Thin film (Ba,Sr)TiO$_3$ (BST) has attracted a lot of attention in recent years because of its high dielectric constant and the fact that when it is in contact with high work function electrodes (such as metal Pt), it can be used to make low-leakage on-chip capacitors used in very large-scale integrated dynamic random access memory. It is generally recognized that these Pt/BST/Pt capacitors have a Schottky barrier at both electrodes. The mechanism of leakage current of the capacitors has been ascribed to the variation of the oxygen vacancies in the BST films. These high-leakage currents present an urgent problem to be resolved in Pt/BST/Pt capacitors.

It was reported that the leakage current of Pt/BST/Pt capacitors could be effectively reduced by annealing in an oxygen ambient with high processing temperatures (>500 °C). The oxygen vacancy in the BST films is supposed to be compensated by influx of oxygen through platinum films where the grain boundaries of the columnar structure act as a fast diffusion path for oxygen. While if the Pt/BST/Pt capacitors go through postannealing above 500 °C under an inert atmosphere (such as N$_2$), oxygen vacancies will be formed and the leakage current will increase.

It has recently been reported by Pontes et al. that postannealing of Pt/BST/Pt capacitors in an oxygen atmosphere at 350 °C increases the dielectric loss and dielectric relaxation, while postannealing in nitrogen at 350 °C reduces the dielectric loss and dielectric relaxation. They concluded that the postannealing treatment in oxygen ambient at 350 °C could increase the trapped charge related to oxygen vacancies and negatively charged oxygen which is caused by charge transfer between the Barium vacancy and the oxygen. Thus, it seems that the results has been totally reversed compared with that of postannealing in oxygen above 500 °C. However, there is no theory or detailed experiment to explain this important phenomenon to date. More research is also needed to understand the difference between the Pt/BST/Pt capacitors being postannealed in oxygen and in nitrogen atmosphere at different temperatures. In this letter, we report an investigation on the dependence of the leakage characteristics and dielectric properties on postannealing temperature in both oxygen and nitrogen atmospheres in order to examine when the low-frequency dielectric relaxation appears and what the mechanism is.
The corresponding current–voltage ($I$–$V$) characteristics are shown in Fig. 2. The as-deposited capacitors have a dielectric constant of near 320 at 1 kHz and show a slight dielectric dispersion within the frequency range of 100 Hz to 2 MHz. The leakage currents are almost flat and are as low as $6 \times 10^{-9}$ A/cm² in the electric field range of $-150$ to $150$ kV/cm, as shown in Fig. 2(a). Similar results have been reported by others for as-deposited films prepared by pulsed laser deposition technique. The as-deposited capacitors have gone through five postannealing processes as described in Table I. First, the BST films were postannealed at 350 °C for $8$ h in oxygen. To our surprise, unlike the results of Pontes et al., there is no dielectric relaxation phenomenon in the low-frequency region in our films. The leakage currents increase a little in the high electric field region compared with the as-deposited films. The second postannealing was performed at 550 °C for $3$ h in nitrogen in order to increase the density of oxygen vacancies. It can be seen from the $I$–$V$ characteristics in Fig. 2 that both the forward and reverse currents were greatly increased. This is caused by the generation of higher density of oxygen vacancies near the interface of BST film and the Pt electrodes, as recognized by many research groups. We noticed that there was almost no change in the dielectric constant, but very large dielectric relaxation in the low-frequency region appeared when the films were again postannealed at 350 °C for $8$ h in oxygen. The leakage currents are also greatly increased after the third annealing. According to the Maxwell–Wagner (MW) model, the results indicate that a layer with lower resistivity is formed in the BST films during the postannealing treatment in an oxygen atmosphere at 350 °C after the formation of higher density of oxygen vacancies. The relaxation phenomenon almost disappeared after the films were postannealed the fourth time at 350 °C for $8$ h in $N_2$, and the leakage currents decreased at the same time. This result indicates that the lower resistivity layer in the BST films disappeared during the fourth postannealing process. In addition, the leakage currents decreased even further after the capacitors being postannealed the fifth time in oxygen for $3$ h at 550 °C. This is because oxygen will compensate for the oxygen vacancies at this temperature. Note that the first postannealing step causes no significant influence on the aforementioned results of other steps because we postannealed the as-deposited Pt/BST/Pt capacitors fabricated in the same conditions directly from the second step to the fifth step and got similar results. In addition, it can be noted from Fig. 1 that the dielectric constant reduces a little after the postannealing processes. This may be due to the stress release at the interface of the as-deposited capacitors and/or the film thickness deviation.

Figure 3 shows the corresponding dielectric loss as a function of frequency. Similar to the results of dielectric constant in Fig. 1, these are significant increases in the low-frequency range after the capacitors were postannealed through the third step. The dielectric loss comes from two mechanisms: resistive loss and the relaxation loss of the dipole. In the resistive loss mechanism, the energy is consumed by mobile charges in the film. The contribution from the mobile charges reduces with the increase of frequency since they can not follow higher frequency field. In other words, the dielectric loss is slowly reduced with the increase of frequency. In order to check whether there are mobile charges in the film after the third postannealing, we added a dc bias on the top electrode during the measurements of dielectric properties. The results are shown in Fig. 4. We found that the dielectric constants at 500 Hz are enhanced by either negative or positive dc bias. The process is reversible, the dielectric constants slowly reduced back to their original values after the dc bias is turned off, as shown in Fig. 5. It was also found that the dielectric loss also has similar behavior. These results indicate that there are mobile charges in the BST films after the third postannealing, and these mobile charges may accumulate near the top and bottom interface between BST film and Pt electrodes. Such phenomenon did not occur in the films after the first three postannealing processes.

![Image](image_url)

**FIG. 2.** Change of leakage currents of Pt/BST/Pt capacitors with respect to applied field for samples corresponding to Fig. 1.

**FIG. 3.** Frequency dependence of the dielectric loss for samples corresponding to Fig. 1.

**TABLE I.** The postannealing conditions of the each step.

<table>
<thead>
<tr>
<th>Step</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Postannealing Conditions</td>
<td>$O_2$, 8 h</td>
<td>$N_2$, 3 h</td>
<td>$O_2$, 8 h</td>
<td>$N_2$, 8 h</td>
<td>$O_2$, 3 h</td>
</tr>
<tr>
<td>$O_2$, 8 h</td>
<td>350 °C</td>
<td>350 °C</td>
<td>350 °C</td>
<td>550 °C</td>
<td></td>
</tr>
</tbody>
</table>
not occur in the as-deposited films and those films after other postannealing steps.

Different from Pontes et al.’s report the low-frequency dielectric enhancement in the present study can not be explained by the existence of barium deficiency in the BST films because we did not find the phenomenon if the second postannealing step was not performed. The BST films fabricated using different methods may cause this discrepancy. Thus, there must be other reasons to explain the results of this work. Most studies showed that annealing Pt/BST/Pt thin-film capacitors in forming gas results in a large increase of both leakage current and low frequency dielectric relaxation. The H$^+$ ions and oxygen vacancies accumulated in the BST thin films are supposed to be responsible for this phenomena. With some analysis, we proposed that the oxygen vacancies formed during the second postannealing step and the charged oxygen ions produced during the third postannealing step accumulated in the BST films are responsible for the high-leakage current and low-frequency dielectric constant relaxation. When the capacitors were subjected to reduced atmosphere during annealing, such as nitrogen and forming gas, it is generally believed that oxygen vacancies are produced by the following process:

$$O_2(\text{oxygen ion at its normal site}) \rightarrow V_o^{++} (\text{oxygen vacancy}) + 2e^- + 1/2O_2$$

However, in the process of compensating oxygen vacancies $V_O^{++}$, two steps might happen:

$$\frac{1}{2}O_2 + e^- \rightarrow O^{2-},$$
$$O^{2-} + V_o^{++} \rightarrow O_2, \quad (T_2 > T_1).$$

First, the oxygen molecules may get electrons and become charged oxygen ions. This chemical step occurs at temperature $T_1$ (near 350 °C) and the dissociation process of the oxygen molecule should be supported by the oxygen vacancies in the BST films. Then, the oxygen ions, which may weakly trapped near $V_o^{++}$ and be mobile under an electric field, will get into its normal site at a higher temperature $T_2$ (above 500 °C). Thus, if Pt/BST/Pt capacitors with a higher density of oxygen vacancies were postannealed in an oxygen ambient at a lower temperature (near 300 °C), a large amount of negatively charged oxygen ions will be produced. The existence of oxygen ions forms a layer with a lower resistivity leading to low-frequency dielectric relaxation and high loss as predicted by the MW model. While annealing in a nitrogen ambient at a lower temperature will reverse this process because of the reduced oxygen atmosphere, this leads to the reduction of dielectric relaxation and leakage current. If annealing at a higher temperature in oxygen, both steps will happen and the oxygen vacancies are compensated.

In conclusion, postannealing in oxygen and nitrogen atmospheres at 350 °C and 550 °C result a significant difference in the dielectric properties and leakage current characteristics of BST films. High-leakage currents and dielectric relaxation in the low-frequency region were found after the as-deposited Pt/BST/Pt capacitors being first postannealed in nitrogen at 550 °C and then in oxygen at 350 °C. The results suggest that postannealing treatment in oxygen at a lower temperature on Pt/BST/Pt capacitors with a higher density of oxygen vacancies in the BST films can increase the oxygen-related mobile charges in the films. The formation mechanism of charged oxygen ions during the postannealing process has been proposed.

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$^{8}$H. Neumann and G. Arlt, Ferroelectrics 69, 179 (1986).


