Electrical Properties of $BaTiO_3$ System Thick Films Prepared by Screen-Printing Method

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Abstract

$(Ba,Sr,Ca)TiO_3$ powders, prepared by the sol-gel method, were mixed with an organic vehicle and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. The grain size decreased with increasing amounts of MnO_2, and the BSCT(50/40/10) thick film doped with 1wt% MnO_2 showed a value of 6.5mm. The thickness of thick films by four-cycle on printing/drying was approximately 100mm. The relative dielectric constant, dielectric loss and tunability of the BSCT(50/40/10) thick films doped with 1.0wt% MnO_2 were 1296, 0.61% and 11.18%, respectively.

Key Words : $BaTiO_3$ ceramics, Screen-Printing method, Thick films, Electrical properties

1. Introduction

The microwave phase shifter is an essential element in many different communication and radar systems. For example, each radiating element of a phased array antenna must have an independent phase shifter in order to electronically steer the radiated beam. Tuning of the microwave devices can be achieved by both electric and magnetic fields [1,2]. The former employs the dielectric nonlinearity of ferroelectrics, and the latter depends on the nonlinear magnetization of ferrites. The ferrite phase shifters require dc current and an induction coil to vary the phase shift and are relatively expensive and complex. However, ferroelectric phase shifters can offer much better performance, for example a high power handling capacity, low drive power and low costs compared with ferrite phase shifters, since the dc biasing is relatively easy to implement and the power consumption is very low. Several ferroelectric materials have been proposed for such applications. However, due to the high inherent material loss and high dielectric constant of $BaTiO_3$ bulk ceramics have been restricted in their application in phased array antennas. On the other hand, thin or thick films of high dielectric constant ferroelectrics in combination with multilayered dielectric substrates are drawing interest for planar integrated microwave circuits. Several publications have reported on thin film ferroelectric phase shifters in microstrip [3] and coplanar waveguide technology [4]. The thick film technology using the screen printing method is most suitable for the preparation of films of about 10~100mm thickness [5].

In this paper, MnO_2-doped $(Ba,Sr,Ca)TiO_3$ powders, prepared by the sol-gel method, were mixed with an organic vehicle and BSCT thick films were fabricated by the screen printing method on alumina substrates. For perovskite structure, doping with small amounts of acceptor dopants can greatly affect the dielectric properties, and the Mn ion can act as an acceptor dopant. Its electrical properties were investigated for microwave device applications.

2. Experimental

The chemical compositions of the specimens are given by the formula $(Ba_{0.6-x}Sr_{0.4}Ca_x)TiO_3$ (BSCT) + ywt% MnO_2 (x=0.10, 0.15, 0.20, y=0~3.0). BSCT powders, started with a mixture of Ba acetate, Sr acetate, Ca acetate and Ti isopropoxide, were prepared by the sol-gel method. Acetic acid and 2-methoxyethanol were used as solvents. Ba, Sr and Ca acetate were dissolved in acetic acid, and then the solution was heated to evaporate the water. After cooling, Ti isopropoxide, dissolved in 2-methoxyethanol, was added to the solution. The mixed solution was refluxed, and then 2-methoxyethanol and water were added to the solution for stabilization and hydrolysis, respectively. The obtained precusor solutions were dried and then calcined at 900℃ for 2h. MnO_2 and the calcined powders were mixed and ground for 24h.

The screen-printable pastes were prepared by kneading the ground BSCT powder with an organic vehicle (Ferro. B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro.). High purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing Pt paste. After screen printing the BSCT paste, printed films were dried. These processes of printing and drying were repeated four times to obtain the desired thickness. The thick films were sintered at 1420℃ for 2h in a closed alumina crucible. The upper electrodes were fabricated by screen printing the Ag paste.

Scanning electron microscopy was used in order to analyze the microstructure of the specimen. The dielectric properties were measured using an impedance analyzer (HP 4294). The tunability was determined using the following equation: tunability = $\{K(0)-K(V_{appl.})\} / K(0)$, where $K(0)$ is the relative dielectric constant without dc bias and $K(V_{appl.})$ is the relative dielectric constant with V_{appl}. The tunability measurements were taken as a function of the applied electric field, which ranged from 0 to 30 kV/cm.

3. Results and discussion

Figure 1 shows the surface and cross-sectional SEM micrographs of the BSCT(40/40/20) thick films for various MnO_2 contents. The BSCT(40/40/20) thick films doped with 1wt% MnO_2 exhibited a dense and uniform grain structure and the average grain size was about 6.5mm. The grain size decreased with

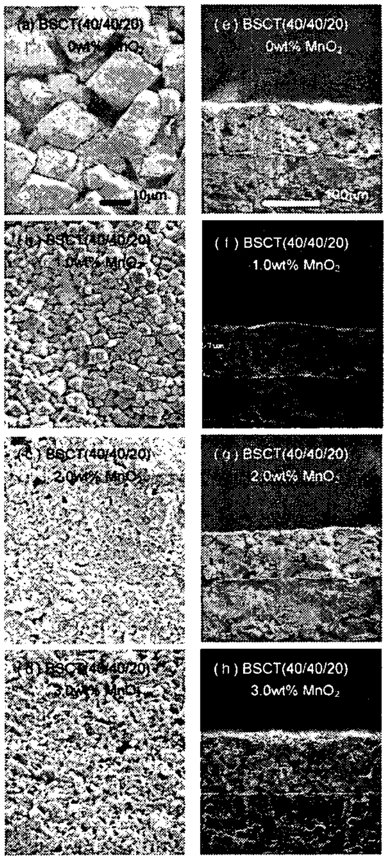

Fig. 1. Surface and cross-sectional SEM micrographs of the BSCT(40/40/20) thick films for various MnO_2 contents.

increasing MnO_2 amounts because a large portion of the doping Mn ions precipitate out of the normal grains and stay at the grain boundaries which subsequently restricts the grain growth. The thickness of all the specimens was approximately 100mm.

Figure 2 shows the variation of relative dielectric constant of BSCT thick films as a function of temperature for various MnO_2 contents at 1MHz. The Curie temperature of

BSCT specimens decreased with the decreasing Ba/(Sr+Ca) ratio. For substitution Sr^{2+}-Ba^{2+}, the bonding force between the A-site ion and the oxygen ion of ABO_3 perovskite structure become

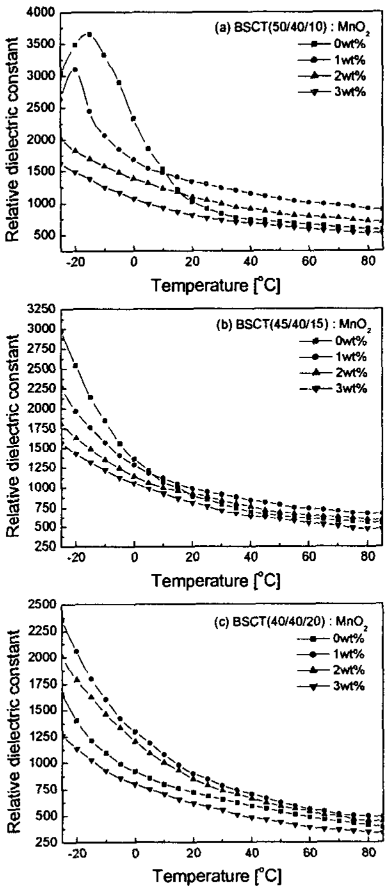

Fig. 2. Relative dielectric constant as a function of temperature for BSCT thick films with various MnO_2 contents.

stronger because the radius of the Ba^{2+} ion is larger than that of the Sr^{2+} ion (0.113nm): the bonding force Ti-O(Sr), therefore, becomes weaker than the Ti-O(Ba) bond. The weakening of the Ti-O bond leads to a weaker distortion of the octahedron and brings about a decrease in the c/a ratio, thus inducing a drop in the Curie temperature [6].

Figure 3 shows the applied dc field dependence of the relative dielectric constant for BSCT thick films at 1MHz. The relative dielectric constant of all specimens decreased with increases in the applied dc field. This is because the applied electric fields suppress the displacement of ions

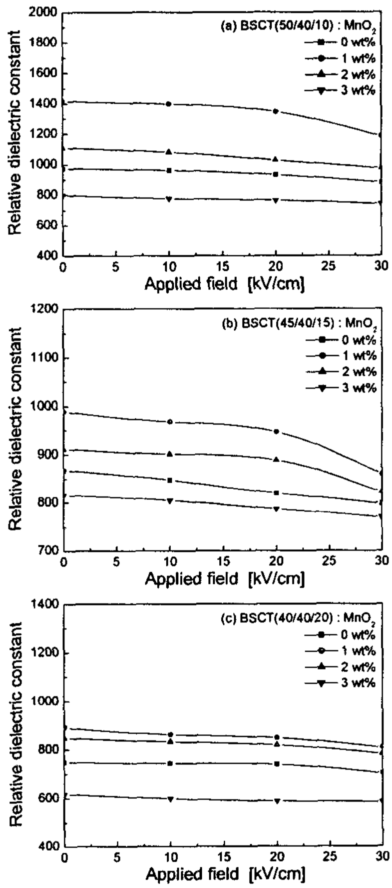

Fig. 3. Relative dielectric constant as a function of the DC electric field for BSCT thick films with various MnO_2 contents.

inside the grains of the paraelectric phase. Also, the non-linear dependence of the dielectric constant on the applied dc electric field results from the chemical inhomogeneities and/or the strain between the grains and grain boundaries in polycrystalline specimens.

Figure 4 shows the tunability of BSCT thick films as a function of MnO_2 content at 1MHz. The tunability of the BSCT thick films increased with decreasing Ca content because the Curie temperature, as shown in Fig. 2, decreased with increasing Ca contents. The displacement of ions was strongly influenced by the external fields at around the Curie temperature. The BSCT(50/40/10) thick film doped with 1.0wt% MnO_2 showed the highest tunability of 11.18%.

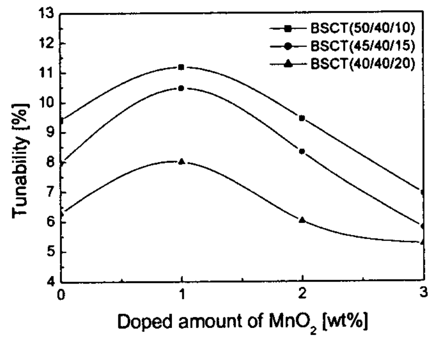

Fig. 4. Tunability of BSCT thick films with various MnO_2 content at 1MHz.

4. Conclusions

$(Ba,Sr,Ca)TiO_3$ powders doped with MnO_2 were prepared by the sol-gel method and BSCT thick films were fabricated by the screen printing technique on alumina substrates. The structural and the electrical properties were investigated for their various composition ratios and MnO_2 doping contents. The Curie temperature of BSCT specimens decreased with decreasing Ba/(Sr+Ca) ratios. The relative dielectric constant and Curie temperature of BSCT thick films decreased with increasing MnO_2 amount. The relative dielectric constant decreases with increases in the applied dc field because the applied electric fields act on the non-ferroelectric grains in such a way as to induce a ferroelectric state in those grains. The tunability of the BSCT specimens was affected by the phase transition temperature and microstructures such as grain size.

Acknowledgements

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