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Different microstructure and dielectric properties of $Ba_{1-x}Ca_xTiO_3$ ceramics and pulsed-laser-ablated films

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Abstract

A comparative study of the microstructure and dielectric properties between $Ba_{1-x}Ca_xTiO_3$ (BCT) ceramics and films were performed in the whole Ca concentration range of $x = 0$–1. The ceramics were prepared by conventional solid-state reaction technique and the films by the method of pulsed-laser deposition. X-ray diffraction (XRD) study of the BCT ceramics exhibited a pure tetragonal phase for $x = 0$–0.25, a tetragonal–orthorhombic diphase for $x = 0.25$–0.85 and a pure orthorhombic phase for $x = 0.90$–1.00. And the dielectric phase transition temperature from tetragonal to cubic was marginally affected by the Ca doping into $BaTiO_3$. However, BCT films deposited on $Pt/Si/SiO_2/Si$ substrates showed a different microstructure and dielectric properties. Tetragonal–orthorhombic diphase was not found in the BCT films for $x = 0.25$–0.85, and a large decrease of the Curie point and diffuse phase transition were observed in the BCT films. Based on the compositional analysis, such phenomena were ascribed to the occupancy of some Ca^{2+} to the Ti^{4+} sites in the BCT films.

Keywords: A. Ceramics; A. Thin films; B. Laser deposition

1. Introduction

Ferroelectric materials have been applied to many electronic and optical devices, utilizing their excellent dielectric, piezoelectric and optical properties. Specially, $BaTiO_3$ and isovalent-substituted $BaTiO_3$ are the promising candidates and have been actively studied. Among them, Ca doped $BaTiO_3$ ($Ba_{1-x}Ca_xTiO_3$, BCT) crystals are considered to be one of the foremost potential candidates for the lead-free electro-optic modulators and memory devices [1]. And the BCT ceramics near the solubility limit of $x = 0.23$ have shown high electrostrictive strain of 0.22% at an electric field of 50 kV/cm [2].

Microstructure and dielectric properties of BCT ceramics prepared by conventional solid-state reaction technique have been reported by several workers [2–8]. It has been found that Ca^{2+} replaces Ba^{2+} in $BaTiO_3$ to form tetragonal BCT solid solutions when x is less than 0.23. Above the solubility limit of $x = 0.23$, the ceramics are in diphasic coexistence and composed of tetragonal $Ba_{0.8}Ca_{0.2}TiO_3$ solid solution and orthorhombic $Ba_{0.07}Ca_{0.93}TiO_3$ solid solution. This insolubility region extended to $x = 0.90$, and above this limit orthorhombic $CaTiO_3$-based solid solutions were formed. This effect is quite puzzling, since other similar elements, like Sr^{2+} and Pb^{2+}, can replace Ba^{2+} in $BaTiO_3$ to form solid solutions without insolubility limitation.

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Modern micro-devices require high-performance materials in the form of films with thickness in the range of a few hundred and even tens of nanometers. However, the reports on the BCT films are lack in open literature. Victor et al. [9] reported the microstructure and dielectric properties of the BCT thin film with x between 0.05 and 0.17, and found that the films showed quite different dielectric behaviors from those of the corresponding ceramics. To the best of our knowledge, no detailed structural and dielectric studies have been reported for the BCT films in the whole Ca concentration (x = 0–1). In this paper, we report on a comparative study of the microstructure and dielectric properties between BCT ceramics and films in the whole Ca concentration range of x = 0–1.

2. Experiment

BCT ceramics with x between 0 and 1 were prepared by conventional solid-state reaction technique. High-purity starting powders of $BaCO_3$, TiO_2 and $CaCO_3$ were mixed with addition of alcohol, ball-milled for 10 h, then dried and heated at 900 °C for 4 h in air. After that, they were remixed and pressed into disk-shaped pellets with 10 mm in diameter, and finally sintered at 1400 °C for 4 h. The sintered pellets were polished to near 0.7 mm in thickness and the silver paste was coated on both sides as electrodes. BCT films were deposited onto the $Pt/Si/SiO_2/Si$ substrates by a 248 nm KrF excimer pulsed laser (Lambda Physik 105i) with an energy density of 1.6 J/cm^2 using the above ceramics as targets. During the deposition, the substrate temperature was maintained at 700 °C and the laser frequency was 5 Hz. The base pressure was initially pumped down to 2.0×10^{-3} Pa and then high-purity oxygen gas was introduced into the chamber to a pressure of 20 Pa prior to the deposition. The thicknesses of all the BCT films were about 450 nm as measured by an ET350 Talysurf profilometer (Kosaka Laboratory Ltd.). For carrying out the electrical measurement, Pt dots of 0.28 mm in diameter were deposited onto the films at room temperature through a shadow mask by a radio-frequency sputtering technique. The temperature-dependence of the dielectric properties was measured by a HP4284 LCR meter in a computer-controlled Delta 9023 oven. The frequency dependence of the dielectric properties was measured by a HP4294A impedance analyzer. The ceramics and films were structurally characterized by a Rigaku D/MAX 3C X-ray diffraction (XRD). Scanning electron microscopy (SEM) of Hitachi S-4700 was used for the observation of the microstructure of the film surface. The composition of the element in targets and films were identified using energy-dispersive spectrometry (EDS) attached to a SEM of Hitachi S-4700 and X-ray photoelectron spectroscopy (PHI-550 Photoelectric Spectrometer, XPS).

3. Results and discussions

The typical microstructure of the BCT ceramics (x = 0, 0.5 and 1.0) is shown in Fig. 1(a). All the patterns show a polycrystalline perovskite nature without impurity phases. The pure $BaTiO_3$ ceramic shows a tetragonal phase with a distinct tetragonal splitting at (0 0 2)/(2 0 0), while the pure $CaTiO_3$ ceramic is an orthorhombic phase, as identified and indexed using the standard XRD data of the corresponding powder. In $Ba_{0.5}Ca_{0.5}TiO_3$ ceramic, the tetragonal and orthorhombic phases were coexisted. The peaks marked ''*'' in Fig. 1(a) are related to the tetragonal Ba-rich phase and the ones marked ''#'' to the orthorhombic Ca-rich phase. Fig. 1(b) shows the refined XRD patterns of BCT ceramics with different x from 0 to 1 near the tetragonal strongest peak (1 1 0) and orthorhombic strongest peak (1 2 1). The structures of the ceramics were determined to be a pure tetragonal phase for x from 0 up to 0.25, tetragonal and orthorhombic phase coexistence for x = 0.30–0.85, and a pure orthorhombic phase for x = 0.90–1.00. The results are similar to those reported [2]. However, the solubility limit for Ca addition in $BaTiO_3$, which is between 0.25 and 0.3, increased a little, and that within 0.85 and 0.9 for Ba addition in $CaTiO_3$ decreased a little, comparing with those reported (x = 0.23 and 0.93, respectively). This may be due to the different processes in the fabrication of the ceramics.

The XRD patterns for the BCT films (x = 0, 0.5 and 1.0) are presented in Fig. 2(a). It can be seen that the XRD results for the BCT films are different from those of the corresponding ceramics. The BCT films did not show a distinct tetragonal splitting when x is equal to 0 or 0.5. For pure $BaTiO_3$ film the lattice parameters were determined to be $a = b$ = 3.995 Å and c = 4.034 Å, which are in agreement with the PDF card, and compare well with $a = b$ = 3.995 Å and c = 4.034 Å as measured by Mitsui and Westphal [6]. So the pure $BaTiO_3$ film is still in tetragonal phase at room temperature, although the tetragonal splitting was not observed in the XRD pattern, which can be due to the grain size or substrate–film interface effect.

From Fig. 2(a), we also found that the double peaks near 32.3° corresponding to the tetragonal Ba-rich (1 1 0) peak and orthorhombic Ca-rich (1 2 1) peak in the BCT ceramics were not observed in the corresponding films with x