Changes in the Crystal Structure of RF-Magnetron Sputtered BaTiO₃ Thin Films

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The crystal structure of BaTiO₃ thin films fabricated by RF-magnetron sputtering has been investigated. As-sputtered films exhibited a cubic structure with a small grain size of about 6-8nm. After annealing at a temperature above 1100°C, the crystal structure changed from cubic to tetragonal, because the annealing process caused grain growth. The critical grain size of the thin films which provided the cubic structure existed in the range of 0.1-0.2 μm. This value agreed well with the critical grain size of BaTiO₃ fine particles, 0.12 μm.

Key-words: RF-magnetron sputtering, BaTiO₃ thin film, Annealing process, Critical grain size, Phase transition

1. Introduction

With increasing the demand for ferroelectric thin films for the applications to optical wave guides, nonvolatile memories and so on, many studies have been attempted using RF-sputtering and other thin film fabrication techniques. However, ferroelectric films fabricated by these methods frequently have not shown so good ferroelectricity as seen in bulk sintered ceramics or single crystals. Although many researchers have attempted to give explanations to this phenomenon, they have been insufficient so far.

Nagatomo et al. have reported that the ferroelectric BaTiO₃ thin film could be prepared at a relatively low substrate temperature of 700°C by using RF-planar-magnetron sputtering, however, the ferroelectricity of those films was weak or absent for the fine-grained film, and it was necessary to anneal at 1000°C in order to obtain ferroelectric BaTiO₃ films with high quality. They have explained these phenomena by the 90° domain model suggested by Arlt et al. However, the reason why the fine-grained film exhibits cubic symmetry and non-ferroelectric properties has not been discussed.

The purpose of this study is to clarify why the as-grown BaTiO₃ thin films do not show ferroelectricity. Our discussion is based upon the “critical grain size” model.

We have reported the particle/grain size dependence of ferroelectricity for powder and polycrystal-line samples of BaTiO₃, and clarified that both the tetragonality, c/a, and the Curie temperature, Tc, are decreased drastically at a particle size of 0.12 μm. Fine particles less than this critical grain size will not exhibit ferroelectricity because the crystal lattice becomes a cubic structure.

In order to explain this phenomenon, we have proposed an “effective surface tension” model. A fine particle with R in radius experiences a hydrostatic pressure of 2γ/R (γ: surface tension), and this hydrostatic pressure decreases the Curie temperature of the particle down below room temperature and changes the structure into cubic. It is interesting that the revealed in perovskite ferroelectrics ((Pb, Ba)TiO₃, (Ba, Sr)TiO₃) shows an almost constant value of 50 N/m. This extraordinarily large value has not been explained yet, however, it may be attributed to the surface layer generated by the permanent dipoles.

2. Experiments

2.1 Sample preparation

The BaTiO₃ film was deposited by using an RF-magnetron sputtering system (Anelva, SPF-430HS). Corning 7059 and fused quartz substrates with 15 mm × 15 mm × 1 mm in size were used. All the substrates were cleaned by using trichloroethane (TCE) and acetone, and then placed in a stainless steel holder by clips prior to film deposition. The target had a stoichiometric composition of BaTiO₃ with purity of 99.9%. The size was 100 mm in diameter and 5 mm in thickness. The sputtering conditions are summarized in Table 1. The thickness of the sputtered films was more than 2 μm, much thicker than the grain size.

In order to control the grain size the as-sputtered
thin films were annealed at the temperature range of 600°C-1200°C for 12 h. Chemical analysis of the composition was made by the ICPS (Inductively Coupled Plasma Spectroscopy) method and the Ba/Ti ratio was proved to be nearly 1.0.

2.2 Measurement

An X-ray diffractometer (JEOL, JDX-11PA) was employed to examine as-grown and annealed thin films. The crystal symmetry and the consequent lattice constants of samples were calculated by averaging the (100) and (200) reflections of the BaTiO₃ perovskite cell. Average grain size in the range of sub-micron was determined from SEM (Hitachi, S-900) micrographs using a line intercept method. In the range of grain size of nano-meter Scherrer’s equation was used for (100) peaks. The grain sizes determined by SEM and X-ray diffraction were almost the same (±0.1 μm) for the sample annealed at 1000°C; this suggests that the crystallite size almost corresponds to the grain size.

3. Results and discussions

Figure 1 shows the X-ray diffraction patterns of as-grown films sputtered at the gas pressure of 1.0 Pa for various substrate temperatures. The film sputtered at room temperature showed an amorphous phase, but the film fabricated above 500°C showed a crystalline phase. The lattice constant decreased with the substrate temperature from 4.15 Å at 500°C down to 4.07 Å at 800°C, but it was still larger than that of sintered BaTiO₃ (a: 3.989 Å, c: 4.029 Å).

Only two peaks due to the preferential orientation along {100} appeared and the preference did not change significantly with the substrate temperature. This result is different from previous researches. It has been reported that if the mobility of atoms during deposition is high (i.e., at a high substrate temperature), the films grow with the orientation of {110} due to its highest occupation density compared to the other planes with low indices. The decrease in the X-ray intensity and the peak broadening for the substrate temperature of 800°C seems to be caused by the slight mis-orientation due to higher substrate temperature.

The samples were annealed at various temperatures to increase the grain size so that they were compared to the fine grain ceramic BaTiO₃. Figure 2 shows the XRD patterns of (200) reflection of films annealed at 1000°, 1100°, and 1200°C. The diffraction pattern of the film annealed at 1000°C shows a symmetrical pattern. On the other hand, the peak of

Fig. 1. XRD patterns of films sputtered on the substrate at various temperatures.

Fig. 2. XRD peaks of the {200} reflections of BaTiO₃ annealed at various temperatures.

Fig. 3. SEM photographs of BaTiO₃ thin films annealed at various temperatures. (a) 600°C, (b) 1000°C, (c) 1100°C, (d) 1200°C.
the film annealed at 1100°C or 1200°C skews to the right side from the center, revealing an additional peak at a lower angle. This seems to be attributed to the appearance of the (002) peak, although the peak was not entirely separated from the (200) peak. In conclusion, the phase transition from cubic to tetragonal was caused by thermal annealing at the temperature above 1100°C. The microstructure of annealed samples was observed by using SEM and the results are shown in Fig. 3. By the annealing process, the grains grew from about 40nm to 350nm.

Figure 4 plots the relationship between the grain size and the annealing temperature, where the crystal structure is also indicated. The crystal structure was cubic below 0.1 μm in grain size, and tetragonal above 0.2 μm. Therefore, it is shown that the critical grain size might exist between 0.1 and 0.2 μm. This result agrees exactly with that obtained by the study on the particle size dependence of the crystal structure of fine powder BaTiO₃, where the critical grain size was indicated to be 0.12 μm. The grain size of as-sputtered thin films ranged over 6-8nm in this study. Iijima has reported that the grain size of evaporated BaTiO₃ thin films ranges over 35-70nm and the film without heat-treatment did not show any ferroelectric properties. Although there are some differences among these values due to fabrication methods, both of them are below the critical grain size, 0.12 μm. Accordingly, it can be thought that the cubic structure and non-ferroelectric properties of as-sputtered films are attributed to the small grain size.

4. Conclusions
The results of this study are summarized:
(1) As-sputtered films prepared on the substrate of 500°C–800°C exhibited a cubic crystal structure.
(2) The crystal structure of sputtered films changed from cubic to tetragonal after annealed at a temperature above 1100°C.
(3) The critical grain size separating cubic and tetragonal phases existed in the range of 0.1–0.2 μm, and was in good agreement with the critical grain size of 0.12 μm determined from the fine powder of BaTiO₃.

References