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Enhanced dielectric tunability properties of $Ba(Zr_xTi_{1-x})O_3$ thin films using seed layers on $Pt/Ti/SiO_2/Si$ substrates

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Abstract

The compositionally graded and homogeneous $Ba(Zr_xTi_{1-x})O_3$ (BZT) thin films were fabricated on $LaNiO_3$ (LNO) buffered $Pt/Ti/SiO_2/Si$ and $Pt/Ti/SiO_2/Si$ substrates by a sol–gel deposition method, respectively. These films crystallized into a single perovskite phase. The BZT thin films deposited on $LaNiO_3/Pt/Ti/SiO_2/Si$ substrates had a highly (1 0 0) preferred orientation and exhibited a preferred (1 1 0) orientation when the thin films were deposited on $Pt/Ti/SiO_2/Si$ substrates. The LNO and $Ba(Zr_{0.30}Ti_{0.70})$ served as seed layer on $Pt/Ti/SiO_2/Si$ substrates and analyze the relationship of seed layer, microstructure and dielectric behavior of the thin films. The compositionally graded thin films from $BaTiO_3$ to $BaZr_{0.35}Ti_{0.65}O_3$ were fabricated on $LNO/Pt/Ti/SiO_2/Si$ substrates. The tunability behavior of compositionally graded films was analyzed in order to produce optimum effective dielectric properties. The dielectric constant of $BaZr_xTi_{1-x}O_3$ compositionally graded thin films showed weak temperature dependence. This kind of thin films has a potential in a fabrication of a temperature stable tunable device.

Keywords: A. Sol–gel processes; A. Films; C. Dielectric properties; Microstructure

1. Introduction

The large electrical field dependent dielectric constant can be used for tunable microwave devices, such as phase shifters, tunable oscillators, tunable filters and varactors. In such devices, it is desirable to have a high dielectric tunability over a given electric field range, a low dielectric loss and high Q value. Commonly, the studies in this field are mainly focused on the $Ba_xSr_{1-x}TiO_3$ (BST) system [1–4].

There are a large number of lead-free $BaTiO_3$-based ceramics and thin films with different composition, some of which exhibit a relax behavior with characteristics related to the type of ionic substitutes and substitution rate [5–8]. Barium zirconium titanate $Ba(Zr_xTi_{1-x})O_3$ (BZT) is obtained by substituting ions at the B site of the $BaTiO_3$ with Zr in compounds of the perovskite structure ABO_3. Depending on the amount of zirconium (Zr) substitution in $BaTiO_3$, it behaves as a ferroelectric or a relaxor [9]. It is reported that an increase in the Zr content induces a reduction in the thin films grain size and dielectric constant, and maintains the leakage current low and stable [5,8].

In the last few years, BZT ceramics has been used as a dielectric material in multi-layer ceramic capacitors (MLCC) and is of considerable interest for use as a new ferroelectric material for the dynamic random access memory (DRAM) and the piezoelectric transducer [5,10,11] in the future and more currently in tunable microwave applications due to their high dielectric constant, relatively low dielectric loss, leakage current and their tunable dielectric properties [12,13]. However, their tunable dielectric properties and the relationships of the orientation and seed layer effect were rarely investigated.

In the present investigation, an improvement in dielectric properties was achieved by the insertion of seed layers between the BZT and bottom electrode. The $LaNiO_3$ (LNO) and $Ba(Zr_{0.30}Ti_{0.70})$ thin films were as seed layer on $Pt/Ti/SiO_2/Si$ substrates. The use of LNO seed layer provides bottom electrode and an excellent template facilitating the grain-on-grain growth so that highly oriented BZT thin films with much improved properties are realized. In order to improve temperature stability from the compositionally graded thin films along with improved tunability, the compositional gradient thin films from $BaTiO_3$ to $BaZr_{0.35}Ti_{0.65}O_3$ were

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fabricated on LNO/Pt/Ti/SiO_2/Si substrates. The relationship of seed layer, microstructure and dielectric behavior of the thin films were studied. The tunability behavior of graded films was analyzed in order to produce optimum effective dielectric properties.

2. Experimental procedure

The barium acetate [$Ba(CH_3COO)_2$] (99%, Sigma–Aldrich), [$Zr(OC_3H_7)_4$] (99.9% Aldrich), and [$Ti(OC_3H_7)_4$] (98%, Aldrich) were used as starting materials. Acetic acid was used as solvent. The details of the preparation of BZT solution have been described in our early publication [14]. The concentration of the final solution was adjusted to about 0.3 M. The LNO layer was deposited on platinumized Si substrates using the magnetron sputtering technique [15]. The thicknesses of the $LaNiO_3$ (LNO), Pt, Ti, and SiO_2 were 150, 150, 50, and 150 nm, respectively.

The seed layer of $Ba(Zr_{0.30}Ti_{0.70})$ was deposited on Pt/Ti/SiO_2/Si substrates by sol–gel processing. The concentration of the solution was adjusted to about 0.1 M. Pyrolysis and heat treatment were carried out in an air muffle furnace at 700 °C for 10 min for each spun-on coating. The different seed layer thickness was achieved by repeated spin coating–drying–annealing process. The different BZT seed layer thicknesses of 0, 10, 20, 30 and 90 nm were obtained, respectively.

After aging the hydrolyzed solution for 24 h, the homogeneous $Ba(Zr_xTi_{1-x})O_3$ (BZT) thin film was carried out on the $LaNiO_3$/Pt/Ti/SiO_2/Si(1 0 0) and $Ba(Zr_{0.30}Ti_{0.70})$/Pt/Ti/SiO_2/Si(1 0 0) substrates by spin coating at 3000 rpm for 30 s each layer, respectively. Each spin coated BZT layer was subsequently heat treated at 500 °C for 5 min. The coating and heat treatment procedures were repeated several times until the desired thickness was reached. A final anneal in flowing O_2 (decrease leakage current) at high temperature of 700 °C for 30 min crystallize the amorphous films. The total film thickness of BZT was about 480 nm.

Compositionally graded $BaZr_xTi_{1-x}O_3$ thin films were formed on the LNO/Pt/Ti/SiO_2/Si substrate by sequentially depositing three layers of each composition (sequence: $BaZr_{0.35}Ti_{10.65}O_3$, $BaZr_{0.18}Ti_{0.82}O_3$, $BaZr_{0.09}Ti_{0.91}O_3$, $BaTiO_3$). Pyrolysis and adequate heat treatment were carried out in an air muffle furnace at 500 °C for 10 min for each spun-on coating. A final anneal in flowing O_2 at high temperature of 700 °C for 30 min. The compositionally graded thin film with Zr/Ti ratio varying from $BaZr_{0.35}Ti_{0.65}O_3$ at the substrate to $BaTiO_3$ at the top surface was formed in this study. The total thickness was about 680 nm.

The crystalline phase of the thin films was identified by X-ray diffraction (SIEMENS D-500 powder diffractometer). The film thickness and the surface morphology were determined by Field Emission Scanning Electron Microscope (FESEM). For electrical measurements the top gold electrode of a 200 μm square was deposited by DC-sputtering. Current–voltage (*I*–*V*) characteristics were measured using a HP 4140B. The capacitance–voltage (*C*–*V*) and capacitance–temperature (*C*–*T*) characteristics were measured using an Agilent 4284A LCR meter. The sample's temperature was varied by using a delta chamber. Dielectric constant and dielectric loss of the films was measured at 100 kHz, with an AC field of 0.4 kV/cm superimposed on a slowly varying direct current (DC) bias field. The DC bias was stepped through 0.2 V intervals and held 1 s prior to capacitance measurement.

3. Results and discussion

Fig. 1 shows the XRD of the $Ba(Zr_{0.35}Ti_{0.65})$ thin films deposited on (a) $LaNiO_3$/Pt/Ti/SiO_2/Si and (b) $Ba(Zr_{0.30}Ti_{0.70})$/Pt/Ti/SiO_2/Si substrates, respectively, after annealing at 700°C for 30 min. The perovskite phase for BZT thin films deposited on Pt/Ti/SiO_2/Si substrates had a preferred (1 1 0) orientation. Films deposited on $LaNiO_3$/Pt/Ti/SiO_2/Si substrates exhibited a highly (1 0 0) preferred orientation. No observable impurity phases were found. The LNO layer not only serves as a useful metal oxide bottom electrode, but also forms a template with preferred (1 0 0) orientation to enable growth of high quality BZT films. Pt-buffer substrate showed highly preferred (1 1 1) orientation (Fig. 1(b)) and enable growth of preferred (1 1 0) orientation BZT films. The XRD patterns revealed that the compositionally graded $BaZr_xTi_{1-x}O_3$ thin film was also (1 0 0) orientation structure and had a single perovskite phase, shown in Fig. 1(c). The degree of orientation of BZT thin films is shown as a function of seed layer thickness in Fig. 1 (inset figure). The relative intensity of the BZT (1 0 0) peak was calculated as $I_{(1\,0\,0)}(\%) = I_{(1\,0\,0)}/(I_{(1\,0\,0)} + I_{(1\,1\,0)})$. It is evidence that the relative intensity of (1 0 0) peaks was increased from 24% to 46% and then decreased to 20% with the increase of seed layer thickness. The (1 0 0) peak intensity of the BZT was obviously enhanced as the thickness of the seed layer increased up to 20 nm. However, as the seed layer thickness was further increased to 30 nm, the (1 0 0) orientation of BZT thin film was decreased. The full width at half-maximum (FWHM) of the (1 1 0) was decreased with the insertion of the seed layer. It can be attributed to the higher degree of crystal

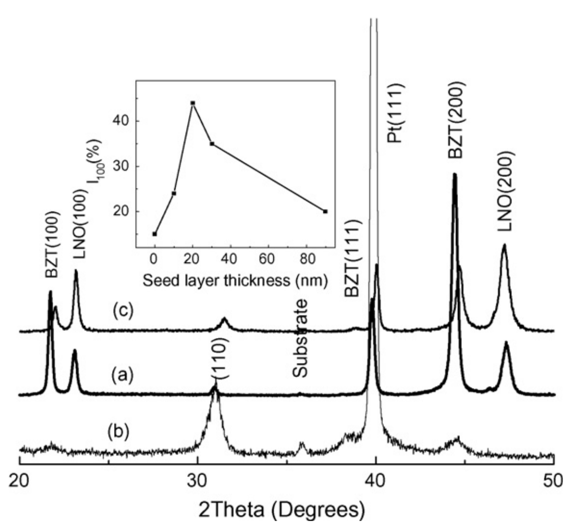

Fig. 1. XRD patterns of sol–gel deposited $BaZr_{35}Ti_{65}O_3$ thin films on (a) $LaNiO_3$/Pt/Ti/SiO_2/Si(1 0 0), (b) $BaZr_{30}Ti_{70}O_3$/Pt/Ti/SiO_2/Si(1 0 0) substrates and (c) BZT compositionally graded films.