Tunable Properties of Ferroelectric Thick Films With MgO Added on (BaSr)TiO_3

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Jun-Ki Chung and Won-Jeong Kim****

Abstract – MgO enhanced $(Ba_{0.6}Sr_{0.4})$ TiO_3 thick films have been fabricated by a tape casting and firing method for tunable devices on the microwave frequency band. In order to improve ferroelectric properties, the composite thick films enhanced with MgO on BST have been asymmetrically annealed by a focused halogen beam method. Dielectric constants of composite thick films are changed from 1050 to 1300 at 100 kHz after 60 s and 150 s annealing by the focused halogen beam. Even though no prominent changes were previously observed from the thick films before and after annealing in terms of chemical composition and surface morphology, it is clear that the average particle size of the thick films calculated by Scherrer's formula were increased by annealing. Furthermore, a strong correlation between particle size and dielectric constant of the composite thick films has been observed; dielectric constant increases with increased particle size. This has been attributed to the increased volume of ferroelectric domain due to increased particle sizes. As a result, the tuning range was improved by halogen beam annealing.

Keywords: BST, $(Ba_{0.6}Sr_{0.4})TiO_3$, Composite, Ferroelectrics, MgO, Microwave device, Thick films, Tuning range, Unable properties

1. Introduction

Ferroelectrics, which exhibit an electric field dependent dielectric constant, have recently been of interest for possible applications on electrically controllable devices. Especially, the dielectric constant of ferroelectrics could be adjusted in a few microseconds in response to an externally applied electric field, which would make it possible to use ferroelectrics in microwave tunable devices [1-8]. However, the dielectric constant of bulk ferroelectrics is too large to be used in microwave devices because it is difficult to design a matching circuit on the bulk ferroelectrics. Therefore, most of the investigation has been focused on thin ferroelectric films because the effective dielectric constant of ferroelectric thin film can be reduced by adjusting the film thickness. However, thin film is not cost effective and its properties are too sensitive on the growth condition to produce reliable films.

Since composite thick film technology has been widely used to fabricate cost effective and reliable microwave components and tunable devices [9-10], the alternative solution to bulk or thin film ferroelectrics could be BST thick film. Incorporation of ferroelectrics with other dielectric and conductive materials will enhance the possibilities of ferroelectric applications, enabling integration of components, such as phase shifters, variable reactors, tunable filters, tunable resonator, etc. BST thick ferroelectric film may have a few drawbacks, such as high dielectric constant. The reported dielectric constants of $(Ba_{0.6}Sr_{0.4})$ TiO_3 thick films range from 5700 to 7000 depending on the annealing conditions [11, 12]. Therefore, it is necessary to reduce the dielectric constant of ferroelectric thick films to be used in microwave devices. In order to reduce the dielectric constant of ferroelectric BST thick films, 20 wt% of MgO (magnesium oxide) has been added in the BST thick films.

In this paper, fabrication of a ferroelectric BST and dielectric MgO composite thick film has been demonstrated by a tape-casting and firing method. Furthermore, enhancement of tunable dielectric properties of composite thick films enhanced with 20 wt% of MgO on BST has been demonstrated by a focused halogen beam annealing method, which may be useful for mass production of ferroelectric tunable devices and high performance tunability at low cost.

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2. Measurement and fabrication of BST thick films enhanced with MgO

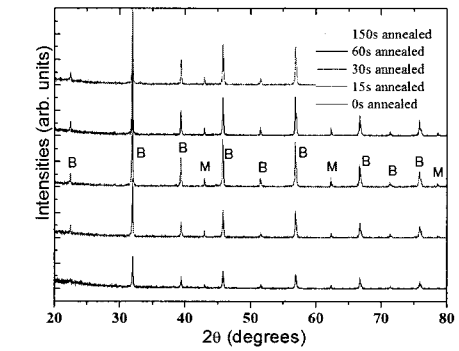
A stoichiometric ceramic BST ($(Ba_{0.6}Sr_{0.4})TiO_3$) powder was sintered by a solid state reaction using ball-milled $BaTiO_3$ and $SrTiO_3$ powders. The BST powder was mixed with 20 wt% of MgO by a ball-milling method for 24 h with a solvent (MEK 60: ethanol 40) and a dispersant. The mixture was ball-milled again for 24 h with a PVB binder and a plasticizer to make slurry for tape cast. Green sheets were made by passing the slurry below a doctor blade followed by drying. Organic materials in the dried green sheets were burned out at 250°C for 24 h. Then, the green sheets were sintered at 1350°C for 2 h. The thickness of the final composite thick films was measured to be approximately 100 μm.

In order to change dielectric properties, one side of as-casted BST composite thick film was annealed by a focused beam radiated from a halogen lamp. The width of the focused beam was about 1 mm, and the sample annealing time was calculated from the sample moving speed. The estimated annealing time, which corresponds to the duration of sample in the focused beam of 1 mm while moving, is 0, 15, 30, 60, and 150 s. The measured temperature in the focused beam is approximately 700°C. By the focused beam annealing, one side of the composite films was heated quickly, while the other side was heated slowly. This would produce a temperature gradient between the top and bottom sides of the thick film. The structure of the BST composite thick film was investigated by an x-ray diffractometer. The surface morphologies of the films were studied by a scanning electron microscope equipped with an energy dispersive spectroscopy for chemical analysis.

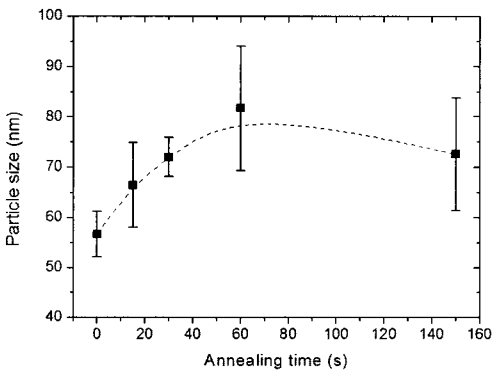
For electrical property measurement of the BST composite thick films, platinum electrodes were deposited on the thick films by RF sputtering using a shadow mask. Capacitance of MOM (metal-oxide-metal) and tuning range of IDC (inter digital capacitor) were measured by an impedance analyzer (HP 4194A) and an electrometer with applying DC bias -40 V to +40 V. Dielectric constants of the BST composite thick films were converted from the dimension of the dielectric layer.

3. Results and discussion

The BST composite thick films before and after annealing were investigated by XRD as shown in Figure 1 (a). The reflected peaks were indexed as those from a cubic perovskite BST and a cubic MgO. Any appreciable peak shift was not observed from either BST or MgO, which suggest that their mutual solubility is negligible. The particle or grain size has been calculated by Scherrer's formula using the full width at half maximum (FWHM) of BST (211) reflection (2θ 57°). The calculated particle size is shown in Fig. 1 (b). Although there is a contribution on peak broadening from the x-ray instrument, FWHM of (211) changes systematically and the particle size increases with increased annealing time. This may suggest that the coherent length scale, corresponding to the particle size, was increased after annealing.



(a)



(b)

Fig. 1. (a) X-ray diffraction patterns, and (b) particle sizes of the BST thick films with added MgO

The surface morphologies of the composite thick films were investigated by SEM. Since only one side of the films were directly exposed on the focused beam, morphology and chemical composition difference between top (exposed on the beam) and bottom (indirectly exposed on the beam) were expected. However, any noticeable differences between top and bottom sides have not been observed as shown in Fig. 2. Since the composite thick films were fabricated from the ball milled powders, the surfaces of the thick films are rough. In Fig. 2, bright particles are corresponding to BST, and the dark ones are corresponding to MgO. Metal ratio of the samples measured by EDS is close to the nominal composition within 5 wt%.

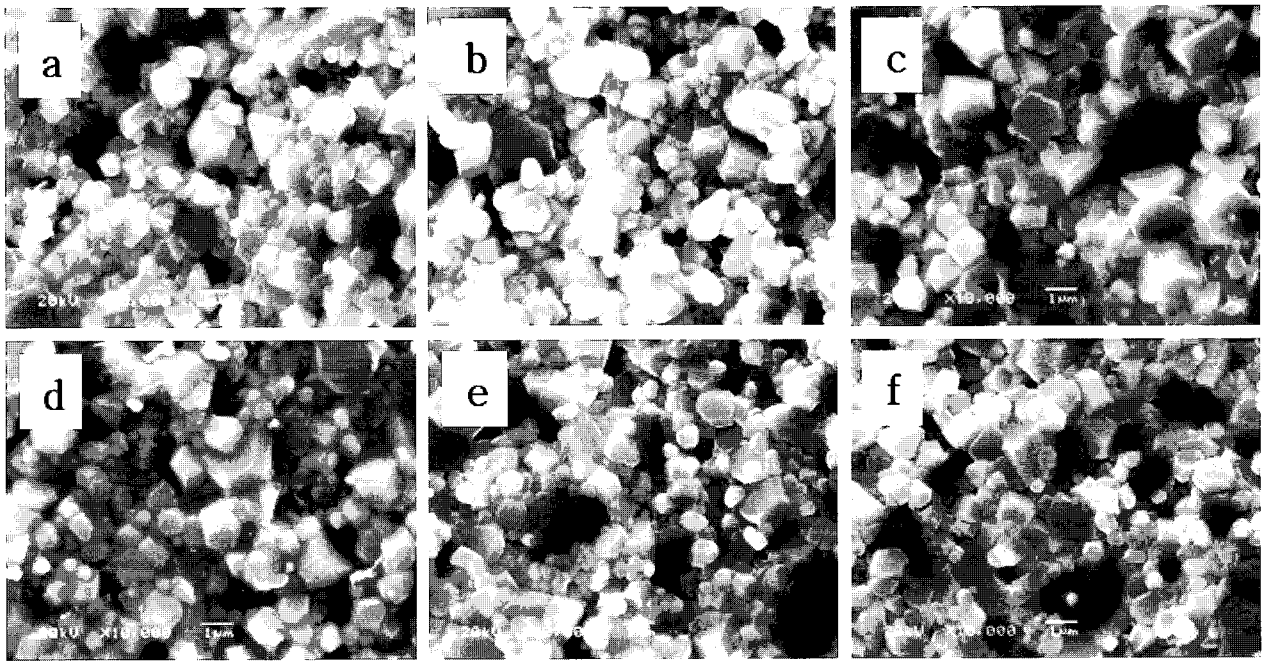


Fig. 2. Surface morphologies of the BST thick films with added MgO. Directly exposed on the focused beam for (a) 0 s, (b) 30 s, and (c) 150 s. Indirectly exposed on the focused beam for (a) 0 s, (b) 30 s, and (c) 150 s.

The particle sizes appearing on the SEM micrograph are much larger than those calculated by Scherrer's formula. This discrepancy may come from the fact that the particle size has been overestimated by SEM, while it has been underestimated by XRD. It is possible that the particle appearing on the SEM micrograph is actually consisted of many small coherent regions.

The real coherent region may be larger than the particle size calculated by Scherrer's formula, because the FWHM used for calculation contains instrumental broadening. To measure the electrical properties of the thick films, a platinum top and bottom electrode have been fabricated on the thick films. Fig. 3 (a) exhibits the frequency dependent dielectric constant of the thick films, and Fig. 3 (b) exhibits the bias electric field dependent dielectric constant measured at 100 kHz. Generally, dielectric constant decreases with increasing frequencies. Furthermore, dielectric constant increases with increasing annealing time.

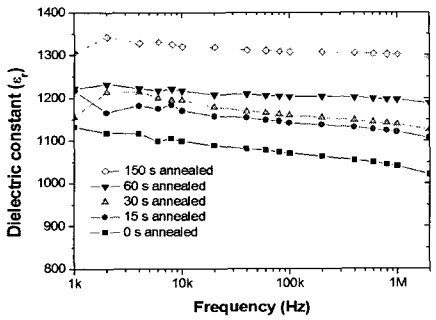
At 100 kHz, dielectric constant 1050, of as-cast thickness increases to 1300 after 150 s of annealing by focused beam annealing. Since the bias voltage of 40 V across the film thickness of 100 μm is low, dielectric constant change with electric field characteristics of ferroelectrics was not observed. However, a slight fluctuation in dielectric constant around 2 kV/cm was observed, hinting at the ferroelectricity of the films.

This indicates that the dielectric constant of the BST thick films with added MgO is close to 1000, which is desirable for microwave devices. If the dielectric constant is about 5000 reported from the thick BST films, it is too high to make co-planar type microwave devices. In this study, it has been clearly demonstrated whether dielectric constant of the thick film can be controlled or not.

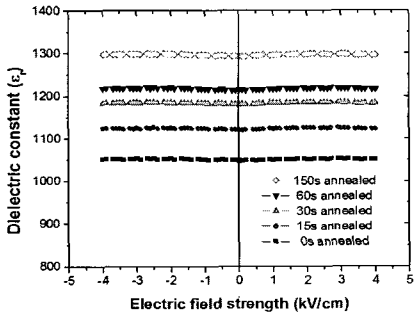
Furthermore, it has been demonstrated that the dielectric constant of the BST thick films with added MgO could be altered by a focused beam annealing, though the annealing temperature (700oC) is much lower than that of sintering (1350oC).

An interesting relation between the measured dielectric constant and the calculated particle size has been observed from the annealed BST thick films with added MgO as shown in Fig. 4; the measured dielectric constant of the thick films increases with the increased particle size calculated from the FWHM of the (211) reflection of BST. This may suggest that the volume fraction of the ferroelectric domain was increased in the larger particle. Further investigation of the particle size argument should be pursued by TEM [3, 9].

Tuning rage 9.5 ~ 10.5 was shown in the case of symmetrical annealing, but it was increased to 12.5~ 14% in the case of asymmetrical annealing for 60 seconds. The ferroelectric properties were distinct when adding MgO to BST thick film, and paraelectric patterns were distinct when annealed for 60 sec. Also, dielectric tuning range of the BST thick films with added MgO show a similar pattern with respect to asysmetric annealing. The change in the tuning range with the BST thick films with added MgO can be understood by the change in the phase substitution with MgO and asymmetry annealing [12, 13].



(a)



(b)

Fig. 3. (a) Frequency dependent dielectric constant, and (b) electric field dependent dielectric constant of the BST thick films with added MgO

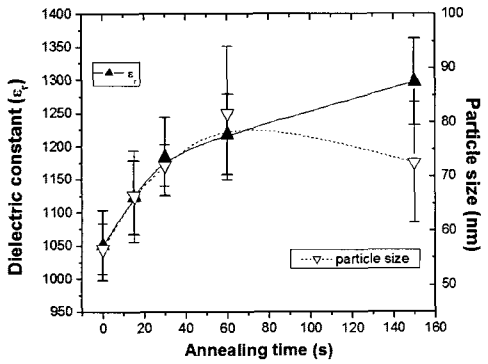


Fig. 4. A strong correlation between dielectric constant and calculated particle sizes of the annealed BST thick films with added MgO

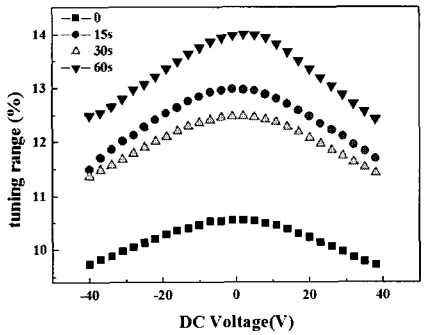


Fig. 5. DC bias voltage dependent tuning range capacitance of the BST thick films with added MgO

4. Conclusions

MgO has been added in ferroelectric $(Ba_{0.6}Sr_{0.4})TiO_3$ to fabricate thick film useful for microwave devices. Composite BST:MgO thick film has been successfully fabricated by a tape casting and firing method. In order to improve ferroelectric properties, the BST thick films with added MgO have been asymmetrically annealed by a focused halogen beam method. Dielectric constants of BST thick films with added MgO are changed from 1050 to 1300 at 100 kHz after 150 s annealing by the focused beam. A strong correlation between the particle size calculated by Scherrer's formula and the measured dielectric constant of the BST thick films with added MgO has been observed; dielectric constant increases with increased particle size. Tunability was dependable on the asymmetrical annealing time and additional MgO.

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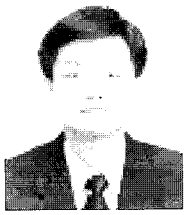

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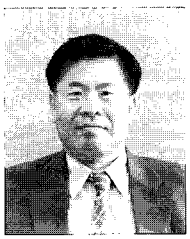

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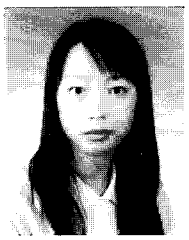

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