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Dielectric properties of barium strontium titanate (BST)/yttrium aluminate ($YAlO_3$) thick films under DC bias field

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Abstract The DC bias dependence of the dielectric properties of BST thick films on $YAlO_3$ substrates has been investigated for possible tunable microwave device applications. Rare earth aluminate (e.g. $YAlO_3$) substrates were used to overcome the interfacial interactions between BST thick films and alumina substrates during high temperature sintering. The results show that the BST films exhibit good chemical compatibility with $YAlO_3$ substrates at sintering temperatures up to 1,500 °C. Improved density and enhanced grain growth in the films have been obtained compared to BST films on alumina substrates sintered at lower temperatures (<1,250 °C). Consequently, the permittivity and tunability are increased significantly. The low frequency losses in the ferroelectric region are also increased due to the contribution of domain wall motion. However, compared to their bulk ceramic counterparts, the films still exhibit a relaxor-like behaviour and DC bias hysteresis in both ferroelectric and paraelectric regions, which indicates some extent of microstructural heterogeneity and existence of micro-/nano- polar phases within the films. Possible reasons are discussed in terms of the substrate constraint induced stress effect in the films during high temperature sintering due to the thermal expansion coefficient mismatch between the BST films and $YAlO_3$ substrates.

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Introduction

Barium strontium titanate (BST) thick films have been investigated as potential candidates for tunable microwave applications because of the benefits of lower fabrication costs compared to their thin film forms and relatively smaller DC bias voltages to achieve large tunability as required by their bulk ceramic analogues [1–3]. Alumina is a commonly used substrate in microwave devices because of its low permittivity (ca. 10 at 10 GHz) and low cost. However, our early studies showed that BST films are very reactive with alumina substrates at sintering temperatures above 1,300 °C [4]. Though BST thick films sintered at lower temperatures possess reasonably good tunability [5], fine line electrode patterning is very difficult and leakage often occurs under high DC bias field due to the porous nature of the films, which hinder the device applications.

Rare earth aluminates have been reported to possess good microwave properties [6]. They generally have low dielectric constant and high Q at microwave frequencies, e.g. $\varepsilon_r = 15.7$ and $Q = 6800$ at 10 GHz for $YAlO_3$, and therefore potentially could be used for substrates of BST films. In this article, the high temperature compatibility of BST films with rare earth aluminates and the microstructure and dielectric properties of the BST films on yttrium aluminate substrates are reported.

Experimental

Two BST powders with the composition of Ba/Sr = 50/50 and 70/30 were employed. Previous study showed that the

Curie point for BST ceramics with composition of 70:30 and 50:50 was ca. 30 and −30 °C, respectively [5] For room temperature applications, it is interesting to investigate the tunability of the BST films at both ferroelectric (FE) and paraelectric (PE) regions since the dielectric tuning mechanisms were rather different at these two regions. The powders were prepared using a conventional solid-state reaction route from barium carbonate, strontium carbonate and titania. Rare earth aluminate ($YAlO_3$) substrates were fabricated using a conventional solid state reaction method and sintered at 1,650 °C for 8 h. Screen printing technique has been used to fabricate BST thick films on $YAlO_3$ substrates. For comparison, BST films on 99.6% alumina (CoorsTek) substrate have also been fabricated. The sintering temperatures were varied from 1,200 to 1,300 °C for the alumina substrates and from 1,400 to 1,500°C for yttrium aluminate substrates with a holding time of 1 h. Pt and Ag coatings have been used as bottom and top electrode materials respectively.

Dilatometry (Netszch 402E) was used to monitor the thermal expansion behaviour of the BST and $YAlO_3$ during heating up and cooling down stages. X-ray diffraction (Philips X'pert) and scanning electron microscopy (JEOL 5410) have been used to characterise the phases and microstructures of the films. Dielectric properties at frequencies <1 MHz have been characterised using an impedance analyser (HP 4194 A) in an environment chamber at temperatures from 70 to −70 °C. Tunability of the films was measured at 10 kHz using an internal DC bias voltage from 0, 10, 20, 30 to 40 V and calculated as following: Tunability $= (\varepsilon_0 - \varepsilon_v)/\varepsilon_0 \times 100\%$, where ε_v and ε_0 are permittivity with and without DC bias, respectively. Hysteresis has been measured by applying a DC voltage from 40 to −40 V for five cycles at temperatures of 60, 25 and −40 °C, respectively.

Results and discussion

Figure 1 shows the XRD patterns of the BST 70/30 films on alumina and yttrium aluminate substrates. The results clearly indicate that rare earth aluminates have good chemical compatibility even at high sintering temperatures (>1,400 °C). No extra peaks are observed for the BST films. In contrast, severe interactions are observed in the BST films on alumina substrates as reported previously [4].

The SEM results (Fig. 2) show distinct interfaces between the BST films and $YAlO_3$ substrates (sintered at 1,450 °C), indicating minimum interactions between them. The grain sizes and density of the films are increased when the films are sintered at higher temperatures compared to those sintered at lower temperatures on alumina substrates

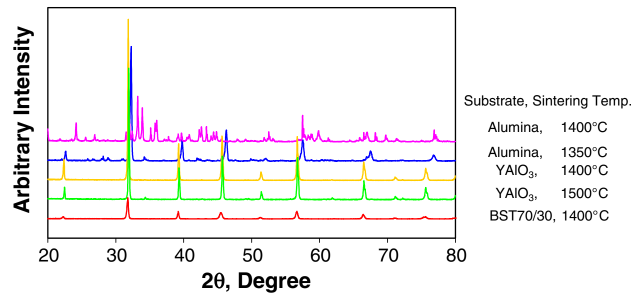

Fig. 1 XRD patterns of BST 70/30 films on different substrates and sintered at different temperatures. The data of BST 70/30 ceramic is also included for comparison

[7], especially for the BST 70/30 films. However, microcracks are observed within both films.

Dilatometry has been used to measure the thermal expansion coefficient of the BST ceramics and $YAlO_3$ substrates during heating and cooling at temperatures up to 1,500 °C. The results indicate large coefficient of thermal expansion (CTE) difference between the BST 50/50 ceramic and $YAlO_3$ substrate (13.2×10^{-6}/K for the BST versus 8.78×10^{-6}/K for the $YAlO_3$ during cooling stage). The smaller CTE for $YAlO_3$ substrate during the cooling down stage means that larger tensile stresses could be developed within the BST films, which may be responsible for the microcracks generated within the films as shown in SEM.

Figure 3 shows the frequency dependence of the dielectric properties of the BST 70/30 film on a $YAlO_3$ substrate which has been sintered at 1,450 °C. Two phase transition temperatures (cubic to tetragonal $T_{c\text{–}t}$ = 35 °C and tetragonal to orthorhombic $T_{t\text{–}o}$ = −54 °C) are clearly present, different from the previous report on low temperature sintered BST films on alumina substrates, where only a broad diffused transition was observed [7]. Both permittivity and dissipation (in the ferroelectric region) are increased compared to the BST films on alumina substrates. The increase could mainly be ascribed to the increase in sintered density and grain sizes due to the higher sintering temperatures used for the films on $YAlO_3$ substrates. Domain wall induced dissipation in the ferroelectric (FE) region becomes more significant in the films with large grain sizes. However, contrary to their ceramic counterparts, where sharp peaks were observed at the phase transition temperatures [8], the BST films on $YAlO_3$ substrates, even though sintered at the same high temperatures (1,450 °C), still show a relaxor-like behaviour: a diffused phase transition and the permittivity shift to higher temperatures with the increase of frequency. These results may indicate some extent of microstructural heterogeneity as observed in relaxor ceramics. The large CTE mismatch between the films and substrates measured in this work

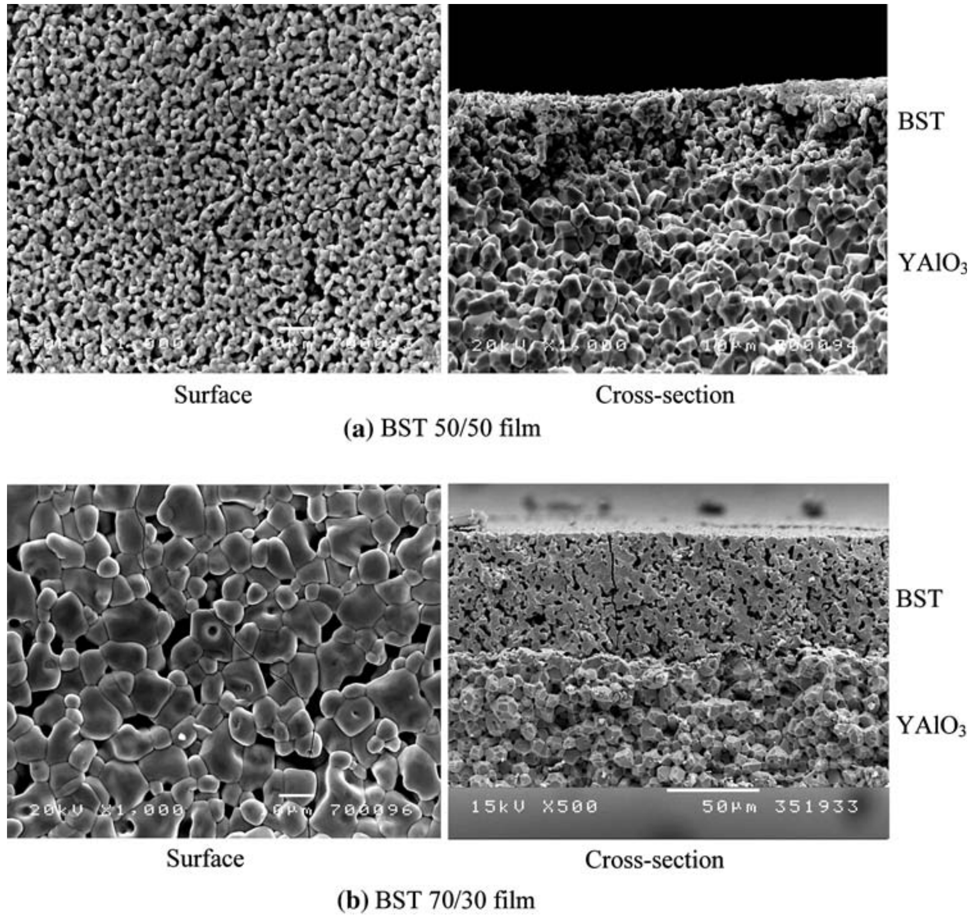

Fig. 2 SEM micrographs of the surface morphology and cross-section of BST 50/50 and BST 70/30 films sintered at 1,450 °C. Microcracks are observed in both films

may cause distorted crystal structure within the films [9]. The substrate constraint effect may result in micro-/nano-polarisation, which is responsible for its unique dielectric properties [10].

The DC bias field dependence of the dielectric properties of the BST 70/30 films sintered at different temperatures is shown in Fig. 4. Both permittivity and dissipation are suppressed with the increase of DC bias voltage due to the 'freezing' of the polar phase reorientation under a DC field. The tunabilities of the high temperature sintered films are increased drastically, mainly in the paraelectric (PE) region near Curie point (≤40 °C above the T_c) and in the ferroelectric (FE) region (see Fig. 5). The increase in the FE region probably results from domain contributions of the larger grains. In the PE region near T_c, possible micro- or nano- polar phase regions may contribute to the effect due to the microstructural heterogeneity within the films as discussed above.

Figures 6 and 7 show DC hysteresis of dielectric properties of the BST 50/50 and 70/30 films measured at different temperatures. 'Butterfly' hysteresis loops, which are typical for ferroelectrics owing to the domain wall motion during switching of polarisation, are observed for both films at three measured temperatures, but the

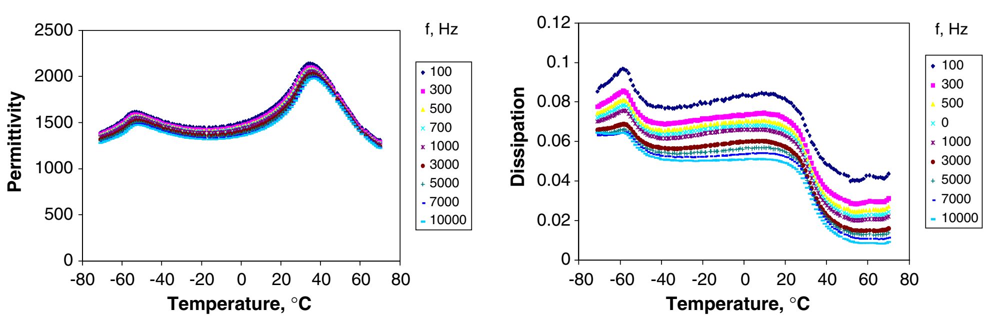

Fig. 3 Frequency dependence of dielectric properties of the BST 70/30 film sintered at 1,450 °C for 1 h on $YAlO_3$ substrate

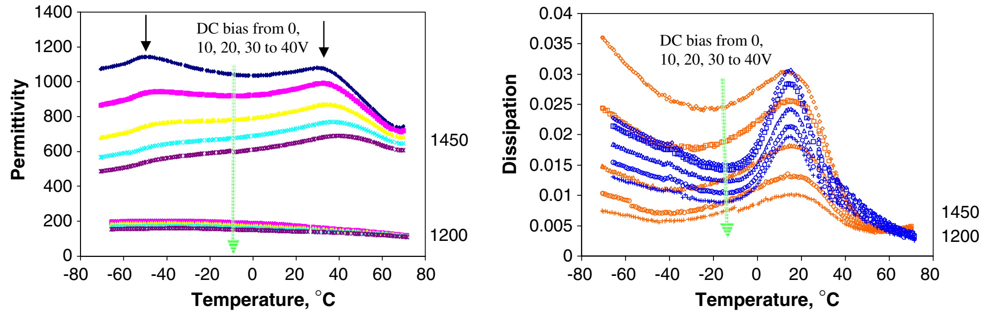

Fig. 4 DC field dependence of dielectric properties of the BST 70/30 films sintered at 1,200 and 1,450 °C for 1 h on Al_2O_3 and $YAlO_3$ substrates respectively

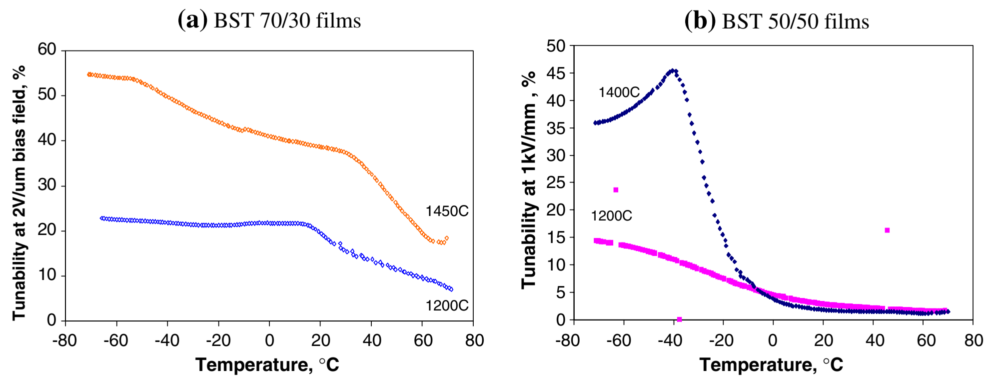

Fig. 5 Tunability versus temperature of the BST 70/30 films and BST 50/50 films sintered at 1,200 and 1,450 °C for 1 h on Al_2O_3 and $YAlO_3$ substrates respectively

magnitudes are quite different depending on the film composition and temperature. In the FE region, films with both compositions exhibit large tunability and hysteresis. However, hysteresis is also present in the PE region though the magnitude becomes much smaller when the temperature moves far away from the Curie point, e.g. at 25 and 60 °C for the BST 50/50 film whose T_c = −35 °C. For the BST 70/30 film whose T_c = 30 °C, large tunability and hysteresis are observed in both FE (−40 and 25 °C) and PE (60 °C) regions. These results indicate that dielectric tuning in the PE region is not solely achieved via a field-induced hardening of the soft phonon [11], contributions from those micro-/nano- polar phase reorientations are also possible, especially near the phase transition temperature.

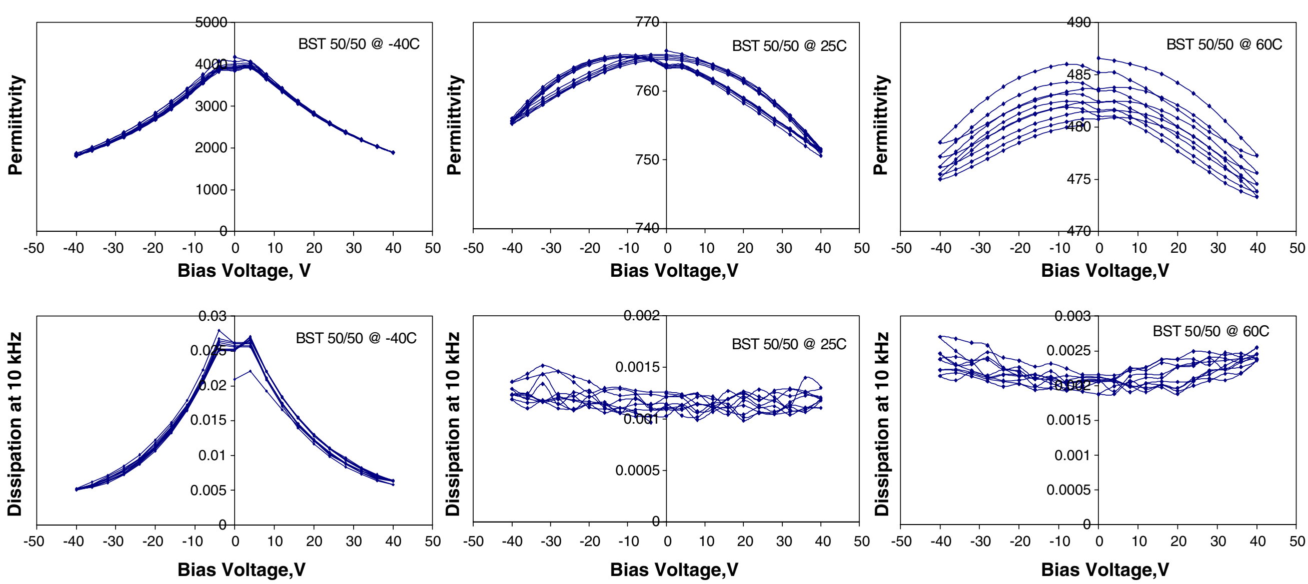

Fig. 6 DC bias hysteresis measured at −40 °C (FE region) and 25, 60 °C (PE region) for the BST 50/50 film sintered at 1,450 °C for 1 h, whose T_c is −35 °C

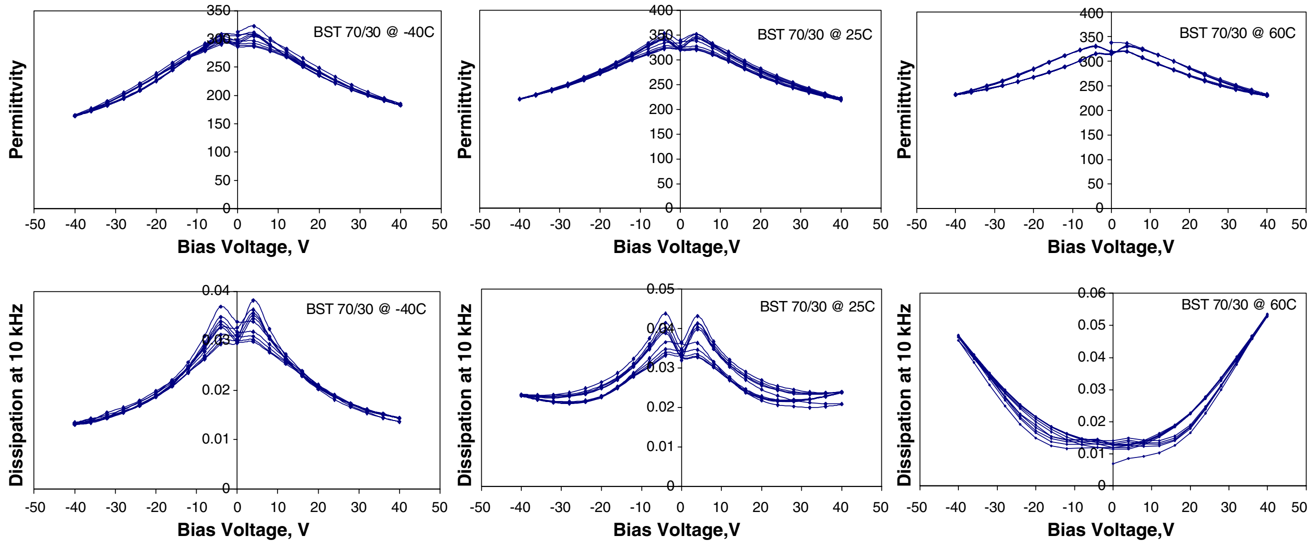

Fig. 7 DC bias hysteresis measured at −40 and 25 °C (FE region) and 60 °C (PE region) for the BST 70/30 film sintered at 1,450 °C for 1 h, whose T_c is 30 °C

Conclusions

High temperature chemical compatibility is good between BST films and yttrium aluminate substrates, which allows the BST films to be sintered at high temperatures (>1,400 °C), resulting in improved density and large grain size in the BST films. Consequently, the permittivity and tunability are increased significantly, especially in the FE region. The dissipation in the FE region is also increased owing to the domain wall contributions in the films with large grains. However, a relaxor-like behaviour and DC bias hysteresis are observed in the BST films, probably due to the micro-/nano- polar regions induced from the possible substrate constraint effect, where the residual strain causes crystal structure distortion and composition heterogeneity at the interface between the BST films and yttrium alumina substrates. This is supported by the fact that microcracks are observed in the films resulting from a large CTE mismatch between the films and substrates on cooling from the high sintering temperature.

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