Structural and electro-optic properties of pulsed laser deposited $Bi_4Ti_3O_{12}$ thin films on MgO

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Ferroelectric $Bi_4Ti_3O_{12}$ thin films have been grown on MgO (100) and MgO(110) substrates by the pulsed laser deposition. X-ray diffraction studies show that the films on both substrates have preferential crystallographic orientation such that most of their c axes are close to the substrate normal direction. The film on MgO(110) shows quadratic and hysteretic electro-optic characteristics with the effective coefficient of about 3.8×10^{-15} m^2/V^2.

$Bi_4Ti_3O_{12}$ thin films have been widely investigated with the pulsed laser deposition techniques due to their potential application for nonvolatile memory and electro-optic (EO) devices.[1–4] Recently, we showed that a ferroelectric $Bi_4Ti_3O_{12}$ thin film grown on a $SrTiO_3$(110) substrate has a large quadratic EO effect.[4] However, this film has a couple of drawbacks for application. First, the refractive index n of $SrTiO_3$ ($n=2.39$) is comparable to that of $Bi_4Ti_3O_{12}$ ($n=2.4$–2.6), so it is difficult to use this film for optical waveguide devices. A substrate with a lower value of n is more desirable. Second, the $Bi_4Ti_3O_{12}$ film is composed of grains with more than two orientations, so its light scattering loss is very large. To reduce the scattering loss, films with more highly aligned grains are required. In this study, $Bi_4Ti_3O_{12}$ thin films are pulsed laser deposited on MgO, whose refractive index is 1.74. It is found that a film grown on MgO(110) has preferential crystallographic orientation as well as large EO effects.

Two kinds of MgO substrates, i.e., MgO(100) and MgO(110), were used. Details of pulsed laser deposition and *in situ* annealing conditions used in this study are similar to those described in our earlier letter.[4] The thickness of the deposited films is about 5000 Å. The structure of the $Bi_4Ti_3O_{12}$ films was characterized by x-ray diffraction (XRD) techniques, such as θ-2θ scan and pole figure measurements. The surface morphology and the roughness were investigated using an atomic force microscope (AFM), and the EO properties were investigated by measuring their linear birefringences.

It is found that laser fluence on the target is a very important parameter to grow $Bi_4Ti_3O_{12}$ films with a preferential crystallographic orientation. Most films deposited with laser fluences above 2 J/cm^2 show strong (00l) and (117) peaks in the XRD θ-2θ scan. In this letter, only films grown with the fluences of 1.5–2 J/cm^2 are described. The problem of $Bi_{12}TiO_{20}$ phase appearance for the fluences less than 2 J/cm^2, reported by Maffei and Krupanidhi,[3] was not found in the study.

Figures 1(a) and 1(b) show the XRD pattern of the film grown on MgO(100) and that on MgO(110), respectively. Both of the XRD patterns show substrate peaks and only (00l) peaks for $Bi_4Ti_3O_{12}$. The appearance of only (00l) reflections for the film on MgO(110) is very interesting, since surface atomic configuration of MgO(110) lattice is not square. A similar observation has been made by Buhay *et al.*[1] However, XRD θ-2θ scan measurements are not sufficient for us to understand structural properties of the $Bi_4Ti_3O_{12}$ films, since they only provide information on crystal orientation normal to substrates.

Lateral registry between crystal axes of the thin film and in-plane vectors of the substrate can be obtained using x-ray pole figure measurement. The pole figure of the $Bi_4Ti_3O_{12}$ film on MgO(100), in Fig. 2(a), shows strong fourfold (117) reflections at $\beta=0°$, 90°, 180°, and 270° with $\alpha\approx40°$, and weak (117) reflections at $\beta=45°$, 135°, 225°, and 315° with $\alpha\approx35°$. The relative ratio of intensities between these two kinds of peaks is about 10:1. The strong reflection peaks come from $Bi_4Ti_3O_{12}$ grains whose (110) plane is parallel to MgO(010) plane. The peaks shown in the XRD θ-2θ scan, i.e., Fig. 1(a), are due to these grains. The weak peaks come from grains whose (110) is nearly parallel to MgO(011). Considering the fact that the lattice mismatch between $Bi_4Ti_3O_{12}$ and MgO is rather large, i.e., about 9% it is interesting to observe the strong tendency of the nearly epitaxial growth.

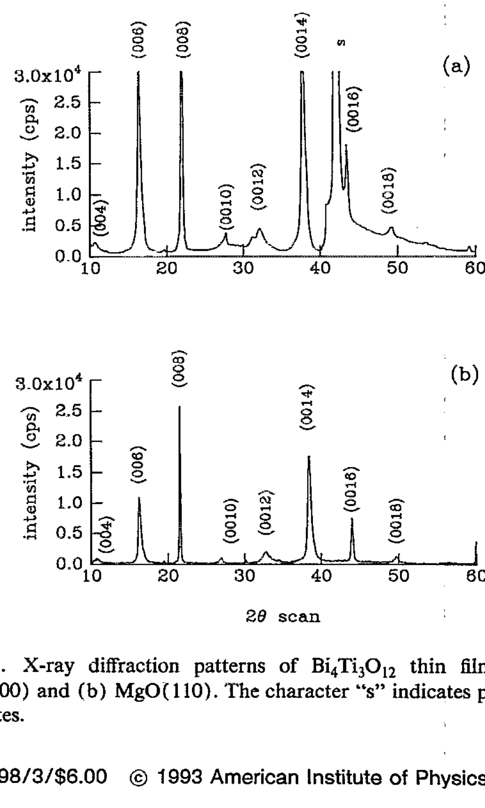

FIG. 1. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ thin films on (a) MgO(100) and (b) MgO(110). The character "s" indicates peaks of the substrates.

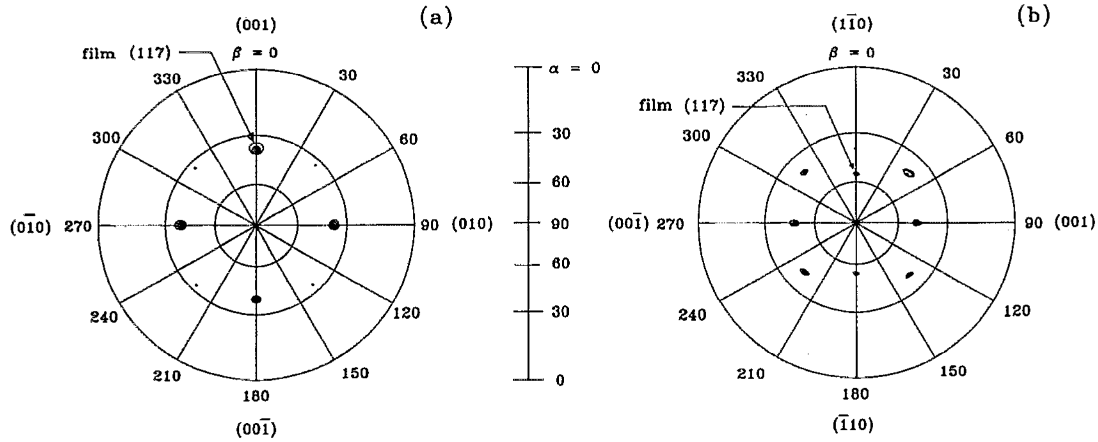

FIG. 2. X-ray pole figures of $Bi_4Ti_3O_{12}$ thin films on (a) MgO(100) and (b) MgO(110).

The pole figure for (117) reflections of the $Bi_4Ti_3O_{12}$ film on MgO(110) is shown in Fig. 2(b). Four reflections are located at $\beta=45°$, 135°, 225°, and 315° with $\alpha=40°$. Since the MgO(110) surface forms a rectangular net with atomic distances 4.21 and 5.95 Å, a or b direction of $Bi_4Ti_3O_{12}$ [$a=5.41$ Å and $b=5.45$ Å] grains have a tendency of aligning along the [1$\bar{1}$0] direction of MgO. As in the case of the film on MgO(100), these reflections come from the grains which provide peaks in the XRD θ-2θ scan. The pole figure shows some additional reflections whose corresponding grains do not provide any peaks in the θ-2θ scan: two reflections appear at $\beta=90°$ and 270° with $\alpha\approx45°$, and another two peaks appear at $\beta=0°$ and 180° with $\alpha\approx50°$. (The intensities of these reflections are similar to those of reflections at $\alpha\approx40°$.) The small differences in the values of α from 40° indicate that the c axes of the grains are slightly misaligned from the substrate normal direction.

Figure 3(a) shows an AFM picture and surface roughness data for the film on MgO(100). The film is composed of closely packed preferential grains, whose typical size is about 2000–3000 Å. Figure 3(b) indicates that roughness along the bar marked in Fig. 3(a) is on the order of 500–1000 Å. The film on MgO(110) has a similar surface morphology. It is quite different from the case of the films on $SiTiO_3$,[4] where surface morphology strongly depends on the substrate surface orientation. Considering that both of the films on MgO are composed of grains preferentially c-axes oriented, it is likely that the surface morphology of $Bi_4Ti_3O_{12}$ films is closely related to the grain growth behavior with c-axis normal to a substrate.

Linear birefringence, Δn, was measured at 0.633 μm by the Senarmont method.[4] Aluminum electrodes were thermally evaporated onto the films with a separation of 100 μm. A dc electric field up to 10 kV/cm was applied parallel to the [001] direction of the MgO(100) and MgO(110) substrates. The light enters with its polarization at an angle of 45° with respect to the direction of the electric field. Figure 4 shows $\delta(\Delta n)$, i.e., $\Delta n(E)-\Delta n(E=0)$, for films on MgO substrates as a function of applied electric field E. Changes of birefringence $\delta(\Delta n)$ for the film on MgO(100) (solid circles) show little dependence on E. On the other hand, $\delta(\Delta n)$ for the film on MgO(110) (solid triangles) show strong electric field dependence.

The large differences in the EO behaviors for these two films are due to their structural differences. $Bi_4Ti_3O_{12}$ crystal is an optical biaxial crystal, which has two kinds of domains related to the direction of the polarization component along the c axis. The domains can be distinguished optically for a light propagating along the b axis.[5] All the grains of the film on MgO(100) have their c axes normal to the substrate, and the light in our experimental configuration propagates along the c axis. The domains cannot be

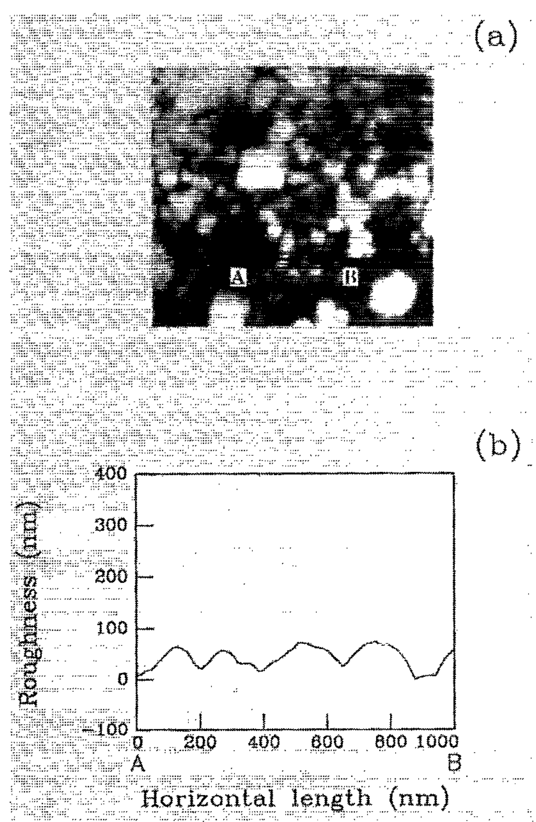

FIG. 3. AFM images of $Bi_4Ti_3O_{12}$ thin films on (a) MgO and (b) surface roughness along the bar marked in figure (a).

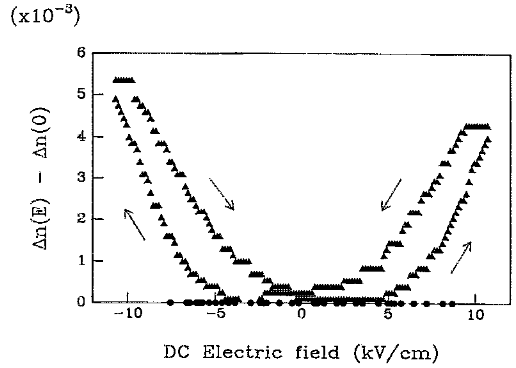

FIG. 4. Changes of $\delta(\Delta n)$ as a function of applied electric field E. Solid circles and solid triangles represent the data for the films on MgO(100) and MgO(110), respectively.

distinguished in this configuration. However, as shown in Fig. 2(b), about half of the grains in the film on MgO(110) have their c axes misaligned from the substrate normal direction, so the effective Δn of this film becomes nonzero. The biased electric field causes the grains to experience the switching of the polarization component along the c axis, which results in the large EO effects in the film on MgO(110).

Figure 4 also shows a hysteresis behavior in $\delta(\Delta n)$ for the film on MgO(110), indicating that the film is ferroelectric. The effective quadratic electro-optic coefficient is estimated from an equation:

$$\delta\Delta n = R(E - E_{\pm})^2,$$

where $E_{\pm}$ is introduced to account for the hysteresis behavior. For each direction of the dc electric fields, the value of R is estimated to be about 3.8×10^{-15} m^2/V^2. This value of R is larger than that of $Bi_4Ti_3O_{12}$ film on $SrTiO_3$(110) and that of a sputtered PLZT thin film ($R=4\times10^{-16}$ m^2/V^2)[6] by an order of magnitude.

In summary, ferroelectric $Bi_4Ti_3O_{12}$ thin films are grown on MgO(100) and MgO(110) by the pulsed laser deposition. A film grown on MgO(110) has highly aligned microstructures and shows very large EO effects with an effective quadratic coefficient of 3.8×10^{-15} m^2/V^2.

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