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Enhancement of ferromagnetic and ferroelectric properties in calcium doped $BiFeO_3$ by chemical synthesis

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Abstract

Calcium (Ca)-doped bismuth ferrite ($BiFeO_3$) thin films prepared by using the polymeric precursor method (PPM) were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), polarization and magnetic measurements. Structural studies by XRD and Rietveld refinement reveal the co-existence of distorted rhombohedral and tetragonal phases in the highest doped $BiFeO_3$ (BFO) where enhanced ferroelectric and magnetic properties are produced by internal strain. A high coercive field in the hysteresis loop is observed for the $BiFeO_3$ film. Fatigue and retention free characteristics are improved in the highest Ca-doped sample due to changes in the crystal structure of BFO for a primitive cubic perovskite lattice with four-fold symmetry and a large tetragonal distortion within the crystal domain.

Keywords: A. Ceramics; A. Thin films; B. Chemical Synthesis; D. Ferroelectricity

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1. Introduction

Multiferroic materials with ferroelectric and ferromagnetic simultaneous ordering are currently attracting significant attention due to their interesting fundamental physics as well as their potential applications [1–5]. Among the single-phase multiferroic materials studied, $BiFeO_3$ (BFO) with a rhombohedrally distorted perovskite structure and a space group of R3c is the only material which exhibits both ferroelectricity and G-type antiferromagnetism at room temperature (with a Curie temperature Tc of 1103 K and Néel temperature T_N of 643 K) which facilitates applications at room temperature [6–8]. However, pure BFO has a serious high leakage current problem resulting from charge defects such as oxygen vacancies and the cancellation of ion magnetic moments due to its spatial periodic inhomogeneous spin structure [9] which hinders its practical applications in multiferroic devices. Considerable efforts have been expended to improve BFO properties; e.g., A-site substitution with La^{3+}, Nd^{3+}, Ce^{3+} and Tb^{3+} [10–15] and B-site substitution with Ni^{2+}, Cu^{2+}, Co^{2+}, Cr^{3+}, Mn^{3+}, Ti^{4+}, Zr^{4+} and V^{5+} [16–18] etc. These studies confirmed that ion doping is an effective method to improve BFO properties. Since ferroelectricity of BFO evolves from a lone pair of A-site Bi^{3+} ion electrons, ferroelectric property effects are very important [19–20]. Ramesh et al. studied the quasi-non-volatile and reversible modulation of electric conduction accompanied by the modulation of the ferroelectric state in Ca-doped $BiFeO_3$ films using an electric field as the control parameter. The mechanism of this modulation in Ca-doped $BiFeO_3$ is based on electronic conduction as a consequence of naturally produced oxygen vacancies that act as donor impurities to compensate Ca acceptors and maintain a highly stable Fe^{3+} valence state [21]. For the low Ca doping regime ($x < 0.1$), films with a

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monoclinic structure undergo a first-order transition to a pseudo-tetragonal phase at higher temperatures with a thermal hysteresis. The extrapolation of the transition temperature results in the well-known ferroelectric Curie temperature (T_c) of $BiFeO_3$ at 1100 K. With increased Ca doping, the ferroelectric T_c rapidly decreases, and a T_c of 600 K with a thermal hysteresis of 240 K is recorded. It has been reported that the T_c of some ferroelectrics such as $BaTiO_3$ and $PbTiO_3$ is very sensitive to the strain state [22,23]. However, because $BiFeO_3$ ferroelectricity is primarily attributed to Bi 6s lone-pair electrons, ferroelectric properties and the T_c are expected to be less sensitive to strain [24]. Many of these studies were focused on improving the electrical and magnetic properties of BFO. Compared with magnetic property, significant achievements were gained in improving electrical property of BFO [25,26]. Therefore, we throw our light mainly on investigating the magnetic property of BFO in this paper, noted that substitutions of Pr^{4+},Ce^{3+}, Zr^{4+} and Ca^{2+} for partial Bi^{3+} at A-site had improved the magnetic properties of BFO to different extent [27–31], and Ca^{2+} was shown to be the best substitution for enhancing the saturation magnetization. However, there is still no agreement on the mechanism of how the magnetic properties of BFO are affected by now [32–34]. Ederer et al. [35] and Ueda et al. [36] thought that both Fe ions and oxygen vacancy help to improve the magnetic property of BFO to some extent. In most applications involving ferroelectric films, there are several parameters to technological adoption, such as fatigue-endurance, remnant polarization (2Pr), coercive field (2Ec), and processing temperature [37,38]. Recently, changes in the crystal structure of BFO for a primitive cubic perovskite lattice with four-fold symmetry and a large tetragonal distortion within the crystal domain were attained for ferroelectric Ca-doped samples. This observation introduces magnetoelectronics at room temperature by combining electronic conduction with electric and magnetic degrees of freedom which are already present in the multiferroic $BiFeO_3$. A comparative study shows that A-site Ca doping with various contents have notable influences on electrical properties, including leakage current and ferroelectric and piezoelectric properties of BFO films which may be related to modification of the structure and elimination of charge defects due to A-site Ca doping [39]. However, the fatigue and retention characteristics of A-site Ca doping films have so far not been reported by the polymeric precursor method. In a memory element, a data bit (1 or 0) should be stored and made available for query at some later time. Retention is the ability of a memory element to maintain a given data state as time elapses. In most retention studies, ferroelectric capacitors exhibited a significant loss in retained polarization within the first one second after writing and then a relatively slight decay thereafter [40]. Retention loss causes a reduction in the difference between switched (P^*) and non-switched ($\hat{P}$) polarizations, i.e $\Delta P = (P^*) - (\hat{P})$ and leads to an inability to distinguish between the two logic states. Therefore, it is quite important to have good retention properties for any ferroelectric material to be utilized for FRAM applications. In this paper, we report the first systematic studies on the fatigue and retention characteristics of A-site Ca doping thin films obtained by the polymeric precursor method. We have also investigated the enhancement magnetism for A-site Ca-doped BFO films with different compositions on $Pt/Ti/SiO_2/Si$ substrates by using the PPM method.

2. Experimental procedure

$BiFeO_3$ (BFO) and $Bi_{1-x}Ca_xFeO_3$ with $x = 0.10$ (BCF010); 0.20(BCF020); 0.30 (BCF030) thin films were prepared by the PPM as described elsewhere [40], using Iron (III) nitrate nonahydrate, (99.5% purity, Merck), Bismuth nitrate ($\geq$99% purity, Aldrich) and Calcium carbonate (99.9% purity, Aldrich) as raw materials. An excess of 5 wt% Bi was added to the solution to minimize bismuth loss during thermal treatment. Films were spin coated on $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 5000 revolutions/min for 30 s (spin coater KW-4B, Chemat Technology). Thin films were annealed at 500 °C for 2 h in a conventional furnace under static air atmosphere. The film thickness was reached by repeating spin-coating and heating treatment cycles ten times. Annealed film thicknesses were measured using SEM (Topcom SM-300) at the transversal section. We have obtained films with thicknesses in the range of 340 to 360 nm. A phase analysis of films was performed at room temperature by XRD using a Bragg-Brentano diffractometer (Rigaku 2000) and Cu-Kα radiation; in this case, back scattering electrons were used. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [41]. The profile function used was the modified Thompson-Cox-Hastings pseudo-Voigt where η (the Lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum. The surface morphology of the thin films was measured by atomic force microscopy (AFM) using a tapping mode technique. Top Au electrodes (0.5 mm diameter) were prepared for electrical measurements by evaporation through a shadow mask at room temperature. The capacitance–voltage characteristic was measured in the MFM configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias. Ferroelectric properties of the capacitor were measured on a Radiant Technology RT6000 instrument and a tester equipped with a micrometer probe station in a virtual ground mode at a frequency of 60 Hz. These loops were traced using the Charge 5.0 program included in the software of the RT6000HVS in a virtual ground mode test device. For the fatigue measurements, internally generated 8.6 μs wide square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies. Retention characteristics of the films were measured by independently observing the time-dependent changes of P^* (switched polarization), and $\hat{P}$ (nonswitched polarization). For P^*, the capacitor was switched with a negative write pulse and read by a positive read pulse after retention time t. For $\hat{P}$, positive pulses were used for both writing and reading. The pulse width for all triangular pulses was 1.0 ms. The time delay between the written pulse and the first read pulse is referred to as retention time.