Preparation of BaTiO₃ Films for MLCCs by Direct Vapor Deposition

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ABSTRACT

BaTiO₃ films were deposited by the direct vapor deposition (DVD) technique to prepare thin dielectric layers for multilayer ceramic chip capacitors (MLCCs). The BaTiO₃ films were successfully prepared by co-evaporation of the BaTiO₃ ceramic and Ti metal source. The films deposited at room temperature and 600°C were amorphous and crystalline phases, respectively. The intensity of (110) and (111) peaks increased as Ba/Ti ratios were close to stoichiometric composition. BaTiO₃ films deposited with e-beam power of 700 W showed the deposition rate of 33 nm/min. The dielectric constant and dissipation factor of BaTiO₃ films measured at 1 kHz were 150∼180 and 2∼5%, respectively. The capacitance decreased with increasing the temperature and varied only between 787pF and 752pF in the temperature range 15∼125°C.

Keywords: MLCC; DVD; barium titanate; deposition rate; capacitance

INTRODUCTION

The research on the miniaturization of electric parts has been widely carried out while miniaturization of electronic and electric products has been proceeded. Especially, the miniaturization of multilayer ceramic chip capacitors (MLCCs) among passive components is remarkable. MLCC manufacturers have focused on development of products with smaller size and higher capacitance[1–3]. The manufacturing of thinner dielectric film is indispensable for higher capacitance. Now the dielectric sheets of MLCCs have been formed by die coater and lip coater and thickness of dielectric sheets has been decreased to about 1 μm

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levels. However, because the preparation of thinner dielectric layers by liquid phase method such as doctor blade is very difficult, it is needed to consider new method except liquid phase method. Barium titanate (BaTiO₃) is used extensively as the dielectric for ceramic capacitors, particularly due to its high dielectric constant and low dielectric loss. Although BaTiO₃ thin films have been studied intensively for application in nonvolatile memory devices, thin film capacitor and electro-optic devices, the studies on dielectric films for MLCCs are uncommon. High quality BaTiO₃ films have been deposited successfully by various deposition methods [4–6], but almost all deposition methods are too low deposition rate to prepare the MLCCs.

Among various techniques, the e-beam evaporation method shows relatively high deposition rate. So, some efforts have been made to prepare BaTiO₃ films by e-beam evaporation. However when BaTiO₃ is used as source for e-beam evaporation, there are problems such as decomposition of BaTiO₃ and considerable difference of vapor pressure between Barium and Titanium. These problems incur large difference of composition in films and make preparation of BaTiO₃ films by e-beam evaporation process difficult. Flash evaporation method, which evaporates instantaneously after dropping a small portion of source material onto a heater, was used to avoid these problems. Although BaTiO₃ films can be made by flash evaporation, the deposition rate of 8–40 Å/min. was too low for preparation of MLCCs [7].

In this work, BaTiO₃ films were deposited using the direct vapor deposition (DVD) technique. The DVD system generates a vapor stream from one or more crucible sources. The flowing carrier gas interacts with that stream and dictates its flow towards the coating surface [8]. The purpose of this study is to evaluate the variation of composition of sources and films with processing condition and to prepare of BaTiO₃ films by DVD technique with high deposition rate. The effect of current applied to each source on composition change and annealing temperature on formation of BaTiO₃ phase was studied also.

**EXPERIMENTAL**

Figure 1(a) shows the general geometric configuration of DVD system. The DVD system uses an e-beam to evaporate a material from source pools. The vapor is then transported to the coating surface in a flowing gas. The system is largely composed of working chamber and gas flow chamber and e-beam gun. Figure 1(b) shows the focused e-beam with diameter of 0.5mm and current pattern of oscilloscope showing high speed beam scanning applied at sources, respectively. To prepare the BaTiO₃ dielectric layer, BaTiO₃ and Ti source were co-evaporated using e-beam scanning technique. BaTiO₃ sources were made to rod form by cold isostatic press and sintering. Helium and oxygen gases were used as carrier gas and reactive gas, respectively. During deposition, the total chamber pressure was maintained at $4.3 \times 10^{-2}$ mbar. The flow
rate of He and O₂ gas was 2 : 0.05 slm. The detailed deposition conditions were described in Table 1. The crystal structure of the films was determined by X-ray diffraction (XRD, Scintag X1 Texture) employing Cu kα radiation and a Ni filter. The microstructure of BaTiO₃ films were determined using scanning electron microscopy (SEM, JEOL JSM 6700F). The composition of the films was determined by energy dispersive x-ray spectroscopy (EDX). The dielectric constant and dissipation factor were measured with a Hewlett-Packard (HP4194A) impedance-gain phase analyzer.

![Diagram of DVD system and focused beam patterns](Image)

**Figure 1.** (a) General geometric configuration of DVD system and (b) focused beam patterns. (See Color Plate XXVIII)

**Table 1**

Preparation condition of BaTiO₃ films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Si wafer</td>
</tr>
<tr>
<td>Source-substrate distance</td>
<td>20 cm</td>
</tr>
<tr>
<td>E-beam power</td>
<td>70 kV/10 mA</td>
</tr>
<tr>
<td>He: O₂ flow rate</td>
<td>2: 0.05 slm</td>
</tr>
<tr>
<td>Pressure of working chamber</td>
<td>4.3 × 10⁻² mbar</td>
</tr>
<tr>
<td>Pressure of gas flow system</td>
<td>1.2 × 10⁻¹ mbar</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>R.T. and 600°C</td>
</tr>
<tr>
<td>Deposition time</td>
<td>10 min</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

When BaTiO$_3$ ceramic is used as a source for e-beam evaporation, it is generally known to decompose to BaO, TiO and TiO$_2$ from BaTiO$_3$ ceramic [9] and then, it is very difficult to control the composition of BaTiO$_3$ films using single source. To overcome this problem, the dual sources of BaTiO$_3$ and Ti were used in this study. The composition of source must not change during continuous evaporation. Figure 2(a) shows the composition profile of BaTiO$_3$ source from surface with depth after evaporation for 1 hour. The Ba/Ti ratio at source surface was about 0.67 and the ratio at 1 mm depth from surface was 0.29. These are values decreased largely from stoichiometric ratio, 1.0. It may be assumed that these results are due to higher vapor pressure of Ba than that of Ti and rapid diffusion of Ba from sub-surface. The barium and oxygen was deficient in source surface, but the oxygen contents and Ba/Ti ratio increased to stoichiometric composition near the non-melted region. The color of source was changed to black from white, implying the change to conductive material from insulator after melting. This indicates that BaTiO$_3$ source was changed to Ti rich and oxygen poor phases. Figure 2(b) shows the change of composition in films prepared as a function of melting time using same source. When made through melting for 15 min. from original source of BaTiO$_3$, the film showed the Ba/Ti ratio of 3.2. However, as the melting time of source was long, Ba/Ti ratio in films was decreased because Ba in source was decreased. After source was melted for 90 min., the Ba/Ti ratios of films could be regarded as being almost constant, having a value of about 2.0. This result suggested that the evaporation rate and diffusion rate of Ba became similar after melting during some period. In order that the process has reproducibility, Ba/Ti ratio in source has to be constant during deposition. Therefore, the BaTiO$_3$ films can be made using the source melted during some period. Also the deficiency of Ti in films was compensated by co-evaporation of Ti.
The X-ray diffraction profile of the initial source and source melted for 2 hours is shown in Fig. 3(a). The BaTiO$_3$ ceramic source had tetragonal phase, but after melting, the BaTiO$_3$ source was changed to BaTi$_2$O$_5$, Ba$_4$Ti$_3$O$_{30}$ and BaTi$_5$O$_{11}$ phases. As can be expected from Fig. 2(a), the source shows Ba deficient phase due to higher vapor pressure of Ba after melting. Figure 3(b) shows the EDX spectrum of BaTiO$_3$ source melted for 2 hours. The Ba/Ti ratio at source surface was 0.53. In considering that the composition of source has to be invariable, Ba deficient source (BTO) such as BaTi$_2$O$_5$ or BaTi$_4$O$_{13}$ are preferable to BaTiO$_3$ source to prepare BaTiO$_3$ films. Therefore, The BaTiO$_3$ source was used after melting for 90 min. to have a constant Ba/Ti ratio as shown in Fig. 2(b).

Figure 4 shows XRD patterns of BaTiO$_3$ films annealed at 700 °C after deposition at 600 °C. The composition of films was controlled with e-beam current applied at BTO and Ti sources. The current ratio applied at each source was changed while a constant beam power was applied. The Ba/Ti ratio was decreased linearly as the current applied to Ti source was increased. The Ba/Ti ratios of films showed 2.09, 1.70, 1.32, and 1.19 when the current ratios applied at BaTiO$_3$ and Ti source were 5, 7, 10 and 20, respectively. As the Ba/Ti ratio increases, the intensity of characteristic peaks of BaTiO$_3$ decreases and new peaks begin to appear. The diffraction patterns showed Ba rich phases marked as ■ Ba$_4$Ti$_2$O$_{27}$ and ● Ba$_2$TiO$_4$. The Ba rich phases were diminished as composition of films was close to stoichiometric. In case of film with Ba/Ti ratio of 1.19, XRD pattern showed only BaTiO$_3$ phase. The intensity of (110) and (111) peaks increased as Ba/Ti ratios were close to stoichiometric composition. This indicates that the fraction of Ba rich phases decreased and the fraction of BaTiO$_3$ phase increased.

Figure 5 shows SEM images of BaTiO$_3$ films coated at 600 °C for 10 min. The as-grown film of Fig. 5(a) and (c) showed smooth surface morphology and columnar structure. The approximate range of grain size is 50–80 nm and the
Figure 4. XRD patterns of BaTiO$_3$ films deposited with different e-beam current. The films show Ba rich phases ($\square$; Ba$_4$Ti$_2$O$_{27}$, $\bullet$; Ba$_2$TiO$_4$). (See Color Plate XXXI)

Figure 5. SEM images of BaTiO$_3$ films (a), (c) as grown at 600$^\circ$C and (b), (d) annealed at 700$^\circ$C.
Figure 6. XRD patterns of BaTiO$_3$ films deposited at different temperature and annealed at 700°C. (See Color Plate XXXII)

The thickness of as-grown film is about 330 nm. The calculated deposition rate is 33 nm/min. In general, the deposition rate of ceramic films by vapor deposition method is below several nm/min. The DVD system may be one of candidates for MLCC preparation due to its high deposition rate. Figure 5(b) and (d) show the microstructure of film annealed at 700°C for 1 hour. The microstructure of surface is denser and smoother than that of as-grown film.

Figure 6 shows the XRD patterns of BaTiO$_3$ films deposited at different temperature and annealed at 700°C for 1 hour. The films deposited at room temperature were amorphous. However, the films deposited at 600°C showed strong (110) and (111) peaks, suggesting that polycrystalline BaTiO$_3$ films without second phases were grown. The intensity of peaks was increased due to the increase of crystallinities after annealing at 700°C.

Figure 7(a) shows the dielectric constant and dissipation factor (tanδ) of BaTiO$_3$ films annealed at 700°C as a function of frequency. The film with
dielectric thickness of 1 µm showed capacitance of 0.783 nF and dissipation factor of 5.3% at 1 kHz. The calculated dielectric constant is 177 at 1 kHz. This value is similar to that of films prepared by other deposition method [10, 11]. Figure 7(b) shows capacitance vs. temperature property of BaTiO$_3$ films. For the X7R type dielectrics, the capacitance must not change by more than ±15% from the value at 25°C over the temperature range −55 to 125°C. Although the capacitance of film decreased with increasing the measuring temperature, the change of capacitance satisfied the specification of X7R type materials.

**CONCLUSION**

After evaporation, Barium in BaTiO$_3$ source was severely decreased due to higher vapor pressure of Barium than that of Titanium. The BaTiO$_3$ source was used after melting for 90min. in order to have a constant Ba/Ti ratio. The composition of films was controlled with ratio of e-beam current applied to Ba-deficient BaTiO$_3$ and Ti source. The intensity of (110) and (111) peaks increased as Ba/Ti ratios were close to stoichiometric composition. The deposited films showed smooth surface morphology and columnar structure and the deposition rate of 33nm/min. The intensity of crystalline peaks was increased due to the increase of crystallinites after annealing at 700°C. The dielectric constant and dissipation factor of BaTiO$_3$ films obtained by DVD are 150~180 and 2~6%, respectively and are comparable to that by other deposition methods. The capacitance decreased with temperature and satisfied the specification of ±15% at 125°C. The BaTiO$_3$ films were successfully prepared by DVD with high deposition rate.

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**REFERENCES**


