

# Low Temperature Fabrication of BaTiO<sub>3</sub> Thick Films by Aerosol Deposition Method and Their Electric Properties

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The Aerosol Deposition Method (ADM) was employed in order to prepare BaTiO<sub>3</sub> thick films at low temperature for the applications to a decoupling capacitor. The optimum deposition conditions were investigated to grow BaTiO<sub>3</sub> thick films on copper metal substrates at room temperature. As a result, it was revealed that the dispersion state of ultrafine BaTiO<sub>3</sub> particles as a starting material was very important to improve surface morphology. It was succeeded in obtaining BaTiO<sub>3</sub> thick films with smooth surface. The as-deposited BaTiO<sub>3</sub> thick films were translucent and their crystal structure was assigned to cubic BaTiO<sub>3</sub>, not tetragonal through the analysis of X-ray diffraction. The dielectric permittivity of the as-deposited BaTiO<sub>3</sub> thick films was around 70 while the dielectric loss tangent of them was around 1 % at 1 MHz regardless of the film thickness. To enhance the dielectric permittivity of BaTiO<sub>3</sub> thick films, the annealing treatment was applied. After annealing at 300°C for 2 hrs, the lattice parameters became closer to those of BaTiO<sub>3</sub> ceramics, and the dielectric permittivity also increased up to approximately 140. We could show the possibility for aerosol-deposited BaTiO<sub>3</sub> thick films to be applied to the embedded decoupling capacitor.

Key words: Aerosol Deposition Method, BaTiO<sub>3</sub> film, embedded decoupling capacitor

## 1. INTRODUCTION

Today's electronic devices, such as cellular phones, personal digital assistants (PDAs) and personal computers, continue to be subjected to the trend of added functionality with wireless interfaces and high operating speeds and of the miniaturization by high integration of electronic components. Especially, the number of passive components increases at very high rates. In the roadmap of the National Electronic Manufacturing Initiative (NEMI)<sup>1</sup>, the surface mounting technology (SMT) of passive components, such as discrete parts, arrays, networks and integrated passive devices will be no longer satisfied due to the limited area left for the passive components. So, the embedded passive technology (EPT) should be developed to overcome this problems. Candidates of the present fabrication technologies for embedded passives are low temperature co-fired ceramics (LTCCs)<sup>2,3</sup> and polymer-ceramic composites<sup>4,5</sup>. LTCCs need still high temperature process at around 850 °C leading to low size accuracy due to shrinkage during firing, limitations on the use of materials caused by interdiffusion and reactions, difficulty in embedding of active devices and chip components. And, polymer-ceramic composites show degraded electric properties, low permittivity and low heat extraction compared with ceramics in spite of being able to fabricate lower than 200 °C and to embed active devices in the multilayer structure circuitry. Among the passive components, the decoupling capacitor with high dielectric permittivity are

one of the most difficult components to fabricate as a embedded passive by means of the present fabrication technologies. For instance, relative permittivity of the embedded decoupling capacitor prepared by polymer composites is less than 100.<sup>6</sup> Decoupling capacitors, which act as a charge reservoir, are required to suppress the power distribution noise which arises due to the fast switching speed of the circuits which result in sudden current demands, noise is generated in the system. However, traditional decoupling capacitors such as MLCCs (multilayer ceramic capacitors) are not effective at frequencies above 1 GHz. As advantages of EPT, decoupling capacitors can be placed directly underneath the high speed active components shortening distance between the passives and active components so that the parasitics associated with SMT passives can be reduced to result in better signal transmission and less cross talk. If BaTiO<sub>3</sub> thick films with high dielectric permittivity can be fabricated on Cu substrates below 300°C, all of the problems mentioned above are expected to be overcome. In this study, we propose a new novel technology to fabricate BaTiO<sub>3</sub> thick films as the decoupling capacitor by employing the aerosol deposition method (ADM)<sup>7-9</sup>.

## 2. EXPERIMENTAL

The ADM is based on shock loading solidification due to the impact of ultrafine ceramic particles accelerated by means of carrier gases and a nozzle. Figure 1 illustrates

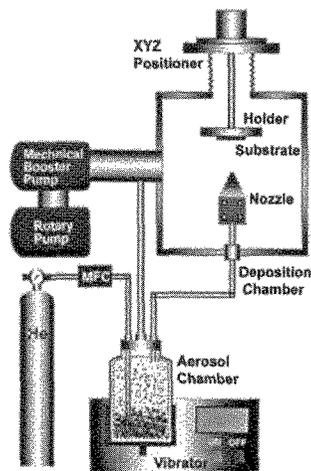


Fig. 1. Schematic diagram illustrating the apparatus of the Aerosol Deposition Method.

the ADM apparatus.  $\text{BaTiO}_3$  thick films were fabricated on glass or Cu substrates by the ADM. Cu substrates were mechanically polished to get a mirror-like plane using alumina powder of  $1\ \mu\text{m}$  in diameter. Fine  $\text{BaTiO}_3$  particles (Sakai Chemical Industry Co., Ltd., BT03) with  $0.3\ \mu\text{m}$  in average diameter and purity of 99.9 % were used as starting materials. Before deposition, the  $\text{BaTiO}_3$  particles were dried at  $150^\circ\text{C}$  for 1 day. The  $\text{BaTiO}_3$  particles become a state of aerosol in the aerosol chamber by means of the vibration and mixing system. The particles are transported by He gases and accelerated through a nozzle. Films are grown at room temperature by the impact of the particles on substrates. The deposition conditions for  $\text{BaTiO}_3$  thick films by the ADM were summarized in Table 1. The microstructure and crystallinity of the  $\text{BaTiO}_3$  thick films were examined by a field emission-scanning electron microscope (FE-SEM) and X-ray diffractometer (XRD), respectively. In order to examine the dielectric properties of the ADM-derived  $\text{BaTiO}_3$  thick films, the upper electrode was formed by Au using a DC sputter. Their dielectric properties were measured from 1 kHz to 1 MHz by an impedance analyzer (Agilent Tech. 4294A) and the coaxial microprobes (Cascade Microtech Japan, INC, DCP100). And temperature dependence of dielectric properties also measured using the temperature controllable probe station (WM365A-1, Measure Jig Co., Ltd.).

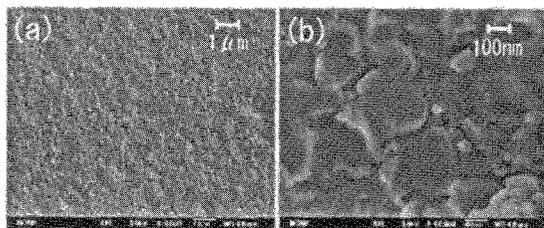


Fig. 2. Plane-view FE-SEM micrographs of  $\text{BaTiO}_3$  films deposited on Cu substrates at room temperature by the ADM. (a) low magnification and (b) high magnification.

Table I. Experimental conditions of  $\text{BaTiO}_3$  thick films by the aerosol deposition process.

Powder	$\text{BaTiO}_3$
Substrate	Glass and Cu
Carrier Gas	He
Size of Nozzle Orifice	$10 \times 0.4\ \text{mm}^2$
Scanning Rate	1.25 mm/sec
Working Pressure	1~1.5 kPa
Consumption of Carrier Gas	4.5~9 L/min
Distance between Substrate and Nozzle	10~35 mm
Deposition Temperature	room temperature
Deposition Time	10~60 min
Deposition Area	$5 \times 5\ \text{mm}^2$
Vibration Speed	150~300 rpm

### 3. RESULTS AND DISCUSSION

#### 3.1 ADM-derived $\text{BaTiO}_3$ thick films prepared at room temperature

Figure 2 shows plane-view FE-SEM micrographs of the ADM-derived barium titanate thick films on Cu substrates using  $\text{BaTiO}_3$  particles with  $0.3\ \mu\text{m}$  in average diameter at room temperature. The thickness of this sample was approximately  $1\ \mu\text{m}$ . In addition,  $\text{BaTiO}_3$  thick films were prepared with various thickness from submicron to  $5\ \mu\text{m}$ . Deposition rate was in the range of  $0.01\text{--}1\ \mu\text{m}/\text{min}$  according to the experimental conditions. It could be confirmed that the barium titanate thick films are dense although their surfaces are somewhat rough. The surface roughness  $R_a$  is approximately  $0.5\ \mu\text{m}$ . By the observation of FE-SEM at higher magnification, as shown in Fig. 2(b), it was clearly revealed that the films are very dense and the grain size is approximately  $10\text{--}300\ \text{nm}$ . However, TEM observation is required to determine more accurately. Figure 3 shows the XRD patterns of the  $\text{BaTiO}_3$  thick films on Cu substrates at room temperature by the ADM and the raw material powder (BT03). Even though the films were prepared at room temperature, only perovskite- $\text{BaTiO}_3$  phase was formed. However, the peak splits indicating the tetragonal structure could not be observed in the XRD patterns of the ADM-derived  $\text{BaTiO}_3$  thick films. Moreover, their XRD peaks were shifted to the lower angle than that of

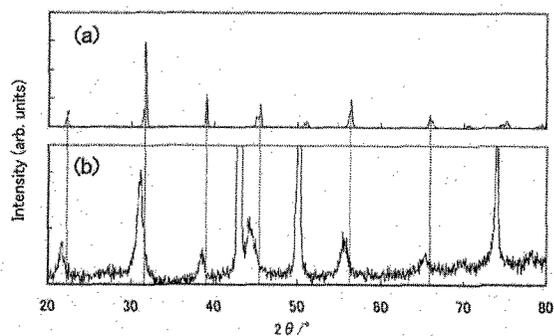


Fig. 3. X-ray diffraction patterns of (a) raw material powder (BT03) and (b)  $\text{BaTiO}_3$  films deposited on Cu substrates at room temperature by the ADM.

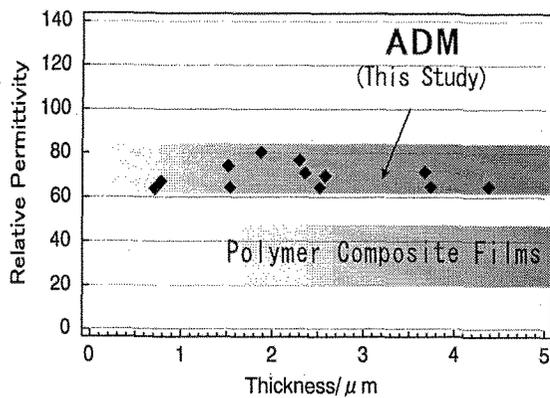


Fig. 4. Thickness dependence of permittivity of BaTiO<sub>3</sub> films deposited on Cu substrates at room temperature by ADM.

BaTiO<sub>3</sub> ceramics. And, the peak broadening was observed for the films, which is caused by the small crystallite size (15 nm in average). From the XRD results, it is considered that the ADM-derived BaTiO<sub>3</sub> thick films have cubic system and their lattice parameters are slightly expanded compared with those of BaTiO<sub>3</sub> bulk ceramics. This phenomenon is very similar to the size effect of BaTiO<sub>3</sub>, but it has not been clearly understood yet and the further study is required to elucidate the phenomenon. At present, we consider that the growth of the films by the ADM is follows. When the BaTiO<sub>3</sub> thick films are grown by the ADM, the raw material BaTiO<sub>3</sub> particles are fractured to 10 nm-order sized particles by the impact so that their activation energy becomes much higher due to the high specific surface area, making the fractured particles to be bonded with the assist of the impact of the subsequent accelerated particles.

Their dielectric properties were investigated by an impedance analyzer. Figure 4 shows the thickness dependence of permittivity of BaTiO<sub>3</sub> thick films deposited on Cu substrates at room temperature by the ADM. The permittivity with various thickness ranging from submicron to several microns was not almost dependent on the film thickness. The average relative permittivity was around 70 and the dielectric loss tangent was 1%. Although the dielectric property is good from the viewpoint of dielectric loss, dielectric permittivity is much lower than that of bulk ceramic, but it is higher than that of polymer composite by the use of BaTiO<sub>3</sub> particles. This is not the satisfied dielectric properties for the application to the embedded decoupling capacitors. In addition, the temperature dependence of dielectric permittivity and dielectric loss tangent of the ADM-derived BaTiO<sub>3</sub> thick films prepared at room temperature. As shown in Fig. 5, the Curie point could not be observed up to 150°C, which phenomenon is considered to be occurred because the crystal structure of the ADM-derived BaTiO<sub>3</sub> thick films was determined to be cubic system as shown in XRD data. At present, we think that it is associated with the size effect. However, the reason has

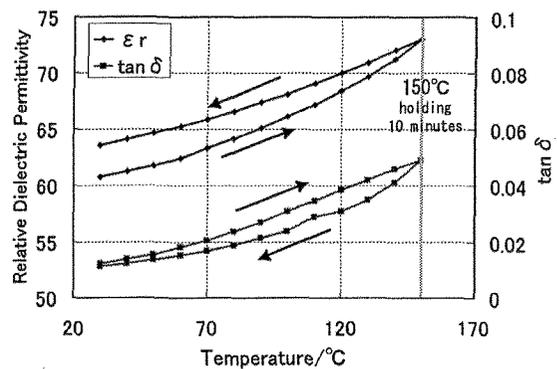


Fig. 5. Temperature dependence of dielectric properties of BaTiO<sub>3</sub> films deposited on Cu substrates at room temperature by ADM.

not been understood clearly. A further study is necessary to clarify the mechanism and to improve the dielectric properties. Moreover, the hysteresis of the dielectric properties appeared as a function of the measurement temperature. This is considered to be from the annealing effect, which will be shown in the next section.

### 3.2 Post-Annealing Effects of ADM-derived BaTiO<sub>3</sub> thick films

In the previous section, we investigated the dielectric properties regarding the ADM-derived BaTiO<sub>3</sub> thick films prepared at room temperature. However, since the dielectric permittivity was too small for the applications, their post-annealing effects on the dielectric properties were also examined up to 300°C. First, the change in the crystal structure from the XRD analysis was examined according to the annealing temperature as shown in Fig. 6. As the annealing temperature increased, the peak shift to the lower angle decreased, indicating the lattice parameters became closer to that of BaTiO<sub>3</sub> ceramics, but the lattice expansion could not be fully recovered to the

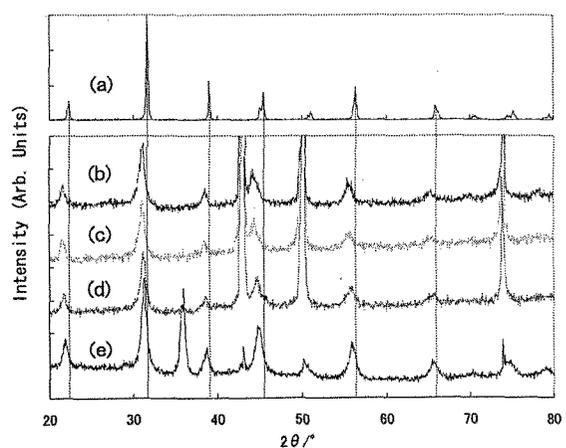


Fig. 6. X-ray diffraction patterns of (a) raw material powder (BT03) and (b) as-deposited BaTiO<sub>3</sub> films, post-annealed BaTiO<sub>3</sub> films at (c) 100°C, (d) 200°C, and (e) 300°C.

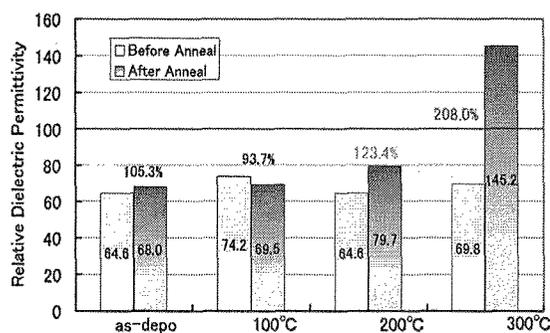


Fig. 7. Post-annealing effects on the dielectric permittivity of ADM-deposited BaTiO<sub>3</sub> films on Cu substrates.

original lattice size through the post-annealing below 300°C. And, their crystallite size was not changed apparently by the annealing at such a low temperature. We think that the change in the lattice parameters is the interesting phenomenon because such low heat energy is generally not enough to change the lattice parameters. At present, we believe that H<sub>2</sub>O molecules in the ADM-derived BaTiO<sub>3</sub> thick films are related to the above results, being considered that the Ba<sup>2+</sup>, Ti<sup>4+</sup> or O<sup>2-</sup> ions are hardly diffused for their lattices to be rearranged at 300°C. Although the starting material powder was dried, H<sub>2</sub>O, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and other contamination were absorbed at the surface of the powder. It is considered that this kind of contaminations cannot be removed easily through the annealing at 100°C or 200°C. However, it can be considered that they are able to begin to be got rid of around 300°C so that their lattice parameters are changed.

Figure 7 shows the post-annealing effects on the dielectric permittivity of ADM-deposited BaTiO<sub>3</sub> films on Cu substrates. At 100°C annealing, there was no enhancement in the dielectric properties compared with as-deposited BaTiO<sub>3</sub> thick films. As the annealing temperature increased above 100°C, the dielectric permittivity increased. In particular, it is noticeable that the increase of the dielectric permittivity at 300°C was approximately 200%. Figure 8 shows the frequency dependence of dielectric properties of the as-deposited and the post-annealed BaTiO<sub>3</sub> films at 300°C. For the both of samples, the frequency dependence was observed, which dependence was not so high. And, the dielectric permittivity and dielectric loss increased by annealing at 300°C. However, its dielectric loss is still less than 3%. We think that this increase is not from the defects such as space charges but from the non-linearity of BaTiO<sub>3</sub> materials themselves.

Through the post-annealing below 300°C, relatively good dielectric properties could be obtained compared to that of polymer composites. Even though some further studies remained, we could show the possibility for the applications to the embedded decoupling capacitors.

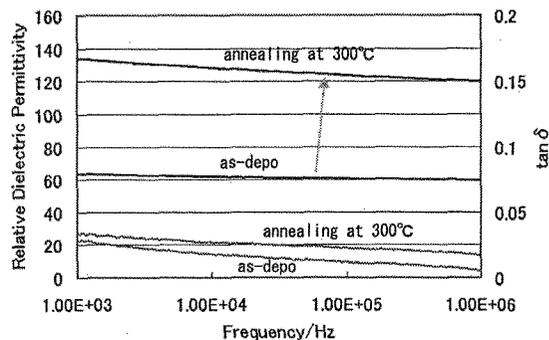


Fig. 8. Comparison of frequency dependence of dielectric properties between (a) as-deposited and (b) post-annealed BaTiO<sub>3</sub> films deposited by the ADM.

#### 4. CONCLUSIONS

The Aerosol Deposition Method (ADM) was employed in order to prepare BaTiO<sub>3</sub> thick films with high dielectric permittivity at low temperature for the applications of the embedded decoupling capacitors. It was succeeded to obtain BaTiO<sub>3</sub> thick films with smooth surface by the application of non-agglomerated BaTiO<sub>3</sub> particles. The as-deposited BaTiO<sub>3</sub> thick films were translucent and their crystal structure was assigned to cubic BaTiO<sub>3</sub>, not tetragonal through the analysis of X-ray diffraction. The dielectric permittivity of the as-deposited BaTiO<sub>3</sub> thick films was around 70 while the dielectric loss tangent of them was around 1% at 1 MHz regardless of the film thickness. After annealing at 300°C for 2 hrs, the lattice parameters became closer to those of BaTiO<sub>3</sub> ceramics, and the dielectric permittivity also increased up to approximately 140. We could show the possibility for aerosol-deposited BaTiO<sub>3</sub> thick films to be applied to the embedded decoupling capacitors.

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