Low dielectric dissipation and enhanced tunability of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films by the modified composition and multilayer structure

Dongwen Peng · Jinrong Cheng · Zhongyan Meng

Abstract $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ (BST, y=0.1, 0.15, 0.2, 0.25, 0.3) thin films were fabricated on Pt-coated silicon substrates by modified sol-gel techniques. It was found that the tunability of BST thin films and dissipation factor decreased with the increase of Ti content. The multilayer structure of $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$(200 nm)/$Ba_{0.6}Sr_{0.4}TiO_3$(100 nm)/ $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ (200 nm; y=0.1, 0.2, 0.25) was designed to enhance the tunability. Our results indicated that the modified composition and multilayer structure were beneficial to lowering the dielectric dissipation and enhancing the tunability simultaneously. The tunability of 26.7% and dielectric dissipation of 0.013 were achieved for modified BST thin films.

Keywords BST thin films · Sol–gel · Ti content · Multilayer structure

1 Introduction

Thin films of $Ba_{1-x}Sr_xTiO_3$ (BST) are being developed for tunable microwave device applications [1–3], such as filters, phase shifters, and delayer lines, due to the fact that the materials exhibit a large dielectric constant change with dc bias voltage. In tunable microwave devices, it is desirable to have a high dielectric tunability and a low dielectric loss. The dielectric properties at microwave frequencies are strongly affected by many factors, such as substrates, films thickness, grain size, Ba/Sr ratio, and film stress. Recently, deviation of the (Ba+Sr)/Ti ratio from the stoichiometric value of unity is reported to have a dramatic effect on the dielectric properties. Susanne Stemmer et al. [4], fabricated $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ thin films grown by chemical vapor deposition. Reasonable film behavior is generally achieved up to y=0.15, which greatly exceeds the solubility of excess Ti in bulk BST, of approximately y<0.001. Q.X. Jia et al. [5] deposited the epitaxial $Ba_{0.6}Sr_{0.4}TiO_3$ films with TiO_2-doped, and found that by controlling the amount of TiO_2 added to BST reduced the dielectric loss of the films. However, in those papers, the dielectric constant and tunability of the films also reduced with the (Ba+Sr)/Ti ratio increased. In order to optimize the reasonable tunability and loss tangent of the BST tunable devices, a multilayer structure was discussed. Hitoshi Tabata et al. [6] formed an artificial $BaTiO_3$/$SrTiO_3$ superlattices. They reported that a large dielectric constant of 900 was observed with a stacking periodicity of 2 unit cells/2 unit cells for large strain introduced at the interface between the BTO and STO layers. Xinhua Zhu et al. [7] also investigated heteroepitaxial BST thin films with compositional gradient on MgO substrates using PLD technology. However, the polycrystalline thin films with multilayer structure have not been discussed by sol–gel technology.

In this paper, the influence of the Ti content on the dielectric properties of BST polycrystalline films is investigated. And multilayer structure of $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$(200 nm)/ $Ba_{0.6}Sr_{0.4}TiO_3$(100 nm)/$Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ (200 nm; y=0.15, 0.2, 0.25) was designed to enhance dielectric properties. Our results indicated that the modified composition and multilayer structure were beneficial to lowering the dielectric dissipation and enhancing the tunability simultaneously.

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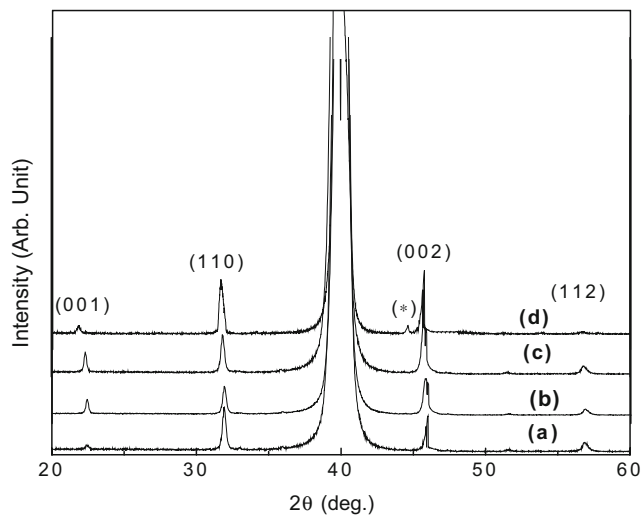e-mail: zymeng@staff.shu.edu.cn

Fig. 1 XRD patterns of $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ thin films: (**a**) $y=0$, (**b**) $y=0.15$, (**c**) $y=0.25$, and (**d**) $y=0.30$

2 Experimental

$Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ ($x=0.1$, 0.15, 0.2, 0.25 and 0.3) films were prepared on Pt(111)/Ti/SiO$_2$/Si substrate by modified sol–gel method, respectively. The details of the experimental procedures have been described in authors' previous paper [8]. For fabricated multilayer structure, firstly, 200 nm $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ layer was deposited on substrate with 750 °C annealing temperature for 30 min in air for complete perovskite phase formation and better crystallization. Then 100 nm $Ba_{0.6}Sr_{0.4}TiO_3$ and 200 nm $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ layers were also deposited in sequence, respectively. Finally, as-deposited films were annealed in air at 750 °C for 2 h.

The crystal structure of films was identified by XRD (DIMAX Model IIIC, Japan). The microstructure and morphology were observed by FE-SEM (XL 30 FEG). To measure the dielectric properties, Pt electrodes with 400 μm in diameter were deposited by sputtering on the film surface through a shade mask to serve as top contacts. The dielectric properties and dielectric tunability were measured at room temperature by using a Precision Impedance Analyzer (Agilent 4294A, Japan).

3 Results and discussion

Figure 1 illustrates the XRD patterns for $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ thin films with different Ti contents. The film with Ti content ranging from 0 to 1.25 shows a perovskite single phase. Only $Ba_{0.6}Sr_{0.4}Ti_{1.3}O_3$ film [Fig. 1(d)] shows peaks (*) near 44.6° besides the perovskite peaks. This second phase is considered to be a TiO$_2$ phase. Although the peak intensity has no obvious change with Ti content, the diffraction angle of peaks shifted as Ti content increased, which implies

the lattice constant increases as Ti content increased. Our result is agreement with that reported by Susanne Stemmer [4] et al. However, Shintaro Yamamichi [9] found the lattice constant did not shift as (Ba+Sr)/Ti ratio in the range from 0.75 to 1.05. As Ti content increasing, the excess titanium in polycrystalline films is accommodated in the grain interior, and the lattice constant increased. When excess Ti in films is higher [as shown in (d)], Ti segregates to the grain boundaries in addition to being partially accommodated in the grain interior and the second phase (TiO$_2$) formed.

The dielectric properties of $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ films as a function of the DC bias electric field at frequency of 1 MHz are shown in Fig. 2. It can be seen that the dielectric constant, tunability and dissipation factor decrease rapidly with the increase of Ti content. In our paper, the (Ba+Sr)/Ti ratio was considered one of the most critical problems, although the dielectric properties are also related to grain size, thickness and inner strain of the films. Excess Ti in films is facilitated by a defect mechanism that involves a lowering of average valence state of Ti. The incorporation of excess tetravalent Ti in bulk titanates in much smaller concentrations is thought to occur by incorporation on Ti sites accompanied by Schottky defect formation. It was well known that Ti with a valence state of less than 4+ reduces ferroelectricity. Therefore, the dielectric constant and tunability and dissipation factor decrease with increasing amounts of excess Ti. $Ba_{0.6}Sr_{0.4}TiO_3$ thin films have tunability of 34.9% (250 KV/cm, 1 MHz) and dissipation
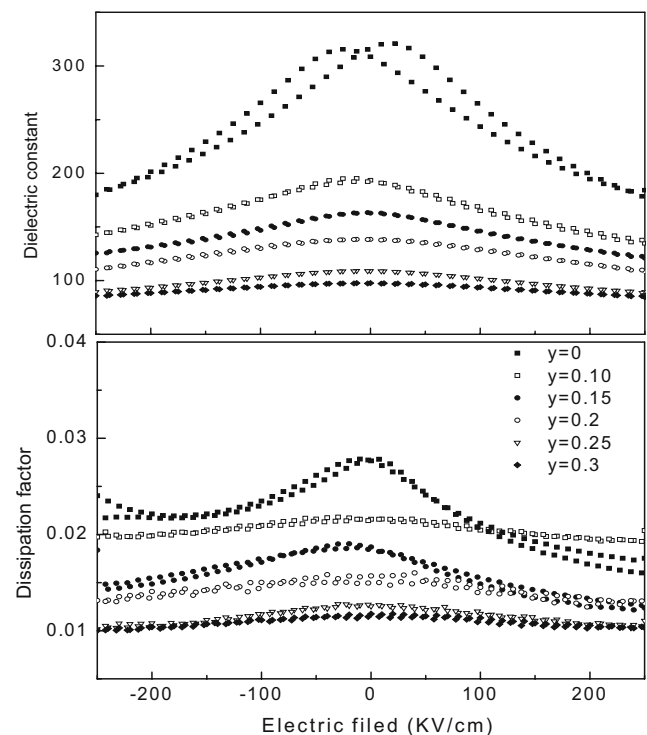

Fig. 2 The dielectric properties of $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ films at frequency of 1MHz as a function of the DC bias electric field
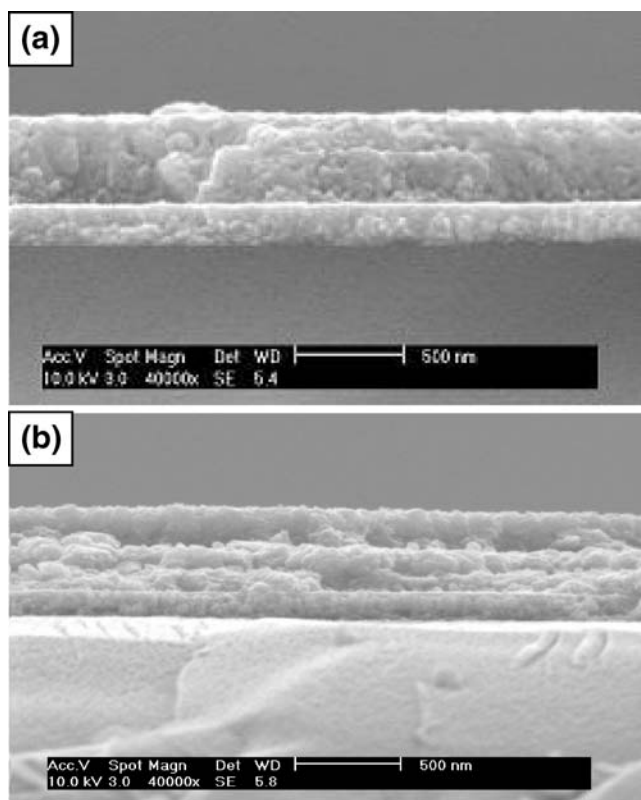
Fig. 3 FE-SEM photographs for cross-section of BST films. (a) $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$, (b) $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3/Ba_{0.6}Sr_{0.4}TiO_3/ Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$

factor of 0.028, and $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$ thin films have lower tunability of 17.1% and lower dissipation factor of 0.012. As more Ti added, the second phase forms, which has lower dielectric constant compared to BST, and thus $Ba_{0.6}Sr_{0.4}Ti_{1.3}O_3$ films have lower tunability of 12.4%.

Although added Ti content depressed films dissipation factor, the tunability of films also decreased enormously. Therefore, a multilayer structure was promoted to enhance films' dielectric constant and tunability. Figure 3 shows the FE-SEM photographs for cross-section of the $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$ and multilayer structure of $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3/Ba_{0.6}Sr_{0.4}TiO_3/Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$ films. The cross-sectional images show that BST films with multilayer structure were grown layer by layer orderly, which indicate each layer of the films was well crystallized at 750 °C for 30 min.

Figure 4 illustrates the dielectric constant and dissipation factor of films as a function of bias field. Some authors [4, 10] have epitaxially deposited BST films with multilayer structure. They reported that tunability and dissipation factor increased enormously, for large strain introduced at the interface between layers. However, in this paper, the strain between layers could be disappeared for the polycrystalline characteristic of films. In comparison with Fig. 2, the tunability of films with multilayer structure increases, and the dissipation factor did not change evidently.

For example, the tunability and the dissipation factor of $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3/Ba_{0.6}Sr_{0.4}TiO_3/Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$ film are 26.7% and 0.013 respectively. Vendik et al. [11] had reported that the films with multilayer structure present as a series connection of capacitors. However, Figs. 2 and 4 indicate clearly that the dielectric constant of films with multilayer structure is larger than that of $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ films. The interface between $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ layers has heterogeneous compositions, and a space charge layer has been introduced in this micro-region. According to Maxwell–Wagner model [12], the dielectric constant of the films with multilayer structure increases and the dissipation factor has no increase evidently. It is manifested that multilayer structure with modified composition is beneficial to enhancing the tunability simultaneously.

4 Conclusion

$Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ (BST, $y=0.1$, 0.15, 0.2, 0.25, 0.3) thin films were fabricated on Pt-coated silicon substrates by modified sol-gel techniques. The dielectric constant, tunability and dissipation factor decrease with increasing amounts of excess Ti. $Ba_{0.6}Sr_{0.4}TiO_3$ thin films have tunability of 34.9% (250 KV/cm, 1 MHz) and dissipation factor of 0.028, and $Ba_{0.6}Sr_{0.4}Ti_{1.25}O_3$ thin films have lower tunability of 17.1% and lower dissipation factor of 0.012. As more Ti added up to 1.3, second phase forms. The polycrystalline thin films with multilayer structure were also prepared. It is found that the dielectric tunability of the films with multilayer structure increases and the dissipation factor does not change evidently. Our results indicated that the multilayer structure with modified composition is beneficial to lowering the dielectric dissipation and enhancing the tunability simultaneously.
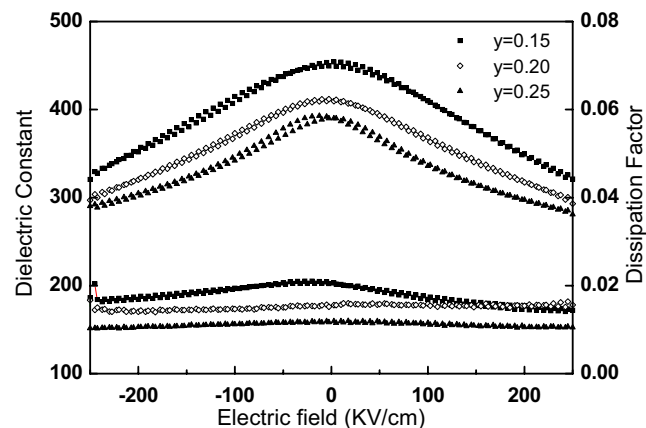

Fig. 4 The dielectric properties of $Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3/Ba_{0.6}Sr_{0.4}TiO_3/ Ba_{0.6}Sr_{0.4}Ti_{1+y}O_3$ multilayer structures as a function of DC bias field

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