

Surface chemical bonding states and ferroelectricity of Ce-doped BiFeO₃ thin films prepared by sol–gel process

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Abstract Bi_{1-x}Ce_xFeO₃ ($x = 0, 0.05, 0.1, 0.15$ and 0.20) (BCFO) thin films were deposited on Pt/TiN/Si₃N₄/Si substrates by sol–gel technique. Crystal structures, surface chemical compositions and bonding states of BCFO films were investigated by X-ray diffraction and X-ray photoelectron spectroscopy (XPS), respectively. Compared to BiFeO₃ (BFO) counterparts, the fitted XPS narrow-scan spectra of Bi 4f_{7/2}, Bi 4f_{5/2}, Fe 2p_{3/2}, Fe 2p_{1/2} and O 1s peaks for Bi_{0.8}Ce_{0.2}FeO₃ film shift towards higher binding energy regions by amounts of 0.33, 0.29, 0.43, 0.58 and 0.49 eV, respectively. Dielectric constants and loss tangents of the BCFO ($x = 0, 0.1$ and 0.2) film capacitors are 159, 131, 116, 0.048, 0.041 and 0.035 at 1 MHz, respectively. Bi_{0.8}Ce_{0.2}FeO₃ film has a higher remnant polarization ($P_r = 2.04 \mu\text{C}/\text{cm}^2$) than that of the BFO ($P_r = 1.08 \mu\text{C}/\text{cm}^2$) at 388 kV/cm. Leakage current density of the Bi_{0.8}Ce_{0.2}FeO₃ capacitor is $1.47 \times 10^{-4} \text{ A}/\text{cm}^2$ at 388 kV/cm, which is about two orders of magnitude lower than that of the BFO counterpart. Furthermore, Ce cations are feasibly substituted for Bi³⁺ in the Bi_{0.8}Ce_{0.2}FeO₃ matrix, possibly resulting in the enhanced ferroelectric properties for the decreased grain sizes and the reduced oxygen vacancies.

Keywords BiFeO₃ thin films · Ce-doping ·
Surface chemical bonding states ·
Dielectric and ferroelectric properties

1 Introduction

ABO₃-type perovskite structure BiFeO₃ (BFO) has attracted much attention because it is a known Pb-free and environmentally friendly material that simultaneously shows electric and magnetic ordering in the same phase [1–3]. Based on the specific characteristics, including magnetoelectric coupling effects [1], high Curie temperature ($T_C \sim 1,103 \text{ K}$) and Néel temperature ($T_N \sim 643 \text{ K}$) [4], and small optical bandgap ($E_g \sim 2.5 \text{ eV}$) [5], BFO thin films have potential applications in magnetic/ferroelectric data storage media, spintronics, nonvolatile memories, photocatalytic compound and ultrafast optoelectronic devices [1, 3, 5, 6]. Though as promising as BiFeO₃ films are, there are still drawbacks, such as large dielectric loss, small remnant polarization, high coercive field, high leakage current and inhomogeneous magnetic spin structure [4, 7, 8], to be overcome before practical applications. One way of doing so is by doping BFO films with other elements. In order to enhance ferroelectric properties, reduce leakage current, modify its spatially inhomogeneous spin-modulated incommensurate structure, and intensify magnetoelectric interaction, several research groups have tried A-site, B-site or (A, B)-sites of BFO films substituting by La [2, 7], Tb [9], Gd [10], Sc [4], Ti [11], Cr [12], La and Ti [13], La and Mn [14] as well as La and Nb [15]. More recently, Shannigrahi et al. reported that impure phase appeared in 0.5 mol% Sc-doped BFO film, and leakage current, ferroelectric and magnetic properties were improved for 0.3 mol% Sc-doped BFO [4]. Wang et al. investigated that Ti⁴⁺ ions were used to substitute some of Fe cations to form Ti_{Fe}^{••} as substituting Fe²⁺ or Ti_{Fe}[•] as substituting Fe³⁺, which could eliminate oxygen vacancies in the Ti-doped BFO films because of the requirements of charge compensation [11]. Cheng et al. found that the

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ferroelectric properties were significantly improved, and the ferromagnetic moments were kept at a high level for the (La, Nb)-codoped BFO films [15]. Being a lanthanide element, however, Ce has remained relatively unexplored in doping BFO films.

In this study, crystal structures, surface chemical compositions and bonding states of pure and Ce-doped BFO films were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. Chemical shifts of Bi 4f_{7/2}, Bi 4f_{5/2}, Fe 2p_{3/2}, Fe 2p_{1/2}, O 1s, Ce 3d_{5/2} and Ce 3d_{3/2} peaks for pure BFO and Bi_{0.8}Ce_{0.2}FeO₃ films were analyzed by fitting the corresponding XPS narrow-scan spectra. Dielectric and ferroelectric properties of the pure and Ce-doped BFO film capacitors were also discussed.

2 Experimental details

Bismuth nitrate [Bi(NO₃)₃ · 5H₂O], iron nitrate [Fe(NO₃)₃ · 9H₂O] and cerium nitrate [Ce(NO₃)₃ · 6H₂O] were suitably dissolved in the mixtures of 2-methoxyethanol (CH₃OCH₂CH₂OH) and glacial acetic acid (CH₃COOH), while Ce contents were determined by composition formulae Bi_{1-x}Ce_xFeO₃ (abbreviated as BCFO), where *x* is equal to 0 (for pure BFO), 0.05, 0.10, 0.15 and 0.20, respectively. Meanwhile, acetylacetonone (CH₃COCH₂COCH₃) and *N,N*-dimethyl formamide [(CH₃)₂NOCH] in 1 to 1 molar ratio with respect to Fe(NO₃)₃ · 9H₂O were used to stabilize BCFO solutions. The stock solutions were stirred at 318 K for 240 min to obtain homogeneous BCFO precursors. BCFO sols were spin-coated onto Pt (111)/TiN/Si₃N₄/Si (100) substrates at 3,000 rpm for 20 s. After each spin-coating, the green BCFO films were dried at 393 K for 10 min, and then prebaked at 693 K for 30 min in the air to remove organic contaminations. This procedure was repeated several times to obtain appropriate thickness. Finally, BCFO films were annealed in a quartz tube furnace at 873 K for 60 min under a N₂ ambience, and then cooled down slowly to room temperature.

Crystal structures of BCFO films were analyzed by XRD (D8 Advance, Bruker Corp.) with Cu K_α radiation. Thicknesses of BCFO films were measured by scanning electron microscope (SEM) (Sirion FEG, FEI Co.). Surface chemical compositions and binding states of the corresponding elements for BFO and Bi_{0.8}Ce_{0.2}FeO₃ films were investigated by XPS (VG MultiLab 2000, Thermo Electron Corp.). The XPS Al K_α source operating at 300 W provided nonmonochromatic X-rays at 1,486.6 eV. Photoelectric peak of C 1s located at 284.6 eV was assigned to carbon from adventitious contaminations, and it was used as the criterion to rectify binding energies of XPS spectra. Software of XPSPEAK Version 4.1 was used to fit the narrow-scan

spectra of Bi 4f, Fe 2p, O 1s and Ce 3d after Shirley-type background subtraction [16, 17]. For comparison, 120-nm-thick Pt top electrodes with diameter of 0.3 mm were sputtered on BCFO films through a metal shadow mask. To understand Ce-doped influence on dielectric and ferroelectric properties of BFO film, capacitance–frequency and dielectric loss–frequency curves for the BCFO (*x* = 0, 0.1 and 0.2) film capacitors were measured by a precision impedance analyzer (Agilent 4294A, Agilent Technologies Ltd.). Polarization–electric field (*P*–*E*) hysteresis loops and leakage current density–electric field (*J*–*E*) curves for the same BCFO capacitors were measured by a precision materials analyzer (RT6000, Radiant Technology Inc.). All measurements were carried out at room temperature.

3 Results and discussion

Figure 1 shows XRD patterns of BCFO films annealed in 873 K for 60 min under a N₂ ambience. It is found that all the BCFO films are polycrystalline and exhibit a single-phase perovskite structure. Non-perovskite phase such as Bi₂Fe₄O₉, Bi₃₆Fe₂O₅₇ and Bi₁₂(Bi_{0.5}Fe_{0.5})O_{19.5} [6, 18] are not detected in the XRD patterns. The obvious peak-splitting XRD pattern for the BCFO film with *x* = 0 indicate that the BFO film is rhombohedral phase (space group *R3c*) [10]. As shown in the broken square of Fig. 1, (104) and (110) peaks of BCFO films move closer together along with broadening, indicating a structural change [19, 20] with increasing Ce content. Since ionic radii of Ce³⁺ (1.18 Å) and Ce⁴⁺ (1.02 Å) are smaller than that of Bi³⁺ (1.20 Å) [21], Ce cations are partially substituted for Bi³⁺

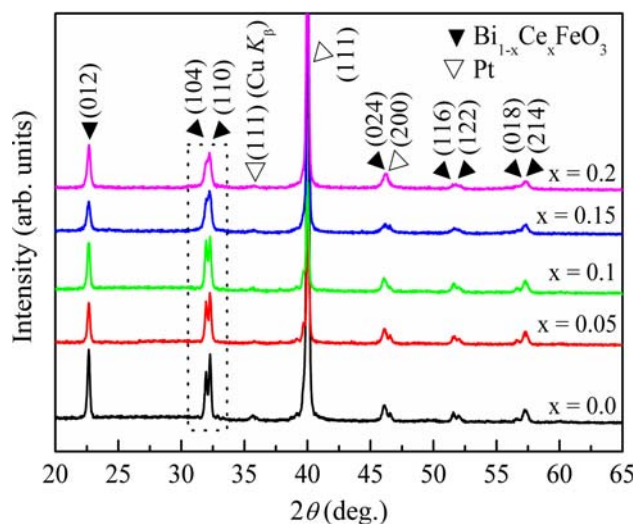
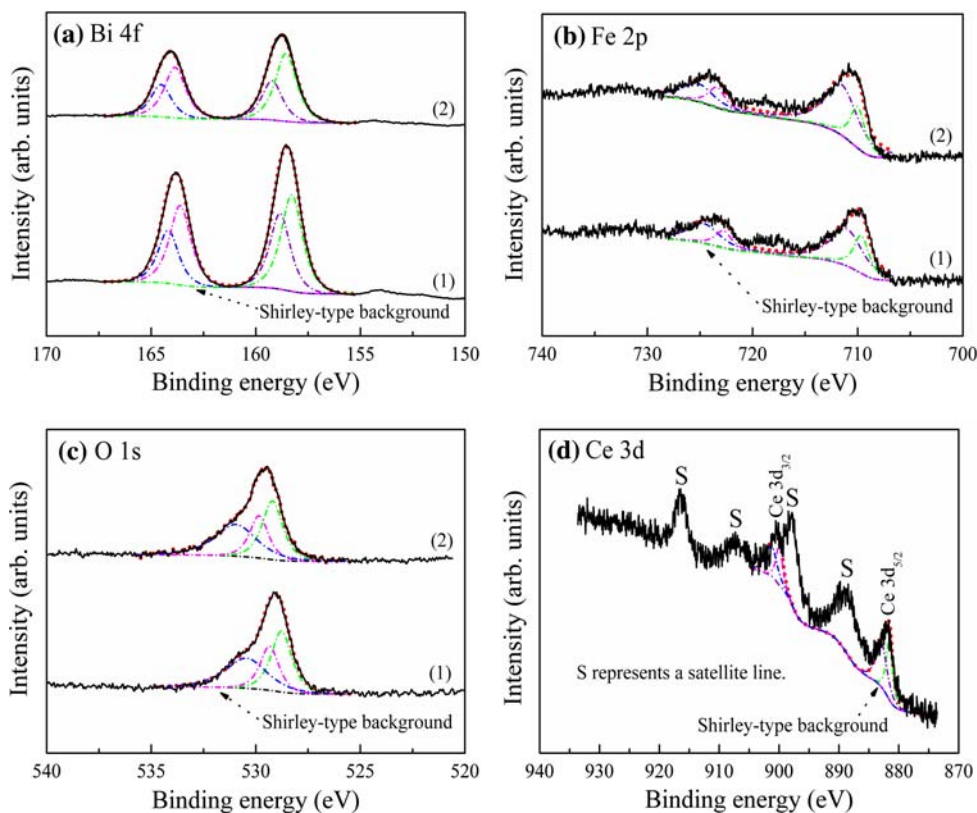


Fig. 1 XRD patterns of Bi_{1-x}Ce_xFeO₃ (*x* = 0, 0.05, 0.1, 0.15 and 0.2) films deposited on Pt/TiN/Si₃N₄/Si substrates. As shown in the broken square of Fig. 1, (104) and (110) peaks merge when *x* increases from 0 to 0.2

Fig. 3 The fitted XPS narrow-scan spectra of (a) Bi 4f, (b) Fe 2p, (c) O 1s and (d) Ce 3d peaks for (1) BFO and (2) $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ films. The black solid lines represent experimental result, red short dots represent the fitting results after Shirley-type background subtraction, the dashed peaks with colors of blue, magenta, violet and green are fitted subpeaks. Iterations are performed until a minimum for square of the difference (χ^2) between the experimental curve and the fitted curve is reached for each fitted sum curve



regions in comparison with the Fe 2p doublet of the BFO film. According to ratio of the fitted peak areas for Fe^{3+} and Fe^{2+} , concentration ratios of Fe^{3+} and Fe^{2+} in the BFO and $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ films are 67:33 and 70:30, respectively, indicating that the presence of Fe^{2+} ions are less in the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ film compared to that of the BFO film. This could be an evidence for the decreased oxygen vacancies in the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ film.

Figure 3c shows the fitted O 1s narrow-scan spectra for the BFO and $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ films. Figure 3c(1) shows that a broad O 1s peak (529.52 eV) for the BFO film consists of three subpeaks located at 528.77, 529.34 and 530.45 eV. Since the BFO film consists of three components (Bi_2O_3 , Fe_2O_3 and FeO) in BFO solid solution, the subpeaks are mainly ascribed to $\text{Fe}_2\text{-(O 1s)}_3$ (529.6 eV), Fe-(O 1s) (529.8 eV), $\text{Bi}_2\text{-(O 1s)}_3$ (530.0 eV) bonds [17] and relaxed O phase, especially for the fitted subpeak located at the higher binding energy region. It may be mainly attributed to the absorbed oxygen (531.0 eV) [17] associated with oxygen vacancies and surface species, such as H_2O and CO_2 absorbed from the air during the sol-gel process [16, 17]. Figure 3c(2) shows that compared to the counterpart of the BFO film, O 1s peak (530.01 eV) for the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ film shifts towards higher binding energy region by amount of 0.49 eV. These subpeaks are mainly ascribed to $\text{Fe}_2\text{-(O 1s)}_3$ (529.6 eV for the O 1s peak), Fe-(O 1s) (529.8 eV), $\text{Bi}_2\text{-(O 1s)}_3$ (530.0 eV) and $\text{Ce}_2\text{-(O 1s)}_3$

(530.3 eV) bonds [17]. Considering that Ce^{3+} ions are partially substituted for Bi^{3+} ions, and binding energy of O 1s in $\text{Ce}_2\text{-(O 1s)}_3$ bond is larger than that of $\text{Bi}_2\text{-(O 1s)}_3$ bond, suggesting that the O 1s peak of the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ film shifts toward the higher binding energy regions in comparison with the BFO counterpart.

Figure 3d shows the fitted Ce 3d_{5/2} peak located at 882.24 eV and Ce 3d_{3/2} peak located at 900.61 eV. Both of them are mainly assigned to Ce–O bonds. Spin-orbit splitting energy of the Ce 3d doublet is equal to 18.37 eV, which is compared to theoretical value ($\Delta_{\text{Ce 3d}}$) of 18.10 eV for Ce or 18.30 eV for CeO_2 [17]. The fitted area ratio for Ce 3d_{5/2} and Ce 3d_{3/2} peaks is about 1.47, which is comparative to theoretical value of 1.50 for Ce 3d doublet [17]. Figure 3d also shows that each of the Ce 3d peak is accompanied by two satellite lines, called 3d⁹4f⁰ and 3d⁹4f² [17, 26]. Furthermore, each of the Ce 3d_{5/2} and Ce 3d_{3/2} peak could be fitted by two subpeaks separated by 1.33 ± 0.01 eV. The subpeaks located at 882.91 and 901.27 eV are assigned to Ce 3d_{5/2}–O and Ce 3d_{3/2}–O bonds for Ce^{3+} . Meanwhile, the subpeaks located at 881.57 and 899.95 eV may be associated with Ce 3d_{5/2}–O and Ce 3d_{3/2}–O bonds for Ce^{4+} [17], (Bi, Ce)–O bonds and/or relaxed Ce phase, probably caused by oxygen vacancies and other defects.

Figure 4 shows typical dielectric properties of the BCFO ($x = 0, 0.1$ and 0.2) film capacitors at the measured frequency ranging from 40 Hz to 1 MHz. The

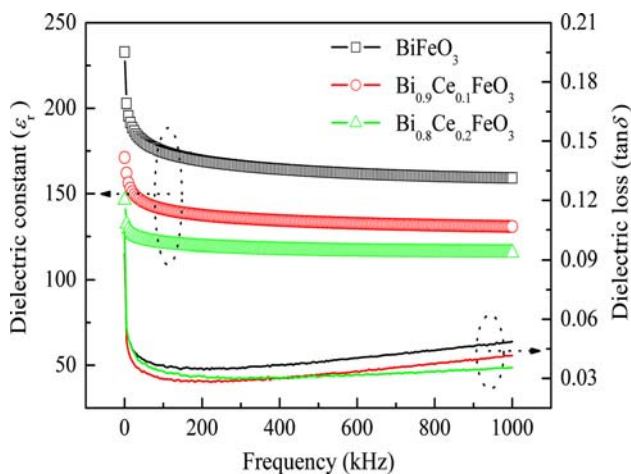


Fig. 4 Dielectric constants and loss tangents of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.2) film capacitors as a function of frequency ranging from 40 Hz to 1 MHz

corresponding dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) for the BFO, $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{FeO}_3$ and $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ capacitors are 159, 131, 116, 0.048, 0.041 and 0.035 at 1 MHz, respectively. It means that compared to the BFO counterparts, both ϵ_r and $\tan\delta$ of the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ capacitor decrease when 20 mol% Ce doped into the BFO matrix. Moreover, this result could be comparable to the values of PLD-derived $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$ ($\epsilon_r = 86$, $\tan\delta = 0.69$) and $\text{Bi}_{0.8}\text{La}_{0.2}\text{Nb}_{0.01}\text{Fe}_{0.99}\text{O}_3$ ($\epsilon_r = 184$, $\tan\delta = 0.038$) films [15] deposited on Pt/Ti/SiO₂/Si substrates at 100 kHz as reported by Cheng et al., respectively.

Figure 5 shows P - E hysteresis loops for the BFO, $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{FeO}_3$ and $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ film capacitors. These capacitors have typical ferroelectric characteristics, and the corresponding remnant polarization [$P_r = (P_r^+ - P_r^-)/2$]

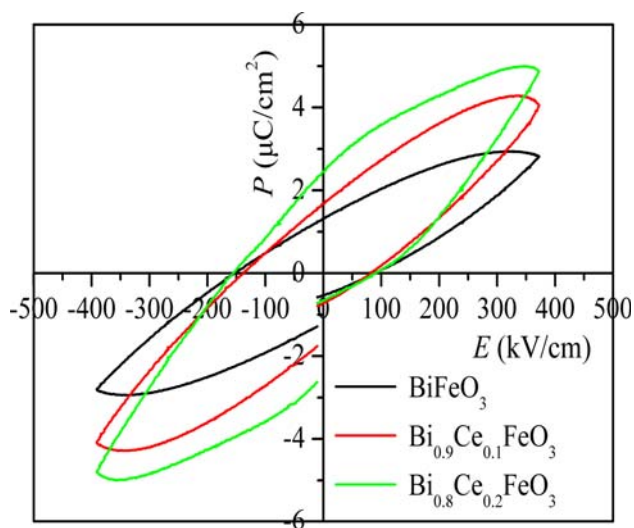


Fig. 5 Polarization-electric field hysteresis loops of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.2) capacitors

of 1.08, 1.43 and 2.04 $\mu\text{C}/\text{cm}^2$ and coercive field [$E_c = (E_c^+ - E_c^-)/2$] of 120, 112 and 123 kV/cm, respectively, are obtained under the applied electric field of 388 kV/cm. P_r value of the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ capacitor is larger than that of the BFO film, or those of the $\text{BiFe}_{1-x}\text{Sc}_x\text{O}_3$ ($x = 0.1$ and 0.3 mol%) films [4] or the Ti^{4+} and Ni^{2+} doped BFO films prepared by PLD process [27], but it is much small than that of the Gd-doped BFO film prepared by metal organic decomposition process [10]. According to Wang et al., ferroelectricity of BFO film originated from the displacements of Bi with respect to the FeO_6 cages along (111) plane [22]. Compared to the BFO counterpart, the increased P_r of the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ film might be attributed to the structural change in the oxygen octahedron, since Ce cations are feasibly substituted for Bi^{3+} as evidenced by the XPS spectra.

Figure 6 shows J - E curves of the BCFO ($x = 0, 0.1$ and 0.2) capacitors. Leakage current densities of BFO, $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{FeO}_3$ and $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ capacitors are 1.38×10^{-2} , 1.06×10^{-3} and 1.47×10^{-4} A/cm² at 388 kV/cm, respectively. It means that the leakage current density of the $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ capacitor is about two orders of magnitude lower than that of the BFO counterpart. One reason for this is that an appropriate amount of Ce doping reduces grain sizes of the BCFO film as evidenced by XRD result, leading to an increase in the density of grain boundaries, which makes contribution to the decreased leakage current density [9]. Another reason is that the decreased Bi volatilization and the restrained reduction of Fe^{3+} to Fe^{2+} are realized by virtue of the reducible oxygen vacancies and cation defects after Ce-doping, as proofed by XPS data.

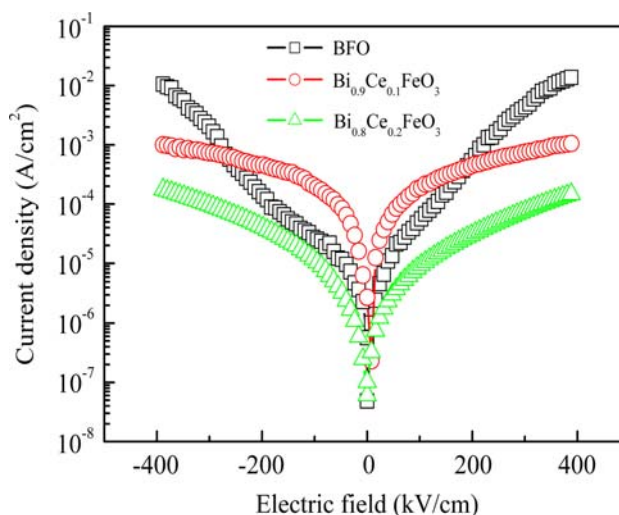


Fig. 6 Leakage current density-electric field curves of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.2) capacitors when electric field ranges from -388 to 388 kV/cm

4 Conclusions

BCFO films were deposited on Pt/TiN/Si₃N₄/Si substrates by sol–gel technique. Compared to the BFO counterparts, the fitted Bi 4f_{7/2}, Bi 4f_{5/2}, Fe 2p_{3/2}, Fe 2p_{1/2} and O 1s peaks for the Bi_{0.8}Ce_{0.2}FeO₃ film shift towards the higher binding energy regions by amounts of 0.33, 0.29, 0.43, 0.58 and 0.49 eV, respectively. The corresponding ϵ_r and $\tan\delta$ of the BFO, Bi_{0.9}Ce_{0.1}FeO₃ and Bi_{0.8}Ce_{0.2}FeO₃ capacitors are 159, 131, 116, 0.048, 0.041 and 0.035 at 1 MHz, respectively. The corresponding P_r of 1.08, 1.43 and 2.04 $\mu\text{C}/\text{cm}^2$ and E_c of 120, 112 and 123 kV/cm are obtained under the electric field of 388 kV/cm, respectively. The leakage current density of the Bi_{0.8}Ce_{0.2}FeO₃ capacitor is about two orders of magnitude lower than that of the BFO counterpart. Compared to the BFO counterparts, the increased P_r and the decreased leakage current density of the Bi_{0.8}Ce_{0.2}FeO₃ film might be attributed to the decreased Bi volatilization and the restrained reduction of Fe³⁺ to Fe²⁺ by virtue of the reducible oxygen vacancies and cation defects after Ce-doping, as proved by the XPS spectra.

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