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Preparation of $Ba_{0.09}Sr_{0.91}TiO_3/YBa_2Cu_3O_{7-x}$ bilayers and investigation of their dielectric properties

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ABSTRACT

$YBa_2Cu_3O_{7-x}$ (YBCO) films of 110 nm thickness were prepared on $LaAlO_3$ (LAO) substrates via the sol–gel method. Subsequently, about 400 nm thick $Ba_{0.09}Sr_{0.91}TiO_3$ (BST) films were epitaxially grown on the YBCO and LNO films surface; the BST films exhibited a strong *c*-axis orientation. The dielectric adjustability and relative dielectric constant was investigated in the range of 300-83 K. Results indicate that the tunability of the $Ba_{0.09}Sr_{0.91}TiO_3/YBa_2Cu_3O_{7-x}$ (BST/YBCO) displayed an increase relative to *c*-axis-oriented BST on $LaNiO_3$ (LNO). The tunability was further enhanced as the operating temperature decreased, yet the loss tangent (tanδ) decreased. The tunability and the tanδ at 100 kHz and 83 K were 58% and 0.029, respectively.

1. Introduction

$Ba_{\delta}Sr_{1-\delta}TiO_3$ (BST) films are ubiquitous in microwave devices, such as filters and phase shifters, due to their high dielectric constant, low loss and adjustable Curie point [1,2]. Conventionally, Pt electrodes are deposited on BST films. However, BST films are vulnerable to fatigue when coupled with Pt. Furthermore, the structural difference between Pt and BST creates an environment suitable for defect formation, which may have an effect on the ferroelectric and dielectric properties of the BST films. Hence, recent efforts have concentrated on electrodes based on semiconductive materials with sufficient electrical conductivity to circumvent this phenomenon [3]. High temperature superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) possesses an identical perovskite structure as BST with similar lattice parameters, a low square resistance at room temperature and negligible resistance at low temperatures. Well-oriented (001) BST films can be epitaxially grown on the top of YBCO and satisfies application requirements of the electrode for room temperature and low temperature use. Furthermore, the microwave devices based on superconducting/ferroelectric (dielectric) heterostructure also demonstrate high tunability and low microwave resistance enabling their application in intelligent communication systems of advanced applications [4–6]. Sol–gel is a common method for industrial thin film preparation due to its low cost, facile doping, and tunable composition control. However, there are few investigations on the preparation of superconducting/ferroelectric (dielectric) films via sol–gel method. In this paper, epitaxially grown superconducting $Ba_{0.09}Sr_{0.91}TiO_3/YBa_2Cu_3O_{7-x}$ (BST/YBCO) heterostructures were prepared via sol–gel method, and the (001)-oriented BST film prepared on LNO by an identical processing was developed for comparison purposes. The tunability of the dielectric property was studied and results verify that the BST deposited on YBCO bottom electrode demonstrated improved dielectric tunability.

2. Experimental

2.1. The preparation of BST films

During the preparation of YBCO via sol–gel method, TFA (Trifluoroacetic Acid) is typically added into the solution to avoid the formation of the barium carbonate phase. However, HF will be released when TFA is heat treated during the elevated temperature process which not only corrodes the substrate but also increases the root mean square roughness of the film's surface. In this study, an independently developed fluoride-free sol–gel YBCO preparation process was utilized to prepare YBCO films. Yttrium acetate, barium acetate, and copper acetate were used as raw materials and dissolved in methanol to prepare a fluoride-free YBCO sol, Barium carbonate phase formation was prevented by supplying water vapor at high temperature, YBCO films with suitable properties were then synthesized. The main reactions are shown in

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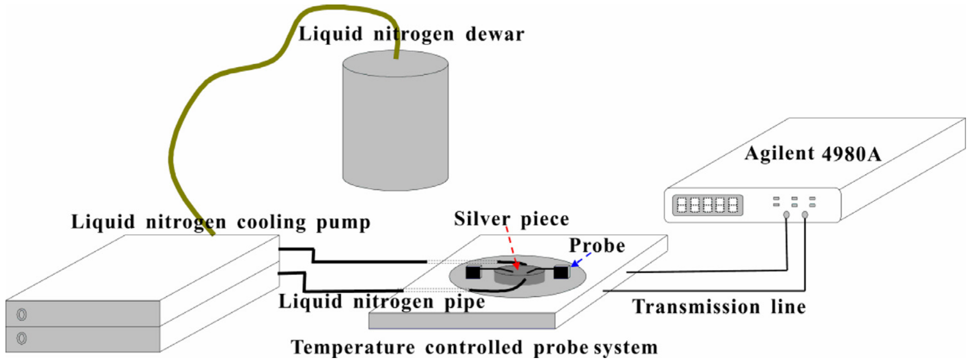

Fig. 1. Diagram of the low temperature measurement system setup.

formula (1) and (2), the detailed preparation method can be found in literature [7].

$$BaCO_3+H_2O \rightarrow Ba(OH)_2+CO_2\uparrow \tag{1}$$

$$4Ba(OH)_2+6CuO+Y_2O_3+xO_2 \rightarrow 2YBa_2Cu_3O_{7-\delta}+4H_2O\uparrow \tag{2}$$

A stable LNO precursor was prepared using lanthanum acetate and nickel acetate as starting materials, acetylacetone (AcAc) as the chemical modifier, and ethanol as the solvent. LNO gel films were held at 750 °C for 20 min (square resistance is less than 50 Ω).

The Curie point of the BST films is a function of the Ba/Sr ratio, which decreases as the content of Sr increases. The BST behaves as a paraelectric material at temperatures above the Curie point and ferroelectric at temperatures below the Curie point. When behaving as a ferroelectric, the existence of the coercive electric field causes dielectric loss of the BST films to dramatically increase. Therefore, as a dielectric tunable film material, the Ba/Sr ratio can be adjusted as required by the application to produce the BST film in the state of paraelectric phase. Moreover, the film possesses improved dielectric tunability as the temperature approaches the Curie point. During low temperature conditions, BST films of Ba/Sr ratio 0.09:0.91 and Curie point of about 80 K [8] (Curie point is different for different preparation methods) can be practically utilized. The detailed preparation method and the heat treatment process are presented herein. Strontium acetate, barium acetate, and tetrabutyl titanate were used as starting materials. Acetylacetone was added to obtain a stable light-yellow BST colloidal solution, the solution concentration was ∼0.5 mol/L. The BST gel films were prepared via dip-coating method followed by drying at 80° for 10 min, and then heat-treatment at 400° for 20 min to allow organic content to fully react in the gel film. The above steps were repeated until a specified thickness was obtained (the thickness of the BST obtained in this study was about 400 nm). Finally, the BST film was heated to 680° for the duration of 1 h to fully crystalize and the BST films were prepared on the YBCO and LNO films by the above heat treatment process.

The superconductivity of $YBa_2Cu_3O_{7-x}$ strongly depends on x, the oxygen vacancy. When x is smaller than 0.5, the structure is orthorhombic possessing superconducting behavior. When x is larger than 0.5, the structure is tetragonal sans superconducting behavior, demonstrating the high dependency of superconductivity on the oxygen content [9–10]. During the high temperature heat treatment process of BST, YBCO produces a large number of oxygen vacancies that degrades its superconducting property. To avoid this phenomenon, an oxygen permeation process of the BST/YBCO and BST/LNO composite films were applied after the preparation of BST films. The detailed process entails a pure oxygen environment at 450–520° for 2 h, effectively reducing oxygen vacancies. The Pt top electrode of 0.2 mm diameter was then sputtered onto the surface of the BST/YBCO and BST/LNO films, in other words, the bottom electrodes were YBCO or LNO and the counter electrodes were Pt.

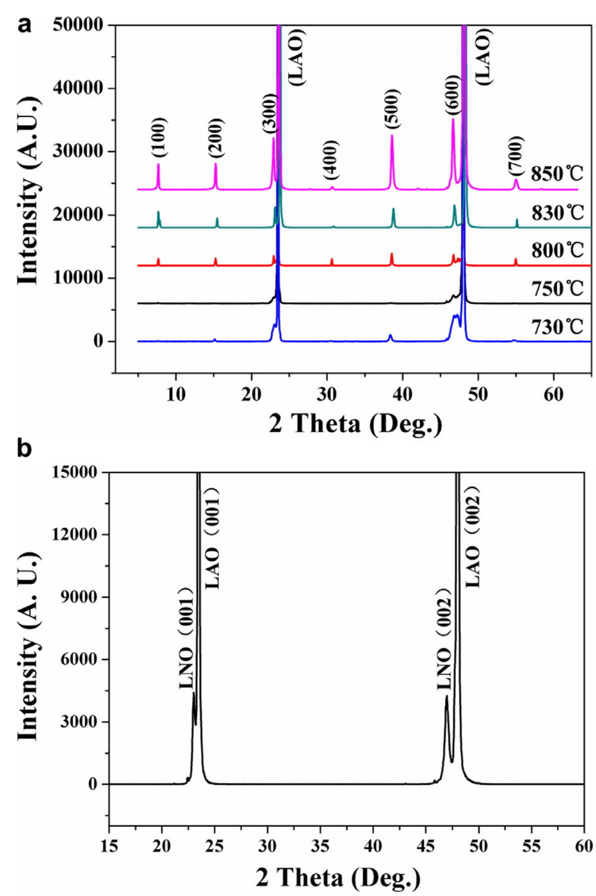

Fig. 2. XRD spectra of YBCO and LNO films. (a) XRD spectra of YBCO films under varying annealing temperatures. (b) XRD spectra of LNO films under 750 °C annealing temperatures.

2.2. Examination of the dielectric property of BST film

The dielectric properties were examined by using an Agilent E4980A LCR meter analyzer. The tunable bias voltage range was −40 V to 40 V and the tunable frequency range was 20 Hz–2 MHz. Test methods can be described as follows: the sample capacitance and the tanδ were measured by Agilent E4980A analyzer at various temperatures, the relative dielectric constant was calculated by formula (3):

$$\varepsilon = \frac{Cd}{\varepsilon_0 S} \tag{3}$$