin films. The films grown on $SrTiO_3(110)$ shows a ferroelectric phase transition near 720 °C and a large quadratic electro-optic effect with the effective coefficient 1.1×10^{-16} m^2/V^2.

$Bi_4Ti_3O_{12}$ is an interesting ferroelectric material with useful properties for nonvolatile memory, piezoelectric, and electro-optic devices.[1] Recently, epitaxial $Bi_4Ti_3O_{12}$ thin films have been successfully grown by pulsed excimer laser deposition on $SrTiO_3(100)$,[2] $MgO(110)$,[3] and $YBa_2Cu_3O_7(001)$.[4] The feasibility for growing lattice-matched heterostructures makes this material very attractive for several applications. In this letter we report effects of substrate surface orientation, i.e., (100) and (110) faces of $SrTiO_3$ single crystal, on structural and electro-optic properties of the laser ablated $Bi_4Ti_3O_{12}$ films.

A visible laser, i.e., second harmonics (532 nm) of a *Q*-switched Nd:YAG laser, was used in this study instead of commonly used ultraviolet lasers.[2–4] The laser was pulsed at a rate of 20 Hz, and the beam was focused with a quartz lens onto a polycrystalline, single-phase $Bi_4Ti_3O_{12}$ target. Fluence of the beam on the target was estimated to be 1.5–2 J/cm^2. Thin-film deposition was carried on a single-crystal substrate, $SrTiO_3(100)$ or $SrTiO_3(110)$, which was maintained at temperature of 730–750 °C in oxygen atmosphere of 200 mTorr. After the deposition, the thin films were *in situ* annealed at 500 °C in oxygen atmosphere of 500 Torr for 30 min. They were characterized using x-ray diffractometry methods (2θ scan, rocking curve, and x-ray pole figure) and scanning electron microscopy (SEM). Their linear birefringences were also measured as a function of temperature and dc electric field.

X-ray diffraction patterns are shown in Fig. 1. The pattern of the $Bi_4Ti_3O_{12}$ thin film on $SrTiO_3(100)$, as shown in Fig. 1(a), has only $(00l)$ peaks in agreement with an earlier report.[2] The rocking curve full width at half maximum (FWHM) is about 0.3° for the (006) peak of the film. This value informs us that grains are well aligned with their *c*-axes normal to the substrate. However, the film on $SrTiO_3(110)$ shows a (117) peak as well as $(00l)$ peaks, as shown in Fig. 1(b). This result indicates that this film is composed of grains with more than one orientation.

A relation between the crystal axes of $Bi_4Ti_3O_{12}$ and the in-plane vectors of $SrTiO_3$ can be obtained using x-ray pole figure. The Schultz geometry[5] was used in this measurement. The α and β rotations are coupled so that a 360° rotation of β corresponds to a 2.5° decrease of α. (The 2θ scan corresponds to $\alpha=90°$.) As shown in Fig. 2(a), the four (117) reflections of the film on $SrTiO_3(100)$ are located at $\beta=0°$, 90°, 180°, and 270° with $\alpha\cong40°$. This indicates that the [117] direction of the $Bi_4Ti_3O_{12}$ grains is aligned in the ac-plane of $SrTiO_3$ lattice with the polar angle of about 50° from the *c*-axis of the substrate. This epitaxial growth behavior can be understood from the fact that the lattice constants of $Bi_4Ti_3O_{12}$ ($a=5.448$ Å and $b=5.410$ Å) are close to the length of the face diagonal of the $SrTiO_3$ lattice ($a=3.905$ Å for $SrTiO_3$).

Figure 2(b) shows a pole figure of the film on $SrTiO_3$ (110) for (117) and (008) reflections of $Bi_4Ti_3O_{12}$. Similar to Fig. 2(a) the resulting (117) reflections, which come from the grains with their *c*-axes normal to the substrate, have fourfold azimuthal orientations along the [100] and $[1\bar{1}0]$ directions of the substrate. This tendency can be understood from the fact that the lattice constant of $SrTiO_3$ along the $[1\bar{1}0]$ direction is very close to that of $Bi_4Ti_3O_{12}$ along *a*-axis. On the other hand, the (008) reflections show strong peaks at $\beta\cong20°$ and 200° with $\alpha\cong40°$–48°. These reflections come from the grains with their (117) planes nearly parallel to the substrate. Most of these grains are

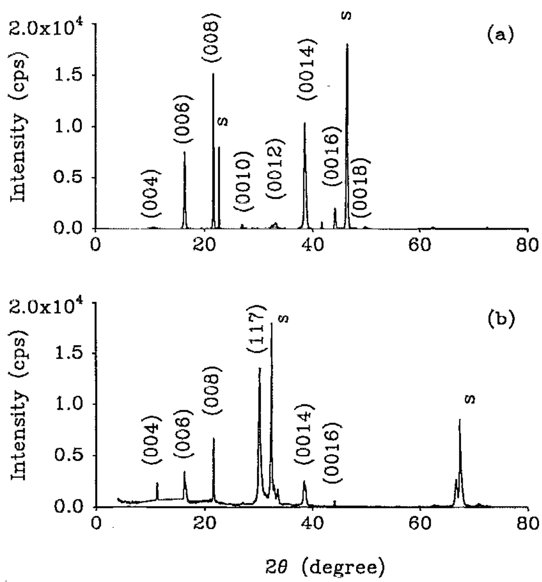

FIG. 1. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ thin films on (a) $SrTiO_3(100)$ and (b) $SrTiO_3(110)$. The character "s" indicates peaks of $SrTiO_3$.

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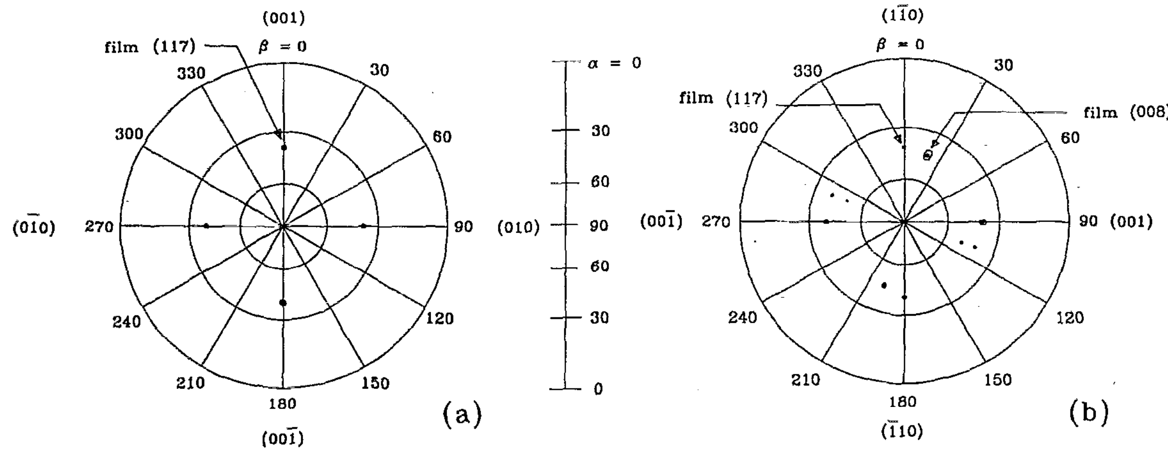

FIG. 2. X-ray pole figures of $Bi_4Ti_3O_{12}$ thin films on (a) $SrTiO_3(100)$ and (b) $SrTiO_3(110)$.

oriented along an angle of 20° from [1$\underline{1}$0] direction of $SrTiO_3$ and an angle around 46° from the normal direction of the $SrTiO_3$ substrate. Therefore, the film on $SrTiO_3(110)$ is composed of grains which are highly oriented along some directions.

SEM micrographs, shown in Fig. 3, also demonstrate an interesting difference in grain growth behavior between the $Bi_4Ti_3O_{12}$ thin films. The film on $SrTiO_3(100)$ shows grain growth without any preferred habit but the film on $SrTiO_3(110)$ shows growth of elliptical grains which are aligned along a direction about 20° away from the [110] direction of the substrate. This tilt angle is similar to that of the strongest (008) peaks in Fig. 2(b). Therefore, the $SrTiO_3$ surface orientation influences grain growth behavior as well as crystal axis orientation.

Linear birefringence, Δn, was measured by the Senarmont method[6] using a 15 mW He-Ne laser. For a thin film of 5000 Å thickness, the resolution of Δn in our system was about 10^{-4}. Birefringence of a blank $SrTiO_3$ substrate was measured separately and showed no significant shift within our experimental error. For the temperature dependence measurement, the samples were heated with a furnace. For the electric field dependence measurement, silver electrodes were thermally evaporated on a thin film with a separation of 0.5 mm. A dc electric field up to 20 kV/cm was applied parallel to the [1$\underline{1}$0] direction of the $SrTiO_3(110)$ substrate. The light enters with its polarization at an angle of 45° with respect to the direction of the electric field.

Figure 4(a) shows the temperature dependent birefringences for the $Bi_4Ti_3O_{12}$ thin films. The birefringence of the film on $SrTiO_3(100)$, $\Delta n_{(100)}$, is similar to that of a single-crystal $Bi_4Ti_3O_{12}$ when the light enters the crystal along the *c*-axis.[7] The birefringence of the film on $SrTiO_3(110)$, $\Delta n_{(110)}$, is much larger than $\Delta n_{(100)}$, and the former comes from the contribution of Δn's along three

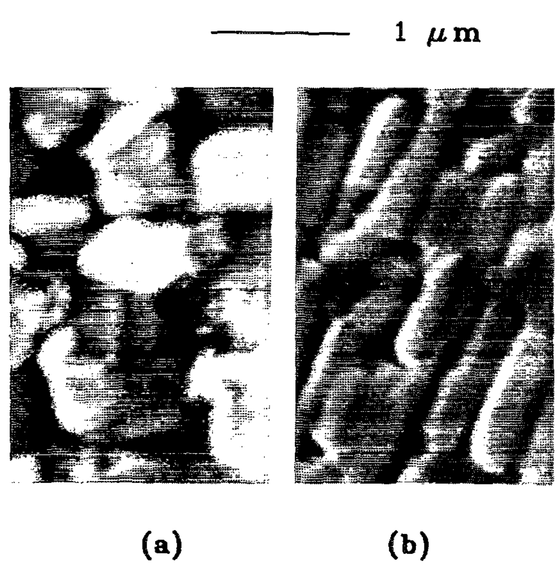

FIG. 3. Scanning electron micrographs of $Bi_4Ti_3O_{12}$ thin films on (a) on $SrTiO_3(100)$ and (b) $SrTiO_3(110)$.

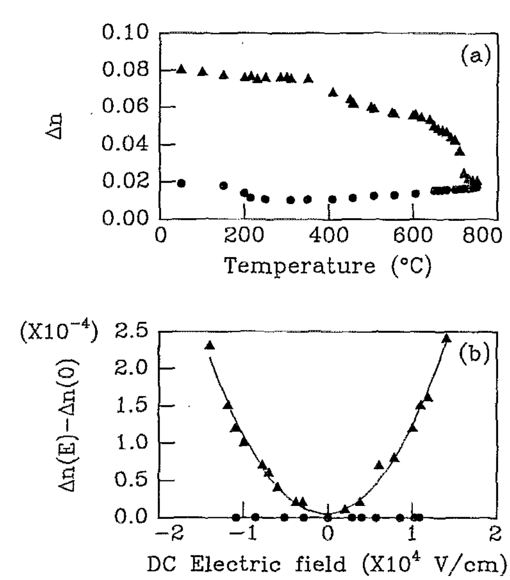

FIG. 4. (a) Temperature dependence of linear birefringence shift, Δn, of $Bi_4Ti_3O_{12}$ thin films. (b) Changes in Δn as a function of applied electric field. In these figures, solid circles represent the data for the film on $SrTiO_3(100)$ and solid triangles represent those on $SrTiO_3(110)$.

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crystal axes.[7] An abrupt change in $\Delta n_{(110)}$, which is related to the ferroelectric transition, is observed near 720 °C. This Curie temperature is higher than that of a single crystal, i.e., 676 °C.[7] A similar shift of 50 °C in the Curie temperature was reported for the epitaxial $PbTiO_3$ thin films,[8] and it was interpreted as a stress induced shift.[9]

Figure 4(b) shows changes in Δn, i.e., $\Delta n(E)-\Delta n(E=0)$, as a function of applied electric field E. Little changes in Δn are observed for the thin film on $SrTiO_3(100)$. However, the film on $SrTiO_3(110)$ shows very large changes in Δn which can be fitted to a quadratic equation of E. The linear electro-optic component is found to be very small and that is in agreement with the fact that our measured Δn's are the average responses from the multidomain material.[10] The effective quadratic electro-optic coefficient is calculated to be 1.1×10^{-16} m^2/V^2. This value is larger than those of most ferroelectric films [typically, 10^{-17}–10^{-19} m^2/V^2 for $(Sr,Ba)Nb_2O_6$, $BaTiO_3$, and $Ba_2NaNb_5O_{15}$],[11] and it is also larger than that of sputtered $(Pb,La)(Zr,Ti)O_3$ thin film [i.e., 4.43×10^{-17} m^2/V^2] by a factor of 2.[11] Therefore, the $Bi_4Ti_3O_{12}$ film on $SrTiO_3(110)$ is a good candidate material for the electro-optic device applications.

In summary, $Bi_4Ti_3O_{12}$ thin films have been grown on $SrTiO_3(100)$ and $SrTiO_3(110)$ by laser ablation. From x-ray diffraction SEM and linear birefringence measurements, it is found that the $SrTiO_3$ surface orientation determines crystal axis orientation, grain growth behavior, and electro-optic properties of the $Bi_4Ti_3O_{12}$ thin films. A ferroelectric phase transition is observed near 720 °C, which is higher than the transition temperature of a bulk $Bi_4Ti_3O_{12}$. The effective quadratic electro-optic coefficient for the film grown on $SrTiO_3(110)$ is evaluated to be 1.1×10^{-16} m^2/V^2.

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