

The Dielectric Properties of BaTiO₃/SrTiO₃ Heterolayered Thick films by Screen Printing Method

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The BaTiO₃/SrTiO₃ heterolayered thick films were fabricated by the screen printing method on alumina substrates. The effect of the sintering temperature on the microstructure and dielectric properties of the BaTiO₃/SrTiO₃ thick films has been investigated. The relative dielectric constant and dielectric loss at 1 MHz of the BaTiO₃/SrTiO₃ heterolayered thick films with sintering temperature of 1350 °C were about 751 and 1.74, respectively. The remanent polarization (P_r) of the pure (Ba_{0.5}Sr_{0.5})TiO₃ and BaTiO₃/SrTiO₃ heterolayered films are approximately 5.1 $\mu\text{C}/\text{cm}^2$ and 10 $\mu\text{C}/\text{cm}^2$. This study suggests that the design of the BaTiO₃/SrTiO₃ heterolayered thick films capacitor with different phase should be an effective method to enhance the dielectric and ferroelectric performance in devices.

Keywords : BaTiO₃/SrTiO₃, Heterolayer, Thick films, Dielectric constant

1. INTRODUCTION

Recently, perovskite-type barium strontium titanate [pure (Ba,Sr)TiO₃ and doped variations] have gained attention for their excellent dielectric properties. They are used to make electronics materials for piezoelectric and capacitor ceramics, especially in multilayered chip ceramic capacitor (MLCC). For commercial applications, BST (Barium strontium titanate) thick films on low-cost substrates are the preferred choice because these can overcome the problems of the large dielectric loss observed in thin films and high voltages required to bias bulk substrates[1-3].

These devices have been used to make thick films such as screen printing, tape casting and modified sol-gel spin coating. When we used in these methods, the sol-gel method must possess the following characteristics: low calcinations temperature, easy doping, productivity, and the very fine and homogeneous powder[4]. So we adopted these characteristics to prepare BaTiO₃ and

SrTiO₃ powders. Also, some of the advantages of going through screen printing method are low cost, high reliability, heat dissipation, wide range of component values, and the ability to produce multilayers which significantly increase circuit density[5-7].

In this study, BaTiO₃/SrTiO₃ heterolayered thick films were deposited on the alumina substrate alternately using BaTiO₃ and SrTiO₃ paste by means of the screen printing method. The purpose of this study is to investigate the role of the lower BaTiO₃ thick films in crystallization of the upper SrTiO₃ thick film during the sintering and the interface structure between the BaTiO₃/SrTiO₃ heterolayered thick films on electrical properties.

2. EXPERIMENTAL

Pure BaTiO₃ and SrTiO₃ powders were prepared using a sol-gel method from Ba-acetate [Ba(CH₃COO)₂], Sr-

acetate hemihydrate [Sr(CH₃COO)₂·0.5H₂O], Ti-isopropoxide [Ti(OCH(CH₃)₂)₄] as the starting materials: acetic acid (CH₃COOH) and 2-methoxyethanol (CH₃OCH₂CH₂OH) were used as solvents. Ba and Sr acetate were dissolved in acetic acid and then the solution was heated to evaporate water. After cooling, Ti isopropoxide dissolved in 2-methoxyethanol was added to the solution. Ti[OCH(CH₃)₂]₄ The mixed solution was refluxed and then 2-methoxyethanol and water were added to the solution for stabilization and hydrolysis, respectively. The BaTiO₃ and SrTiO₃ powder precursors were dried and then calcined for 2 h. at 900 °C and 1100 °C, respectively. These powders were used to make the respective slurries for processing thick films. The screen-printable pastes were prepared by kneading the ground BaTiO₃ and SrTiO₃ powder with 30 wt% of organic vehicle (Ferro. B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro.). High purity (99.9 %) alumina was used as a substrate. The calcined powders were characterized using XRD (X-ray Diffraction) and the particle size was analyzed using SEM (Scanning Electron Microscopy). The bottom electrodes were prepared by screen printing Pt paste and fired it at 1400 °C for 10 min. After screen printing the BaTiO₃ and SrTiO₃ paste using a 325 mesh screen mask, printed films were allowed to level for 10 min. and then dried at 100 °C for 10 min. The processes from printing to drying were repeated four times to obtain a desired thickness. The thick films were sintered at 1300~1375 °C for 2 h. in a closed alumina to crucible, with an intermediate 2 h. isothermal at 600 °C to remove any organic components.

The upper electrodes were fabricated by screen printing the Ag paste and then fired at 590 °C for 10 min. The calcined particle size analysis after mechanical activation has shown that the obtained particles were less than 0.2 μm. After calcination, milling and sieving the particle size ranged from 0.2 to 0.5 μm. The rather strong agglomerates were destroyed by multi-step ultrasonic treatment. The thicknesses of the films were measured from a cross-sectional analysis of the samples using scanning electron microscope (SEM). The micro-structure and chemical composition were analyzed using SEM coupled with an energy dispersive spectrometer (EDX).

The dielectric constant and dielectric loss were measured by using an impedance/gain phase analyzer (HP4192A). Ferroelectric properties of the BaTiO₃/SrTiO₃ heterolayered thick films were measured by a RT66A tester (Radiant Technologies).

3. RESULTS AND DISCUSSION

The XRD pattern of the BaTiO₃/SrTiO₃ heterolayered thick films sintered at different temperatures are shown in Fig. 1.

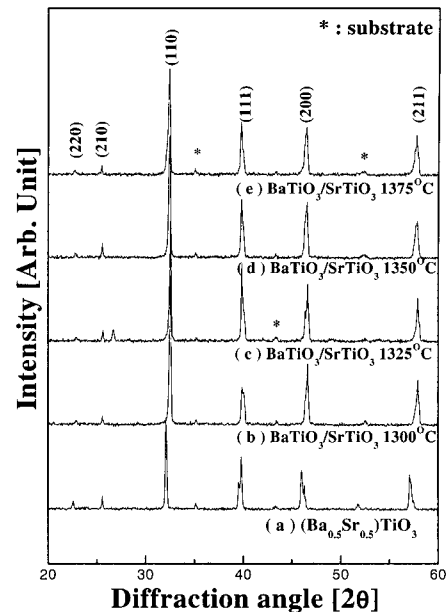


Fig. 1. XRD patterns of pure BaTiO₃, SrTiO₃, (Ba_{0.5}Sr_{0.5})TiO₃, and BaTiO₃/SrTiO₃ heterolayered thick film.

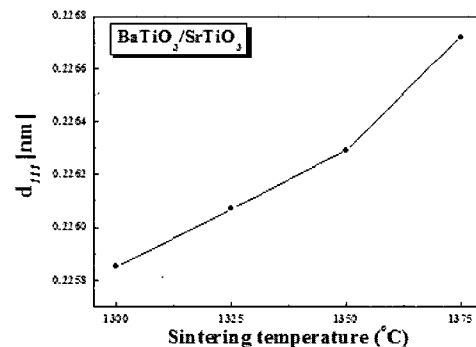


Fig. 2. The change of spacing of BaTiO₃/SrTiO₃(111) plane (d_{111}) sintered at different temperature.

The BaTiO₃/SrTiO₃ heterolayered thick film shows typical XRD patterns with a polycrystalline perovskite structure. At higher temperature, the phase structure is the tetragonal perovskite phase of (Ba,Sr)TiO₃. No secondary phase is detected by XRD and the broadening of diffraction peak is obvious at a lower temperature. As compared with (Ba_{0.5}Sr_{0.5})TiO₃ thick films, the diffraction peaks of BaTiO₃/SrTiO₃ heterolayered thick film shifted slightly to the higher diffraction angle and the peak became sharper, as shown in Fig. 1. In addition, as the sintering temperature increased to 1375 °C the diffraction peaks shifted slightly to the higher diffraction angles and the peak became sharper.

The variation of the spacing of (111) (d_{111} value) of the

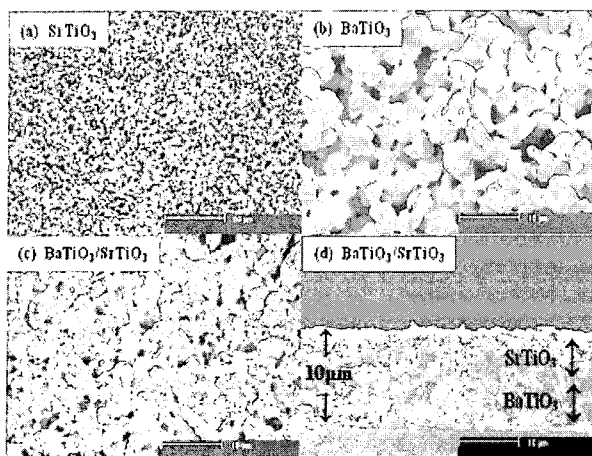


Fig. 3. SEM micrographs of thick films: surface morphologies of (a) SrTiO₃, (b) BaTiO₃, and (c) SrTiO₃/BaTiO₃ heterolayered thick film and cross section of (d) SrTiO₃/BaTiO₃ heterolayered thick film.

BaTiO₃/SrTiO₃ heterolayered thick films sintered at different temperature is shown in Fig. 2. The d_{111} value determined from the diffraction angle of the (111) peak increase from 0.2258 to 0.2267 nm with increasing of the sintering temperature. d_{111} value of the heterolayered thick films sintered at 1350 °C is similar to d_{111} value (0.2262) of (Ba_{0.5}Sr_{0.5})TiO₃ thick film[8].

Figure 3 shows the surface and cross-sectional SEM micrographs of the BaTiO₃/SrTiO₃ heterolayered thick films sintered at 1350 °C. A mixture of various grain sizes was evident for the BaTiO₃/SrTiO₃ heterolayered thick films sintered at 1350 °C, which showed very large grains coexist with very small ones. It could be seen that sintering temperature was also effective for increasing the grain size and improving the microstructure homogeneity. All thick films showed large size pores due to the evaporation of the organic components. The adhesion between Pt and the BaTiO₃ layer is good, as shown in Fig. 3(d). Also, this figure shows the clear interface between the BaTiO₃ and SrTiO₃ layers. The average thickness of the BaTiO₃/SrTiO₃ heterolayered thick film sintered at 1350 °C was approximately 10 μm.

Figure 4 shows the dielectric constant and the dielectric loss of pure BaTiO₃, SrTiO₃, (Ba_{0.5}Sr_{0.5})TiO₃ thick film and BaTiO₃/SrTiO₃ heterolayered thick film as a function of frequencies ranging from 1 kHz to 1 MHz.

The dielectric constant was decreased with increasing the applied frequency and the BaTiO₃/SrTiO₃ heterolayered thick films showed the typical dielectric dispersion properties. The dielectric constant of pure (Ba_{0.5}Sr_{0.5})TiO₃ and BaTiO₃/SrTiO₃ heterolayered thick films were measured as 698 and 751, respectively, at an applied frequency 1 kHz. The enhanced dielectric constant of the heterolayered thick films can be explained

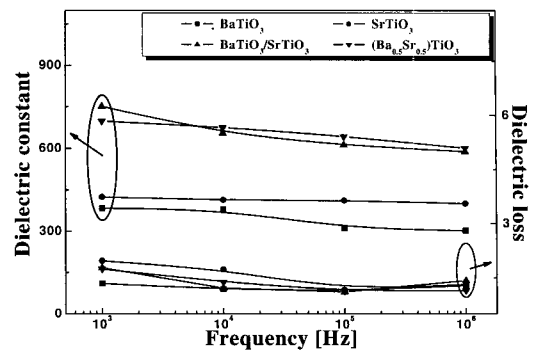


Fig. 4. Dielectric constant and dielectric loss of BaTiO₃/SrTiO₃ heterolayered thick films as a function of frequency.

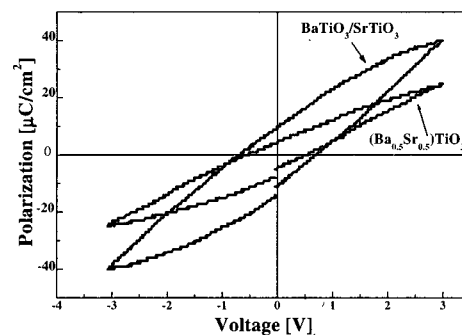


Fig. 5. Hysteresis loops of the (Ba_{0.5}Ti_{0.5})TiO₃ and BaTiO₃/SrTiO₃ heterolayered thick films.

by a series connection of individual components. We considered that there was a coexistence of the modified (Ba,Sr)TiO₃ phase at the interface between BaTiO₃ and SrTiO₃[9]. The dielectric loss of the pure (Ba_{0.5}Sr_{0.5})TiO₃ and BaTiO₃/SrTiO₃ hetero-layered thick films are 1.34 and 1.74, respectively at 1 kHz. The BaTiO₃/SrTiO₃ heterolayered thick film exhibited higher dielectric loss than that of the pure (Ba_{0.5}Sr_{0.5})TiO₃ thick film. The dielectric loss increased due to imperfect crystallization at interface.

Figure 5 shows polarization versus electric field (P - E) hysteresis loops of the (Ba_{0.5}Sr_{0.5})TiO₃ films and BaTiO₃/SrTiO₃ heterolayered thick films. When saturated, the remanent polarization (P_r) of the pure (Ba_{0.5}Sr_{0.5})TiO₃ and BaTiO₃/SrTiO₃ heterolayered films were approximately 5.1 μC/cm² and 10 μC/cm², respectively. The increased remanent polarization may be a result of understood to the existence of the interfaces between the BaTiO₃ and SrTiO₃. Other reasons could be the interdiffusion of the two phases near interfaces. These results confirmed that diffraction peaks with polycrystalline perovskite were increased in the XRD analysis.

4. CONCLUSION

In this paper, the BaTiO₃/SrTiO₃ heterolayered thick films were fabricated by a screen printing method on alumina substrates. The average thickness of all thick film was about 20 μm. The dielectric properties such as dielectric constant and remnant polarization of the BaTiO₃/SrTiO₃ heterolayered thick films were superior to those of single composition SrTiO₃, BaTiO₃ and (Ba_{0.5}Sr_{0.5})TiO₃ thick films, values for the BaTiO₃/SrTiO₃ heterolayered thick films were 751 and 10 μC/cm², respectively.

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