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Ferroelectric and dielectric properties of $Ba_{0.5}Sr_{0.5}(Ti_{0.80}Sn_{0.20})O_3$ thin films grown by the soft chemical method

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Abstract

Polycrystalline $Ba_{0.5}Sr_{0.5}(Ti_{0.80}Sn_{0.20})O_3$ (BST:Sn) thin films with a perovskite structure were prepared by the soft chemical method on a platinum-coated silicon substrate from spin-coating technique. The resulting thin films showed a dense structure with uniform grain size distribution. The dielectric constant of the films estimated from $C-V$ curve is around 1134 and can be ascribed to a reduction in the oxygen vacancy concentration. The ferroelectric nature of the film indicated by butterfly-shaped $C-V$ curves and confirmed by the hysteresis curve, showed remnant polarization of $14\,\mu C/cm^2$ and coercive field of 74 kV/cm at frequency of 1 MHz. At the same frequency, the leakage current density at 1.0 V is equal to $1.5 \times 10^{-7}\,A/cm^2$. This work clearly reveals the highly promising potential of BST:Sn for application in memory devices.

Keywords: Crystallization; Film deposition; Space charge effects; Thin films

1. Introduction

Recently, ferroelectric thin films have been investigated as a key material for application to dynamic random access memories (DRAMs), in addition to non-volatile random access memories or other applications [1]. Ferroelectric barium strontium titanate [$Ba_{1-x}Sr_xTiO_3$ (BST)] film is of great interest for the most promising capacitor material in future DRAM applications because of its low leakage current at operating voltage as well as high dielectric constant [2,3]. BST can be categorized as a solid solution between $BaTiO_3$ (BT) and $SrTiO_3$ (ST). BT is a ferroelectric material with a Curie temperature of 120 °C, while ST is a paraelectric material at room temperature. In the past several years, much research has been carried out focusing on deposition techniques and electrical properties of the BST films [4–7].

Zhai et al. studied the dielectric and ferroelectric characteristics of $Ba(Ti_{1-x}Sn_x)O_3$ thin films deposited on $LaNiO_3$ electrodes by the sol–gel process [8]. The authors observed that by increasing Sn concentration, the temperature of the ferroelectric–paraelectric phase transformation decreases and becomes more diffuse within a wide temperature range. When the Sn ratio is between 10% and 20%, the ferroelectric transition occurs between 0 and 60 °C. These compositions have no other structural phase transition in their ferroelectric state. Thus, a solid solution of BTS is expected to exhibit good ferroelectric characteristics and to be a good candidate for use not only in stable ferroelectric devices but also in the study of general ferroelectric properties in the vicinity of Curie temperatures T_c around room temperature [9,10]. Although the deposition of BST films and their dielectrical properties have been reported [4,5] those of the BST:Sn thin films deposited on

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$Pt/Ti/SiO_2/Si$ substrate by the soft chemical method have not yet been studied in detail.

Among various methods such as MOCVD, pulse laser deposition and sol–gel, the polymeric precursor method has a better potential for technological applications, because of their precise control of composition and homogeneity and good conformality [11]. In the present work, we present the preparation of BST:Sn films on platinum-coated silicon substrates by the soft chemical method with excellent structural, microstructural and electrical properties.

2. Experimental procedure

Titanium isopropoxide (Hulls AG), strontium carbonate (Aldrich), barium carbonate (Aldrich) and tin chloride ($SnCl_2.2H_2O$-Reagen) were used as raw materials. The precursor solutions of barium, titanium, strontium and tin were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. We reported studies of $Ba_{0.5}Sr_{0.5}(Ti_{0.80}Sn_{0.20})O_3$ (BST:Sn) with the appropriate amount of Ti, Sr, Ba and Sn solutions that were mixed and homogenized by stirring at 90 °C. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 15 cP controlling the water content using a Brookfield viscometer. From this solution the films were deposited by the spin-coating technique on (1 1 1) Si/Ti/Pt substrates. A platinum layer (140 nm) was used as bottom electrode. The BST:Sn films were then annealed at 700 °C for 2 h in oxygen atmosphere resulting in a film thickness from 60 to 400 nm. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C, in oxygen atmosphere for 1 h. Here, the desired effect is to reduce oxygen vacancies. Phase analysis of the films were performed at room temperature by X-ray powder diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and CuKα radiation. The thickness of the annealed films was examined using scanning electron microscopy (SEM) (Topcom SM-300) by looking at the transversal section. The thickness results obtained from SEM represent an average value of three measurements. The capacitance–voltage characteristic was measured in the MFM configuration using a small AC signal of 10 mV at 100 kHz in an impedance analyzer (model 4192 A, Hewlett Packard). The AC signal was applied across the sample, while the DC was swept from positive to negative bias. From $C-V$ measurements the dieletric constant ε and charge storage density were determined. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology 6000 A). The leakage current–voltage ($I-V$) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns for the BST:Sn thin films deposited on platinum-coated silicon substrates at 700°C for 2 h. The annealed thin film was a single phase of a layer-structured perovskite with pseudo-cubic crystallographic structure. The polycrystalline film showed the highest intensity peak at $2\theta = 31°$. The main peak is very sharp, suggesting the presence of large crystalline grains in the film. Characteristic peak for platinum-coated silicon (1 1 1) substrates was observed in the range of $38° \leqslant 2\theta \leqslant 41°$.

The average grain size and the surface roughness of the BST:Sn thin films were estimated using an atomic force microscope (AFM). The surface morphology was obtained using an area of $1 \times 1\,mm^2$, as shown in the inset of Fig. 2. Analysis of AFM data indicated that the BST:Sn thin films were characterized by a small surface roughness (4 nm) with a crack-free uniform microstructure and average grain size equal to 100 nm.

Hysteresis loops measured at room temperature for BTS:Sn thin films annealed at 700 °C is shown in Fig. 3. A saturated $P-E$ loop with larger remnant polarization and lower E_c was obtained for the BST:Sn films deposited from the soft chemical method. The P_r and E_c observed in this study was much better compared to the $(Ba_{1-x}Sr_x)(Ti_{0.9}Sn_{0.1})O_3$ (BS_xTS) thin films prepared by radio frequency (RF) magnetron sputering [9]. The authors explain that the low remnant polarization is caused by diffusion of some activated oxygen in the (BS_xTS) thin films into the bottom electrode leading to the formation of oxygen vacancies which increase leakage current of the $Pt/BS_xTS/Pt/Ti/SiO_2/Si$ capacitors. The high remnant polarization can be ascribed to their larger grains and reduction of interfacial defects due to the annealing in oxygen atmosphere. This results in a decrease of oxygen vacancy concentration and increase of electron holes which incorporates oxygen molecules at positively charged oxygen vacancies. Also, the origin of a high remnant polarization can be caused by the stress in the lattice once

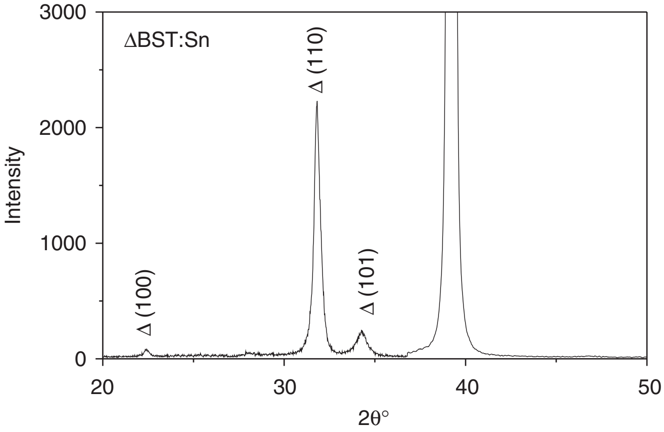

Fig. 1. X-ray diffraction for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

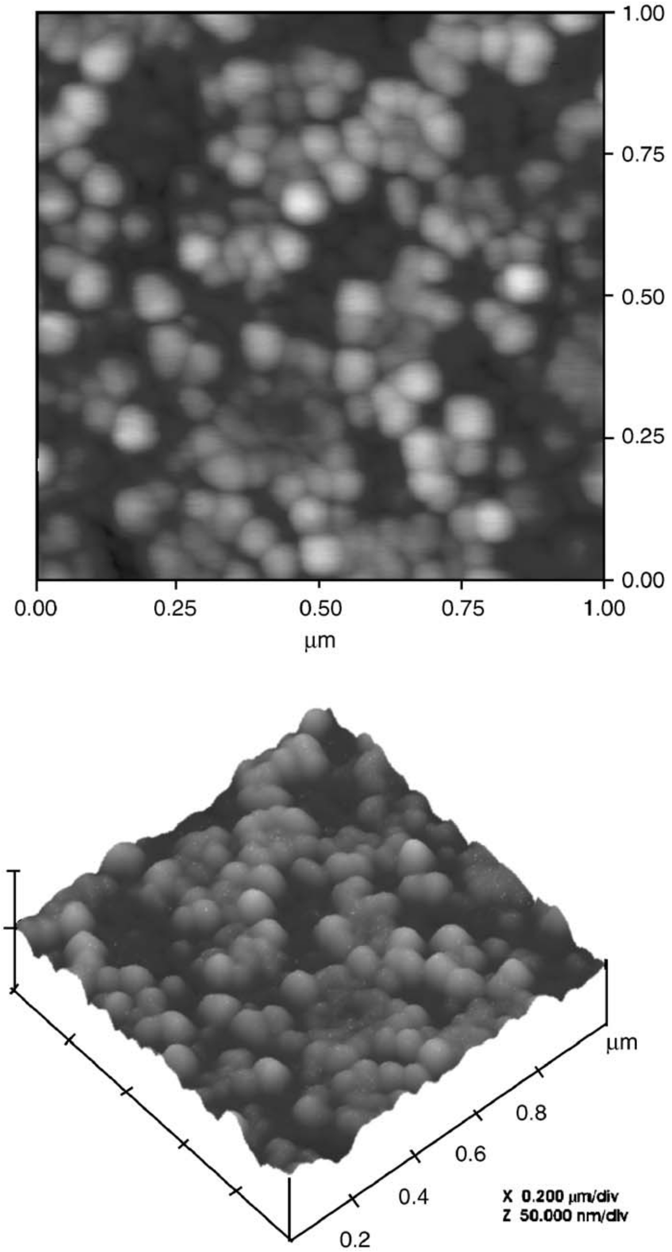

Fig. 2. AFM micrograph for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

tin forms more strong covalent bonds than titanium and therefore causes a slight structural change.

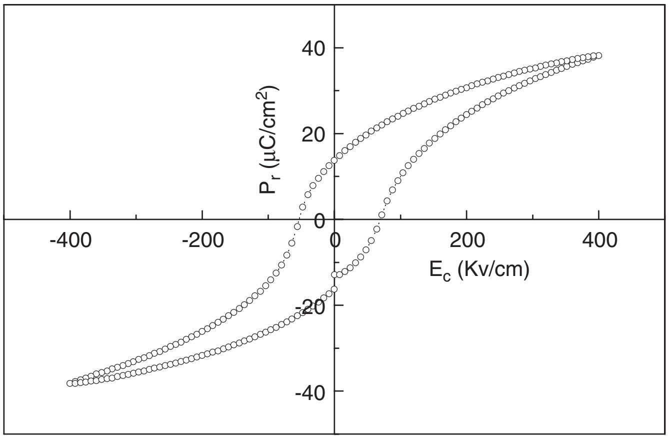

Fig. 3. $P-E$ hysteresis loops for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

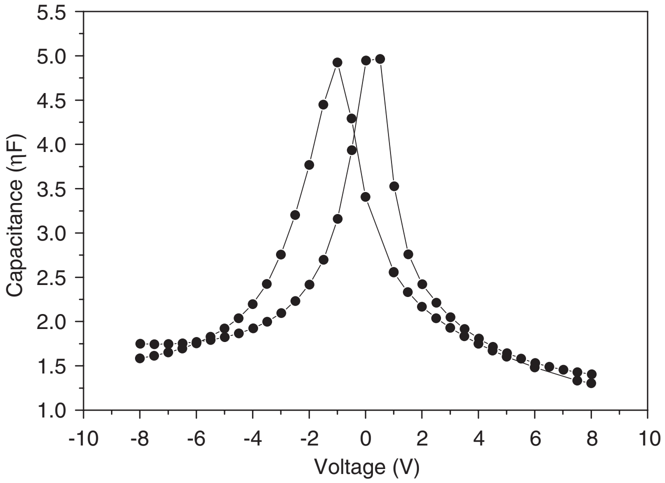

Fig. 4. Capacitance in dependence of voltage for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

Current–voltage ($C-V$) characteristics (at 1 MHz) for the BST:Sn film annealed at 700 °C for 2 h is shown in Fig. 4. The voltage-step and the delay-time after applying each voltage-step were fixed at 0.5 V and 1 s, respectively. A general bell-shape of $C-V$ measurement was obtained with a cycling of the bias voltage up and down at room temperature. The capacitance–voltage dependence is strongly nonlinear, confirming the ferroelectric properties of the film resulting from domain switching. The $C-V$ curve is symmetric around the zero bias axis, indicating that the films contain only few movable ions or charge accumulation at the film–electrode interface. From $C-V$ curve the dielectric constant value at the frequency of 1 MHz is 1134, which is much higher than the one reported by Wang et al. [9] (250) for the BS$_x$TS thin films deposited on platinum-coated silicon substrates by RF magnetron sputtering. This enhancement may be due to the improvement between the thin film and the platinum electrode interface as well as to the large grain size of our films. This supports the idea that our BST:Sn films annealed in oxidant atmosphere suppress the formation of a very low dielectric constant layer at the thin film–electrode interface, which is the main cause of the lower value of the dielectric constant related to many ferroelectric thin films.

Fig. 5 shows the reciprocal capacitance as a function of film thickness at 1 MHz with 20 mV amplitude. As shown, a linear relationship intersecting at zero was noted. The dielectric constant reveals no dependence with the film thickness confirm the linear relationship. This result indicates the non-existence of an interfacial layer having low dielectric constant between the ferroelectric film and

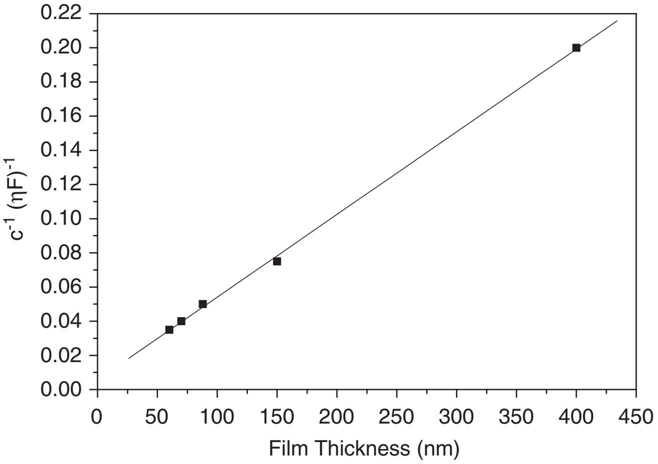

Fig. 5. Capacitance in dependence of voltage for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

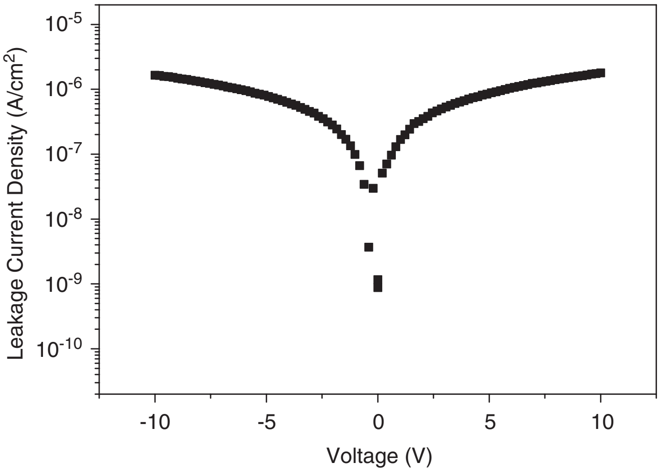

Fig. 7. Leakage current density in dependence of voltage for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

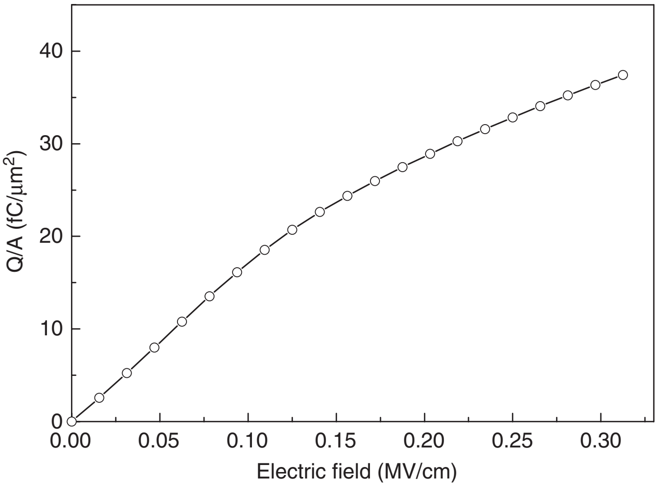

Fig. 6. Charge storage density versus applied electric field for BST:Sn film annealed at 700 °C for 2 h in oxygen atmosphere.

the bottom electrode confirm that the oxygen atmosphere suppress the formation of the dead layer.

The charge storage densities were estimated from the $C-V$ characteristics using the relationship $Q_c = \varepsilon_0\varepsilon_r E$, where ε_0 is the permittivity of free space, ε_r is the relative permittivity and E is the applied field. A practical DRAM capacitor [12] requires a leakage current density (LCD) of $3\,\mu A/cm^2$ and a charge storage density of about $35\,fC/\mu m^2$. From Fig. 6 it may be seen that this would be satisfied already at $E = 0.27\,MV/cm$.

For DRAM applications it is very important to understand the major conduction mechanism occurring in a given dielectric film. A high leakage current generally leads to the loss of the stored data written in DRAM cells and, thus, requires a frequent refresh and a high power consumption. It has been estimated that the upper limit of the allowable LCD of $3\,\mu A/cm^2$ is generally required for a 200-nm thick film. Here the measured logarithmic current density (log J) versus the voltage (V) is shown (Fig. 7). The mechanisms of carriers transport though thin insulator films have been the subject of extensive theoretical and experimental investigations. The steady-state field dependent DC conductivity was examined through the measurement of the $I-V$ characteristics in MFM capacitors. Several processes allow a charge movement in insulators, leading to sizable current densities.

The low field electrical properties are usually of Ohmic nature which means the current I is a linear function of voltage V. At high fields, these films exhibit nonlinear $J-V$ relationships. The BST:Sn thin films exhibited good leakage current characteristics. The LCD at 1.0 V is equal to $1.5 \times 10^{-7}\,A/cm^2$ establishing good insulating characteristics. The low leakage current observed for the film may be attributed to the larger grain size, small roughness and improved crystallinity. Also, it was noted a symmetric $J-V$ characteristic for both voltage polarity indicating that the bulk controls the properties once we have used different top and bottom electrodes and having different processing conditions. Since the conductivity is strongly affected by the characteristics of the film–electrode interface, the surface morphology of BST:Sn thin films is one of the major factors determining the leakage current in capacitors.

4. Conclusions

BST:Sn thin films were successfully deposited on Pt/Ti/SiO_2/Si substrates by the soft chemical method. The single phase film has a large-grained microstructure resulting in a high dielectric constant. Leakage current density at 1.0 V is equal to $1.5 \times 10^{-7}\,A/cm^2$ which is fundamental for DRAMs. The BST:Sn thin film shows ferroelectricity behavior at room temperature. A remarkable improvement in the dielectric constant (1134) suggests that BST:Sn thin films deposited on platinum-coated silicon substrates are suitable for integrated device applications and can be used for DRAMs.

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