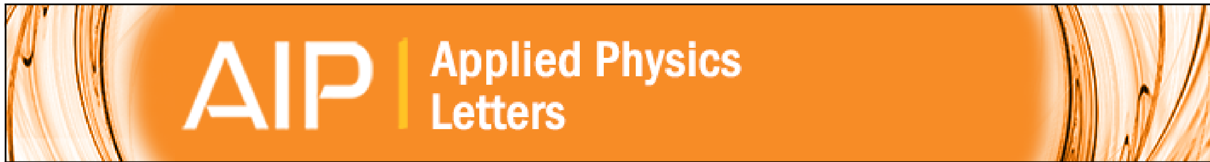

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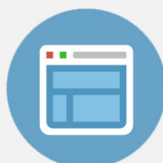

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Effects of the postannealing atmosphere on the dielectric properties of $(Ba,Sr)TiO_3$ capacitors: Evidence of an interfacial space charge layer

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The dielectric properties of $(Ba,Sr)TiO_3$ films were found to be remarkably sensitive to the postannealing treatment atmosphere. This study demonstrates that postannealing in an oxygen atmosphere increases the dielectric relaxation phenomenon and that postannealing in a nitrogen atmosphere produces a slight dielectric relaxation. Such dependence of the dielectric relaxation was related both to oxygen vacancies and to the presence of negatively charged oxygen, trapped at the grain boundary and/or at the electrode/dielectric film interface. © *2000 American Institute of Physics.* [S0003-6951(00)00817-2]

Because of its high dielectric constant, $(Ba,Sr)TiO_3$ (BST)[1–4] thin film has important potential applications in a variety of technologies that require high charge storage density materials in thin film devices.

The main advantages of $(Ba_{0.6}Sr_{0.4})TiO_3$ are its paraelectric properties in the operating temperature range. It is a generally acknowledged fact that these capacitors, formed by the metal—dielectric—metal configuration, present Schottky barriers at both electrodes (top and bottom).

Hwang *et al.*[5] reported that different production processes and processing conditions produce different trap states at the film/electrode interface that are responsible for different electrical interfacial characteristics. In addition, BST thin films show a remarkable dielectric relaxation phenomenon that strongly affects the dielectric properties of the films.[8]

Many researches have reported the effect of the postannealing treatment under an O_2 and/or N_2 atmosphere in the behavior of BST film leakage currents. Joo *et al.*[6] have reported oxygen vacancies in BST films, obtained by the sputtering technique, that are usually generated during the production of Pt/BST/Pt capacitors. These vacancies are responsible for the higher leakage currents of BST films, as well as for the degradation of dielectric properties.[7–9] Moreover, some recent studies have revealed that electron trapping in thin films induces a voltage offset in the polarization-voltage characteristics.[10]

This letter investigates the influence of postannealing treatments on the dielectric properties of BST thin films, after top electrode deposition, in oxygen and nitrogen atmospheres.

$(Ba_{0.6}Sr_{0.4})TiO_3$ films were prepared by the polymeric precursor method[11–14] and deposited by the spin-coating technique on a $Pt/Ti/SiO_2/Si$ substrate. A platinum layer (140 nm) was used as the bottom electrode. The BST film was then sintered at 700 °C for 2 h in air (film thickness of 480 nm).

Using the sputtering technique, the 0.3 mm diameter top Au electrode was then deposited through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a postannealing treatment in a tube furnace, at 350 °C, in an O_2 and N_2 atmosphere for 8 h.

In this work, the first annealing treatment, after BST production, was performed in O_2, the second annealing in N_2, and the last in O_2. All the postannealing treatments were carried out on the same sample. Electric measurements were taken after each treatment in different atmospheres. Dielectric constant and dissipation factor values, in the 100 Hz–10 MHz frequency range, and capacitance–voltage ($C-V$) were measured with a HP 4194A impedance analyzer.

For $C-V$ measurements, a small alternating current signal of 10 mV of amplitude and 100 kHz frequency was applied across the sample, while the direct current (dc) electric field was swept from the positive bias to negative bias and back again. Ferroelectricity was investigated using a modified Sawyer–Tower circuit attached to a Tektronix 2232 digital oscilloscope.

Figure 1 shows the variation of the dielectric constant as a function of frequency for the BST film as-deposited, postannealed at 350 °C for 8 h in oxygen, second postannealing in nitrogen, and final postannealing in oxygen. It can be observed, in Fig. 1, that the sample postannealed in an O_2 atmosphere presents an intense drop in the dielectric constant in the low frequency region (100 Hz–100 kHz). It is possible that this decrease in the dielectric constant in this frequency range is caused by space charge polarization or Maxwell–Wagner type interfacial polarization. The space charge polarization is inherently related to the nonuniform charge accumulation. These charges can be originate during the postannealing treatment in an oxygen atmosphere.

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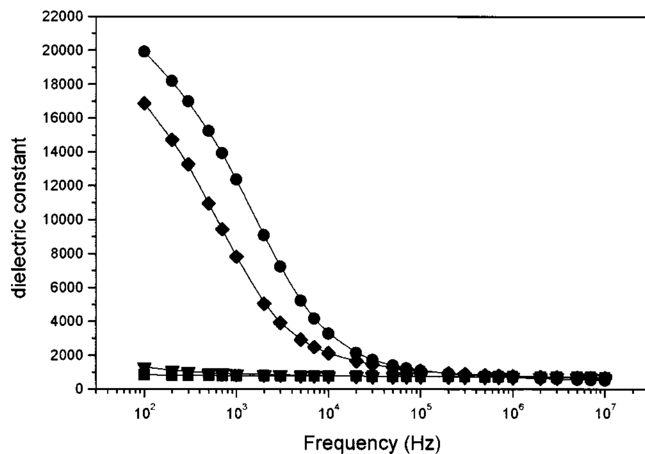

FIG. 1. Dielectric constant vs frequency characteristics of (▼) as-deposited, (♦) postannealed in oxygen, (■) postannealed in nitrogen, and (●) postannealed in oxygen.

When the film was postannealed in nitrogen, a reduction of the dispersion of dielectric constant was observed at a low frequency. This result indicates that there was a reduced charge space effect in the dielectric properties. When the film was again postannealed in oxygen, the phenomenon of the space charge polarization appeared and a large dielectric relaxation was once more observed. This result strongly indicates that the dielectric relaxation observed is not a bulk-related phenomenon, but an oxygen-related interface phenomenon.

Figure 2 shows the influence of postannealing under different atmospheres on the dissipation factor (tan δ) as a function of frequency for BST films. These curves showed a distinctly visible characteristic peak around the frequency range of 100 Hz–10 kHz when the film was postannealed in oxygen. These curves demonstrate that the oxygen atmosphere contributes to the relaxation phenomenon in the dielectric behavior. The curves became flat (Fig. 2) after postannealing in a nitrogen atmosphere. This result strongly suggests that the relaxation phenomenon arises from the postannealing treatment in an oxygen atmosphere. These results are in agreement with the dielectric constant measurement.

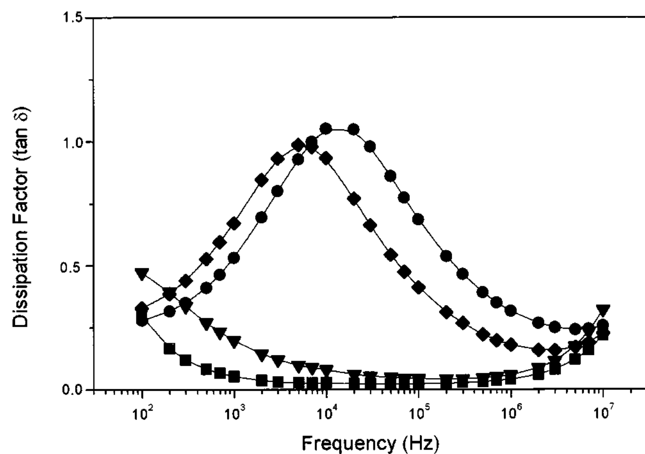

FIG. 2. Dissipation factor vs frequency characteristics of (▼) as-deposited, (♦) postannealed in oxygen, (■) postannealed in nitrogen, and (●) postannealed in oxygen.

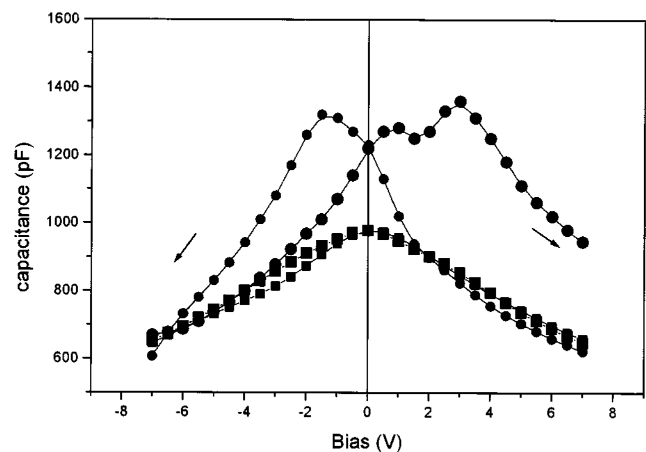

FIG. 3. $C-V$ curve for (■) as-deposited film and (●) postannealed in oxygen.

Figure 3 shows the relationship between the dc bias and capacitance ($C-V$ curve) applied. Although the curves were measured with both an increasing and a decreasing bias voltage, only a slight hysteresis was observed in a curve (as-deposited) film. This indicates that there is a low concentration of movable ions or charge accumulation at the interface between the dielectric and the electrode.

The $C-V$ curve showed typical paraelectric behavior for the as-deposited film. On the other hand, when the capacitor was treated in an oxygen atmosphere, the V_m voltage at which the capacitance is at its maximum C_m value is not located at the zero bias field, but shifted toward the negative and positive bias region. The higher capacitance, which depends on the bias polarity, suggests that the existence of additional capacitance at the interface arises from the space charge, originating from the postannealed film in an oxygen atmosphere.

Two maxima can be observed on the positive side of the $C-V$ curve for the sample postannealed in oxygen, one at 3 V and the other at 1 V. Another maximum can be seen on the negative side of the $C-V$ curve, which may be caused by the presence of some positive charges, such as oxygen vacancies. These oxygen vacancies may originate during the process of heat treatment of the films due to the organometallic decomposition of the polymeric precursor. The negative charges may be associated with the presence of negatively charged oxygen trapped at the grain boundary and/or the film's electrode/dielectric interface. The negative charge of the oxygen may be caused by charge transference between the metal vacancy and the oxygen, as shown in

$$V''_M + 1/2O_2^x \Rightarrow V_M^x + 1/2O''_2, \tag{1}$$

where O^x, V''_M, V_M^x, and O'' represent, respectively, the neutral oxygen ions in their normal position, metal site vacancies doubly negatively charged, neutral metal site vacancies, and oxygen ions doubly negatively charged.

In BST film, the V_M must be a barium vacancy (V_{Ba}), since a barium deficiency was identified by an inductively coupled plasma chemical analysis of the precursor solution with an approximate barium deficiency of 3%.

Figure 4 shows the polarization versus electric field ($P-E$) hysteresis loops of BST films postannealed in different atmospheres. A typical hysteresis loop, related to ferro-

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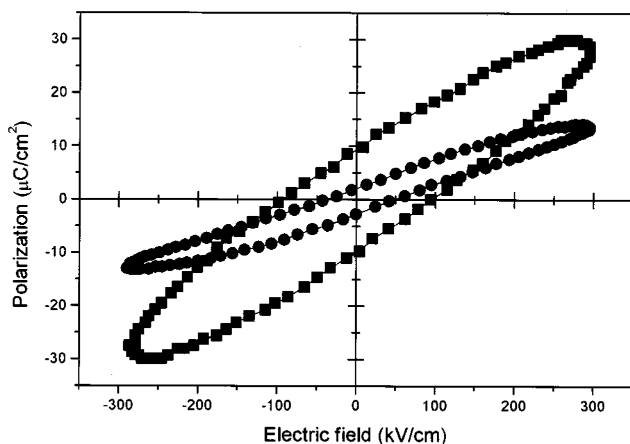

FIG. 4. $P-E$ hysteresis characteristics of BST film (■) postannealed in oxygen and (●) postannealed in nitrogen.

electric materials, can be observed. In addition, the crystallographic structure of the films was examined using the x-ray diffraction technique (XRD), where all the peaks are ascribed to the cubic perovskite structure. A polycrystalline thin film is observed in the pattern.

A further analysis of the XRD data indicated a lattice parameter (a) of $a = 0.396$ nm. This value is close to the bulk material ($a = 0.3965$ nm); thus, the film is by nature paraelectric. This hysteresis is not due to the ferroelectric nature of the film, but rather, to a space charge effect. A slim hysteresis loop is observed after postannealing in nitrogen. This result supports the hypothesis that the hysteresis loop observed stems from the space charge. We believe that the trapped charge (O_2'') located in the grain boundary or and electrode/film interface can promove a local stoichiometric deviation. The O_2'' associated with other defects ($V_O^{\cdot\cdot}$ or even defect dipole complexes such as oxygen vacancies associeted with barium vacancies $V_{Ba}''-V_O^{\cdot\cdot}$) located near the grain boundary or and electrode/film interface can promove the hysteresis loops.

In summary, postannealing in oxygen and nitrogen atmospheres contributed significantly to the dielectric properties of BST films. Postannealing in an oxygen atmosphere increased the dielectric relaxation phenomenon, while a slighter dielectric relaxation phenomenon was observed when the capacitor was postannealed in a nitrogen atmosphere. These results suggest that the postannealing treatment in an oxygen atmosphere can increase the trapped charge and the relaxation phenomenon. On the other hand, the results also demonstrate that the best atmosphere for BST films to reach good dielectric properties, free of the relaxation phenomenon, is postannealing in a nitrogen atmosphere.

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