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Fabrication of patterned $Ba_{0.71}Sr_{0.29}TiO_3$ thick film on Si substrate by tape casting method

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Abstract

Patterned barium strontium titanate (BST) thick films are fabricated in the grooved silicon substrate using tape casting method and sintered from 800 to 1250 °C for 2 h. The slurry used for the tape casting is from sol-precipitation method, and the crystallization of the as precipitated BST powders is improved by hydrothermal treatment at 200 °C for 5 h. The patterned BST thick films have a size of 800 × 300 μm and homogeneous thickness of 30 μm. After sintering below 1000 °C, the obtained BST thick films have a dielectric abnormality at about 30 °C and the dielectric loss is about 0.02.

Keywords: $BaTiO_3$ and titanates; Powders-chemical preparation; Films; Tape casting; Dielectric properties; $(Ba,Sr)TiO_3$

1. Introduction

Thick films are believed to fill out the gap between bulk materials and thin films because the thick films have similar properties with the bulk materials. Especially, the thick films have been widely applied in tunable phase shifter,[1] accelerometers,[2] chemical sensors and biosensors.[3] Previous researchers have employed screen printing,[4] tape casting,[5] spin coating[6] and so on to fabricate thick films, however, there still are difficulties in patterning the thick films due to the thickness obstacle. Thus, developing patterning process of thick films is quite essential to accommodate the demands of miniaturization in their applications. In this paper, we investigate a tape casting method on the grooved silicon wafer to fabricate patterned BST thick films, and in order to lower the sintering temperature and avoid crack, sol-precipitation method together with hydrothermal treatment are used to obtain nano-sized BST powders for the tape casting processing. The sintering characteristics and dielectric properties are also characterized for the obtained patterned BST thick films.

2. Experimental

2.1. Powder preparation

The preparation procedure of BST ($Ba_{0.71}Sr_{0.29}TiO_3$) powders is similar with the reported literature by Diaz-Guemes.[7] Barium acetate, strontium acetate and titanium tetrabutoxide are used as the starting materials. Titanium tetrabutoxide is first mixed with appropriate amount of acetic acid, and then distilled water is added and agitated until this hydrolyzed mixture becomes clear. After that, Barium acetate and strontium acetate are added in and agitated to dissolve completely. The resultant stable precursor solution is then added slowly to a hot stirred aqueous solution (T = 85–95 °C) of sodium hydroxide (10 M) to obtain white precipitates. After the addition is completed, the precipitates solution is transferred into Teflon autoclave and hydrothermally treated at 150–200 °C for 5–10 h. The finally obtained precipitates

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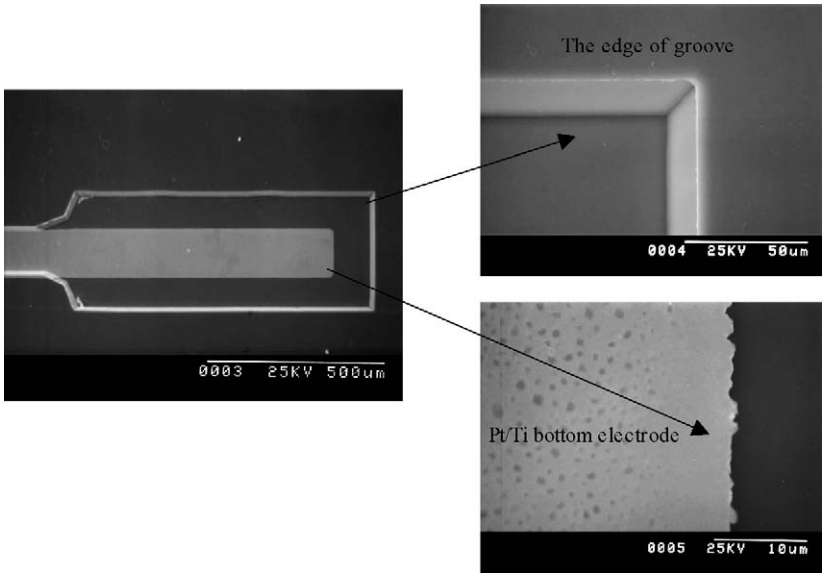

Fig. 1. The SEM photos of groove with patterned bottom electrode in the silicon substrate.

after hydrothermal treatment are centrifuged, washed by distilled water and alcohol to be free of Na^+, and dried at 70 °C for investigations.

2.2. Slurry preparation

The hydrothermally treated (200 °C, 5 h) BST powders (washed and without drying) are dispersed in appropriate toluene/ethanol (66:34 vol.%) solvents containing Polyethylene glycol and phosphate by ball milling for 20 min to form BST slurry for tape casting processing.

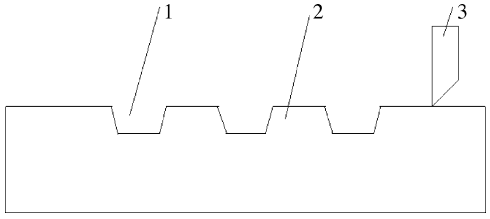

Fig. 2. Schematic diagram of tape casting: (1) grooves; (2) silicon substrate; (3) blade.

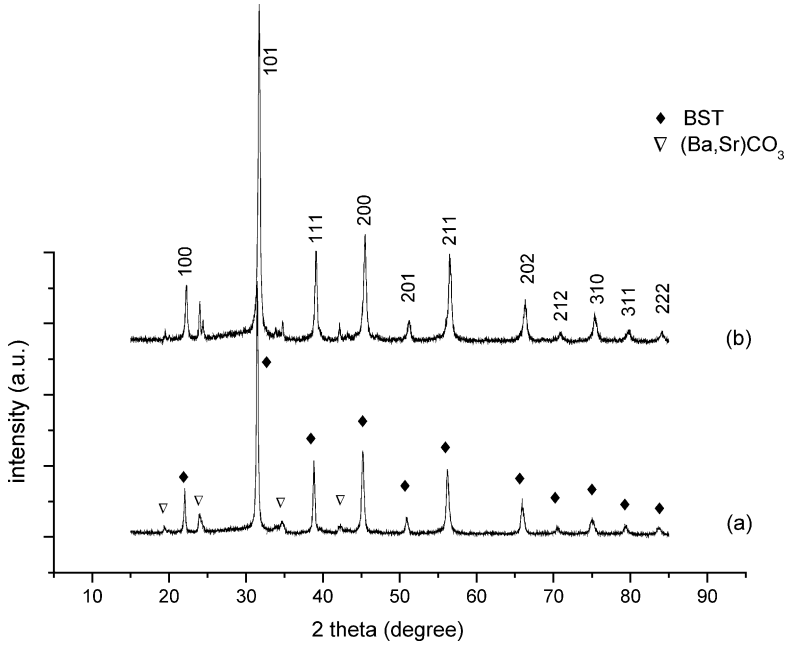

Fig. 3. XRD results of the BST powders: (a) as precipitated; (b) hydrothermally treated at 200 °C for 5 h.

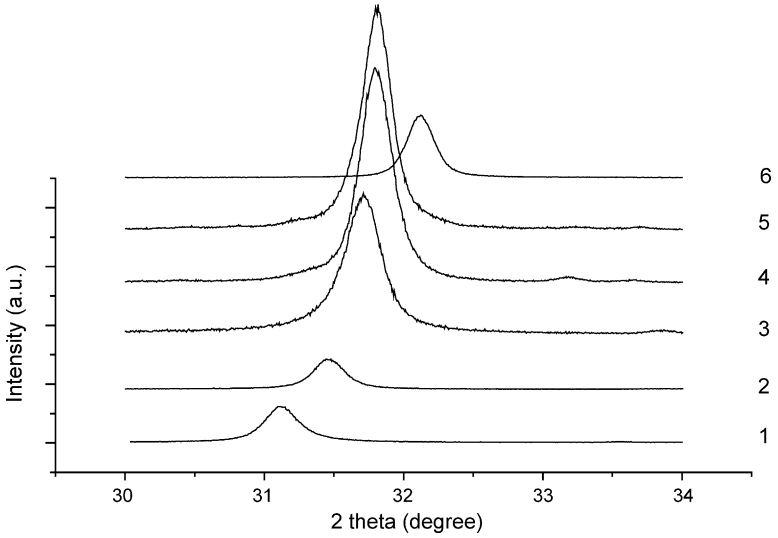

Fig. 4. Slow scan of (1 0 1) peak of the obtained BST powders: (1) as precipitated $BaTiO_3$ powder; (2) as precipitated $Ba_{0.71}Sr_{0.29}TiO_3$ powder; (3) hydrothermally treated $Ba_{0.71}Sr_{0.29}TiO_3$ powders at 200 °C, 5 h; (4) $Ba_{0.71}Sr_{0.29}TiO_3$ powder sintered at 1000 °C after hydrothermal treatment at 200 °C, 5 h; (5) as precipitated $Ba_{0.71}Sr_{0.29}TiO_3$ powder sintered at 1000 °C; (6) as precipitated $SrTiO_3$ powder.

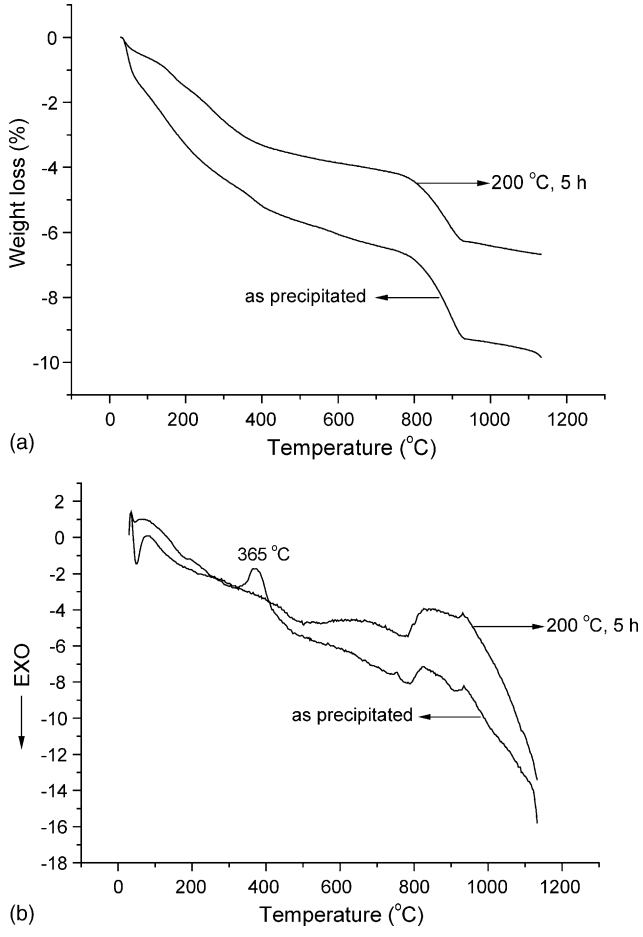

Fig. 5. TG (a) and DTA (b) analysis of as precipitated and hydrothermally treated BST powders (200 °C for 5 h).

2.3. Substrate and electrode

The silicon wafer is etched by wet chemical method to form micro grooves (800 × 300 μm, 30 μm in depth). The Pt/Ti electrode is fabricated by DC sputtering and patterned by lift-off method (Fig. 1). The bottom electrode covers partially on the bottom of the groove in case of short circuit between bottom electrode and up electrode.

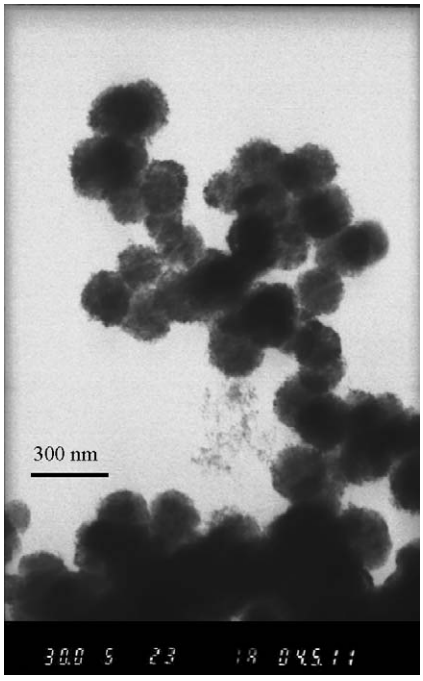

Fig. 6. TEM photo of hydrothermally treated BST powders at 200 °C for 5 h.

2.4. Film fabrication

In the tape casting processing, the blade touches the silicon substrate and the patterned thick film forms in the grooves (Fig. 2). The obtained thick films are dried at 100 °C for 2 h and then sintered from 800 to 1250 °C for 2 h.

2.5. Characterization

The crystalline phases of the obtained BST powders were recorded on X-ray diffraction (XRD). TG-DTA plots are measured under flowing dry air at a constant heating rate of 5 °C/min (SSC/5200, Seiko Instruments, Tokyo, Japan). Particle size and morphology were determined using transmission electron microscope (TEM) and scanning electron microscope (SEM). The dielectric properties are measured using HP4192 coupled with a furnace.

3. Results and discussion

3.1. Hydrothermal treatment of sol-precipitated BST powders

Fig. 3 is the XRD patterns of obtained BST powders. All the powders are cubic crystallized with a little carbonate which is introduced by the dissolved CO_2 in sodium hydroxide solution. And the intensity of the BST powders after hydrothermal treatment is slightly increased compared with that of the as precipitated. Slow scan results of the (1 0 1) peak (Fig. 4) show a shift to higher theta angle for the hydrothermally treated BST powders, which is closer to the sintered BST powders at 1000 °C. Since it is reported that the XRD peaks position of BST materials can be strongly affected by the Ba/Sr ratio,[8–10] therefore, the shift of (1 0 1) peak to higher theta angle can be explained by that more Sr^{2+} is incorporated into the crystalline structure of BST powders through hydrothermal treatment. TG and DTA analysis (Fig. 5) shows that the as-precipitated BST powders have larger weight loss and have extra endothermal peak at about 365 °C which is corresponding to the pyrolysis of the absorbed organic com-

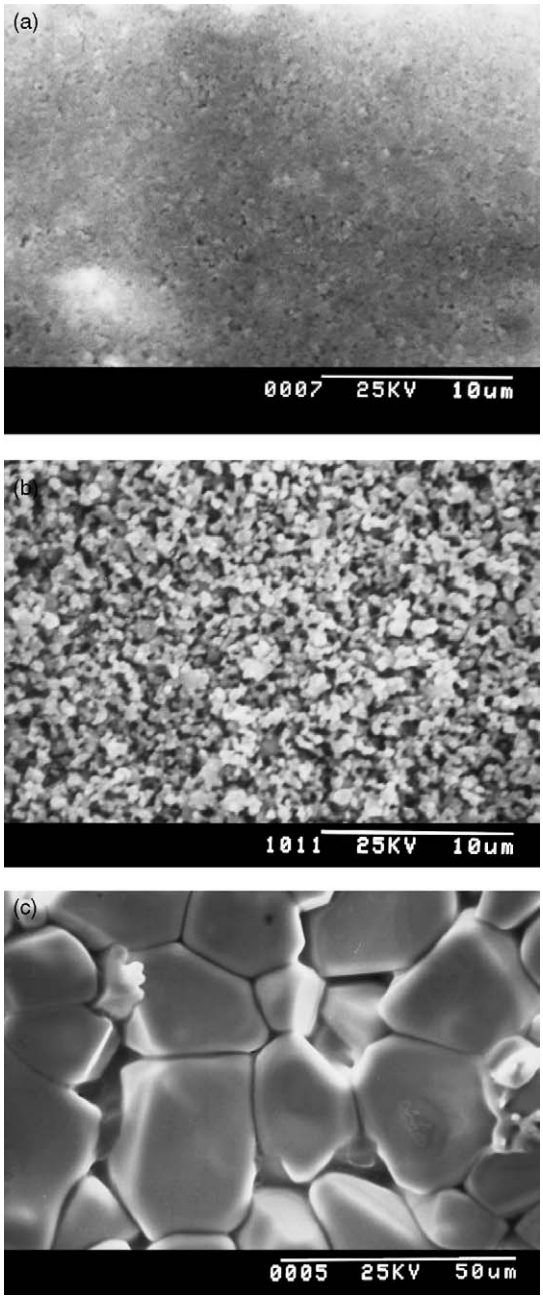

Fig. 7. SEM photos of BST thick films sintered at different temperature: (a) 800 °C, 2 h; (b) 1000 °C, 2 h; (c) 1250 °C, 2 h.

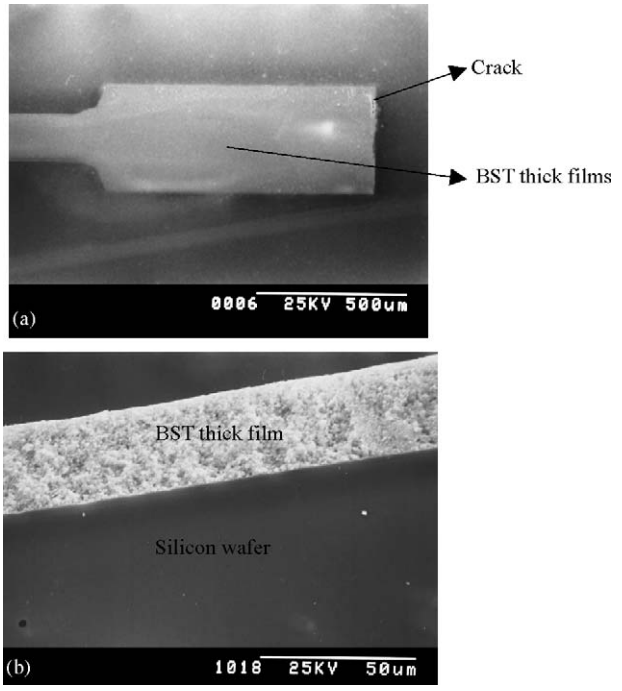

Fig. 8. SEM photos of the surface: (a) and cross section (b) of patterned BST thick film sintered at 1000 °C for 2 h.

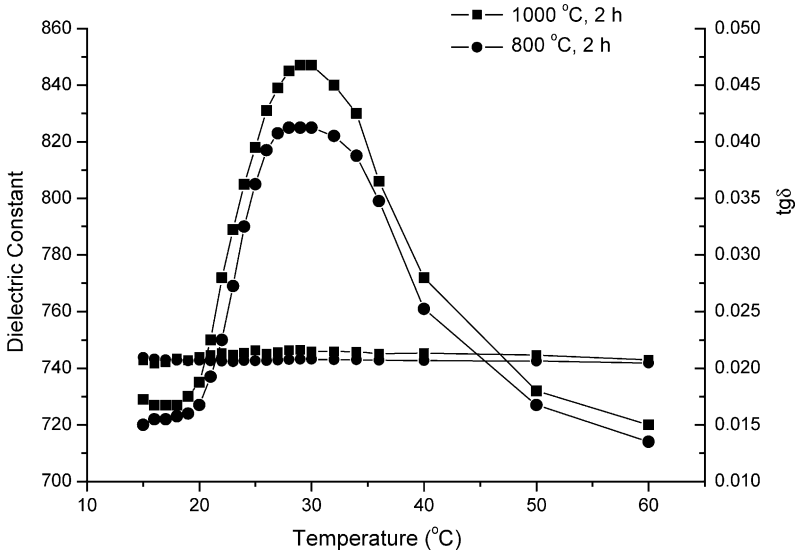

Fig. 9. Temperature dependent of dielectric constant of BST thick film (1 KHz) sintered at 800 and 1000 °C for 2 h, respectively.

pounds. Thus, some Sr^{2+} may be blocked to diffuse by the absorbed organic ligands during the precipitation.

From the above results of XRD and TG-DTA, it supports that hydrothermally treated BST powders are better crystallized than those as precipitated and have more homogeneous stoichiometry. The finally obtained BST powders after hydrothermal treatment at 200 °C for 5 h have the homogeneous particle size distribution around 200 nm (Fig. 6).

3.2. Fabrication of patterned BST thick films by tape-casting method

Conventional thick film fabrication methods are difficult to obtain patterned thick films due to the etching problem. The tape casting method in grooved silicon substrate can solve this problem because little slurry will be left on ungrooved substrate due to the touch between blade and substrate. The slurry used for the BST thick film fabrication is from hydrothermally treated BST powders because the as precipitated powders can cause large cracks in the BST thick films in our experiments.

Fig. 7 is the SEM photos of obtained BST thick films sintered at 800, 1000 and 1250 °C for 2 h, respectively. The BST thick films sintered at 1000 °C for 2 h have a particle size of about 0.5 μm (Fig. 7b) and the particle size increases to about 38 μm (Fig. 7c) after sintering at 1250 °C for 2 h which indicates the sintering temperature has been much lowered by using nano sized starting powders compared with the reported 1350 °C by conventional solid state method.[10] The patterned BST thick film (Fig. 8a) sintered at 1000 °C have homogeneous thickness about 30 μm (Fig. 8b) with a little crack at the edge of the groove which is ascribed to the shrinkage during sintering.

The temperature dependent dielectric constant is measured at 1 kHz for sintered BST thick film (Fig. 9). It should be noted that the bottom Pt/Ti electrode is destroyed after sintering at 1250 °C. The curie temperature of about 30 °C is observed for BST thick films sintered at 800 and 1000 °C, respectively, and the latter one have larger dielectric constant which indicates better crystallization. The dielectric loss of obtained BST thick films is around 0.02, however, the dielectric loss from 1000 °C is slightly higher than that from 800 °C, this can be ascribed to the increased porosity sintered at 1000 °C (shown in Fig. 7a,b). The dielectric peak known as phase transition from tetragonal to cubic indicates that the BST thick films have better ferroelectricity than BST thin films.

4. Conclusions

We have produced BST powders using simple chemical precipitation method. XRD and TG-DTA analysis prove that the crystallization of the as precipitated BST powders can be improved by hydrothermal treatment at 220 °C for 5 h. The hydrothermally treated BST powders with homogeneous particle size distribution around 200 nm are used to fabricate patterned BST thick films in the grooved Si substrate using tape casting method. The patterned BST thick films have a size of 800 × 300 μm and homogeneous thickness of 30 μm. The sintering temperature of the obtained BST thick films is about 1250 °C. The phase transition temperature after sintering at 800 and 1000 °C for 2 h is about 30 °C and the dielectric loss is about 0.02. Therefore, the tape casting processing in the grooved silicon substrate could be a potential way to fabricate patterned thick films.

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