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Formation of c-Axis-Oriented $Bi_4Ti_3O_{12}$ Films with Extremely Flat Surface by Spin-Coating

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Formation of c-axis-oriented $Bi_4Ti_3O_{12}$ (BIT) films by spin-coating has been investigated. The crystallinity of BIT films depends on the Bi to Ti molar ratio of the starting BIT solution as well as annealing temperature. The BIT film spin-coated with 10% Bi-rich solution and annealed at 850°C shows highly c-axis-oriented crystallinity. Additionally, it is found that a BIT layer spin-coated on this c-axis-oriented film becomes highly c-axis-oriented even if the starting solution is not Bi-rich, and that the obtained films have extremely flat surface when the thickness of the first BIT layer is relatively thin. The resulting films have good properties for MFMIS structural memory devices: low leakage current density of $7x10^7$ A/cm^2 at 3 V, remanent polarization of 2.5 μC/cm^2, coercive field of 8 kV/cm, and dielectric constant of 120.

1. Introduction

Recently, many kinds of ferroelectric thin film have been investigated for application to nonvolatile memory devices. Memory cell structures for nonvolatile memory consisting of 1 transistor and 1 capacitor (1T/1C)[1] and 1 transistor (1T) have been proposed[2]. The 1T type structure such as metal-ferroelectric-metal-insulator-semiconductor (MFMIS) is very simple and has the advantages of nondestructive read out and high-level integration. However, the MFMIS structure requires low remanent polarization, small coercive field, and low dielectric constant to the ferroelectric thin film. c-Axis-oriented bismuth titanate ($Bi_3Ti_4O_{12}$:BIT) film has sufficient properties for use in MFMIS structural nonvolatile memories[3),4)]. However, it is well known that c-axis-oriented BIT films have a terrace structure[5)], i.e., the surface is very rough.

In this study, we investigated the formation of BIT films oriented along the c-axis by spin-coating and propose a method for the formation of c-axis-oriented BIT films with extremely flat surface.

2. Formation of c-axis-oriented $Bi_4Ti_3O_{12}$ film

Effects of the Bi : Ti molar ratio of BIT solution for spin-coating on the formation of c-axis-oriented BIT film were investigated. Starting BIT solutions for spin-coating with Bi : Ti molar ratios of 4:3 (stoichiometry), 4:3.3 (10% Ti-rich), and 4.4:3 (10% Bi-rich) were prepared. Pt(60nm) / SiO_2(200nm) /Si(100) were used as a substrates. The solutions were spin-coated onto the substrates at a rate of 500 rpm for 10 s and 2500 rpm for 30 s. The coated films were dried at 150°C for 1 min and 230°C for 10 min in air using a hotplate. This procedure was repeated five times. The spin-coated films were calcined at 450°C for 15 min in air using a hotplate, and then annealed in the range of 750°C to 850°C for 3 min in O_2. After these processes, the thickness of BIT films was about 390nm.

Figure 1 shows the peak intensity ratio, (006)/(117), obtained by X-ray diffraction (XRD). The BIT films formed using stoichiometric and Ti-rich solution had random orientation after annealing in the range of 750°C to 850°C. In the case of Bi-rich solution, the crystallinity of BIT film depends on the annealing temperature. After annealing at temperatures lower than 800°C, the BIT films had random orientation. However, after annealing at 850°C, the crystallinity of the

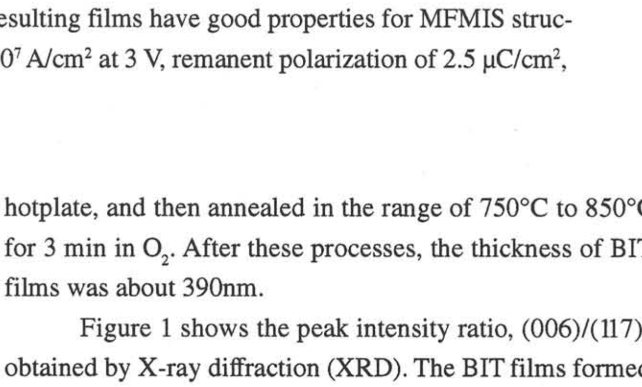


Fig. 1 Peak intensity ratio, (006)/(117), obtained by XRD.

Table I Bi/Ti composition of BIT films.

	after calcining		after annealing at 850°C
stoichiometric solution	1.33	→	1.25
Ti-rich solution	1.21	→	1.20
Bi-rich solution	1.47	→	1.35

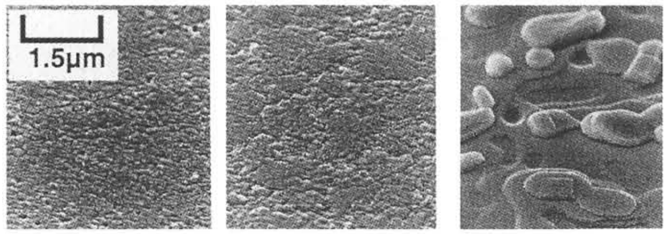
BIT film was changed, i.e., the BIT film became highly c-axis oriented. The Bi/Ti composition was estimated from AES measurements, as shown in Table I. After annealing at 850°C, the composition of the BIT films formed using Ti-rich solution was not changed, while that when stoichiometric and Bi-rich solution was used, the composition was changed. In the case of using Bi-rich solution, the composition 1.35 (≈stoichiometry) was obtained. However, the composition of the BIT film formed using the stoichiometric solution was 1.25, which was Ti-rich.

Figure 2 shows SEM micrographs of the surface morphology of the BIT films after annealing at 850°C. The grain size of the random orientation BIT films formed using stoichiometric and Ti-rich solutions was small and the surface was relatively flat. In contrast, the grain size of the BIT film oriented along the c-axis was very large, but the surface was rough.

The leakage current density of the BIT films after annealing at 850°C was measured using a HP model 4155A, as shown in Fig 3. The leakage current density of randomly oriented BIT film formed by using Ti-rich solution was as low as $1x10^{-8}$ A/cm^2. However, in the case of c-axis-oriented BIT films, the leakage current density was very high. It seems that the leakage current density is affected by the surface morphology of BIT films.

3. Improvement of the c-axis-oriented $Bi_4Ti_3O_{12}$ surface

The surface of c-axis-oriented BIT films is very rough, as shown in Fig. 2(c). In order to obtain c-axis-oriented BIT film with a flat surface, a new spin-coating process was adopted. Figure 4 shows the flow diagram of the new spin-coating process. First, a thin BIT layer was formed using a Bi-rich solution. The thickness of the layer was about 30nm. The thin layer was highly oriented along the c-axis. This layer had a relatively flat surface, as shown in Fig. 5, which became flatter with decreasing film thickness. Next, a BIT film was formed on the highly c-axis-oriented thin BIT layer using a stoichiometric solution (film thickness: 410nm). This BIT film was strongly oriented along the c-axis, as shown in Fig 6. A (117) peak was not observed, i.e., this film contained only c-axis-oriented grains. The surface was extremely flat in comparison with that formed by the conventional process [shown in Fig. 2(c)], as shown in Fig. 7. It is considered that the BIT film formed using the stoichiometric solution had strong c-axis orientation due to the presence of the highly c-axis-oriented thin BIT layer, i.e., the spin-coated BIT grows the solid-phase epitaxially along the c-axis-oriented BITlayer, and an extremely flat surface was achieved.



a) stoichiometric solution b) Ti-rich solution c) Bi-rich solution

Fig. 2 The surface morphology of BIT films after annealing at 850°C for 3 min.

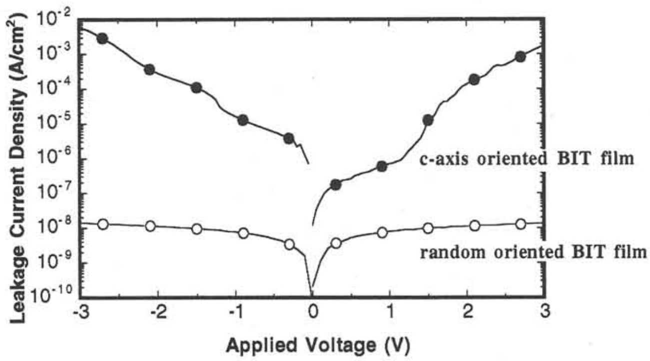


Fig. 3 Leakage current density of the BIT films.

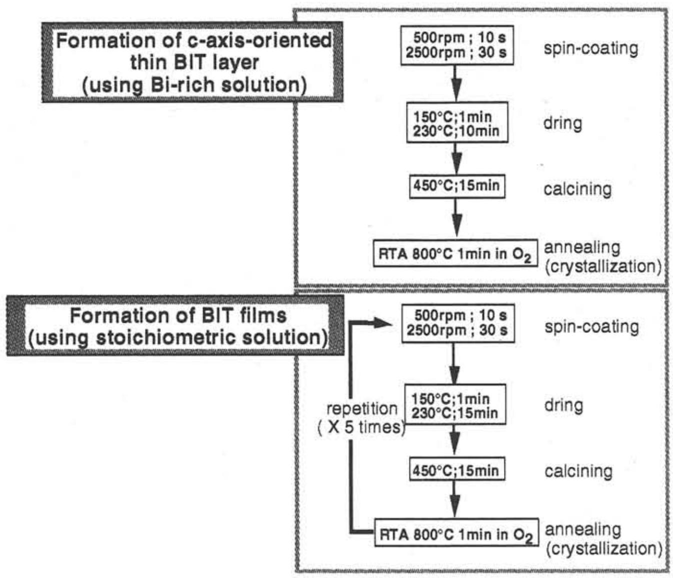


Fig. 4 Flow diagram for new spin-coating process.

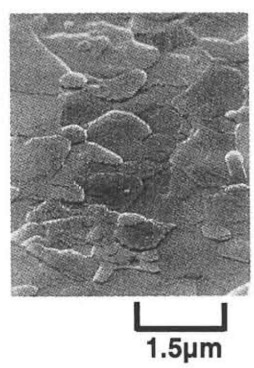


Fig. 5 The surface morphology of c-axis-oriented buffer layer.

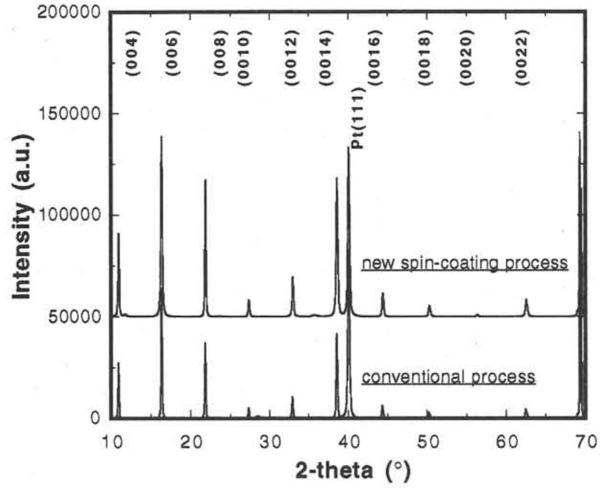


Fig. 6 XRD spectra of c-axis-oriented BIT films.

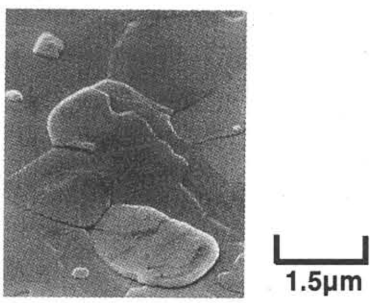


Fig. 7 SEM micrograph of the surface of BIT film on the highly c-axis-oriented thin BIT layer.

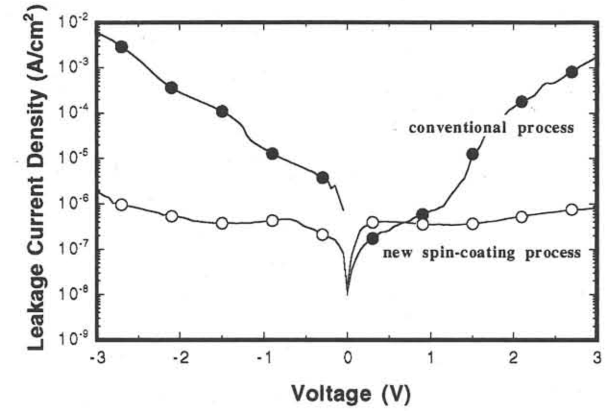


Fig. 8 Leakage current density of the BIT films.

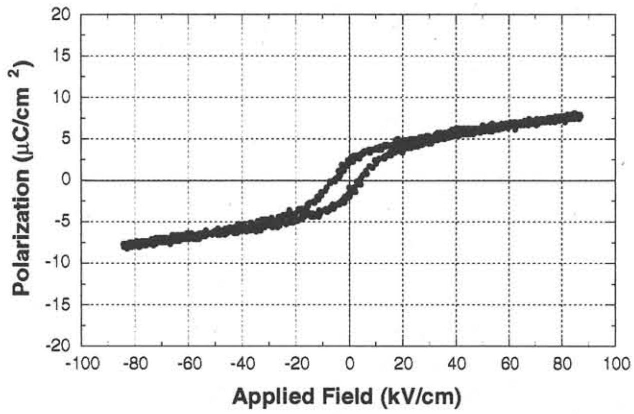


Fig. 9 D-E hysteresis loop of c-axis-oriented BIT films formed by new spin-coating precess.

Figure 8 shows the leakage current density of BIT films measured using HP model 4155A. The leakage current density of the BIT film with the new spin-coating process was as low as $1x10^{-6}$ A/cm^2 at $\pm$3V This value is 10^{-3} times as small as that of BIT films formed by the conventional process. This result indicates that the surface morphology of c-axis-oriented BIT film affects the leakage current density. Figure 9 shows the D-E hysteresis loop of a c-axis-oriented BIT film at $\pm$ 100 kV/cm, measured using a Sawyer-Tower circuit. The remanent polarization Pr and coercive field Ec were estimated to be 2.5 μC/cm^2 and 8 kV/cm, respectively. The dielectric constant was 120. These results indicate that the good ferroelectric properties for MFMIS structural memory devices were achieved for c-axis-oriented BIT film with an extremely flat surface.

4. Conclusions

Formation of c-axis-oriented $Bi_4Ti_3O_{12}$ films with extremely flat surface by spin-coating has been investigated. The crystallinity of BIT films depends on the Bi : Ti molar ratio of the starting BIT solution and the annealing temperature. c-Axis-oriented BIT film was formed by using Bi-rich solution and annealing at temperatures higher than 850°C. It was found that the BIT layer spin-coated on the c-axis-oriented thin BIT layer became highly c-axis oriented even if the starting solution was not Bi-rich, and that the obtained films had extremely flat surface. The c-axis-oriented BIT films on the thin BIT layer had good properties: low leakage current density of $7x10^{-7}$ A/cm^2 at 3 V, remanent polarization of 2.5 μC/cm^2, coercive field of 8 kV/cm, and dielectric constant of 120. These results indicate that c-axis-oriented BIT films formed by spin-coating have high potential for use in MFMIS nonvolatile memories.

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