Large reduction of leakage current by graded-layer La doping in $(Ba_{0.5},Sr_{0.5})TiO_3$ thin films

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A large reduction in the leakage current behavior in $(Ba, Sr)TiO_3$ (BST) thin films was observed by graded-layer donor doping. The graded doping was achieved by introducing La-doped BST layers in the grown BST films. The films showed a large decrease (about six orders of magnitude) in the leakage current in comparison to undoped films at an electric field of 100 kV/cm. The large decrease in leakage current was attributed to the formation of highly resistive layers, originating from compensating defect chemistry involved for La-doped films grown in oxidizing environment. Temperature-dependent leakage-current behavior was studied to investigate the conduction mechanism and explanations of the results were sought from Poole–Frenkel conduction mechanism.

Thin films of $(Ba, Sr)TiO_3$ (BST) compositions have been extensively studied in recent years, upsurged by the strong demand for high dielectric constant materials for dynamic random access memories, high frequency devices, and a variety of other applications.[1–3] Several issues, however, are still being studied to provide better performance in the final device form. The incorporation of aliovalent cations in $BaTiO_3$, $SrTiO_3$, and BST both bulk and thin film form have been shown to bring about remarkable change in their electrical properties.[4–7] The presence of inherent Schottky defect concentrations in these compounds is highlighted in their electrical properties and is influenced by the processing conditions. To this extent, the introduction of different aliovalent substitution show improved leakage and breakdown properties.[7,8] In most cases it has been found that donor substitution enhances the electrical properties of titanate perovskites,[8] owing to their ability of carrying extra oxygen with them, which suppresses the inherent oxygen vacancy concentration. However, several reports show that an excess of doping leads to gradual changes in the properties of the original compound,[9,10] hence, the motivation lies in retaining the original properties and improving them through further means.

In this letter we report the cationic substitution of La in Ba, Sr site, which has been used to study the effect of dopant incorporation in BST for a graded doped film mentioned later. The doping concentration has been varied such that it introduces a gradient in the composition of the deposited film. A multilayer structure has been used to study the effect of donor concentration gradient in the films, starting from the undoped BST layer to a 5 at. % doping in the inner most layers. Both dc and ac measurements have been carried out on the grown samples showing distinct change in their electrical properties. A possible explanation of the change in electrical properties have been sought from the viewpoint of the defect chemistry present, and a study of the conduction processes in terms of their activation energies.

The graded-doped BST thin films have been grown using a pulsed laser deposition process described in detail elsewhere.[11] The substrates were Pt-coated Si and the films were deposited at 600 °C at an oxygen pressure of 10–50 mTorr. After deposition the sample was slowly cooled to room temperature within the chamber at 5 Torr oxygen pressure. The individual layers were grown from different targets having different doping concentrations without breaking the vacuum to eliminate the formation of any surface layers, which might extrinsically affect the film properties. The final film consisted of 0–3–5–3–0 at. % of La doping in the BST films. Each layer thickness was around 30 nm giving a final thickness of around 150 nm. The grown films were successively characterized for phase using x-ray diffraction and electrical properties such as leakage current and ac dielectric response. Gold dots of 1.9×10^{-3} cm^2 area deposited by thermal evaporation were used as top electrodes in a metal–insulator–metal configuration for the electrical measurements. For the dielectric measurement a Keithley LCR meter was used with an oscillating voltage of 50 mV. Leakage current was measured using a computer interfaced Keithley programable source measure unit. Variation in sample ambient temperature for leakage current measurement was provided, where the temperature was stabilized prior to each measurement.

The crystalline structure of the as-deposited films, determined by x-ray diffraction is shown in Fig. 1. A primary observation reveals that for graded doped films the crystal structure remains cubic in nature without any unwanted phase formation. The film shows a strong reflection along the (100) crystal plane. Similar crystal structures have been reported earlier for films grown under *in situ* crystallization conditions where the necessary energy for crystallization is provided by the heated substrate.[12] The undoped case show highly oriented films with a strong reflection along the (100) crystal plane, while in the doped case a reduction in the peak intensity for both (100) and (200) peaks is observed. The perceptible change in the peak intensities may be attributed

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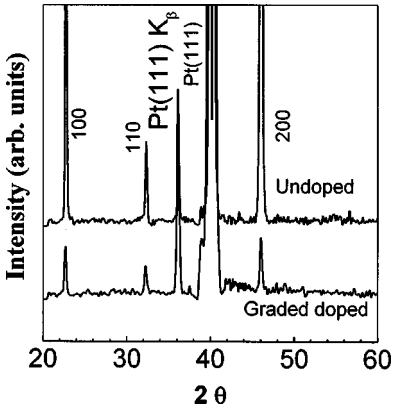

FIG. 1. X-ray diffraction pattern of undoped and graded La-doped BST thin films.

to the underlying microstructure. However, cross-sectional scanning electron microscopy studies revealed columnar grain structure in all the doped and undoped films.[12]

The frequency dispersion of the measured dielectric constant is almost negligible as observed from Fig. 2, except at very low frequency where we see a sudden fluctuation of the data. The dielectric constant as determined from the capacitance measurement of the graded films was 427 (at 100 kHz), which was much reduced in comparison to the undoped films ($\varepsilon > 500$) and a dissipation factor of 0.02.

Figure 3 shows the variation in leakage current density with applied electric field for undoped and graded-doped BST films. The technique followed for measuring the true leakage current, avoiding polarization current and field induced degradation components has been reported earlier.[11] The figure shows an appreciable decrease in the leakage current for the graded-doped BST thin films. It is necessary to mention here that, homogenous or uniform donor doping also results in decreased leakage current,[10] but not to that extent as obtained in the present case. The decrease in leakage current (around six orders less in comparison to undoped films at an electric field of 100 kV/cm) in such a graded-doped structure can be attributed to the compensating defect chemistry involved in a donor doped sample. Lanthanum acting as a donor in the system suppresses the inherent oxygen vacancy concentration when processed under an oxidizing environment,[13] leading to a reduction in the concentration of charge carriers. The aspect of defect chemistry involved in such perovskite titanates as BST is given in detail in Ref. 13.

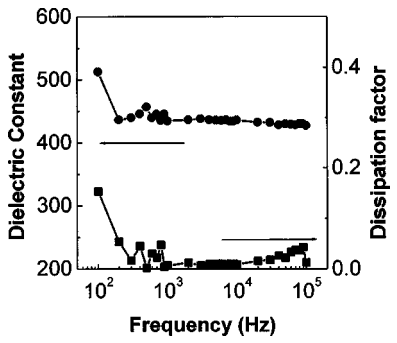

FIG. 2. Pot of dielectric constant and dissipation factor as a function of frequency in graded La-doped BST thin films measured at room temperature.

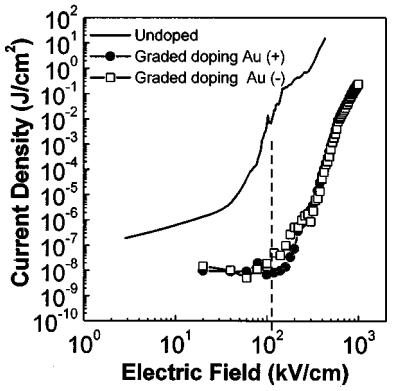

FIG. 3. Leakage current as a function of applied field for undoped and graded La-doped BST thin films. The (+) and (−) sign signifies the top Au electrode is kept at positive and negative bias with respect to the bottom Pt electrode. The leakage characteristics at room temperature of graded doped films show almost six orders of magnitude decrease in the leakage current at 100 kV/cm marked by the dashed line.

Since the donor doping concentration varies throughout the film thickness, it is bound to alter the normal charge transport process, leading to various bulk phenomena. Bulk mode of conduction is verified from the fact that the leakage current in the high field region is polarity independent as shown in the figure (Fig. 3).

Several modes of conduction for BST thin films have been suggested in the literature.[14] The Poole–Frenkel conduction mechanism, which is a bulk phenomenon, is characterized by the following equation:[15]

$$J = \frac{4\pi m q k^2}{h^3} E \exp - \left[\frac{\phi - \alpha_{\mathrm{P-F}} E^{1/2}}{kT} \right], \qquad \alpha_{\mathrm{P-F}} = \sqrt{\frac{q}{\pi \varepsilon_0 \varepsilon_r}}, \tag{1}$$

where J is the current density (A/m^2), m is the electronic mass, q is the electronic charge, k is the Boltzmann's constant, h is the Planck's constant, E is the applied electric field, ϕ is the depth of the potential well, ε_0 is the permittivity of free space, and ε_r is the high frequency dielectric constant. Figure 4 shows the variation in leakage current with applied electric field (plotted as J/E vs $E^{0.5}$ in V/m) as

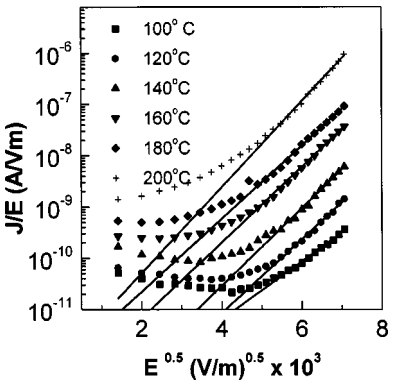

FIG. 4. Leakage current as a function of applied field measured at different temperatures [plotted as (J/E vs $E^{0.5}$)] in a Poole–Frenkel plot shows agreement with theory at high applied fields and deviation in the low field regime. The voltage ramping rate for the experimental data was kept at 0.1 V/s. The scattered data represents experimental values while the solid lines represent theoretical fits to the experimental data.

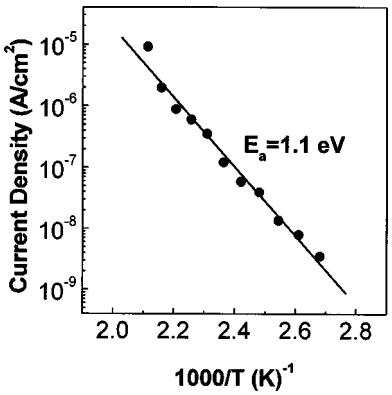

FIG. 5. Arrhenius plot of the leakage current measured at 500 kV/cm showing the linear behavior with 1000/T. The calculated activation energy from the slope of the linear fit is around 1.1 eV.

a function of the ambient temperature. One observes an increase in the leakage current with increase in temperature suggesting a thermally assisted conduction process. The theoretical fits for the Poole–Frenkel mechanism is shown as solid lines in Fig. 4. The graph shows good match with the theoretical fits at higher electric fields while we observe a deviation at lower fields. This implies that the Poole–Frenkel mechanism is only dominant in the high-field regime. The high frequency dielectric constant as obtained from the theoretical fits is in the range of 3.3 to 0.9 decreasing as the temperature is increased. The results agree very well with published data for the high frequency dielectric constant of BST taking into account the lowering due to La doping.[16]

The plot of the leakage current in an Arrhenius representation is shown in Fig. 5 for a temperature range 100–200 °C. The value of the activation energy obtained from the linear fit of the data is around 1.1 eV. This further supports the analysis based on the Poole–Frenkel conduction mechanism. According to published reports the doubly ionized oxygen $V_{\ddot{O}}$ vacancy level lies in the band gap of $BaTiO_3$ at around 1 eV below the conduction band edge.[17] Thus ionization energy required for an electron to be released from such a donor level is then 1 eV. Considering the conduction process as observed from the earlier results one finds it feasible enough to assume an electronic conduction with a trap level 1 eV below the conduction band edge. This satisfies the physical model for a Poole–Frenkel conduction process.

In summary, graded La doped BST thin films were grown using a pulsed laser ablation technique showing a large decrease of leakage current in comparison to undoped BST films. An analysis was provided to study the actual conduction process revealing a Poole–Frenkel type conduction.

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