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Effect of oxygen to argon ratio on defects and electrical conductivities in $Ba_{0.47}Sr_{0.53}TiO_3$ thin-film capacitors

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Abstract. The ionic and electronic conductivity characteristics and defects in the $Ba_{0.47}Sr_{0.53}TiO_3$ (BST) thin films that were rf-sputtered at 450 °C on a Pt bottom electrode at various $O_2/(Ar + O_2)$ mixing ratios (OMR) were studied. The dielectric properties specific to the BST films can be explained by considering the influence of the dielectric relaxation phenomenon. Through the measurement of the dielectric dispersion as a function of frequency (100 Hz $\leqslant f \leqslant$ 10 MHz) and temperature (27 °C $\leqslant T \leqslant$ 150 °C), we studied the dielectric relaxation and obtained the defect quantity of the films, on the basis of the capacitance, admittance and impedance spectra. The defect density of BST films decreases with an increase of OMR. The majority of electrical conductivity is carried by electrons (electronic conductivity) and not the ionic defects (ionic conductivity).

1. Introduction

Barium strontium titanate, $Ba_{0.47}Sr_{0.53}TiO_3$ (BST) thin films are one of the most promising materials for practical use in the capacitor of giga-bit dynamic random access memories (DRAMs) because of its high dielectric constant, low leakage current density, high dielectric breakdown strength, para-electric perovskite phase that does not exhibit fatigue, ageing and the ease of composition control [1–4].

There are at least three possible defects namely, the interface defect at the metal–BST Schottky junction, the grain boundary defect and the shallow trap level existing in the metal/BST/metal capacitors. These may lead to a dielectric relaxation as a function of frequency. These defects are mainly due to the accumulation of the oxygen vacancies in the BST thin-film capacitors [5–11]. The complex plane (capacitance, admittance and impedance spectra) analysis is a valuable tool for the characterization of the dielectric relaxation and the ionic and electronic conductivity characteristics in ceramic capacitors. The titanate perovskites play a very important role in electronic devices technology [12, 13] as well as in basic solid state chemistry. This is, in large, part due to a pronounced mixed (ionic/electronic) conductivity which allows oxygen to be incorporated into the material and to change the intrinsic electronic properties significantly, owing to the sensitive dependence of the electronic conductivity on oxygen partial pressure [14–16].

Several investigations were recently carried out using the alternating current (ac) electrical response in thin-film capacitors, (such as RuO_2/BST [17], RuO_2/PZT (lead zirconate titanate) [18] and Pt/BST [7]) to explain the nature of dielectric relaxation, ionic and electronic conductivity characteristics and the diffusion of the oxygen vacancies in the dielectric bulk materials such as $SrTiO_3$ [19, 20] and $Ba_{0.03}Sr_{0.97}TiO_3$ [14]. Oxygen vacancy diffusivities between 1×10^{-15} and 1×10^{-12} cm^2 s^{-1} have been reported in titanate ceramics for different temperatures, oxygen pressures and dopants [14–16, 19, 20].

The $O_2/(Ar + O_2)$ mixing ratio (OMR) during rf sputtering greatly affects the electrical characteristics of BST thin-film capacitors [5, 8]. However, systematic and detailed studies of the ionic and electronic conductivities for various OMR BST thin films are scarcely reported. In this work, we investigate the effects of OMR on the electrical conductivity in rf-sputtered BST thin films by employing an ac electrical response analysis. This paper also reports the total defect quantity of interface defects and grain–boundary defects, which helps in a better understanding of the effect of dielectric relaxation on the electrical properties of BST films.

2. Experimental details

BST thin films were deposited on Pt coated SiO_2/(100)Si substrates by rf magnetron sputtering. The Pt film was prepared at a fixed power of 50 W (power density is 2.55 W cm^{-2}), constant pressure of 5 mTorr and substrate temperature of 350 °C. The measured resistivity of Pt was about 16.9 $\mu\Omega$ cm at room temperature. The BST 50/50 targets were synthesized using standard solid-state reaction process. The sputtering chamber was evacuated to a base pressure of 2×10^{-6} Torr. All films were prepared at a fixed power of 100 W (power density is 2.26 W cm^{-2}) and constant pressure of 10 mTorr, which was maintained by a

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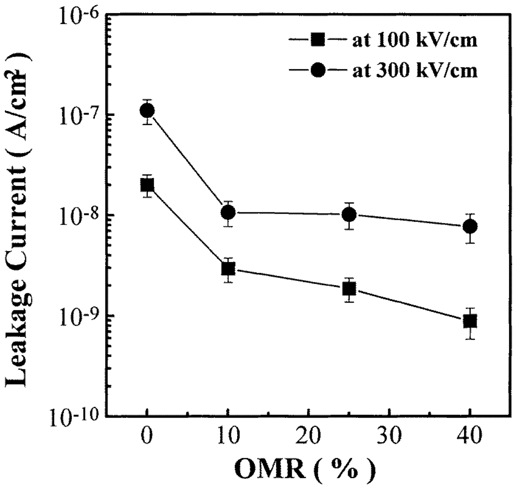

Figure 1. The dependence of the leakage current density at 27 °C measured at 100 and 300 kV cm^{-1} with a delay time of 30 s at various OMR.

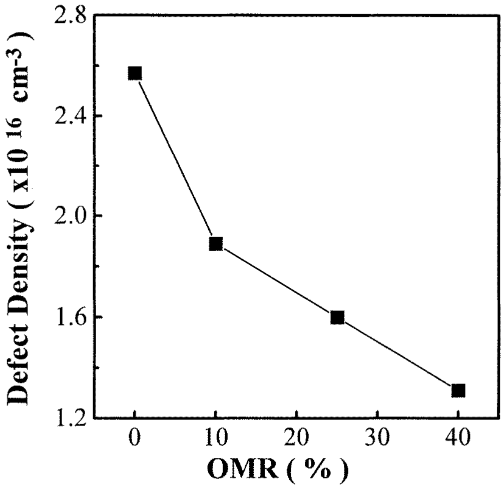

Figure 2. The defect density of various OMR BST thin films at 27 °C.

mixture of argon and oxygen in the mixing ratios of 1:0–3:2 with a total flow of 20 sccm. All the BST films have the same thickness of around 100 nm. The substrate temperature of the sputtered BST films was 450 °C. The composition of BST thin films is $Ba/Sr = 0.47/0.53$. Finally, the 50 nm thick Pt top electrodes with diameters of 165, 255 and 350 μm were patterned by the shadow mask process.

The capacitance, admittance and impedance spectra were measured as a function of frequency with a Hewlett Packard (HP) 4194A impedance gain phase analyser and the temperature was varied in the range 27–150 °C. The ac electrical data, in the form of parallel capacitance and conductance, were recorded in the frequency range 100 Hz to 10 MHz at an ac signal amplitude of 0.1 V. The current–voltage (I–V) and current–time (I–t) measurements were performed by measuring the current through the sample using the HP4145B and the temperature was varied in the range 27–200 °C.

3. Results and discussion

Figure 1 shows the dependence of the leakage current density at 27 °C measured at 100 kV cm^{-1} and 300 kV cm^{-1}, with a delay time of 30 s, with 100 nm thick BST deposited at 450 °C and with the 0%, 10%, 25%, and 40% $O_2/(Ar + O_2)$ OMR. Leakage current density decreased with increasing OMR, which may result from the reduction in concentration of the oxygen vacancies and mobile charge (electrons) that may exist in the films sputtered at higher OMR [5, 8]. The leakage current of BST thin films greatly depends on the composition of the BST thin films, the bottom electrode materials and grain size. However, the leakage current of our films was not significantly affected by the grain size, which was described in earlier reports [5, 8]. On the other hand, it also indicates that the resistive loss dominates the electrical properties of the films sputtered at under 40% OMR. Their relaxation losses would be small and constant, on the basis of the fact of nearly constant dielectric constant at under 40% OMR [8].

The defect traps of perovskite titanates often lead to a dielectric relaxation as a function of frequency, in which the dielectric constant decreases and loss tangent increases with increasing frequency. It has been reported that the oxygen vacancies were the major defect in BST thin films [5–11, 17–20]. The electrical behaviour of a BST thin-film capacitor may be expressed in terms of an admittance (Y) of a unit cube (with parallel plane electrodes) which can be defined by the following equations

$$Y = I(\omega)/V(\omega) = G_p(\omega) + \mathrm{j}B_p(\omega) \quad (1)$$

$$Y = \mathrm{j}\omega C(\omega) = \mathrm{j}\omega(C' - \mathrm{j}C'') = \mathrm{j}\omega C_0(\varepsilon' - \mathrm{j}\varepsilon'') \quad (2)$$

By comparison of (1) and (2), we have

$$G_p(\omega) = \omega C'' = \omega C_0\varepsilon'' \quad (3)$$

$$B_p(\omega) = \omega C' = \omega C_0\varepsilon' \quad (4)$$

where: ω is the angular frequency; $I(\omega)$ and $V(\omega)$ are the electrical current and applied voltage, respectively; $G_p(\omega)$ and $B_p(\omega)$ are the parallel relative real admittance (conductance) and imaginary admittance, respectively; C_0 is the geometric capacitance in free space; ε' and ε'' are the relative real and imaginary dielectric constants; and C' and C'' are the real and imaginary capacitance. A semicircular fit of the ac data (Cole–Cole plot) in any plane for our films suggests an appropriate equivalent resistance–capacitance (R–C) circuit, consisting of a parallel defect trapping resistance and dielectric capacitance in combination with a series electrode resistance, which represents the observed spectra [6]. An equivalent circuit was established which can well explain the ac response and identify the contribution of the defects on the electrical properties of BST thin film. The $G_p(\omega)$ term was analysed by using the complex plane analysis as a function of frequency (100 Hz $\leqslant f \leqslant$ 10 MHz) and temperature (27 °C $\leqslant T \leqslant$ 150 °C) [6] and found to be contributed to only by the grain boundary defects and the interface defects of BST/metal. A shallow trap level located at 5–10 meV below the conduction band was observed from the admittance spectral studies in the temperature range 27–150 °C and can be neglected at the normal temperature range of DRAM operation: 0–70 °C ambient and 0–100 °C

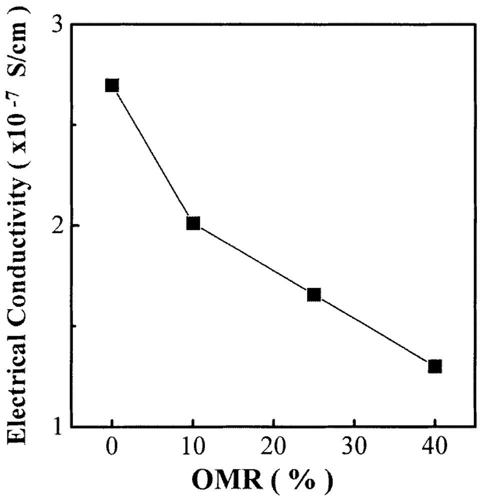

Figure 3. The electrical conductivity of various OMR BST thin films at 27 °C.

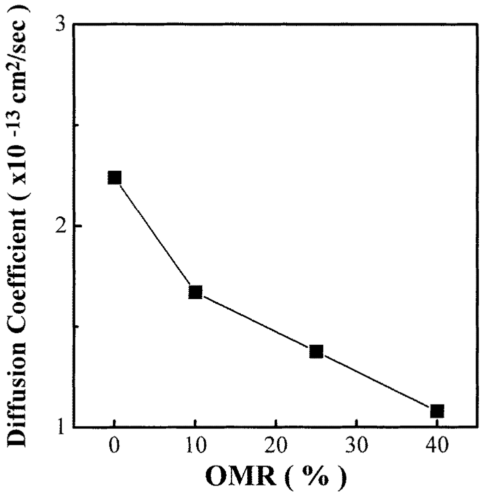

Figure 4. The diffusion coefficient of oxygen vacancies in various OMR BST thin films at 27 °C.

on chip. Hence, we propose that the shallow trap level term is not included in the equivalent circuit of a BST thin film. The equivalent circuit of the BST thin film was considered to be contributed from the grain boundary defect and interface defect of the BST/metal. The details were mentioned in [6]. These defects were mainly due to the accumulation of the oxygen vacancies in the BST thin-film capacitors [5–11]. The grain boundary defect and the interface defect (the total defect density) of BST/metal are considered to be a donor when it becomes neutral or positive by donating two electrons. When an ac voltage is applied at a Schottky junction, the depletion layer width varies about its equilibrium position due to the trapping and detrapping of electrons from the oxygen vacancies. A change of charge in the defect occurs when the depletion layer width varies. The value of G_p/ω is C'' by (3). Once C'' is known, the defect density D_{df} is obtained by using the relation $D_{df} = C''/qA$, where A is the metal plate area and q the elementary charge [21]. Figure 2 shows the defect density of various OMR BST thin films at 27 °C. Defect density decreases with an increase of OMR and the defect density of 0%, 10%, 25% and 40% OMR BST films is 2.6×10^{16}, 1.9×10^{16}, 1.6×10^{16} and 1.3×10^{16} cm^{-3}. Maruno *et al* [11] assumed that a model of leakage current and capacitance characteristics can evaluate the defect density of BST films of 2.7×10^{17} cm^{-3}, which is reasonably close to our values.

High-temperature deposition of BST films under a non-oxidizing atmosphere, such as Ar, generally produces oxygen vacancies in the film according to

$$O_o \leftrightarrow V_o^{\cdot\cdot} + 2e' + \tfrac{1}{2}O_2 \quad (5)$$

where O_o, $V_o^{\cdot\cdot}$ and e′ represent the oxygen ion on its normal site, oxygen vacancy and electron, respectively. As shown by (5), the BST material tends to show an n-type conductivity, although the conductivity is usually small due to the electrons associated with the formation of oxygen vacancies [5, 8]. The leakage current and defect density were decreased with increasing OMR as indicated in figures 1 and 2, which may result from the reduction in concentration of the oxygen vacancies and mobile charge (electrons) existing in the high-OMR sputtered films [5, 8]. The electrical conductivity of the films can be determined under small applied ac signal. The ac conductivity of the films is mainly due to the trapping and detrapping of the electrons from the oxygen vacancies. Therefore, the ac electrical conductivity is expected to correlates with the concentration of oxygen vacancies. The experimental result indicated in figure 3 demonstrates that the ac electrical conductivity decreases with increasing OMR, which results from the reduction in concentration of the oxygen vacancies existing in the high-OMR films. This observation shows a good agreement with the result shown in figure 2, where the defect density decreases with an increase of OMR.

The mobility of the oxygen vacancies in BST thin films was measured using space-charge-limited (SCL) current transients analysis, which was employed by Zafar *et al* [10]. The OMR dependence of current–time (I–t) characteristics of our BST thin-film capacitors was undertaken at the temperature range 75–200 °C and applied fields range 1–3 MV cm^{-1}. Possible causes for the time-dependent current are one or more of the followings: (i) ionic drifting within the films, (ii) dipole polarization of the dielectric and/or (iii) electronic charge trapping within the films. On the basis of the theory for SCL current transients, a current transient with a peak shown in I–t characteristics is due to a large reservoir of charge available at the BST/metal electrode interface (metal electrode, that is, ionic blocking electrode). The creation of oxygen vacancies at the interface during film deposition and under applied field is the source of the charge reservoir [5, 10]. It was reported in [10], that the oxygen vacancies mobility was evaluated from the peak position according to SCL current transients theory. The measured current is the sum of the ionic and electronic currents. Before peaking, the ionic current density is dominant. After peaking, the electronic current is dominant. An extrapolation of the mobility against the temperature curve gives the mobility at 27 °C. The diffusion coefficient of oxygen vacancies in BST films at 27 °C can be obtained on the basis of above measured data and the Einstein's relation of mobility and

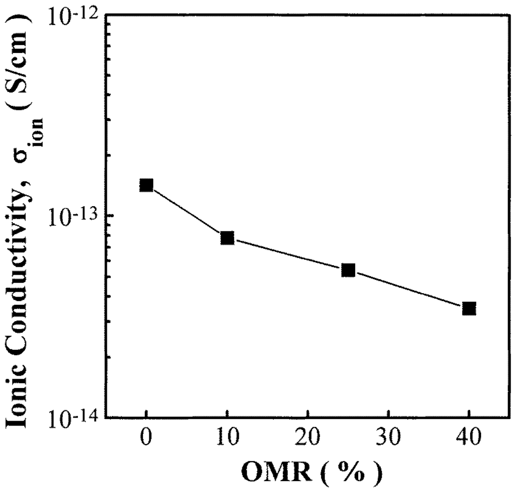

Figure 5. The ionic conductivity of various OMR BST films at 27 °C.

diffusion coefficient. Figure 4 indicates that the diffusion coefficient decreases with increasing OMR. It has been reported [10, 15, 22] that the value of the diffusion coefficient of oxygen vacancies for BST on Pt at 27 °C was evaluated to be 10^{-12}–10^{-15} cm^2 s^{-1}, which is reasonably close to our values. The oxygen vacancy density is considered to correspond to the oxygen vacancy diffusion coefficient [22, 23], and the difference in the oxygen vacancy diffusion coefficients due to the variation of vacancy concentration represents the relative difference in the oxygen vacancy density. Therefore, the oxygen vacancy diffusion coefficient increases with increasing defect density (oxygen vacancies) on the basis of the combination of the results shown in figures 2 and 4.

The temperature dependence of the diffusion coefficient and the electrical conductivity of a perovskite structure, such as $BaTiO_3$, when thermodynamic equilibrium of the crystalline material is achieved, are given by the following equations [22],

$$D = D_0 \exp[-(E' + E''/2)/kT] \tag{6}$$

$$\sigma = (\sigma_0/T) \exp[-(E' + E''/2)/kT]. \tag{7}$$

The quantity D and σ are the diffusion coefficient and the conductivity, respectively. D_0 and σ_0 are constants. The activation energy for the jump of an ion into a vacancy is represented by E', while E'' is the work necessary to create a vacancy by moving the ions from the interior to the surface of the crystal. The ratio σ/D has the simple form

$$\sigma/D = N(qZ)^2/kT \tag{8}$$

which is known as the Einstein relation. The charge-carrier density is given by N and qZ is the particle charge. The electrical conductivity σ_{total} of a ceramic capacitor can be described as the sum of the electronic conductance σ_{ele} and the ionic conductivity σ_{ion} [24]. The fraction of the total conductivity carried by each charged species is termed as the transference number, t_i, where

$$t_i = \sigma_i/\sigma_{total}. \tag{9}$$

The ionic conductivity σ_{ion} of BST film can be calculated from the number of defect density, N (figure 2) and diffusion coefficient data (figure 4) according to (8). Figure 5 shows the ionic conductivity σ_{ion} of various OMR BST films at 27 °C. The σ_{ion} is much smaller in comparison with the electrical conductivity (figure 3), so the majority of the electrical currents is carried by the liberated electrons associated with the formation of oxygen vacancies, as shown in (5). Hence the BST is an electronic conductor ($t_{ele} \sim 1$). The oxygen vacancies are the major defect in the BST thin film, but the mobility of oxygen vacancies (ionic conductivity) is much smaller than the mobility of electrons (electronic conductivity). Hence, the majority of electrical conductivity is contributed by the electrons.

4. Conclusions

This paper describes the dielectric and electrical properties of BST thin films deposited by rf magnetron sputtering with various OMR. The defect density decreases with increasing OMR and the defect density of 40% OMR BST films is 1.3×10^{16} cm^{-3}. Correlation of the diffusion of oxygen vacancies with the ionic/electronic conductivity in the films was presented. Through the measurement of conductivity as a function of frequency (100 Hz $\leqslant f \leqslant$ 10 MHz), the diffusion coefficients of oxygen vacancy at 27 °C for BST on Pt were evaluated to be 10^{-12}–10^{-13} cm^2 s^{-1}. The oxygen vacancy diffusion coefficient was considered to be proportional to the oxygen vacancy density and the difference in the diffusion coefficients of oxygen vacancies represents the relative difference in the oxygen vacancy density. The majority of the electrical current was carried by electrons and, hence, the BST is an electronic conductor ($t_{ele} \sim 1$).

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