Defects control for improved electrical properties in \((\text{Ba}0.8\text{Sr}0.2)(\text{Zr}0.2\text{Ti}0.8)\text{O}-3\) films by Co acceptor doping

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In this letter, the effect of doping with low concentration of Co on the dielectric and leakage properties of (Ba,Sr)(Zr,Ti)O$_3$ (BSZT) films is investigated. Details of Co doping on electrical properties of the films have been reported elsewhere. Figure 1(a) shows the 0-20 XRD patterns of the BSZT films on LSCO buffered (001) STO single crystals. Only the (h00) peaks of the BSZT:Co films and the (000) peaks of the LSCO films are observed, indicating that those films grew perpendicular to the surface of STO substrate. Lattice parameters along the (h00) direction of the BSZT:Co thin films can be estimated from the (200) peaks ($2\sin \theta = \lambda$). The inorganic of Co$_2^+$ (0.75 Å) is larger than that of Zr$_4^+$ (0.72 Å) and Ti$_4^+$ (0.61 Å), but it is smaller than that of Ba$_2^+$ (1.35 Å) and Sr$_2^+$ (1.18 Å). The lattice parameter of the BSZT0, BSZT0.6, and BSZT13 are 3.971 Å, 3.984 Å, and 4.011 Å, respectively. An increase in the lattice parameter with increase of Co-concentration in the films implies that the Co$_2^+$ ions should be substituted into the B-site of ABO$_3$ perovskite structures.
Figure 1(b) shows the ϕ-scans of the BSZT6 (202), LSCO (202), and STO (202) reflections. The azimuthal diffraction patterns of the BSZT6 film, LSCO bottom layer, and STO substrate clearly reveal the four-fold symmetry with the same orientation. No other peaks can be found in the intervals between those peaks, implying a highly oriented growth mode of BSZT6 and LSCO layers on STO substrate. Figure 1(c) depicts a typical Williamson-Hall plot for the 0.6% Co-doped BSZT films. Four planes (i.e., (103), (203), (303), and (402)) are selected for the Williamson-Hall plots analysis
\begin{equation}
(\beta \cos \theta)^2 = (K\lambda/D)^2 + (4e_\varepsilon \sin \theta)^2,
\end{equation}
where \(\beta\) is the measured diffractions peak width by subtracting the instrumental contributions; \(K\) is a geometrical constant close to 1; \(\lambda\) is the x-ray wavelength; and \(D\) is the coherence length along the scattering vector. The defect-induced inhomogeneous strain \((\varepsilon_i)\) is extracted from the slope of linear fits of \((\beta \cos \theta)^2\) as a function of \((2 \sin \theta)^2\). According, the values of \(\varepsilon_i\) are estimated to be 0.31 ± 0.02%, 0.26 ± 0.01%, and 0.17 ± 0.01% for BSZT0, BSZT6, and BSZT13 films, respectively. The result indicates a reduction of defect-induced inhomogeneous strain in the films due to the existence of Co-dopants.

In order to gain further insight on the effect of Co doping on the inhomogeneous strain in the BSZT films, we examine the ac electric-field dependence of dielectric constant at 1 MHz, as shown in Fig. 2. In the measurement, the samples were preliminarily polarized by cycling 10^5 times at 25 kV/cm to obtain a linear dielectric response.12 Under subswitching fields, the domain-wall contribution to the dielectric permittivity \(\varepsilon(E)\) can be examined by the Rayleigh law,13
\begin{equation}
\varepsilon(E) = \varepsilon_0\varepsilon_{\text{init}} + \varepsilon_\sigma E,
\end{equation}
where \(E(E < E_C)\) is the applied ac field and \(E_C\) is the coercive field; \(\varepsilon_0\) is the vacuum permittivity; \(\varepsilon_{\text{init}}\) is the initial permittivity without external field; and \(\varepsilon\) is the Rayleigh coefficient due to the irreversible displacement of domain wall. Our study reveals that the Rayleigh coefficient \(\varepsilon\) of BSZT:Co films increases with increasing Co dopant concentration. A theory of Boser13 indicates that the reciprocal of the Rayleigh coefficient \(\varepsilon^{-1}\) is proportional to the defect concentration, implying that the concentration of defects that affecting the domain wall motion in BSZT films decreases with increase Co-dopant in the films.

The influence of Co-doping on the current density \(J\) versus electric field \(E\) characteristics of BSZT films is shown in Fig. 3(a). The leakage current in the undoped BSZT film is remarkably reduced upon addition of Co at each given electric field. Such a phenomenon is consistent with previous study that Co dopants can significantly decrease the leakage current in BST films.5 Another interesting feature in Fig. 3(a) is that in different electric field regions, the Co-doping dependence of leakage current shows different characteristics. The bias polarity dependence of the \(J–E\) characteristics reveals that different leakage mechanisms operated in the positive and negative bias region.

Figure 3(b) shows the relationship of \(\ln(J/E) \sim E^{1/2}\) for BSZT-Co films under a positive bias, which can be divided into two regions corresponding to Poole-Frenkel (P-F) conduction and Fowler-Nordheim (F-N) tunneling regions. At a low field region, the leakage current can be characterized using the P-F conduction mechanism,
\begin{equation}
J_{PF} \sim E \exp \left(-\frac{\varepsilon_0 E_1}{kT} - \frac{e\varepsilon_0 E_{02}}{\pi e_\sigma \varepsilon_{\text{op}} kT}\right),
\end{equation}
where \(E\) is the barrier height; \(k\) is the Boltzmann constant; \(e\) is the charge of an electron; and \(\varepsilon_{\text{op}}\) is the optical dielectric permittivity. By extracting the optical dielectric constant from the slopes of the curves, the conduction mechanism can be identified. It is found that \(\varepsilon_{\text{op}}\) range from 3.8 ~ 5.6 at \(E^{1/2} < 0.42\) MV/cm, which are quite close to the expected dynamic permittivity of BSZT films \((\varepsilon_{\text{op}} \sim 4)\).15 At the high field region, \(\varepsilon_{\text{op}}\) deviates from the ideal value of \(4\) and follows the F-N tunneling behaviors,
\begin{equation}
J_{FN} \sim E \exp \left(-\frac{2e^2m^*}{\pi e_\sigma \varepsilon_{\text{op}} k^2 T}\right),
\end{equation}
where \(m^*\) is the effective electron mass; \(\varepsilon_{\text{op}}\) is the potential barrier height. A good fitting of leakage current data was found at \(E^{1/2} > 0.42\) MV/cm. Thus, the F-N tunneling appears as the dominant leakage current mechanism at the high field region due to electric-field concentration.

In Fig. 3(d), the \(\log J\) is plotted as a function of \(\log E\) for the leakage current data of BSZT:Co films for the negative bias region. The curves clearly show different slope regions for the \(J-E\) characteristics. It can be seen that all curves...
follow a space-charge-limited (SCL) conduction behavior, which is expressed as \[ J_{\text{SC}, \text{LC}} = 9e_0\varepsilon_0\mu d^2/8d, \]
where \( \varepsilon_\text{i} \) is the permittivity of the insulator; \( \mu \) is the free electron mobility; and \( d \) is the film thickness. At the low bias region I, the slopes of \( \log J \sim \log E \) curve are all close to 2, indicating a transition from Ohmic to SCL behaviors. With increasing electric fields, a transition region characterized by a large slope of \( \sim 5 \)–6 is seen (region II). Upon further increasing, the electric field, the slopes of \( J \sim E \) curves change to about 2–3 again (region III). The deviations of the slope in regions I and III can be attributed to the scattered distribution of the trapping levels because of structural and chemical disorders in the films.

Now we explore the possible applications of these materials in tunable microwave applications. Figure 4 shows the dc electric-field \( E_\text{dc} \) dependence of dielectric permittivity \( \varepsilon' \) and loss tangent \( \tan \delta \) at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved. For example, the loss tangent at zero electric field of the films were improved.

where \( \beta \) is the Landau parameter; \( \varepsilon_\text{i}(0) \) and \( \varepsilon_\text{i}(E) \) are the dielectric permittivity at zero and applied electric field \( E \), respectively. The values of \( \beta \) for BSZT0, BSZT6, and BSZT13 samples are estimated to be \( 2.7 \times 10^9 \), \( 5.3 \times 10^9 \), and \( 9.1 \times 10^9 \) \( \text{m}^2\text{F}^{-1}\text{V}^{-2} \), respectively. The dielectric tunability is defined as \( \eta = \varepsilon_\text{i}(0) - \varepsilon_\text{i}(E) \) and the figure of merit (FOM) can be obtained using FOM = \( \eta / (\tan \delta)_{\text{max}} \).

It is found that the dielectric tunability (@375 kV/cm) of BSZT0, BSZT6, and BSZT13 samples are 54.5%, 69.1%, and 63.7%, respectively, and the FOM are 15.1, 38.5, and 65.7, respectively. The result shows that a small quantity of Co can improve the tunable properties in BSZT films.

In summary, Co-doping has been shown to be an efficient way to improve the electrical properties of the BSZT films. Changes in inhomogeneous strains in BSZT films caused by Co doping were investigated through the W-H plot analysis. The dependence of Rayleigh coefficient under subswitching fields on the doping concentration was examined. The leakage current properties were investigated by systematically studying the \( J \)-\( E \) characteristics under positive and negative biases. This study suggest that the defects concentrations is responsible for the improved electrical properties in the BSZT:Co films.

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