Preparation and evaluation of microwave dielectric ceramic thick films by aerosol deposition process

Jianyong LI, Daisuke TSUKIORI, Hirofumi KAKEMOTO, Satoshi WADA and Takaaki TSURUMI

Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552

The objective of this study is to develop microwave dielectric ceramic thick films with a temperature coefficient of the resonant frequency ($T_{cf}$) near to zero. $\text{Ba}_4\text{Sm}_3\text{Ti}_5\text{O}_{15}$ and $\text{TiO}_2$ fine powders are used as main materials to prepare thick films by aerosol deposition (AD) process. In order to evaluate the dielectric properties of thick films in frequency of microwave region, a new measurement procedure based on resonator techniques using a two-port microstrip ring resonator is developed in this study. In this procedure, an electromagnetic field software simulator is used to avoid the complicated calculation that based on experiential formula. The results show the evidences clearly that the $T_{cf}$ can be modulated by changing the molar ratio of raw powders.

©2008 The Ceramic Society of Japan. All rights reserved.

Key-words: Thick film, Aerosol deposition method, Dielectrics, Microwave, Ring resonator

1. Introduction

Microwave dielectric ceramics generally act as passive components such as resonators, waveguides for microwave radiation in most telecommunication systems. Embedded passive technology (EPT) has been developed to fabricate integrated RF modules, in which passive components are built in one printed wiring board (PWB). As conventional fabrication technologies of integrated RF modules, low-temperature cofired ceramics (LTCCs) and polymer composites have been intensively researched. However, LTCCs technology causes diffusion and reaction between different materials or warp of substrate due to different thermal expansion coefficients, and polymer composites generally have not enough dielectric constant values. To overcome these problems, aerosol deposition (AD) process is introduced in this study to fabricate ceramic thick films. These films have modulated thickness from several $\mu$m to tens $\mu$m, have same order of dielectric constants as bulk sample and good microwave transmission properties, are suitable to application in fabrication of integrated RF modules. On the other hand, microwave dielectric ceramics are desirable to have a zero temperature coefficient of frequency ($T_{cf}$) such that the resonator frequency is stable over a broad temperature range. The $T_{cf}$ depends on how the material properties, dimensions, and stresses change with temperature. It is difficult to obtain such a ceramics because almost all materials have a negative or a positive $T_{cf}$ value.

In this study, to obtain ceramic thick film with a near zero $T_{cf}$ value, a mixture powder of two kinds of raw powders with a negative and a positive $T_{cf}$ value, respectively, were used. Ceramic thick films were prepared by changing the volume ratio of these two raw powders. A new measurement procedure based on resonator techniques using a two-port microstrip ring resonator is developed to evaluate the dielectric properties in microwave frequency range. Possibility of preparing ceramic thick film with a near zero $T_{cf}$ value is explored.

2. Experimental procedure

As $\text{Ba}_4\text{Sm}_3\text{Ti}_5\text{O}_{15}$ (BSmT) has high $\varepsilon_r$ of 80, high $Q$ of 10000 and $T_{cf}$ of $-12$ ppm/°C while $\text{TiO}_2$ has a positive $T_{cf}$ value of $+420$ ppm/°C, BSmT fine powders (Hayashi Chemical Industry Co., Ltd.) with particle size of about 2.6 $\mu$m and $\text{TiO}_2$ fine powders (Showa Denko) with particle size of 0.5 $\mu$m were used as main raw materials. To avoid agglutination and size reduction of powders, BSmT and $\text{TiO}_2$ (BSmT:$\text{TiO}_2$ = 50:50 vol%) were dry-mixed in a mortar and then were dried at 200°C for 24 h. Thick films of pure BSmT and thick films of mixture powders were prepared at room temperature using AD process. Table 1 shows the deposition conditions. Figure 1 shows a schematic diagram illustrating of apparatus for AD process. The aerosol was generated by vibrating the aerosol chamber and was accelerated by $\text{O}_2$ carrier gas through the nozzle. These accelerated particles impacted on a flame retardant (FR-4) substrate with the dimension of $10 \times 10$ mm$^2$ in deposition chamber, and then the films were formed and grown. The crystallinity of thick films was investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). A two-port microstrip ring resonator (Fig. 2) was designed and formed on the surface of thick film by photo lithography followed by lift-off method after Au sputtering with thickness of about 0.3 $\mu$m.

<table>
<thead>
<tr>
<th>Table 1. Conditions of the Aerosol Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
</tr>
<tr>
<td>Flow of carrier gas</td>
</tr>
<tr>
<td>Pressure in deposition chamber</td>
</tr>
<tr>
<td>Size of nozzle orifice</td>
</tr>
<tr>
<td>Scanning speed</td>
</tr>
<tr>
<td>Scanning times</td>
</tr>
<tr>
<td>Deposition temperature</td>
</tr>
</tbody>
</table>
The measuring system developed in this study which consists a vector network analyzer (Anritsu, 37397C). The transmission coefficients $S_{21}$ of the ring resonator were measured up to 10 GHz from 30°C to 150°C. In order to examine and certify the validity of this measuring method, Al$_2$O$_3$ single crystal substrate (1120), ($\varepsilon = 9.5$, Shinkosha Co., Ltd.) and BSmT ceramic bulk sample were also measured. Commercial electromagnetic simulation analysis software (Microwave studio, CST) was used to comparing the simulation data with the measured data, dielectric constants and $T_{cf}$ were determined from resonance frequency and the shift of resonance frequency with temperature, respectively.

3. Results and discussion

Figure 3 shows the SEM images of surface of FR-4 substrate before (a) and after be deposited by pure BSmT powders (b), mixture powders (c), respectively. It is clearly that thick films formed and grown on the surface of FR-4 substrate. The thickness of films was determined to about 4–5 $\mu$m from cross sectional SEM observation. Figure 4 shows the XRD profiles of these two kinds of thick film. Comparing with raw powders, both thick films show week crystallinity, this might be explained by the residual stress existed in crystal grains, because the impact of raw particles to substrate occurred within very short time. We also could not consider that the mixture films have the same composition as raw powders, because the concentrations of BSmT and TiO$_2$ in aerosol are different from that of in raw powders due to their different air performances.

The measured transmission coefficients $S_{21}$ of Al$_2$O$_3$ single crystal substrate and BSmT ceramic bulk sample were shown in Fig. 5. Resonance peaks at different frequency were observed from these two samples, this means they have different dielectric constants. In measuring circuit with a ring resonator, parasitic elements are caused by a gap between the microstrip feed line and the ring, and are introduced into circuit resulting in the unloaded behavior of the ring perturb, then the resonator couple to external circuit were caused and the resonance occurs. The resonance condition can be described by the following equation.

$$l = n\lambda_e = \frac{c}{f_{1/2}}$$

where $l$ is perimeter of ring resonator, $\lambda_e$ is the guided wavelength, $n$ is the order of the resonance, $c$ is light velocity, $\varepsilon_{eff}$ is effective dielectric constant which are related to dielectric constant of sample $\varepsilon_r$ following Hammerstad and Bekkadal’s empirical equation. In fact, it is difficult to derive the real dielectric properties of sample from this empirical equation because of insufficient accuracy. A simulation model of ring resonator was designed by electromagnetic simulator and the simulation results were shown in Fig. 5. The simulation results show resonance peaks at the same frequency as that of measured data, and the dielectric constants of Al$_2$O$_3$ and BSmT were determined to 10.2 and 79. The $T_{cf}$ of Al$_2$O$_3$ and BSmT were determined to $-44$ and $-4.8$ ppm/°C from the resonance frequency shift by chang-

---

**Fig. 1.** Schematic diagram illustrating of apparatus for AD process.

**Fig. 2.** Two-port microstrip ring resonator Designed for dielectric properties measurement.

**Fig. 3.** SEM images of surface of FR-4 substrate before (a) and after be deposited by pure BSmT powders (b), mixture powders (c), respectively.
take the A1 site in crystal lattice of Ba6
ppm might be explained by that the Ba6 wea
stress in crystal lattice at Bronze type crystal structure.11
same
interesting that the pure BSmT thick film showed almost the
from other materials reported in previous research. 10
\[ + \text{modulated to positive value successfully by mixing the TiO}_2 \]
\[ \text{The negative values of } \]
\[ \text{preparing ceramic thick film with a near zero } \]
\[ \text{ing temperature in measurement. These results show almost} \]
\[ \text{the same values as literature data and this give proofs to} \]
\[ \text{Figure 6 shows the temperature dependence of resonance} \]
\[ \text{frequency of thick films prepared with pure BSmT and mix-} \]
\[ \text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{films with thickness of about } 4 \mu \text{m} \]
\[ \text{TiO}_2 \text{were used to modulate the dielectric} \]
\[ \text{properties by mixing it with Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{fine powder.} \]
\[ \text{By using a two-port ring resonator and electromagnetic} \]
\[ \text{simulator, the} \]
\[ \text{By using a two-port ring resonator and electromagnetic} \]
\[ \text{References} \]
\[ \text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{films with thickness of about } 4 \mu \text{m} \]
\[ \text{were prepared on flame retardant 4 substrate by aerosol} \]
\[ \text{deposited on FR-4 substrate.} \]
\[ \text{films prepared with pure BSmT and mixture powders.} \]
\[ \text{4. Conclusions} \]
\[ \text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{films with thickness of about } 4 \mu \text{m} \]
\[ \text{were prepared on flame retardant 4 substrate by aerosol} \]
\[ \text{deposited on FR-4 substrate by aerosol deposi-} \]
\[ \text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{film show almost the same} \]
\[ \text{It is interesting that the pure BSmT thick film showed almost} \]
\[ \text{it might be explained by that the } \]
\[ \text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{at } x = 2/3, \text{which have a similar } 2 \times 2 \text{perovskite block as} \]
\[ \text{Ba}_{4.2}\text{Sm}_{9.2}\text{Ti}_{18}\text{O}_{54} \text{show the} \]
\[ \text{JCS-Japan} \]
\[ \text{Li et al.: Preparation and evaluation of microwave dielectric ceramic thick films by aerosol deposition process} \]

---

Fig. 4. XRD profiles of pure BSmT thick films and mixture films deposited on FR-4 substrate.

Fig. 5. Transmission coefficients S21 of Al2O3 single crystal sub-
strate (a) and BSmT ceramic bulk sample (b).

Fig. 6. Temperature dependence of resonance frequency of thick films prepared with pure BSmT and mixture powders.