PTCR Characteristics of $BaTiO_3$ Thin Films made by rf/dc Magnetron Sputter Technique

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$BaTiO_3$ ceramic thin films doped with Mn were manufactured by rf/dc magnetron sputter technique. We have investigated crystal structure, surface morphology and PTCR(positive- temperature coefficient of resistance) characteristics of the specimen depending on second heat-treatment temperatures. Second heat treatments of the specimen were performed in the temperature range of 400 to 1350℃. X-ray diffraction patterns of $BaTiO_3$ thin films show that the specimen heat treated below 600℃ is an amorphous phase and the one heat treated above 1100℃ forms a poly-crystallization. In the specimen heat-treated at 1300℃, a lattice constant ratio (*c/a*) was 1.188. Scanning electron microscope(SEM) image of $BaTiO_3$ thin films of the specimen heat treated in between 900 and 1100℃ shows a grain growth. At 1100℃, the specimen stops grain-growing and becomes a poly-crystallization. A resistivity-temperature characteristics of the specimen depends on the doping concentrations of Mn. A resistivity ratio between the value at room temperature and the one above Curie temperature was 10^4 for pure $BaTiO_3$ thin films and 10^5 for $BaTiO_3$: additive 0.127mol% MnO

Keywords : $BaTiO_3$ thin film, magnetron sputtering, XRD, interplanner distance, PTCR

1. INTRODUCTION

Due to a rapid development of semiconductor technologies and electronic ceramics, the smaller and the lighter devices are able to be manufactured. Since C. Feldman[1] manufactured ferroelectric $BaTiO_3$ thin films by vacuum evaporation in 1955, various kinds of functional devices using $PbZrTiO_3$(PZT)[2], $BaTiO_3$(BTO)[3], $SrTiO_3$[4], and $PbTiO_3$[5] materials are being made by vacuum evaporation, sputter method, chemical vapor deposition(CVD) method, and etc. With the addition of AST(Al_2O_3, SiO_2, and TiO_2) to $BaTiO_3$ thin films, Y. Matsuo[6] observed a large increase in resistance near Curie temperature T_C. In 1981, T. Nagatomo[7] made the $BaTiO_3$ thin films on platinum(Pt) substrate by rf sputter method. He investigated preferential orientation of the films depending on a variation of substrate temperatures near 700℃. G. T. Houmyuni[8] studied PTCR(positive-temperature coefficient of resistance) characteristics of $BaTiO_3$ thin films made by rf sputter technique in 1989. The PTCR characteristics is the following. In the temperature range below T_C, the resistance is almost constant because the amount of oxygen diffused to the crystal grain is saturated. Thus potential barrier maintains almost constant. Rapid increase in resistance near Curie temperature is explained by the diffusion of oxygen to the grain boundary. Thus the potential barrier becomes higher.

There are several advantages in sputter technique.

Condensation energy is high in the formation of thin film. We can make clean surface of substrates. And it is able to manufacture the insulating materials such as complex oxides.

It is, in general, reported that the substrate temperature requires over 700℃ and the second heat treatment over 900℃ for the $BaTiO_3$ thin films to be poly-crystallized. A study to reduce the substrate and second heat-treatment temperature was actively going on.

In this paper, we are going to present the phase changes, micro-structures and PTCR characteristics of the $BaTiO_3$ thin films manufactured by rf/dc magnetron sputter method with a variation of second heat-treatment temperatures. The substrate temperature is fixed to 295℃ when the films are made.

2. EXPERIMENTAL DETAILS

A desired composition formula of $BaTiO_3$ target was obtained from a preliminary experiment.

$$Ba_{0.998}\,Y_{0.002}Ti_{1.01}O_{3.02} + 0.5wt\%\ SiO_2 + xMnO$$

Here, Mn element was added to improve the PTCR characteristics(x=0, 0.073, 0.100, 0.127, and 0.154mol%). Starting materials are high-purity oxides TiO_2 and $BaCO_3$. The general manufacturing process was followed in making targets. Raw materials are calcined at 1100℃ for 1 hour, and then 3wt% of polyvinyl-alcohol(PVA) was added for solidification and dried it at 150℃ for 12 hours. After pressing it with a pressure of 3,000kg/cm^2, a target with 2 inch diameter and 3mm thickness was obtained. Since the substrate temperature reaches 295℃ by the heat radiation and second electron bombardment when the 210W of rf sputter forward power is applied, no additional power was applied to heat the substrate.

Sputtering conditions are listed in Table 1, and Fig. 1 shows the second heat-treatment conditions of the specimen. In the heat-treatment of $BaTiO_3$ thin film, temperature was increased to the setting point with an increment of 300℃/hr and kept hold time for one hour and then cooled down to room temperature naturally. The thickness of the film was measured by spectroscopic ellipsometry (Rudolph S2000) and it was around 2 μm. X-ray diffractometer(XRD, 35kV, 20mA, CuK_α, λ=10Å, D-Max3 Rigaku) was used to identify crystal structures of the films. Scanning-electron microscope(SEM) was used to observe microstructures of the specimen. For a measurement of SEM, a 200Å thick electrode with gold coating was deposited by vacuum evaporation under 1400V and 6mA for 4 min. A resistance-temperature characteristics of the specimen was measured in the temperature range of 80 to 180℃.

Table 1. Sputtering conditions for a preparation of pecimen.

Parameter	Condition
Initial pressure	3.4 × 10^{-5} Torr
Pressure	2.5 × 10^{-3} Torr
Target(T)	2 inch
Substrate(S)	20 × 10 mm^2 Si wafer
	30 × 5 mm^2 Pt plate
	25 × 13 mm^2 Al_2O_3 ceramics
S - T distance	45 mm
Input power	210 W
Deposition time	10 hr
Substrate temp.	295℃
Oxygen gas	16 sccm
Argon gas	40 sccm

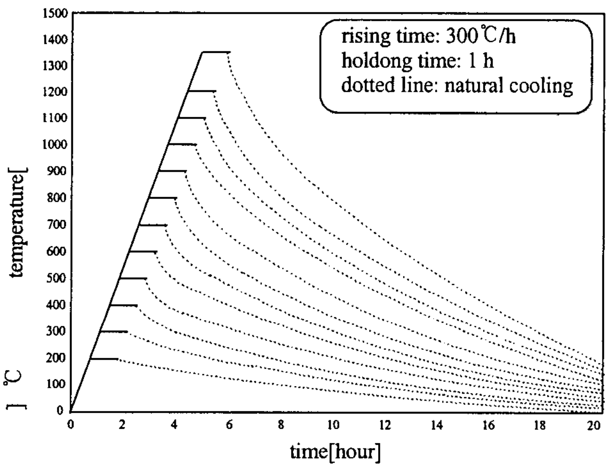


Fig. 1. Second heat-treatment conditions of the $BaTiO_3$ thin films.

3. RESULTS AND DISCUSSION

Fig. 2 displays the X-ray patterns of the $BaTiO_3$ thin films specimen depending on the second heat-treatment temperatures. The kind of varying substrate for below 600℃, 600℃~1200℃ and over 1200℃ of second heat treatment temperature are the Si wafer, Pt plate and Al_2O_3

ceramic substrate, respectively. It shows that the specimen heat treated below 600℃ is an amorphous and the one heat treated above 1100℃ forms a poly-crystallization. It indicates that the specimen requires the second heat treatment temperatures over 1100℃ to become a poly-crystallization. While the specimen heat treated at 700℃ shows a Bragg peak in (110) crystal plane, the specimen heat treated at 1350℃ displays the similar Bragg peaks as those of bulk.

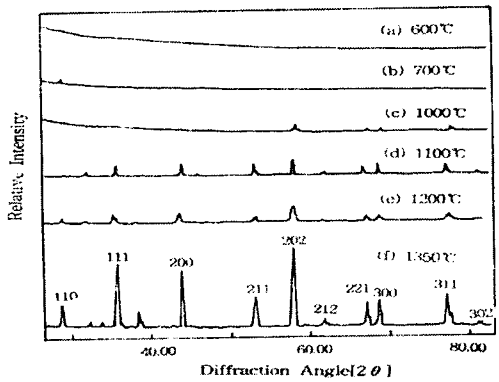


Fig. 2. X-ray diffraction patterns of the $BaTiO_3$ thin films depending on the second heat-treatment temperatures.

Fig. 3 displays interplanar distances as a function of plane indices for a $BaTiO_3$ thin films heat treated at 1300℃. The "+" symbol denotes the measured values and the solid square represents the calculated ones based on the tetragonal crystal structure. The plane with large interplanar distance has a low plane index and the high density of lattice points. The obtained lattice constants *a* and *c* of the specimen are 4.14 Å and 4.92 Å, respectively $c/a = 1.88$

Fig. 4 shows the microstructures of the specimen observed by SEM. Fig. 4(a) shows that specimen heat treated below 600℃ is the amorphous and has the dense morphology. Fig4(b) shows that specimen heat treated in between 900 and 1000℃ shows a grain growth, which indicates that there is a starting point of grain growth. Fig. 4(c) shows that specimen stops grain-growing and becomes a crystal at 1100℃.

Fig. 5 shows the resistivity-temperatures characteristics of the $BaTiO_3$ bulk and thin films depending on the five different amounts of Mn element (0mol%, 0.073mol%, 0.100mol%, 0.127mol%, and 0.154mol%). Fig. 5(a) shows the resistivity-temperature characteristics of the $BaTiO_3$ bulk. As is shown in the figure, the Curie temperature Tc is around 140℃. In pure $BaTiO_3$ bulk, the resistivity below T_C is almost constant, and the value is about 10^2 Ω·cm. The saturated value of resistivity above T_C is about 5×10^4 Ω·cm. Thus the resistivity ratio between the value at room temperature and the saturated one above T_C is $\rho(T>Tc)/\rho(RT) = 5 \times 10^2$ for pure $BaTiO_3$ bulk. In the $BaTiO_3$ bulk doped with 0.127mol% of Mn, the resistivity ratio is $\rho(T>T_C)/\rho(RT) = 10^6$. We can clearly see that with the addition of Mn element to the $BaTiO_3$ there is an increase in resistivity ratio by 10^4. Thus we can say that Mn element improved the PTCR characteristics of the $BaTiO_3$ bulk. Fig. 5(b) shows the resistivity-temperature characteristics of the $BaTiO_3$ thin films with the addition of Mn element. The room-temperature resistivity of the pure $BaTiO_3$ *thin film is*

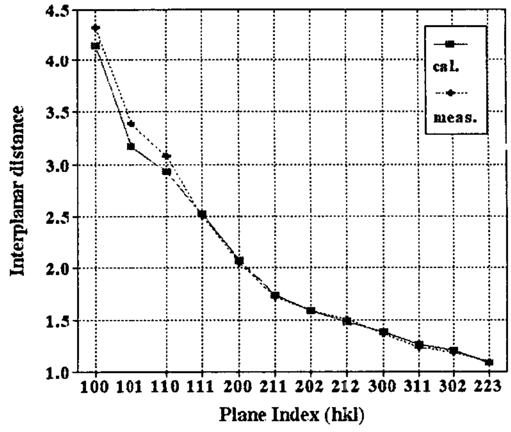
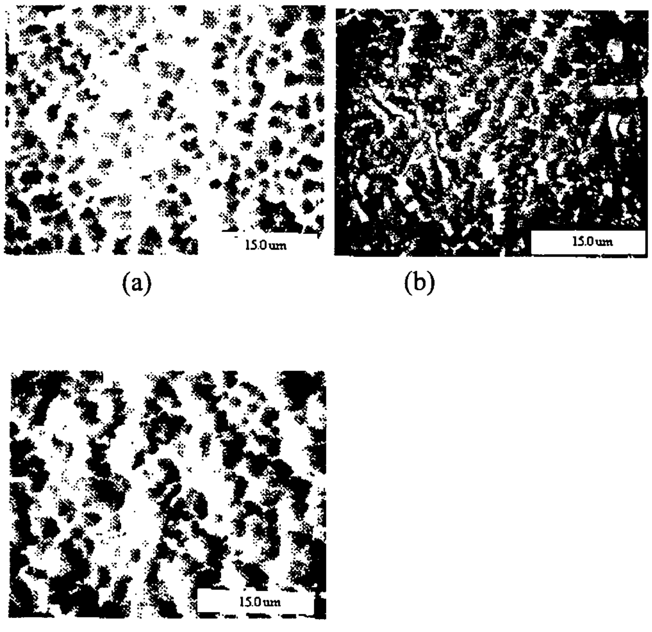


Fig. 3. Interplanar distances of the $BaTiO_3$ thin films heat treated at 1300℃ as a function of plane indices.

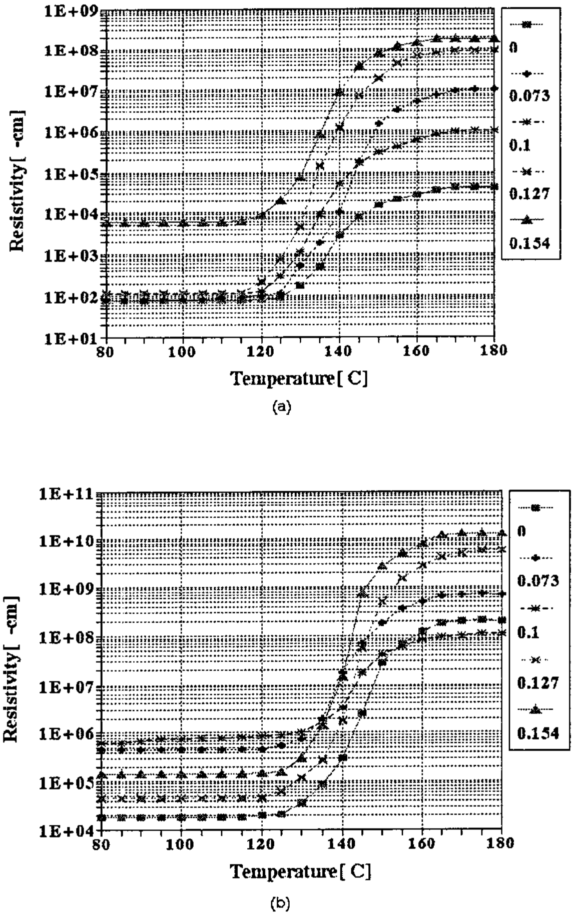


(a) (b)

(c)

Fig. 4. Microstructures of the $BaTiO_3$ thin films taken by SEM.

about $2\times10^4\Omega\cdot$cm. And the saturated resistivity above T_C is almost $2\times10^8\Omega\cdot$cm. Thus the resistivity ratio for pure $BaTiO_3$ thin films is $\rho(T>T_C)/\rho(RT) = 10^4$. When the 0.127mol% of Mn was added, the resistivity ratio $\rho(T>T_C)/\rho(RT) = 10^5$. We here obtained ten times higher resistivity ratio for $BaTiO_3$ thin films added 0.127mol% of Mn. The increase of resistivity ratio in thin film is smaller than that of the bulk. That may be due to the less pores in thin films.



(a)

(b)

Fig. 5. Resistvity-temperature characteristics depending on the amount of Mn in (a) the $BaTiO_3$ bulk and (b) thin films. The number inside the figure represents the mol% of Mn

4. CONCLUSION

We have manufactured $BaTiO_3$ thin films by rf/dc magnetron sputter technique varying second heat-treatment temperatures in the range at 400 to 1350℃. After studying crystal structure, microstructures and PTCR characteristics, we have obtained the followings. X-ray diffraction patterns and SEM micrographs show that the second heat temperature over 1100℃ is required for the films to be crystallized. The PTCR characteristics of the $BaTiO_3$ films doped with 0.127mol% Mn is ten times higher resistivity ratio compared to that of pure $BaTiO_3$ films. We are studying PTCR characteristics of $BaTiO_3$ thin films with different dopants. We can suggest that the $BaTiO_3$ thin films is able to be used as a thermistor.

ACKNOWLEDGMENT

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