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Influence of crystallization on the spectral features of nano-sized ferroelectric barium strontium titanate ($Ba_{0.7}Sr_{0.3}Tio_3$) thin films

S. Bobby Singh*, H.B. Sharma, H.N.K. Sarma, Sumitra Phanjoubam

Department of Physics, Manipur University, Imphal 795003, Manipur, India

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Abstract

Ferroelectric barium strontium titanate ($Ba_{0.7}Sr_{0.3}TiO_3$)(BST) thin films have been prepared from barium 2-ethylhexanoate [$Ba[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2$], strontium 2-ethylhexanoate [$Sr[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2$] and titanium(IV) isopropoxide [$TiOCH(CH_3)_2]_4$ precursors using a modified sol–gel technique. The precursor except [$TiOCH(CH_3)_2]_4$ were synthesized in the laboratory. Transparent and crack-free films were fabricated on pre-cleaned quartz substrates by spin coating. The structural and optical properties of films annealed at different temperatures have been investigated. The as-fired films were found to be amorphous that crystallized to the tetragonal phase after annealing at 550 °C for 1 h in air. The lattice constants "*a*" and "*c*" were found to be 3.974 A and 3.990 A, respectively. The grain sizes of the films annealed at 450, 500 and 550 °C were found to be 30.8, 36.0 and 39.8 nm respectively. The amorphous film showed very high transparency (~95%), which decreases slightly after crystallization (~90%). The band gap and refractive index of the amorphous and crystalline films were estimated. The optical dispersion data are also analyzed in the light of the single oscillator model and are discussed.

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Keywords: Sol–gel; Ferroelectric films; Refractive index and band gap

1. Introduction

Ferroelectric thin films have found wide applications in many electronic and electro-optic devices [1–5]. Among these materials, barium strontium titanate (BST) is currently one of the most interesting ferroelectric materials due to its high dielectric constant, low dielectric loss, high transparency and composition-dependent Curie temperature (from 30 to 400 K)[6–8]. The BST thin films can be used in non-linear optical devices such as planar wave guides or optical switches with minimal optical propagation losses [9,10]. Various deposition techniques such as sputtering [11], metallo-organic chemical vapordeposition (MOCVD) [12], pulsed laser deposition (PLD) [13], sol–gel process [14], etc. have been employed for the fabrication of BST thin films. Compared to other deposition methods, sol–gel process offers many advantages, such as homogeneity, easy stoichiometry control, low-cost equipment and ability to coat large area and complex-shaped area substrates [15]. In majority of the reports, crystalline films were obtained at relatively high annealing temperatures (~700 °C). The lowering of temperature is a challenging task for integration of the ferroelectric thin films with other devices. Also, very recently enhancement of the second-harmonic generation (SHG) efficiency has been observed in nanocrystallites of ferroelectric $Sr_6Ti_2Nb_8O_{30}$ and $Sr_6Ti_2Ta_8O_{30}$ [16]. Thus the study on the effects of crystallite sizes on the optical properties of nanocrystalline ferroelectric thin films will open an era in their wide applications. In this paper, we report the processing of BST films at relatively low temperature (~550 °C) using a modified sol–gel processing technique. We also report the influence of crystallization on the optical properties of nano-sized BST thin films.

*Corresponding author.
E-mail address: bsoram@rediffmail.com (S. Bobby Singh).

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2. Experimental procedure

2.1. Synthesis of precursors

In the sol–gel processing technique, precursors play a very important role in determining the quality of the deposited films. Metal-alkoxides and metal-salts are among the most commonly used sol–gel precursors for the preparation of the films. Undoubtedly, the metal alkoxides are assumed to be the best precursors as they are very reactive and easy to form complexes. However, unequal hydrolysis rates of different metal alkoxides and their low solubility make them unsuitable for multicomponent ferroelectric oxide films such as BST. In this study we made an attempt to use a new type of precursors, namely barium 2-ethylhexanoate $[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2Ba$, strontium 2-ethylhexanoate $[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2Sr$ and titanium (IV) isopropoxide $[TiOCH(CH_3)_2]_4$ as the source of materials for Ba, Sr and Ti, respectively.

Barium 2-ethylhexanoate and strontium 2-ethylhexanoate were synthesized in the laboratory by reacting the barium hydroxide $[Ba(OH)_2]$ and strontium hydroxide $[Sr(OH)_2]$ with 2-ethylhexanoic acid $[CH_3(CH_2)_3CH(C_2H_5)COOH]$ in an alcohol medium according to the following reaction:

$$Ba(OH)_2 + 2CH_3(CH_2)_3CH(C_2H_5)COOH \rightarrow Ba[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2 + H_2O \quad (1)$$

$$Sr(OH)_2 + 2CH_3(CH_2)_3CH(C_2H_5)COOH \rightarrow Sr[CH_3(CH_2)_3CH(C_2H_5)CO_2] + H_2O \quad (2)$$

Titanium (IV) isopropoxide $[TiOCH(CH_3)_2]_4$ was imported from Sigma Aldrich Pvt. Ltd., USA.

2.2. Processing of BST thin films

Desired amounts of barium 2-ethylhexanoate and strontium 2-ethylhexanoate were first dissolved in ethanol (C_2H_5OH) and then refluxed at 60 °C for half an hour. The refluxed solution was then cooled down to room temperature. An equimolar amount of titanium (IV) isopropoxide was added drop wise to the above solution, constantly stirring it. Acetylacetone and formamide were added to the above mixture in order to increase the stability of the solution and to control the rate of pyrolysis. The viscosity of the solution was controlled by the ethanol content. The solution was then filtered using a glass microfibre filter paper. The filtered solution was spin coated onto precleaned quartz substrates at 3000 rpm for 20 s using a photo-resist spinner. The coated film was then fired at 350 °C in air for 10 min to eliminate the residual solvent and organic groups. The thickness of the as-fired single-coated film was about 0.154 μm. Thin film of desired thickness was prepared by repeating the deposition–pyrolysis cycle. The samples were annealed at different temperatures, 350, 450, 500 and 550 °C in air for 1 h. These samples will be, respectively, called as BS1, BS2, BS3 and BS4 hereafter. X-ray diffraction (XRD) and scanning electron microscopy studies were using conducted a Phillips X-ray diffractometer and a Jeol (model JSM-840) scanning electron microscope. The optical property was investigated using a Perkin Elmer Lambda-35 UV–visible spectrophotometer.

3. Result and discussion

3.1. Structural properties

The thickness of the as-fired single-coated film was found to be 0.154 μm, which increases linearly with the increase in the number of coatings. The thickness of the film shows a slight decrease after annealing at 550 °C. The as-fired film was found to be amorphous. At the low annealing temperature (BS1) a glassy amorphous film was formed as a result of the densification of the spin-coated film related to the elimination of residual solvents and organic groups. Fig. 1 shows the XRD pattern of four samples BS1, BS2, BS3 and BS4. As evident from Fig. 1, the onset temperature for crystallization was 450 °C (BS2). The films were crystallized to the polycrystalline phase after annealing at 550 °C (BS4).

The lattice constants of the film were calculated from the XRD pattern of Fig. 1 and were found to be $a = b = 3.974$ Å and $c = 3.990$ Å, showing a tetragonal structure. The error in the estimation of the lattice constant was about ± 0.004 and was reproducible within the data limit. Similar results have been observed by earlier workers [17–20].

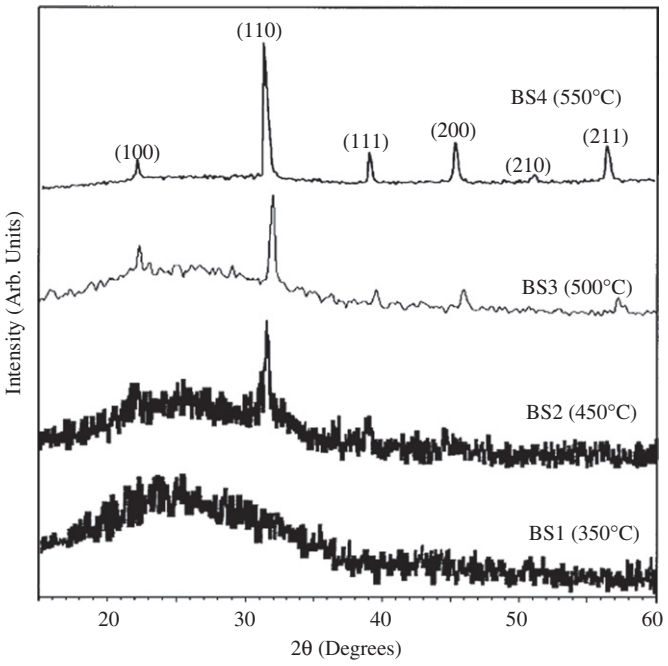

Fig. 1. X-ray diffraction of BST thin films annealed at four different temperatures.