High-oxygen-pressure Crystal Growth of Ferroelectric $Bi_4Ti_3O_{12}$ Single Crystals

Ferroelectric bismuth titanate ($Bi_4Ti_3O_{12}$, BiT) has been regarded as a promising material for innovative semiconductor-based applications such as nonvolatile memories, electro-optic devices and uncooled infrared detectors because of its high Curie temperature, large spontaneous polarization (P_s) and large electro-optic coefficient [1]. The control of polarization states is the underlying basis of these functional devices, and polarization switching is achieved through the nucleation of domains and the following domain-wall motion by applying an electric field (E). Leakage current arising from defects, however, interferes with the polarization switching of BiT-based materials [2]. In addition, oxygen vacancies are known to act as an obstacle to the polarization switching, and a resultant remanent polarization (P_r) is suppressed by the clamping of the domain walls by oxygen vacancies [2]. The leakage current and domain clamping by oxygen vacancies make BiT unsuitable for the practical applications. Thus, a guiding principle of defect control is required to be established for obtaining high-quality BiT-based devices with a large P_r as well as a low leakage current. Here, we show that high-oxygen-pressure crystal growth is an effective process for obtaining high-quality BiT crystals with a large P_r and a low coercive field (E_c) as well as low leakage current [3].

Synchrotron radiation powder diffraction experiments on the crushed powder of the crystals were performed using a large Debye-Scherrer camera installed at **BL02B2** to investigate the precise crystal structure of BiT synthesized by the processing method. We used high-energy SR with a wavelength of λ = 0.035639(2) nm (E ~ 35 keV) to reduce absorption by the samples. The BiT crystals under different Po_2 atmospheres had almost the same lattice

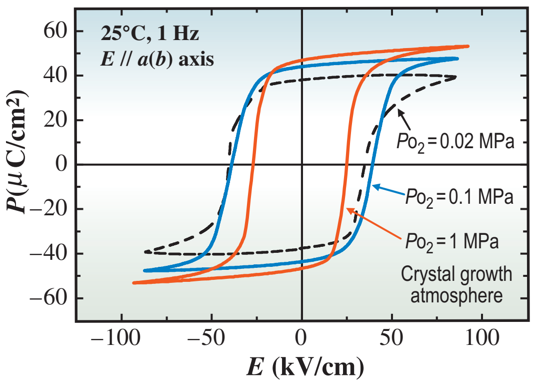

Fig. 1. Polarization hysteresis loops along the ***a***(***b***)-axis for the BiT crystals grown at a Po_2 of 0.02, 0.1, and 1 MPa. These crystals were annealed at 900°C for 10 h in air. The measurements were conduced at 25°C using an E at a frequency of 1 Hz.

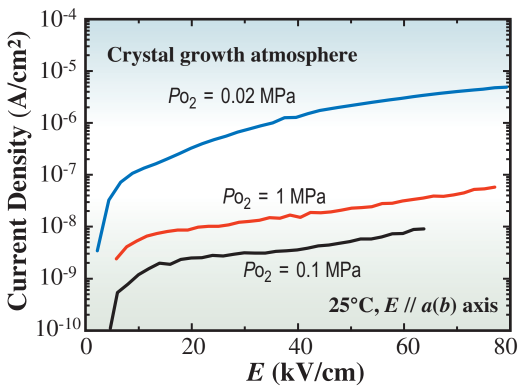

Fig. 2. Remanent polarization (P_r) and coercive field (E_c) as a function of Po_2 during crystal growth (25°C, 1 Hz). The values of P_r and E_c are average in positive and negative regions in the polarization hysteresis loops (Fig. 1).

parameters: a = 0.54505(5) nm, b = 0.54108(4) nm, c = 3.2834(3) nm. Rietveld analyses demonstrated that there was no significant difference in crystal structure in crystals grown under different pressures [3]. These experimental results indicate that high-oxygen-pressure crystal growth is suitable for obtaining defect-controlled ferroelectric crystals without any significant change in the main crystal structure.

Domain observations by piezoresponse force microscopy (PFM) demonstrate that the clamping of 90° domains deteriorates P_r for the crystals grown at 0.02 MPa oxygen, which is suggested to originate from the strong attractive interaction between 90° domain walls and oxygen vacancies. The vacancy formation of Bi and O during crystal growth at high temperatures is suppressed at a higher oxygen pressure, leading to a larger P_r of 47 μC/cm^2 and a lower E_c of 26 kV/cm for the crystals grown at 1 MPa oxygen [3].

Figure 1 shows the polarization hysteresis loops measured along the ***a***(***b***)-axis (25°C, 1 Hz) [3]. The crystals (Po_2 = 0.02 MPa) exhibited hysteresis with P_r = 38 μC/cm^2 and an E_c = 38 kV/cm. The high-Po_2-grown crystals had larger values of P_r of 44 μC/cm^2 (Po_2 = 0.1 MPa) and 47 μC/cm^2 (Po_2 = 1 MPa). Note that the crystals grown at Po_2 = 1 MPa exhibited well-saturated polarization hysteresis with E_c = 26 kV/cm. This E_c value was much lower than those of the other crystals. Figure 2 shows P_r and E_c as a function of Po_2 during crystal growth [3]. With increasing Po_2, P_r monotonically increased, while the decrease in E_c was marked over Po_2 = 0.1 MPa.

Figure 3 shows the leakage current density (J) as a function of E along the ***a***(***b***)-axis (25°C) [3]. The

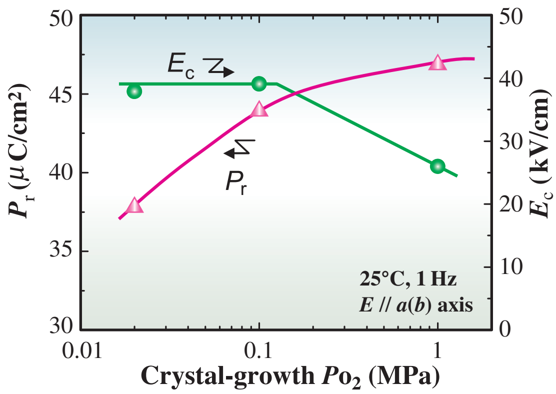

Fig. 3. Leakage current density (*J*) as a function of *E* along the ***a***(***b***)-axis for the BiT crystals (25°C, 1 Hz).

crystals (Po_2 = 0.02 MPa) exhibit a high *J* of the order of 10^{-7} to 10^{-6} A/cm². The increase in Po_2 to 0.1 MPa led to a drastic decrease in *J* to the order of 10^{-9} A/cm². The crystals grown at Po_2 = 1 MPa exhibited a relatively low *J* of the order of 10^{-8} A/cm².

Here, we discuss the mechanism of domain clamping during the polarization switching along the ***a***(***b***)-axis. Figure 4 shows the PFM images observed on the ***a***(***b***)-***c*** surface of the crystals grown at Po_2 = 0.02 MPa [3]. The in-plane PFM image of the as-annealed (nonpoled) crystals (Fig. 4(a)) exhibits 180° DWs parallel to the ***a***-***b*** plane. After an *E* of 100 kV/cm was applied along the ***a***(***b***)-axis at 25°C, the out-of-plane PFM image of the poled crystals was observed (Fig. 4(b)). A single domain state was not established for the poled crystals even though the applied *E* (100 kV/cm) is much higher than the E_c value (38 kV/cm). Domains with $P_{s(a)}$ parallel to the poling direction were found. This is direct evidence that 90° domains are switched by applying an *E* of 100 kV/cm. Note that unswitched regions, i.e., 90° domains with $P_{s(a)}$ normal to the poling direction remained, and 90° DWs with an irregular structure appeared. The irregular-shaped 90° DWs have been reported to originate from the attractive interaction between $V_O^{\cdot\cdot}$ and the electric field established near the 90° DWs due to the discontinuity of the P_s component normal to the DWs. In the domains with $P_{s(a)}$ parallel to the poling direction, a small number of 180° domains with $P_{s(a)}$ antiparallel to the poling direction were observed. These 180° domains are a result of the domain backswitching due to the depolarization field. Our PFM observations lead to the conclusion that the clamping of 90° DWs plays a detrimental role in the $P_{s(a)}$ polarization switching in the BiT crystals. The vacancy formation at high temperatures is suppressed under a higher-Po_2 atmosphere, and then $[V_O^{\cdot\cdot}]$ becomes lower for the crystals grown at a higher Po_2. The larger P_r observed for the crystals (Po_2 = 1 MPa) is found to originate from suppressed 90° domain clamping because of a lower $[V_O^{\cdot\cdot}]$.

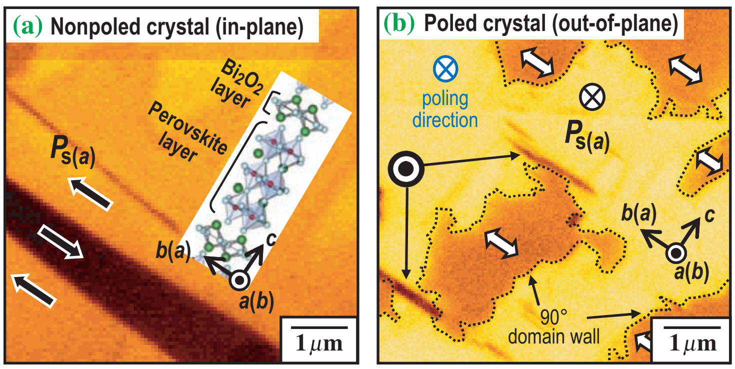

Fig. 4. PFM images of the ***a***(***b***)-***c*** surface of the BiT crystals grown in air (Po_2 =0.02 MPa); **(a)** in-plane image of the nonpoled (as-annealed) crystal, and **(b)** out-of-plane image of the poled crystal. The poling was conducted by applying an *E* of 100 kV/cm along the ***a***(***b***)-axis at 25°C.

In summary, the effects of Po_2 during the crystal growth of BiT on domain-switching behavior have been investigated through polarization measurements and domain observations by PFM. The crystal structure is investigated by high energy synchrotron radiation powder diffraction. The crystals grown at a high Po_2 of 1 MPa showed a large P_r of 47 μC/cm² and a low E_c of 26 kV/cm. PFM observations demonstrate that the clamping of 90° DWs plays a detrimental role in polarization switching, leading to a low P_r. High-Po_2 sintering is proposed as an effective process for suppressing the formation of vacancies of Bi and O without any change in the main crystal structure, leading to the realization of high-quality BiT-based devices with enhanced polarization-switching properties as well as low leakage current.

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