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The dielectrical properties of (B,Si) doped (Ba,Sr)TiO_3 thin films fabricated by sol–gel technique

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Abstract

The dielectrical properties (B,Si) doped barium strontium titanate (BSTS) thin films were investigated. Thin films of BSTS were fabricated on Pt/Ti/SiO_2/Si substrate by spin coating. The multicomponent precursor solutions were prepared using sol–gel method. The relative dielectric constant of a 400 nm BSTS thin film fired at 700 °C decreased with the increasing content of tributyl borate (B) and TEOS (Si). The leakage current of the BST films decreased as the content of (B,Si) dopant was low (≤10 mol%), while it increased as the content of (B,Si) dopant was high (≥15 mol%).

Keywords: BSTS thin films; Dielectric constant; (B,Si) dopant

1. Introduction

In the recent years, thin film perovskite materials with high dielectric constant such as $SrTiO_3$ and (Ba,Sr)TiO_3 (BST) have been investigated as dielectric materials for future dynamic random access memory (DRAM) [1–6]. The best suited dielectric material would have a low leakage current and a high dielectric constant. BST thin films are being widely investigated as alternative dielectrics for ultra large-scale integrated circuits (ULSI) due to their high dielectric constant and low leakage current.

Due to high sintering temperature of BST, the inner electrode must be a noble metal, and a barrier layer to block the oxygen penetration is needed between Pt electrode and plugged poly-silicon. Studies of BST thin films have focused on decreasing the sintering temperature by adding sintering aids and improving the dielectric properties by controlling the sintering conditions and microstructure.

One method of decreasing the sintering temperature is to add sintering aids that have low melting points. The sintering aids promote densification at low temperatures. However, sintering aids degrade dielectric properties due to their low dielectric constants. Furthermore, reactions between the sintering aids and BST cause the formation of a secondary phase with a low dielectric constant [7,8]. It is easy to control the composition and to synthesize high quality thin film by using sol–gel method, thus, the sol–gel process coupled with the use of sintering aids are particularly attractive in the fabrication of dense and uniform BST thin films.

In this article, we report the influence of the sintering temperatures and dopant concentration of tributyl borate (B) and TEOS (Si) on the dielectric properties of $Ba_{0.7}S_{r0.3}TiO_3$ thin films.

2. Experimental details

Barium acetate $Ba(CH_3COO)_2$ (purity ≥99%, Shanghai Chemical Reagent Co.), strontium acetate $Sr(CH_3COO)_2{\cdot}1/2H_2O$ (purity ≥99.5%, Shanghai Chemical Reagent Co.), titanium butoxide $Ti(C_4H_9O)_4$ (purity ≥98%, Shanghai Chemical Reagent Co.), tetraethyl orthosilicate (TEOS, purity ≥99%, Shanghai Chemical Reagent Co.), and tributyl borate $B(OC_4H_9)_3$ (CP, Shanghai Chemical Reagent Co.) were used as starting materials. Glacial acetic acid was used as a solvent. Barium acetate and strontium acetate in the ratio of 7:3 were dissolved into heated acetic acid in a reflux condenser to get clear solution; then, titanium butoxide and Acetylacetone (AcAc) were dropped into the

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solution in proper molar ratio to get a precursor solution. The 0, 5, 10, 15, and 20 mol% (tributy1 borate (B)-tetraethyl orthosilicate(Si)) doped BST, respectively, clear yellowish solutions were prepared, which were stored in sealed bottles for several months without precipitation. The BSTS thin films were prepared as follows: at first, BSTS thin film were deposited by spin coating at 3000 rpm for 30 s on Pt/Ti/SiO_2/Si substrates, and then the wet films were dried in air at 200 °C for 30 min and pre-baked at 400 °C for 30 min in O_2 atmosphere. This coating process was repeated five times. At last, the samples were annealed at 600, 650, and 700 °C, respectively, for 60 min in O_2 atmosphere, and the BSTS thin films were obtained.

To investigate the thermal behavior, the sol was analyzed by DSC and TG (DSC/TG NETZSCH STA449C) in air with a heating rate of 10 °C/min. Dielectric measurements were carried out using the metal–insulator–metal (MIM) capacitor configuration. Au top electrode having a diameter of 1 mm was deposited by direct current sputtering to measure electrical properties. A D8 Advanced X-ray diffractometer with Cu Kα radiation is used to analyze the microstructure of the films. Dielectric constant and loss were measured using an HP4284 impedance analyzer. The leakage current was measured using a Keithley 6517A source measurement unit.

3. Results and discussion

The 0, 5, 10, 15 and 20 mol% (tributyl borate (B)-tetraethyl orthosilicate (Si)) added films were subsequently abbreviated as BST, BSTS5, BSTS10, BSTS15, and BSTS20, respectively.

Fig. 1 shows DSC data of three BSTS (BST, BSTS10, and BSTS20) xerogels dried at 80 °C for 3 h. In BST, BSTS10, and BSTS20 gel curves, most parts of the two curves are essentially alike. The endothermic peak at near 80 °C in BST curve mainly results from the rapid volatilization of water. The exothermic peaks at 388.2, 362.9, and 361.8 °C are related to the pyrolysis of organic compound (to produce CO_2 and H_2O). The exothermic peak at near 500 °C results from the formation of Ti–O–Ti–O–· · · [TiO_2]. The exothermic peaks at 607.7, 625.3, and 689.3 °C are associated with the formation temperature of BSTS. The formation temperature of BSTS10 film is lower than that of pure BST film about 60 °C.

Fig. 2 shows the XRD patterns of BST, BSTS5, BSTS10, BSTS15, and BSTS20 thin films on the Pt/Ti/SiO_2/Si substrate annealed at 650 °C. It can be seen from Fig. 2 that the strongest peak at (1 1 0) for the BSTS10 and BSTS15 thin films is stronger than that in other films. All films have no secondary phase except for BSTS20.

Fig. 3 show XRD patterns of the 10 mol% (B,Si) added BST (BSTS10) thin films annealed at 550, 600, 650, and 700 °C, respectively, for 1 h. The diffraction peak of the thin films increases with annealing temperature.

Fig. 4 shows the dielectric constant and the dielectric loss of the BST thin films as a function of the B_2O_3–SiO_2

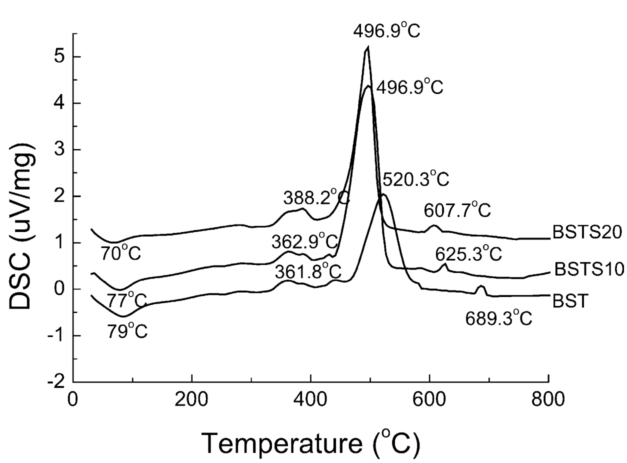

Fig. 1. DSC curves of three BST-based xerogels heat-treated with a heating rate of 10 °C/min.

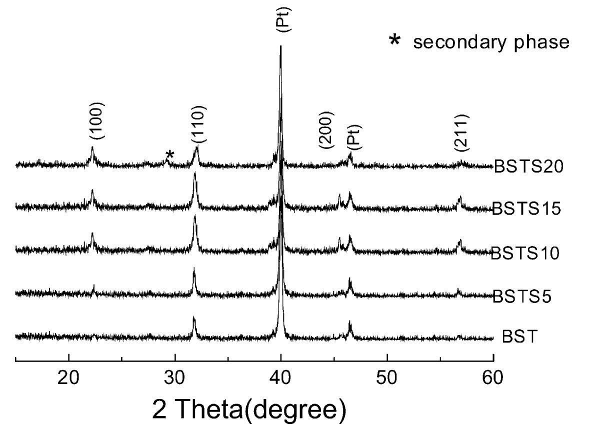

Fig. 2. X-ray diffraction patterns of the (B,Si) doped (0–20 mol%) BST thin films annealed at 650 °C for 1 h.

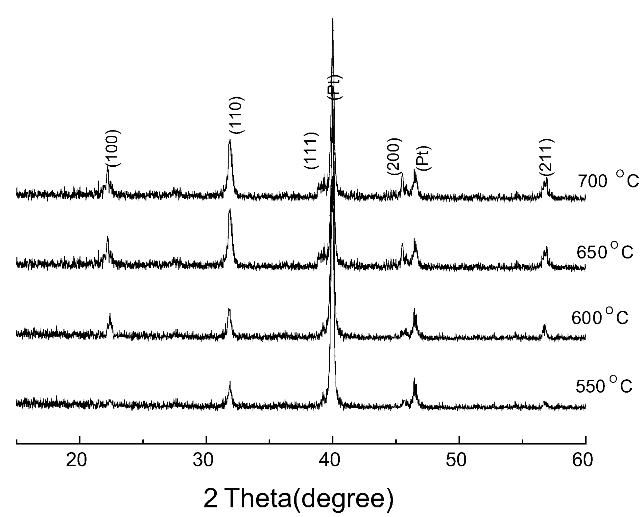

Fig. 3. X-ray patterns of the 10 mol% (B,Si) added BST thin films annealed at different temperatures for 1 h.

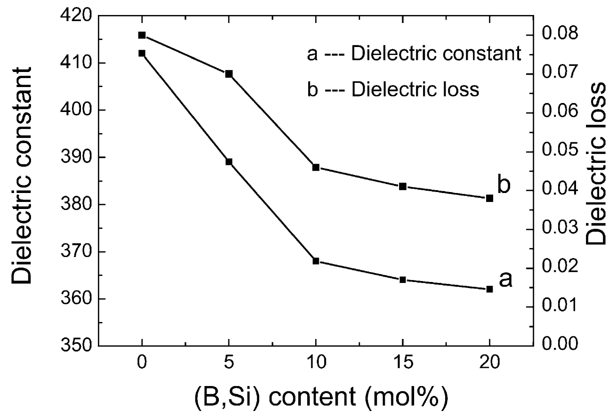

Fig. 4. Dielectric constant and the dielectric loss of the thin films as a function of the (B,Si) content added at a frequency of 100 kHz.

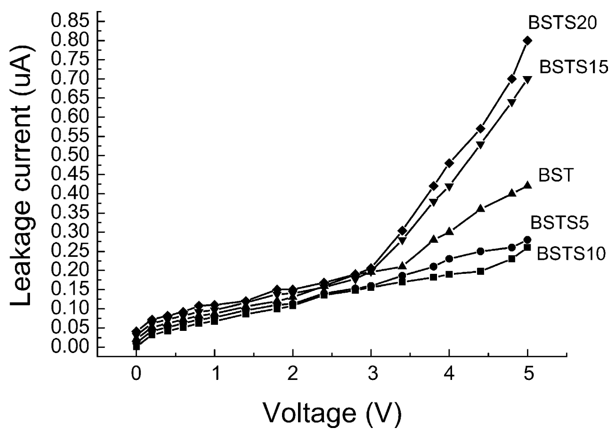

Fig. 5. The leakage current characteristics of five BST thin films with different amount of (B,Si) addition fired at 700 °C for 1 h.

content at a frequency of 100 kHz. The thin films with a thickness of 400 nm were fired at 700 °C for 1 h. Both the dielectric constant and dielectric loss decreased with the increase of B_2O_3–SiO_2 content added in the films. Fig. 5 shows the leakage current–voltage characteristics of the un-doped and doped BSTS films as a function of voltage applied to the top electrode. It can be seen from Fig. 5 that as the (B,Si) content increased from 0 to 10 mol%, the value of leakage current for the BST thin films decreased, while as the (B,Si) content increased from 15 to 20 mol%, the value of leakage current for the BST thin films increased and was higher than the un-doped BST film. The increase of leakage current of BSTS15 and BSTS20 is probably because the amount of (B,Si) added is too much; an additional phase (B,Si) formed in the film as a second phase.

4. Conclusions

In this study, we have studied dielectric properties of BST thin films doped with (B,Si). Our results demonstrated that (B,Si) dopant concentration has a strong influence on the sintering behavior of BST thin films, dielectric constant, and dielectric loss. When B_2O_3–SiO_2 was added, the sintering temperature was decreased. Both the relative dielectric constant and dielectric loss decreased with the increasing B_2O_3–SiO_2 content. The leakage current of the BST films decreased as the content of (B,Si) dopant was low ($\leq$10 mol%), while it increased as the content of (B,Si) dopant was high ($\geq$15 mol%).

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