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Fabrication of ferroelectric $Bi_4Ti_3O_{12}$ thin films by dipping-pyrolysis of metal naphthenates and micro patterning process using an electron beam

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Fabrication of $Bi_4Ti_3O_{12}$ thin films and the micro patterning process using an electron beam were investigated. The films were prepared on Pt/Ti sputtered silicon substrates by dipping-pyrolysis of the mixed solution of bismuth and titanium naphthenates with Bi:Ti = 4:3 in molar ratio. Annealing of the films in air at 800 ℃ for 1 hour crystallized them into the ferroelectric $Bi_4Ti_3O_{12}$ structure with the c-axis orientation. Micro patterns were drawn on the metal naphthenate film by irradiation of an electron beam operated by a computer. An electron dose of $\sim 10^{-2}$ C/cm^2 makes the films unsoluble for toluene. The profile of patterns with a linewidth of smaller than 1 μm obtained by development in toluene has shown good formation capability and high resolution.

1. INTRODUCTION

Ferroelectric thin films have attracted much attention for applications to memory devices such as non-volatile memories and high-density dynamic random access memories (DRAMs) owing to the spontaneous polarization and the high dielectric constant.[1] Over the past few years a considerable number of studies have been made on fabrication of the thin films with good ferroelectric properties by rf-magnetron sputtering, metalorganic chemical vapor deposition, sol-gel and other methods.

We should notice that it is also very important to give a fabrication process of ferroelectric micro patterns on silicon substrates because of the construction of integrated circuits. It is difficult to fabricate micro patterns of ferroelectric oxides by the conventional photolithographic process for silicon, because ferroelectric thin films, which are mostly prepared with composite metal oxides, are too hard to etch. Only few attempts, however, have been made at patterning of the metal oxide ferroelectric materials.

We have proposed a patterning process for high-T_c superconductor $YBa_2Cu_3O_{7-x}$ (YBCO), in which an electron beam (EB) is irradiated to the metal naphthenate thin film which is a precursor of the composite oxide.[2] Bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT), is one of the typical ferroelectric materials with layered structure which is similar to that of high-T_c superconducting cuprates. Therefore, it is very interesting to apply the same patterning process to ferroelectric BIT thin films.

This paper describes the fabrication of the ferroelectric BIT thin film by dipping-pyrolysis of metal naphthenates and the micro patterning process using an electron beam.

2. EXPERIMENTAL

2.1. Preparation of the dipping solution

Bismuth naphthenate (Nihon Kagaku Sangyo Co., Ltd.) and titanium one (Soekawa Chemical Co., Ltd.) which were sticky liquid at room temperature were used as starting materials to prepare the homogeneous dipping solution. Bismuth and titanium contents of the metal naphthenates were estimated to be 7.0 and 4.4 %, respectively, by the suppliers. The dipping solution was prepared by mixing the metal naphthenates with Bi:Ti = 4:3 in molar ratio and diluting with toluene to achive the appropriate viscosity of the solution. The pyrolysis

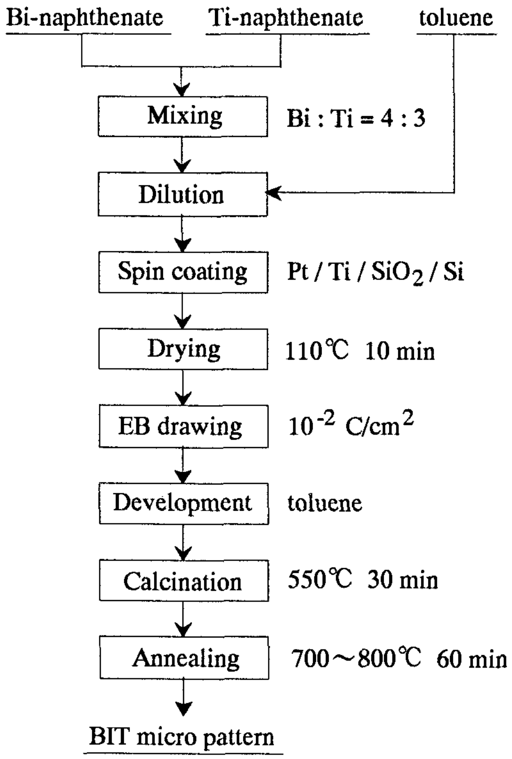

Fig. 1. Patterning process of the ferroelectric BIT.

temperature of the dipping solution was determined from thermogravimetry-differential thermal analysis (TG-DTA).

2.2. Fabrication of BIT thin films

Silicon wafers with a silicon dioxide layer (600 nm) were used as substrates. A titanium layer (50 nm) and then a platinum layer (200 nm) were formed on the surface of the wafers by sputtering. The substrates were washed in acetone and successively in ammonia added pure water using an ultrasonic cleaner for 5 minutes.

The substrates were spin-coated with the above-mentioned solution at a rate of 1000 rpm so that homogeneous films were formed on the substrates and dried in air at 110 ℃ for 10 minutes to evaporate the solvent. Successively, the films were heated to 550 ℃ at a rate of 1 ℃/min in order to obtain crack-free films and calcined at the temperature for 30 minutes to remove the organic components by the pyrolysis. Then they were annealed in air at 600 ～ 800 ℃ for 1 hour to form ferroelectric BIT films.

The crystal structure of resultant films was confirmed by powder X-ray diffraction (XRD) using CuKα. The surface morphology was observed by a scanning electron microscopy (SEM).

2.3. Patterning process

Figure 1 shows the patterning process for metal naphthenate films on Pt/Ti/SiO_2/Si substrates. The EB drawing system was constructed with a conventional SEM and a personal computer. The blanking signal, horizontal and vertical deflecting voltages to the EB were controlled by the computer. The EB spot size was 0.01 μm with a probe current of 10 pA. The electrons were given the energy at the accelerating voltage of 30 kV.

At the first step, the substrates were spin-coated with the dipping solution and dried at 110 ℃ on the same way as the case of the fabrication of the BIT thin films. At the second step, an EB on tracing a given pattern was irradiated to the films. Then, the samples were developed in toluene to remove the non-irradiated parts. Finally, the samples were calcined and annealed to form the ferroelectric BIT micro patterns. The aspect of the developed micro patterns was observed using an SEM.

3. RESULTS AND DISCUSSION

3.1. TG-DTA for the dipping solution

The result of TG-DTA for the dipping solution with Bi:Ti = 4:3 in molar ratio is shown in Fig. 2.

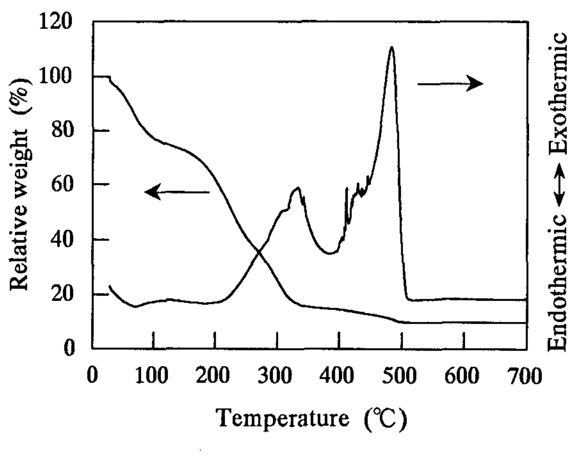

Fig.2. TG-DTA curves for pyrolysis of dipping solution with Bi:Ti = 4:3 in molar ratio.

The decrease of weight from room temperature to 100 ℃ is caused by the evaporation of toluene. The large weight loss occurred in the range from 200 to 350 ℃ is due to the pyrolysis and the burning of organic components. The large exothermic anomaly appeared in the range from 250 to 500 ℃ arises from the pyrolysis of naphthenates and the oxidation of bismuth and titanium. It is confirmed that the dipping solution is perfectly pyrolyzed and turned into Bi_2O_3 -TiO_2 at 510 ℃, because the weight is constant above the temperature. From this result, the calcination temperature of 550 ℃ was chosen in this study.

3.2. Structure of BIT films

The thickness of spin-coated films was estimated to be about 1 μm from the SEM observation. After annealing, the thickness decreased to 20 % of the initial thickness.

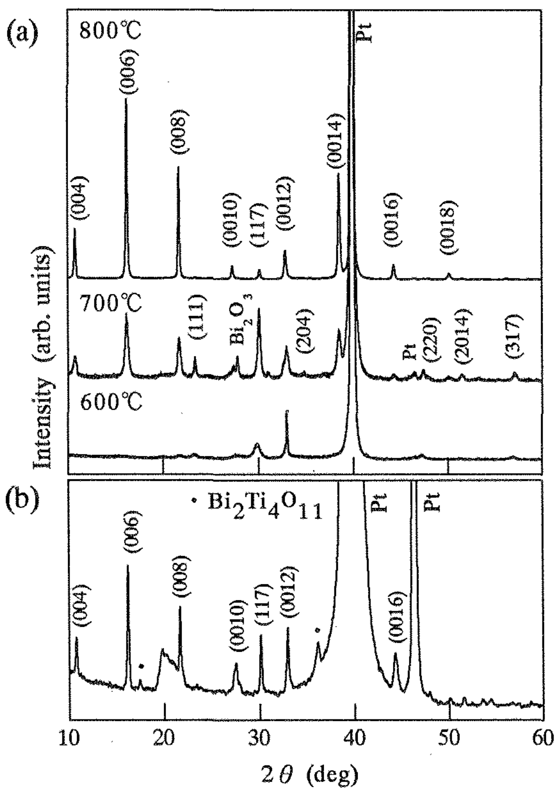

Fig. 3. XRD patterns of (a) BIT films annealed in air at 600, 700 and 800 ℃ for 1 h, and (b) BIT pattern fabricaed using an electron beam and annealed in air at 800 ℃ for 1 h.

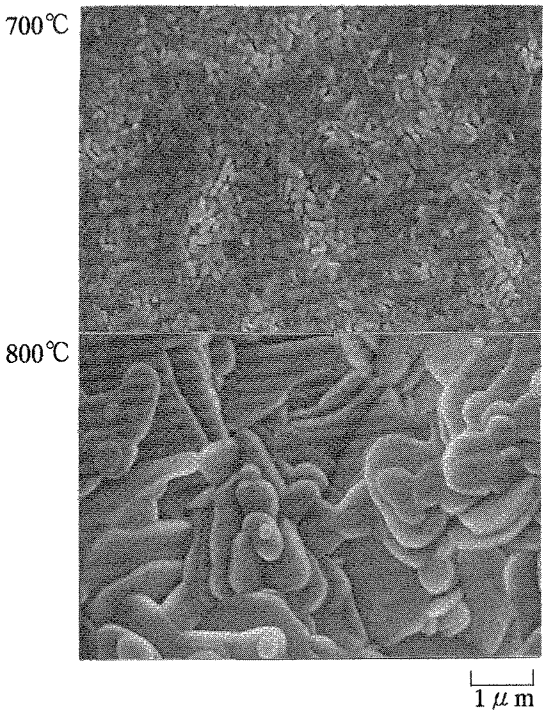

Fig. 4. SEM photographs of BIT films annealed in air at 700 and 800 ℃ for 1 h.

Figure 3(a) shows the XRD patterns of resultant films annealed in air at 600, 700 and 800 ℃ for 1 hour. The clear peaks of the BIT structure are found in the patterns for the films annealed above 700 ℃. The full width at half maximum of the peaks becomes narrow with increase of the annealing temperature. Thus, the crystallinity increases with increasing the annealing temperature. Although the film annealed at 700 ℃ has no orientation, the film annealed at 800 ℃ is crystallized into the BIT structure with the c-axis orientation perpendicular to surface of the substrate.

The SEM photographs of the surface of the films annealed at 700 and 800 ℃ are shown in Fig. 4. Small grains of 0.1 μm in size are observed in the film annealed at 700 ℃. On the other hand, plate-like crystals of 1 μm in size are piled up in the film annealed at 800 ℃.

It is concluded that the BIT thin films with c-axis orientation are fabricated by annealing in air at 800 ℃ for 1 hour.

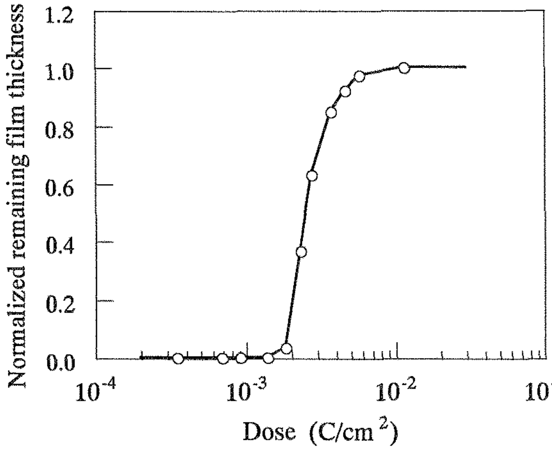

Fig. 5. Electron dose dependence of the remaining film thickness after development. Film thickness is normalized as thickness of the spin-coated film is equal to 1.

3.3. Micro patterning

The electron-irradiated parts in the film could be never removed by the development in toluene. The reaction between the metal naphthenate film and energized electrons has not been clear.

The EB dose dependence of the remaining film thickness is shown in Fig. 5. It is confirmed that the sensitivity to form micro patterns is 2.5×10^{-3} C/cm^2. This value is the same order of the sensitivity for the YBCO naphthenate film and ten times lower than that for PMMA which is a typical resist material in the EB lithography field.

Figure 6 shows the aspect of developed micro patterns observed by the SEM. The sharp 1 μm square dot patterns were formed in this process. The pattern after annealing decreased about 60 % in size to the initial size owing to the pyrolysis. The developed rectangular pattern was calcined and successively annealed at 800 ℃ to form the ferroelectric BIT patterns. The XRD pattern indicates the peaks of BIT structure, as shown in Fig. 3(b).

4. CONCLUSIONS

$Bi_4Ti_3O_{12}$ thin films were fabricated on Pt/Ti/SiO2/Si substrates by dipping-pyrolysis method using bismuth and titanium naphthenates. The films were crystallized into the $Bi_4Ti_3O_{12}$ structure with the c-axis orientation perpendicular to the substrates by annealing in air at 800 ℃ for 1 hour. The films had a layered structure of the plate like BIT single crystals.

Dot patterns of 1 μm square in size were formed using an electron beam. The sensitivity of the metal naphthenate films for the irradiation of an electron beam was 2.5×10^{-3} C/cm^2, at which the metal naphthenates reacted with electrons accelerated at 30 kV. After annealing at 800 ℃, detailed patterns of $Bi_4Ti_3O_{12}$ were fabricated.

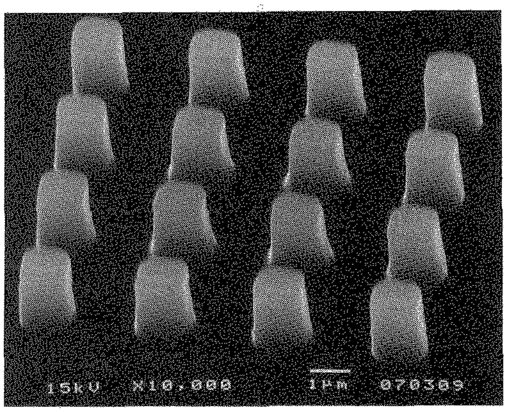

Fig. 6. SEM photograph of the micro pattern of metal naphthenate. The metal naphthenate is precursor for BIT.

ACKNOWLEDGEMENT

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REFERENCES

1) J. F. Scott and D. A. Paz de Araujo: Science **26** (1989) 1400.
2) K. Mori and S. Okamura: Jpn. J. Appl. Phys. **31** (1992) L1143.