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Dielectric properties of lead zirconate titanate thin films seeded with barium strontium titanate nanoparticles

Tomokazu Tanase[a], Yoshio Kobayashi[a], Toshihide Nabatame[b], Takao Miwa[c], Mikio Konno[a,*]

[a] Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 07 Aoba, Aramaki-aza, Aoba, Sendai 980-8579, Japan
[b] Process Development Department, Renesas Technology Corp., Horiguchi, Hitachinaka, Ibaraki 312-8504, Japan
[c] Hitachi Research Laboratory, Hitachi, Ltd., Omika, Hitachi, Ibaraki 319-1292, Japan

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Abstract

A low temperature synthetic method recently proposed by the authors was applied to the fabrication of lead zirconate titanate (PZT) thin films containing crystalline seeds of barium strontium titanate (BST) nanoparticles. PZT precursor and the BST particles were prepared with complex alkoxide methods. Precursor solution suspending the BST particles was spin-coated on $Pt/Ti/SiO_2/Si$ substrate to film thickness of 500–800 nm at particle concentrations of 0–25.1 mol%, and annealed at various temperatures. Seeding of BST particles prevented the formation of pyrochlore phases, which appeared at temperatures above 400 °C in unseeded PZT films, and induced crystallization of PZT into perovskite structures at 420 °C, which was more than 100 °C below the crystallization temperature of the unseeded PZT films. Measurement of dielectric properties at 1 kHz showed that the 25.1 mol% BST-seeded PZT films annealed at 450 °C had a dielectric constant as high as 300 with a dissipation factor of 0.05. Leakage current density of the film was less than 1×10^{-6} A/cm^2 at applied electric field from 0 to 64 kV/cm.

Keywords: Lead zirconate titanate; Crystalline seeds; Crystallization temperature; Dielectric properties

1. Introduction

Ferroelectric thin films of lead zirconate titanate (PZT) are promising materials for high dielectric capacitors, pyroelectric sensors and non-volatile memories [1]. It has been reported that the crystal phase of ferroelectric barium titanate (BT) or lead titanate (PT) transformed from tetragonal to cubic and ferroelectric property disappeared for the grain sizes smaller than 1 μm [2]. Accordingly, much attention has been paid to a paraelectric property of PZT films for an application of high dielectric capacitors with the grains smaller than a critical value for the transformation. PZT films can be prepared by several methods such as metalorganic chemical vapor deposition (MOCVD) [3,4], pulsed laser deposition (PLD) [5], rf-sputtering [6,7] and sol–gel [8–11]. Since the sol–gel method has features of easy composition control, low temperature processing and easy attainment of high-purity [12], this method is receiving increasing attention as a good candidate for future processes.

However, as-prepared sol–gel PZT films generally have amorphous structures and require high temperature annealing for crystallization into the perovskite phase to produce high dielectric properties. Lowering of the annealing temperature is desired to reduce thermal stress, volatilization of PbO, interdiffusion between the PZT film and electrode/substrate and to prevent electric devices from thermal damage.

To lower the crystallization temperature, extensive work has been made that includes rapid heating or high pressure annealing of the amorphous films, interlayer deposition between substrate and film, and the use of materials with appropriate lattice parameters similar to those of the crystalline PZT [13,14]. Recently, the present authors studied seeding effects on the crystallization behavior of PZT with the use of barium strontium titanate (BST) crystalline

* Corresponding author. Tel.: +81-22-217-7239; fax: +81-22-217-7241.
E-mail address: konno@mickey.che.tohoku.ac.jp (M. Konno).

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particles [15]. X-ray analysis made in that work showed that crystallization temperatures could be lowered by the addition of BST particles as the seeds. The present work aims at measuring dielectric properties of the PZT films seeded with BST nanoparticles. The films were prepared following the low temperature synthesis in the previous work. Measurements were performed on the structures, dielectric constant and dissipation factor of the films.

2. Experimental details

2.1. Materials

Starting reagents were metallic barium (Kanto Chemical), strontium (Kanto Chemical), tetraethylorthotitanate (TEOT) (Tokyo Kasei Kogyo, 97%), lead (II) acetate (Kojundo Chemical Lab., 99.999%), zirconium (IV) butoxide (Wako, 85% 1-butanol solution) and titanium tetraisopropoxide (Wako, 99%). Special grade reagents (Wako) of ethanol (99.5%), benzene (99.8%), 2-methoxyethanol (99.0%) and acetyl acetone (99.0%) were used as solvent. All the chemicals except for ethanol were used as received. Ethanol was dehydrated by the Lund-Bjerrum method [16]. Pt/Ti/SiO_2/Si substrate (Pt substrate) prepared by Hitachi was used as a substrate electrode. Water was distilled and deionized to have an electric resistance higher than 18 MΩ cm^{-1}.

2.2. Synthesis of BST ($Ba_{0.5}Sr_{0.5}Ti_1O_3$) nanoparticles

A complex alkoxide solution of barium–strontium–titanium was prepared as the precursor of BST particles. At first, a solution (0.1 dm^3) that dissolved metallic barium (5 mmol) and strontium (5 mmol) in a 50% (v/v) ethanol/benzene cosolvent was refluxed at 73 °C for 1 h to form a double alkoxide. Then, TEOT (10 mmol) was added to the solution, and refluxed for 2 h, which yielded a transparent complex triple alkoxide. To hydrolyze the complex alkoxide, an ethanol/water mixture (0.1 dm^3, 20 $kmol/m^3$ water) was added to an equal volume (0.1 dm^3) of the complex alkoxide solution. The mixed solution was stored at 70 °C for 5 h to age. The solution turned opaque indicating the formation of BST particles.

2.3. Preparation of BST-seeded PZT ($Pb_1Zr_{0.5}Ti_{0.5}O_3$) thin film

For the preparation of a PZT complex alkoxide solution, lead acetate anhydride, zirconium (IV) butoxide and TEOT were dissolved in a 2-methoxyethanol/acetylacetone mixture at a molar ratio of 1:0.5:0.5 and a total concentration of 1.0 $kmol/m^3$. This mixture was refluxed at 120 °C for 24 h to form a brownish PZT complex alkoxide, which was mixed with the BST particles that was washed with a 2-methoxyethanol/acetylacetone mixture. The molar ratio of BST to PZT ranged from 3.9 to 25.1 mol% in the BST suspension at a total concentration of Pb, Zr and Ti. The BST suspension was spin-coated onto a Pt electrode at 2000 rpm for 30 s and dried at 200 °C for 1 min. The spin-coating drying processes were repeated five times. Total thicknesses of the films were from 500 to 800 nm depending on the BST concentration. The films fabricated were heated in air at 380–540 °C for 1 h. The annealing temperature was programmed to increase from 20 °C to the intended temperature at 7 °C/min, and held at that temperature for 1 h, and then cooled down to 200 °C at 3 °C/min.

2.4. Measurements

BST particles and the films were characterized by transmission electron microscopy (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD). TEM photographs were taken with a Zeiss LEO 912 OMEGA microscope operated at 100 kV. Samples for TEM were prepared by dropping and evaporating the particle suspensions on a collodion-coated copper grid. The samples were sputtered with Pt–Pd and observed with SEM (Zeiss LEO 1420 microscope) operated at 15 kV. X-ray diffraction measurements (Rigaku RU-200A) were carried out at 40 kV and 30 mA with CuKα radiation using a monochromator. For powder XRD measurement, the BST colloid was centrifuged to remove supernatant and then the residue was dried at 50 °C for 24 h in vacuum.

To measure electrical properties, a Pt-electrode was patterned on top of the films with sputtering. The films were annealed at 350 °C for 1 h in 100% O_2 to remove sputtering damage. Dielectric constant and dissipation factor of the films were measured with an NF Electronic Instruments 2322 LCZ meter. Leakage current density of the films was measured with a Hewlett-Packard 4142B impedance analyzer.

3. Results and discussion

3.1. Crystallization behavior of PZT thin film

The TEM image and XRD pattern of BST particles are shown in Figs. 1 and 2. Most of the BST particles had sizes of less than 100 nm. All the peaks were attributed to perovskite cubic BST with the crystallite size of 24 nm estimated from Scherrer equation using the broadening of the (111) plane diffraction peak. This size is close to that of the BST particle observed by TEM image, which suggested that the each BST particle probably consisted of a single crystal. The lattice constant of the BST particles calculated from the XRD was 0.396 nm, which was close to a reported value (0.395 nm) in the literature [17].

Fig. 3 shows the XRD patterns of the seeded and unseeded PZT films annealed at various temperatures. The unseeded film at each annealing temperature had a peak at $2\theta = 29.4°$ ($d = 0.304$ nm) that was assigned to the pyrochlore phase of PZT. Peak intensity of the pyrochlore phase