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Investigation of crystallinity and microstructure of $YMnO_3$ single crystal grown by floating zone method

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Abstract $YMnO_3$ single crystals have been grown by a floating zone technique and the optimal growth conditions were investigated. Their crystallinity and microstructure were characterized by the chemical etch pit patterns, their distribution and the compositional difference depending on the G value. In particular, the microstructural feature was interpreted in terms of compositional deviation along radial direction on $(10\bar{1}0)$ growth plane.

Key words $YMnO_3$, Single crystal, Floating zone, KOH, Microstructure

1. Introduction

For last several decades, lead zirconium titanate (PZT) has been used as ferroelectric layer materials of heterostructural devices for nonvolatile memory applications. However, recently $YMnO_3$ thin films seem to attract more attention as the key material for nonvolatile memories with higher efficiency [1-4]. Since the ferro-electric characteristics was proved by Bertaut *et al.* [5], it has been reported that Curie temperature (T_C) is about 640°C and the dielectric anomaly was observed near the Neel temperature (T_N) [6]. Therefore, it has been expected that the coupling effect of the magnetic and the electric ordering could be applied to various physical application [4]. The properties of $YMnO_3$ such as strong unipolarization parallel with the c-axis, relatively low dielectric permittivity in a rage of 2.5-5C/cm^2 and the absence of volatile elements that cause point defects are promising advantages for the device application required for the high operation speed and low voltage [7].

Because almost all investigations to date have been given to the $YMnO_3$ thin films, there are few reports on the $YMnO_3$ bulky single crystals [1, 5]. Although, for $YMnO_3$ single crystals grown by a flux method, their crystal structure and dielectric property were already reported, a further investigation on defect and structural feature of $YMnO_3$ single crystals is needed. In this article, we report on first investigation of the crystallinity and microstructure of $YMnO_3$ single crystals grown by a floating zone (FZ) method.

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2. Experimental Procedure

$YMnO_3$ powder thermally synthesized using Y_2O_3 (99.99 %) and Mn_2O_3 (99.99 %) starting materials was sealed in a rubber tube, and isostatically pressed to a cylindrical rod under a hydrostatic pressure of 450 MPa. The pressed rods were sintered in an electrical furnace at 1500°C for 10 hrs in air. $YMnO_3$ single crystals were grown by a conventional FZ method using an infrared convergence-type image furnace with double ellipsoidal mirrors. A flow of O_2 gas was applied to control the growth atmosphere. The growth rate was 3 mm/h using counter rotation of 20 rpm for both the feed rod and the seed crystal.

Lattice parameters of grown $YMnO_3$ single crystal were determined by a conventional X-Ray diffractometer (XRD). Dislocation etch pits and ferroelectric domains were revealed by observations of optical microscope and scanning electron microscope (SEM) for freshly polished both (0001) and $(10\bar{1}0)$ surfaces of $YMnO_3$ crystals etched in molten KOH of 450°C for 2 minutes. Compositional deviations depending on the radial direction of growth $(10\bar{1}0)$ plane were measured by an electron probe microanalysis (EPMA).

3. Results and Discussion

From several runs for growth of $YMnO_3$ single crys-

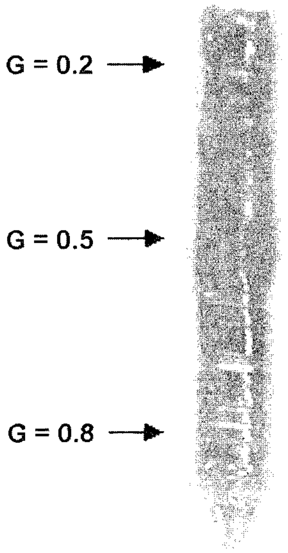

Fig. 1. A photograph of $YMnO_3$ single crystal grown by the floating zone technique (The size is 5 mm in diameter and 50 mm in length).

tals using polycrystal rod as a seed crystal, the preferential growth direction was found to be $[10\bar{1}0]$. Figure 1 shows a photograph of $YMnO_3$ single crystal grown by $[10\bar{1}0]$ seed crystal. The grown $YMnO_3$ crystal shows bluish black in color and its typical size is 5 mm and 50 mm in diameter and length, respectively. The lattice parameters measured by XRD were a = 6.147 Å, c = 11.351 Å, and c/a = 1.847. These results show a little deviation from the JCPDS data (card #: 81-1945, a = 6.130 Å, c = 11.505 Å, c/a = 1.861).

Figure 2 shows SEM images of etch patterns of (0001) (Fig. 2a) and $(10\bar{1}0)$ plane (Fig. 2b-d) revealed by etching in molten KOH. For (0001) plane, a etch pit of hexagonal shape with six edges perpendicular to $<10\bar{1}0>$ are shown clearly, which is a typical etch pattern of hexagonal structure. The $(10\bar{1}0)$ plane shows occasionally negative etch pits of diamond shape and positive etch pits of ellipsoidal shape (see Fig. 2b and c, respectively). Also domain structure was observed as shown in Fig. 2d. The most interesting thing is characterized by a fact that both negative and positive etch pits and the domains present in the $(10\bar{1}0)$ planes are elongated toward [0001] direction in their shape and are aligned same direction. This feature means that $YMnO_3$ has only one strong polarization along c-axis of its hexagonal structure.

The etch pit distribution and the alignment on the (0001) plane were observed by an optical microscope, and the etch pit density at three different positions along the radial direction were measured (Fig. 3). The etch pit density is about $10^4/cm^2$ at the center of the specimen marked as A and about $5 \times 10^4/cm^2$ near the surface

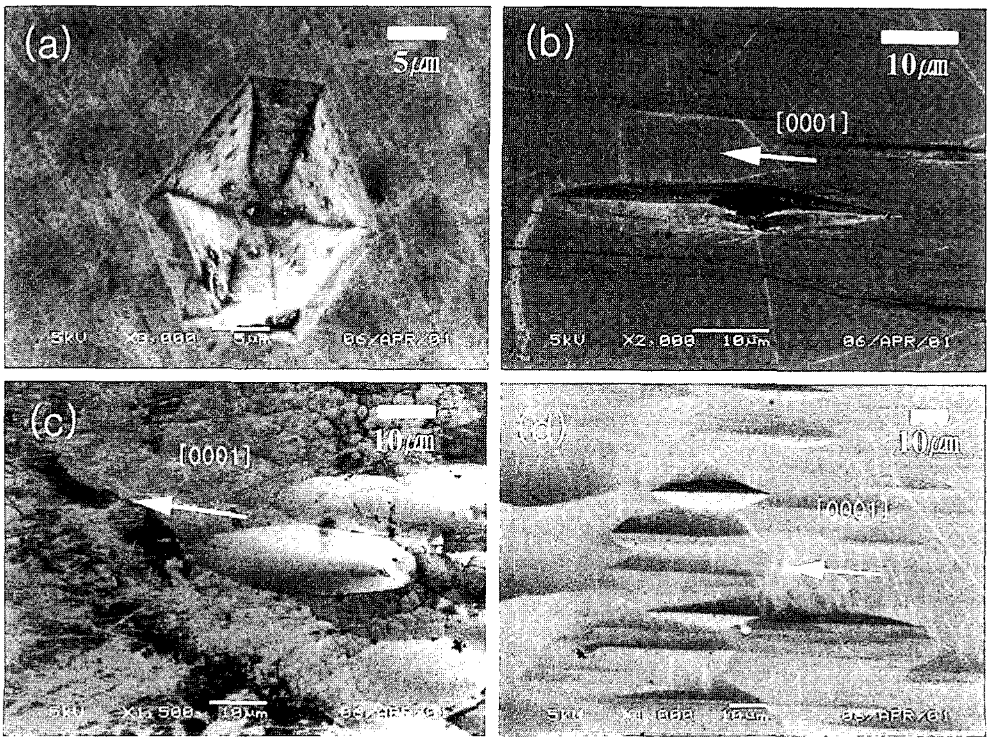

Fig. 2. SEM images showing etch patterns of FZ-grown $YMnO_3$ single crystal after the chemical etching (the molten KOH, 2 min); (a) the (0001) plane, and (b), (c), (d) $(10\bar{1}0)$ plane.

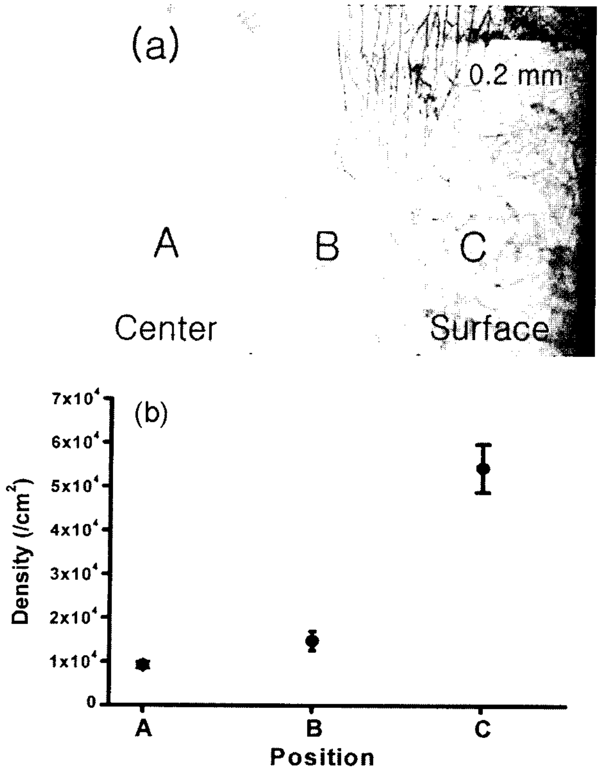

Fig. 3. (a) A photograph of etch pit distribution on the (0001) plane, and (b) a plot of etch pit density values at three different positions, A, B, and C of (a).

area marked as C, depending on the position of the radial direction of the (0001) plane. In the surface area in Fig. 3a, it was observed that lots of dislocations were aligned toward peripheral region and occasionally networked each other. It is thought that the formation of dislocation network would be formed by the temperature gradient developed in the surface area of the crystal. Whereas, in the middle area and the center of the specimen marked as A and B, the dislocation density was decreased as approaching toward the center, and dislocations are lined up parallel to each other but with the different direction from the surface area.

For the investigation of the influence of composition on the defect formations, the compositional deviations of Y and Mn were examined by EPMA. It was found that the composition of the $YMnO_3$ single crystal was different depending on the position in the crystal marked as A, B, C in Fig. 3a and the direction of the growing as shown G = 0.2, 0.5, 0.8 in Fig. 1. The EPMA results show that the grown $YMnO_3$ single crystal is oxygen-deficient Y-rich composition (Fig. 4) and the compositional fluctuation of Y and Mn was increased as the G value increased. Also, the composition of the center and middle area varied depending on the G value but that of the surface area was almost invariant. These results are thought to be affected by the evaporation of Mn component during crystal growing. It is reported that the process of defect formations and the distribution of these defects are affected by the composition of the zone melt established during floating zone method growth process. Also, in case of rare-earth manganite, the composition of the zone melt is influenced by the non-stoichiometry of the feed rod and evaporating losses of Mn from the melt. As the Mn evaporates from zone melt, the increase of Y/Mn ratio changes the composition of the melt to be $YMnO_3$-Y_2O_3 composition. This composition is easier to crystallize Y_2O_3 phase by the temperature fluctuation and Y concentration in the diffusion layer [8]. These facts are well agreed with the etch pit distribution and alignment on (0001) surface shown in Fig. 3 and the compositional deviation shown in Fig. 4. The incensement of the compositional deviation between Y and Mn is considered to be influenced by the continuous Mn evaporation during growing process. Also, the etch pit distribution in the center and the middle area in the specimen on (0001) plane is thought to be affected by the concentration effect in the liquid/solid interface, and the directions of the alignment are almost parallel with the solid/liquid interface formed during the growing process. In case of the surface area the alignment of the etch pit is more strongly influenced by the temperature fluctuation developed near the surface area during growing process.

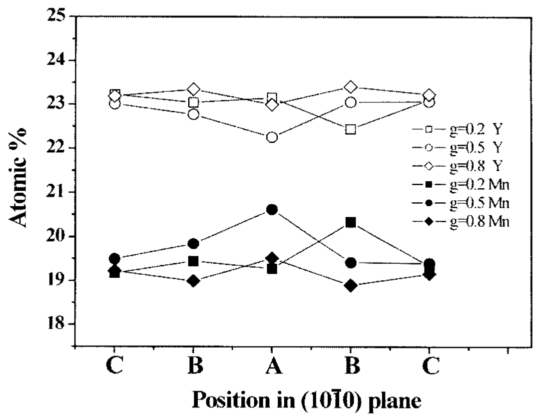

Fig. 4. Compositional deviation depending on the radial directional positions on (10$\bar{1}$0) plane and G values (A : center, B : middle and C : surface area).

4. Summary

The microstructure of $YMnO_3$ single crystal grown by the floating zone technique was investigated by various methods such as the wet chemical etching, OM and EPMA. It was found that the etch pit density and the composition varied depending on the measured position and the G value. Also, EPMA results showed that the grown $YMnO_3$ single crystal is oxygen- deficient Y-rich composition that was originated from the Mn evaporation. Therefore, the formations of defects are considered to be affected by the solid-liquid interface and the temperature fluctuation during growing process and it is necessary to restrict or compensate the evaporation of Mn from the melt for the improvement of the crystallinity.

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