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Lattice distortion of holmium doped bismuth ferrite nanofilms

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Abstract: Single-phase multiferroic $BiFeO_3$ and rare-earth metal of holmium (Ho) doped $BiFeO_3$ nanofilms were prepared on Pt (100)/Ti/SiO_2/Si wafer via solution-gelation technique. It was suggested that the lattice distortion happened with the lattice parameter of d decreasing after doping rare-earth metal of Ho. Meanwhile, the structure of nanofilms transformed from hexahedron phase to tetragonal phase after doping Ho. The analysis on X-ray photoelectron spectroscopy (XPS) indicated that the ratio of Fe^{3+} cations to Fe^{2+} cations increased with the increase of binding energy between Fe and O and decrease of that between Bi and O after doping Ho. The present work provided an available way on enhancing multiferroic of $BiFeO_3$ nanofilms.

Keywords: lattice distortion; holmium; bismuth ferrite; nanofilms; rare earths

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There has been an increasing interest in multiferroics due to their fundamental properties, in which at least two ferroic orderings (ferromagnetism, ferroelectricity and ferroelasticity) appear simultaneously[1,2]. However, most single-phase materials such as Cr_2O_3, $YMnO_3$, $TbMnO_3$ etc.[2–4] exhibit multiferroic only at low temperature, which limits their further application in magnetoelectric devices. As one of the most outstanding single-phase lead-free multiferroics, $BiFeO_3$ has attracted continuous attention due to its high ferroelectric Curie (T_{FE}~1103 K) and Neel (T_N~643 K) temperature, which makes it one of the most important candidate from the views of the multifunctional applications perspective and engineering possibilities[5,6].

$BiFeO_3$ based nanomaterials has been prepared with various methods and investigated greatly[7–9] owing to its highly ferroelectric ordering temperature and magnetic ordering temperature. However some issues still need be solved before it is able to be practically applied in magnetoelectric devices such as leakage current and low ferromagnetism. Especially, for $BiFeO_3$ materials, the good ferroelectric is difficult to obtain due to the leakage current coming from Fe^{2+} within the $BiFeO_3$ films, which all restricts its multiferroic properties. Many attempts have been devoted to demonstrate that it is a very effective method to address such difficult problems by changing the structure from hexahedron phase to tetragonal phase[10–15]. These efforts inspire an available way of decreasing leakage current and enhancing ferroelectric properties for single-phase multiferroics.

So in this work, we prepared pure and Ho doped $BiFeO_3$ nanofilms by a simple solution-gelation method, and reported their crystalline structure. The analysis on X-ray diffraction and Raman scattering spectra analyses indicated that the crystal structure of nanofilms transformed from hexahedron phase to tetragonal phase and accompanied with lattice distortion that happened after doping rare-earth metal of Ho. The analysis on X-ray photoelectron spectroscopy (XPS) indicated that the ratio of Fe^{3+} cations to Fe^{2+} cations was on the rise, which could further decrease the leakage current. The origin of thus lattice distortion would be discussed in detail.

1 Experimental

1.1 Preparation of pure BiFeO₃ and Ho doped BiFeO₃ nanofilms

The pure $BiFeO_3$ and rare-earth metal of Ho doped $BiFeO_3$ nanofilms were prepared by solution-gelation process. The preparation method of the Ho doped $BiFeO_3$ precursor solution is as follows. $Bi(NO_3)_3 \cdot 5H_2O$, $Ho(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, which are of analytical grade, were dissolved in the glycol in proper proportions of 0.99:0.1:1, with excess 10% Bi for compensating the loss during annealing. Stir the solution until the solution is clear transparent, at this time, one by one add dilute nitric acid into the solution. Continue to stir until

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solution is clear transparent. The preparation method of pure $BiFeO_3$ solution is similar to the Ho doped $BiFeO_3$ solution. $Bi(NO_3)_3{\cdot}5H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in the glycol in a proportion of 1.1:1, with excess 10% Bi to prepare $BiFeO_3$ solution.

Then the pure $BiFeO_3$ and Ho doped $BiFeO_3$ nanofilms were fabricated on Pt/Ti/SiO_2/Si (100) substrate with the precursor solution by spin coating the solution, and the films were dried at 280 ℃ on the thermostatic oven for 180 s. The dried deposited films were annealed at 600 ℃ for 5 min under the oxygen atmosphere with flow of 2 L/min. Repeat the above steps 12 times, and at the last time, the films were annealed at 600 ℃ for 30 min. The final thickness of nanofilms was about 300 nm.

1.2 Characterization of pure $BiFeO_3$ and Ho doped $BiFeO_3$ nanofilms

The surface morphology examinations for the pure and Ho doped $BiFeO_3$ nanofilms were carried out on a scanning electron microscope (SEM, Hitachi s-4800). The phase structures of samples were characterized by X-ray diffraction (XRD, Panalytical-Empyrean) on a D/MAX-RA diffractometer using Cu Kα radiation. The Raman spectra were recorded on a confocal Raman spectroscope (NT-MDT NTEGRA Spectra) using a 473 nm excitation laser with an initial power of 10 mW. The binding energies of atoms and orbits for the samples were characterized by X-ray photoelectron spectroscopy (XPS, KRATOS-AMICUS). The cleaning treatments of nanofilms were carried out using Ar ion bombardment. And all binding energies were calibrated with respect to C 1s spectral line at 284.8 eV. The leakage current of pure and Ho doped $BiFeO_3$ nanofilms capacitors were measured using a multiferroic tester system (MultiFerroic100V, Radient Technology, USA) at room temperature.

2 Results and discussion

2.1 XRD analysis

Fig. 1 shows the XRD patterns of the pure $BiFeO_3$ and Ho doped $BiFeO_3$ nanofilms. It is clear that both present nanofilms are polycrystalline and all of the observed diffraction peaks can be indexed to perovskite structure. Moreover, pure $BiFeO_3$ and Ho doped $BiFeO_3$ nanofilms are single phase while no other impurity phases such as Fe_2O_3, Bi_2O_3 or $Bi_2Fe_4O_9$ are detected.

Fig. 1(b), (c), and (d) further present the expanded view XRD patterns, which shows the changes in the location and angle of diffraction peak after doping Ho. Firstly, from the magnified XRD patterns in the vicinity of 2θ around 23° and 32°, the separated (104) and (110) diffraction peaks are merged in the single peak after doping rare-earth metal of Ho, which suggests a phase transaction appears after doping. To be specific, compared to pure $BiFeO_3$ nanofilms, the films were crystallized from the rhombohedral structure with space $R\text{-}3c$ (161) to the orthorhombic structure after doping rare-

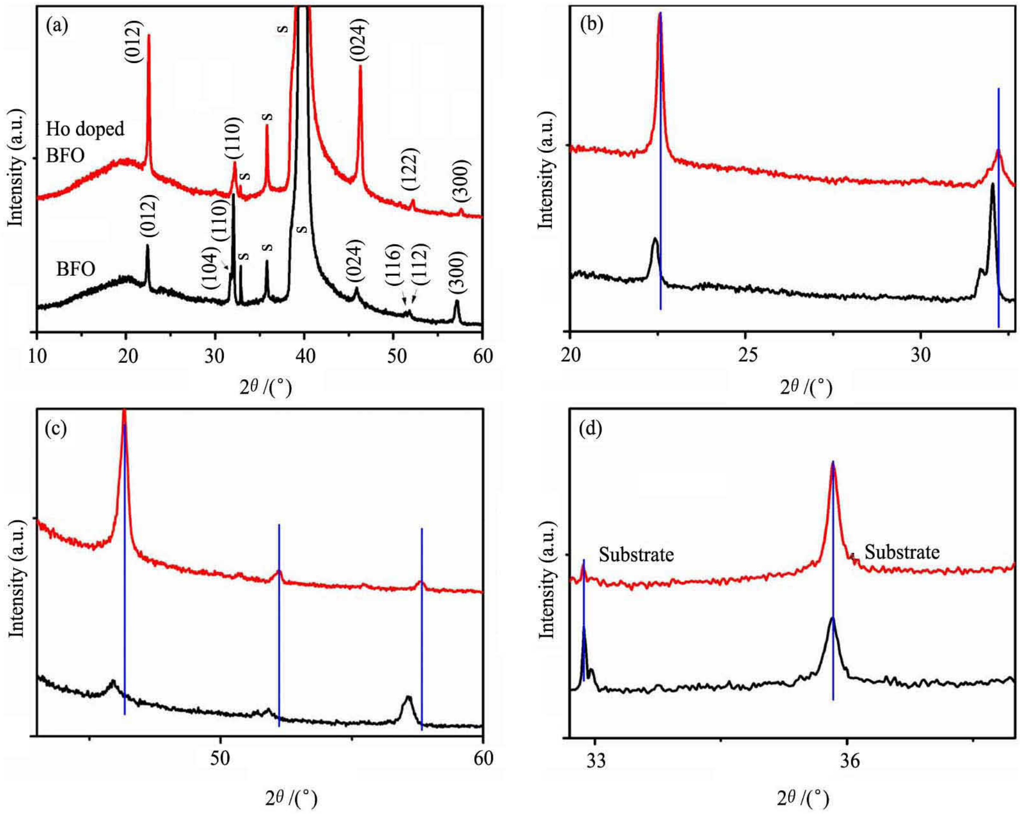

Fig. 1 XRD patterns of the typical pure $BiFeO_3$ and Ho doped $BiFeO_3$ nanofilm (a), expanded view XRD patterns around 20° to 33° (b), expanded view XRD patterns around 43° to 60° (c) and expanded view XRD patterns around characteristic peak of wafer (d)