

Fabrication of ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films by electron beam heating evaporation

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Ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films were fabricated on Pt/SiO₂/Si substrates by electron beam heating evaporation and successive heat treatment. Bi and Ti metal powders with high purity were used as source materials. They were co-deposited on the substrates at rates of 0.27 and 0.10 nm/s, respectively, for 1200 s. The deposited films were successively heat treated in air at 700 °C for 30 min. The resultant $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film with a thickness of 470 nm and preferential *c*-axis orientation exhibited good ferroelectric properties: the remanent polarization of 13.7 $\mu\text{C}/\text{cm}^2$ and the coercive field of 96.4 kV/cm.

1. INTRODUCTION

Ferroelectric bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystals have a typical perovskite-layered structure and show strong anisotropic properties: coercive field values of 3.5 and 50 kV/cm, and spontaneous polarization of 4.0 and 50 $\mu\text{C}/\text{cm}^2$ along the *c*- and *a*-axes, respectively[1]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films with *c*-axis orientation are expected to be applied to electronic memory devices. The small coercive field along the *c*-axis is suitable for low voltage driving. The small dielectric constant and the unique polarization reversal along the *c*-axis are profitable to realize fatigue-free nonvolatile memories. Therefore, it is important to fabricate high quality $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films with *c*-axis orientation on Si wafers.

Over the past few years, many efforts have been made on the fabrication of ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films by several methods such as electron cyclotron resonance (ECR) sputtering[2,3], rf-sputtering[4], sol-gel process[5,6], metalorganic chemical vapor deposition (MOCVD)[7,8] and laser ablation[9-11].

We have fabricated $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films by spin-coating pyrolysis of metal naphthenates[12,13] and MOCVD[14,15]. The resultant $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films with *c*-axis orientation exhibited good ferroelectric properties. However, the remanent polarization deteriorated after polarization reversal at 3×10^8 cycles[13]. It is necessary to investigate the origin of the deteriorating remanent polarization and improve the fatigue characteristics. It seems that there were not a few carbon atoms in the films fabricated by the above processes we used. In order to solve the fatigue problem of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films, we should fabricate carbon-free $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films and compare their properties with these of previous ones.

This paper describes the fabrication of ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films with high purity by electron beam heating evaporation.

2. EXPERIMENTAL

Bismuth and titanium metal powders were used

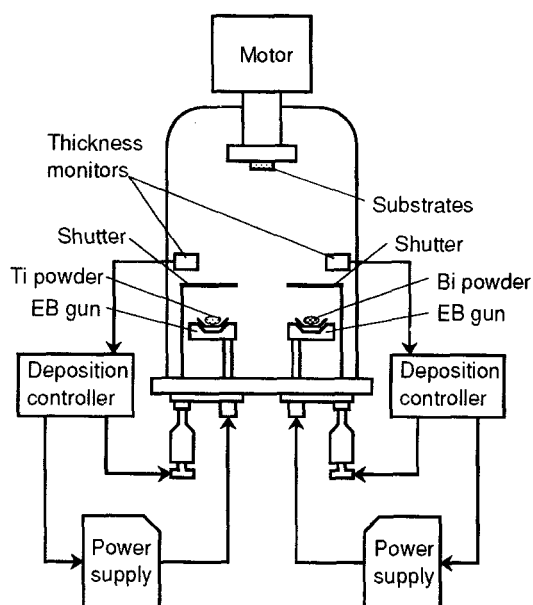


Figure 1. The schematic diagram of the electron beam heating evaporation system.

as source materials. Purity of the powders were 99.99 and 99.98 %, respectively. The process of oxidation and crystallization into ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase of the mixed metal powders containing Bi and Ti atoms at a molar ratio of 4:3 was investigated by thermogravimetry-differential thermal analysis (TG-DTA).

Platinum sputtered silicon wafers with native oxide were used as substrates. The source materials and substrates were put in a vacuum evaporation system shown as Fig. 1. It had no equipment for oxidation. The vacuum chamber was evacuated to of the order of 10^{-8} Torr by a turbo molecular pump (TMP). The metals were simultaneously evaporated from copper crucibles by electron beam guns. Deposition rates of Bi and Ti were independently controlled by two systems of quartz crystal transducer type deposition process controllers. The film thickness which these systems indicated was calibrated by measuring real thickness of the films deposited on the substrates. The film thickness is proportional to mass of deposited materials. Deposited films with a thickness of $1 \mu\text{m}$ contain Bi atoms of $4.69 \times 10^{-6} \text{ mol/cm}^2$ and Ti ones

of $9.39 \times 10^{-6} \text{ mol/cm}^2$, respectively. Therefore, to deposit Bi and Ti at a molar ratio of 4:3, deposition rates of Bi and Ti were set to be 0.27 and 0.10 nm/s, respectively. Deposition time was 1200 s. The substrates were rotated at 5 rpm and not heated during deposition. After deposition, the deposited films were taken out from the vacuum chamber and heat treated in air at $700 \text{ }^\circ\text{C}$ for 30 min.

The crystal structure of the resultant films was estimated by X-ray diffraction analysis (XRD). Surface morphology of the films was observed by a scanning electron microscope (SEM). Circular gold dots with a diameter of 0.5 μm were deposited on the film surface by register heating vacuum evaporation. The Au dots and Pt layers on the surface of Si wafers were used as top and bottom electrodes, respectively, to evaluate electrical properties. Dielectric constants and losses were measured by an LCR meter at 1 kHz, and $D-E$ hysteresis loops were observed using a Sawyer-Tower circuit with a triangle field of 1 kHz.

3. RESULTS AND DISCUSSION

Figure 2 shows the TG-DTA curve of the mixed

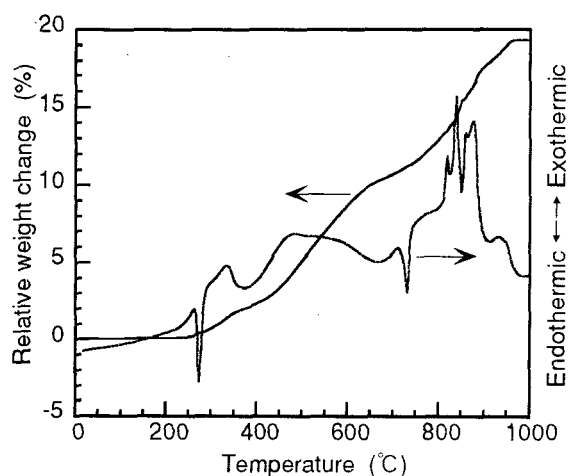


Figure 2. The TG-DTA curve of the mixed metal powder containing Bi and Ti atoms at a molar ratio of 4:3.

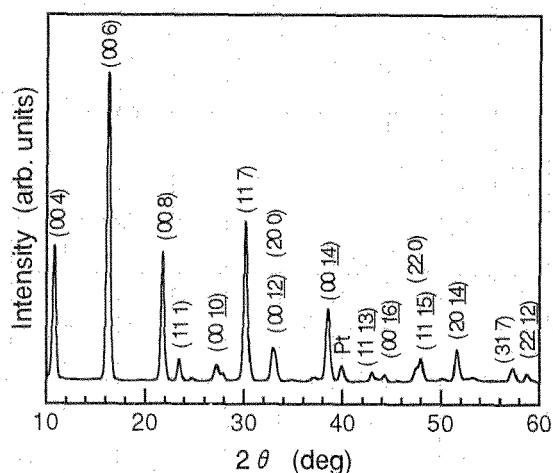


Figure 3. The XRD pattern of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film formed on the Pt/ SiO_2 /Si substrate by electron beam heating evaporation and successive heat treatment in air at 700 °C for 30 min.

metal powder containing Bi and Ti atoms at a molar ratio of 4:3. The sharp endothermic anomaly appeared at about 280 °C arises from the melt of Bi. Increase of the weight due to the oxidation of Bi began at 300 °C. It seems that the broad endothermic anomaly appeared in the range from 330 to 480 °C relates to the oxidation of Bi. It seems that the sharp endothermic dip at about 720 °C and the thermal anomaly ranging from 800 to 900 °C are owing to the oxidation of Ti and the crystallization into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. Relative weight change which stopped at 950 °C was estimated to be 19.3 %. It corresponds with the theoretical value of 19.6 % estimated from $4\text{Bi} + 3\text{Ti} + 6\text{O}_2 \rightarrow \text{Bi}_4\text{Ti}_3\text{O}_{12}$. It means that Bi and Ti atoms hardly evaporated by heat treatment up to 1000 °C.

The metal thin films containing Bi and Ti atoms at a molar ratio of 4:3 were deposited on Pt/ SiO_2 /Si substrates by electron beam heating evaporation. Then, they were heat treated in air at 700 °C for 30 min. Thickness of the resultant films was 470 nm. Figure 3 shows the XRD pattern of the film. It is found that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film with preferential *c*-axis orientation was obtained. It seems that the heat treatment causes the melt and the oxidation of Bi, the

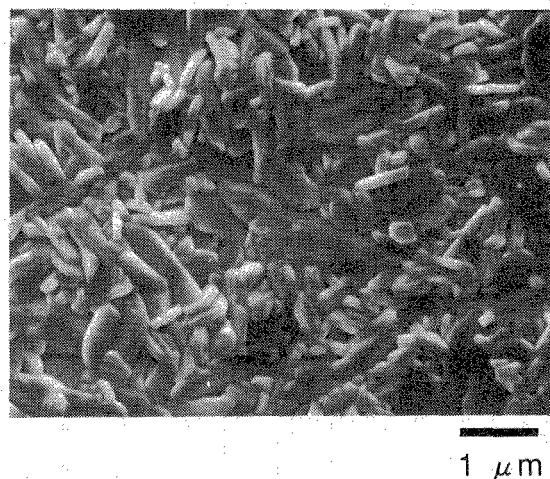


Figure 4. The surface morphology of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film formed on the Pt/ SiO_2 /Si substrate by electron beam heating evaporation and successive heat treatment in air at 700 °C for 30min.

oxidation of Ti and the crystallization into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase on the substrates. The heat treatment at 700 °C made $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystals in the case of thin films although it was forecasted from the TG-DTA results that the heat treatment at 1000 °C was required. It suggests that the metal thin films easily react with oxygen. In fact, Ti thin films were strongly reacted like firing with oxygen in air even at room temperature.

Surface morphology of the resultant film is shown in Fig. 4. It is found that the dense film consisted of platelike crystals was obtained. Roughness of the surface, however, was not so good. In the spin-coating pyrolysis process of metal octylates, it was possible to control orientation and surface morphology of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films by changing the heat treatment temperature[16]. It seems that it is possible in this process.

In the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films fabricated by spin-coating pyrolysis process or MOCVD, sometimes it is impossible to evaluate the electrical properties due to large leakage current. On the other hand, in the films fabricated by this process, the electrical properties were easily measured. It suggests that carbon atoms

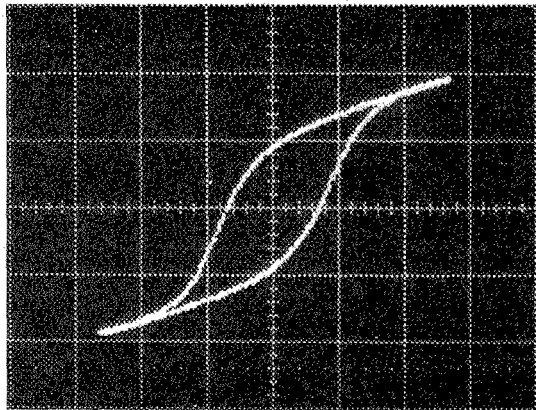


Figure 5. The D - E hysteresis loop of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film formed on the $\text{Pt}/\text{SiO}_2/\text{Si}$ substrate by electron beam heating evaporation and successive heat treatment in air at 700°C for 30 min. The remanent polarization and the coercive field were $13.7 \mu\text{C}/\text{cm}^2$ and $96.4 \text{ kV}/\text{cm}$, respectively.

in the films make some effects on the leakage current. Dielectric constant and loss of the resultant film were estimated to be 39.9 and 0.05, respectively. A D - E hysteresis loop of the film is shown in Fig. 5. From this figure, the remanent polarization and the coercive field of the film were estimated to be $13.7 \mu\text{C}/\text{cm}^2$ and $96.4 \text{ kV}/\text{cm}$, respectively.

4. CONCLUSIONS

The ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films were fabricated on the $\text{Pt}/\text{SiO}_2/\text{Si}$ substrates by electron beam heating evaporation and successive heat treatment. Bi and Ti metals with high purity were co-deposited on the substrates. The heat treatment in air at 700°C for 30 min caused the melt and the oxidation of Bi, the oxidation of Ti, and the crystallization from Bi_2O_3 and TiO_2 into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. The resultant $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film with a thickness of 470 nm and preferential c -axis orientation exhibited good ferroelectric properties: the remanent polarization of $13.7 \mu\text{C}/\text{cm}^2$ and the coercive field of $96.4 \text{ kV}/\text{cm}$.

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