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Stoichiometry control and structure evolution in hydrothermally derived (Ba,Sr)TiO_3 films

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Abstract

(Ba,Sr)TiO_3 films were synthesized on the titanium metal substrates in solution of $Ba(OH)_2$ and $Sr(OH)_2$ by hydrothermal method. Crystallinity and microstructure of the films changed with time, concentration and temperature. Effects of the mole ratio of barium and strontium in solution on the composition of film have been studied. The barium contents in the BST films are fairly lower than those in the original solutions. This indicates that strontium is more readily incorporated into the BST films, relative to barium. The results of narrow-scan of XPS spectrum confirm that the valences of Ba, Sr, Ti and O elements of hydrothermally prepared BST films are +2, +2, +4, and −2, respectively. SEM photographs show that the BST films are dense and well-compact. AFM analyses show that the average surface roughness of the films is 40–50 nm. It is concluded that BST films of different mole ratio of barium and strontium with thickness of up to 2 μm have been prepared successively by the environmentally benign hydrothermal method.

Keywords: Barium strontium titanate; Hydrothermal syntheses; Ceramic films

1. Introduction

The film of perovskite barium strontium titanate (Ba,Sr)-TiO_3 (BST) is an important material in the electronics industry due to its high dielectric constant and ferroelectric properties. It is among the most promising candidates for dynamic random access memories (DRAMs) and other integrated capacitors [1–3]. A variety of techniques including sol–gel, metal organic chemical vapor deposition (MOCVD), pulsed laser deposition sputtering and electrophoretic deposition have been used to prepare (Ba,Sr)TiO_3 films. Almost all these methods require high temperature to get crystalline films. Use of high temperature to deposit or heat-treat the films not only causes compatibility problems with silicon technology, but also induces thermal stress in the films. In order to overcome these problems, fabricating ceramic films at lower temperature such as hydrothermal and electrochemical methods are gaining more attention. $BaTiO_3$, $SrTiO_3$ and (Ba,Sr)TiO_3 films have been prepared by hydrothermal, electrochemical and so-called hydrothermal–electrochemical methods [4–6]. Electrochemical and hydrothermal–electrochemical processes have been widely studied due to its advantages of rapid speed and lower reaction temperature. Unfortunately the films are less crystallized and easy to form inhomogeneities and cracks due to breakdown under increased voltages [7–9]. Unlike electrochemical method, hydrothermal process causes fewer cracks and can be performed on any kind of substrates deposited with titanium metal. (Ba,Sr)TiO_3 films have been fabricated on both titanium substrates or metal-organic precursor deposited glass substrates by hydrothermal method [10,11]. The ability to produce BST films of various compositions and thickness via hydrothermal synthesis is of particular interest, but the processing parameters have not been well understood till now. Detailed researches have been done on the influential factors of hydrothermal synthesis of BST films through metal-organic precursor [10]. However, no systematic studies are

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available on the hydrothermal formation of $(Ba,Sr)TiO_3$ films on titanium substrates. Little work has been done on control over hydrothermal solutions conditions, such as composition, pH value and temperature, etc. On the other hand, chemical considerations such as stoichiometry control and structure evolution have received less attention.

The purposes of the present work are to systematically analyze the effects of processing parameters on the stoichiometry and structure evolution of the hydrothermal derived BST films. Here are reported studies on the various conditions under which $(Ba,Sr)TiO_3$ films can be prepared. The influences of the concentration of barium and strontium ions, reaction temperature and time on $(Ba,Sr)TiO_3$ crystallinity and microstructures have been studied.

2. Experimental procedure

Hydrothermal syntheses of $(Ba,Sr)TiO_3$ films were carried out using a 0.1 dm^3 high-pressure autoclave. Prior to hydrothermal syntheses, titanium substrates with purity more than 99.9% and dimension of 7 mm × 14 mm × 0.5 mm were mechanically polished to a mirror finish. Experiments were performed in the mixture of $Ba(OH)_2$ and $Sr(OH)_2$ (analytical purity) solutions of different concentrations. The solutions were prepared with deionized water previously boiled for at least 30 min to eliminate dissolved CO_2. The titanium substrates were clamped in a Teflon cushion uprightly. Then the Teflon cushion was put into the bottom of Teflon beaker. 0.05 dm^3 mixture of Ba $(OH)_2$ and $Sr(OH)_2$ solution was poured into the beaker, which was immediately put in the high-pressure autoclave. The autoclave was sealed at once and put into oven at suitable temperature. After hydrothermal reaction the samples were taken out of the beaker, rinsed with CO_2-free deionized water for three times and dried for characterization.

The surface morphologies of the samples were investigated both by scanning electron microscopy (SEM) (JSM-6301, JEOL Inc., Japan) and by atomic force microscopy (AFM) (Picoscan, Molecular Imaging, USA). X-ray diffraction measurements were performed on D/max-RB diffractometer (Rigaku, Rotafles). X-ray photoelectron spectroscopy (XPS) analysis was conducted on AEM PHI5300 spectrometer using Al Kα (1468.6 eV) radiation.

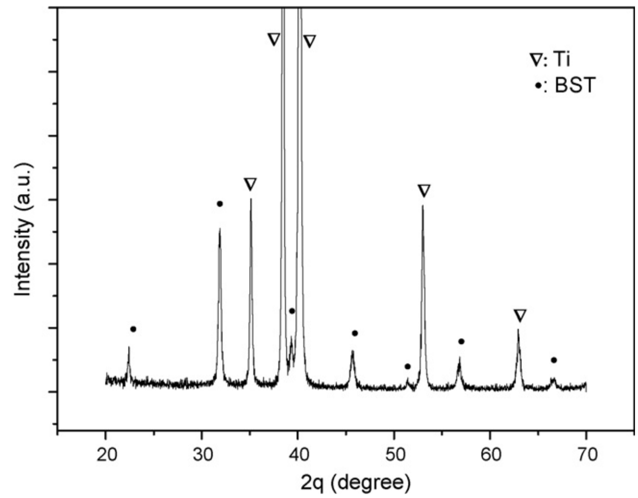

Fig. 1. X-ray pattern of BST films prepared by hydrothermal method.

3. Results and discussion

3.1. Effects of reaction conditions on the crystallinity of BST film

The typical X-ray diffraction pattern of BST films obtained by hydrothermal method is given in Fig. 1. The diffraction pattern shows the presence of crystalline cubic BST without any preferred orientation.

The crystallinity of the films alters with reaction time, temperature and concentration of solutions. Following related Refs. [12–14], a qualitative estimate of the crystallinity is obtained by taking the ratio of the intensity of BST (1 0 1) reflection to that of Ti (0 1 1). According to this criterion, the crystallinity of BST films prepared at different conditions is given in Fig. 2.

From Fig. 2 it is found that the crystallinity of the films altered with time, concentration and temperature. The crystallinity increases along with the increasing temperature and concentration. Along with the increasing of time, the crystallinity increases first, reaches the maximum value and then decreases. Reasons of the decrease of crystallinity at longer time are not very clear now. Preliminary analysis points to side reaction or dissolution of BST films in the mixture of $Ba(OH)_2$ and $Sr(OH)_2$ solution [13,15].

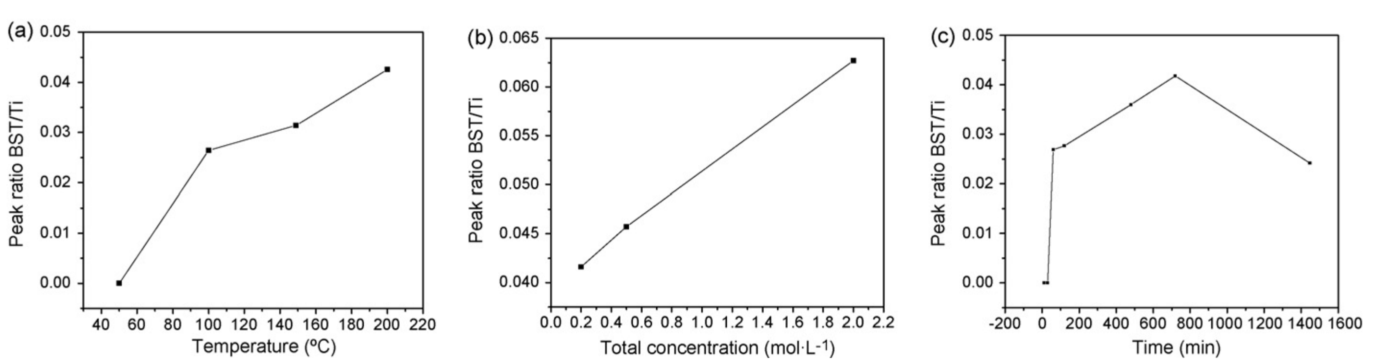

Fig. 2. Crystallinity of BST films at different conditions. (a) Crystallinity vs. temperature; (b) crystallinity vs. total concentration of alkaline earth metal ion; (c) crystallinity vs. reaction time.