Self-assembly growth and structure study of BiFeO$_3$-CoFe$_2$O$_4$ nanostructure film

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Abstract. Pulsed laser deposition method was used to prepare (0.67) BiFeO$_3$- (0.33) CoFe$_2$O$_4$ nanostructure thin film. The XRD analysis shows that lower growth temperature will not obtain separation of BiFeO$_3$ and CoFe$_2$O$_4$ phase. Post-annealing treatment will induce the phase separation. XRD data and SEM image both confirm these phase separation.

1. Introduction

Multiferroic materials have attracted great research interest due to the coexistence of magnetic and ferroelectric properties and the coupling of these two kinds properties, which providing a brand-new functionalities.$^{1,2,7,8,9}$ Biphase vertical nanostructure has been studied, not only for its large interaction area of magnetic and ferroelectric phase, but also the huge candidates of these two phases, such as the immiscible perovskites (BaTiO$_3$, BiFeO$_3$, PbTiO$_3$) and spinels (CoFe$_2$O$_4$, NiFe$_2$O$_4$). In these candidates, BiFeO$_3$ (BFO) possesses a high Curie Temperature (about 820°C), while CoFe$_2$O$_4$ (CFO) has excellent magnetostrictive property, thus as our research object. Zheng et al. reported that different growth temperature in the range of 550-700°C will have well phase-separation with distinct lateral size of CFO nanopillar.$^3$ Several papers also reported the influence of growth temperature both on the crystalline structure and the morphology of the film in this system.$^{24}$ However, no reports about the influence of annealing condition on the corresponding characterization.

In the present paper, BFO-CFO (BCFO) nanostructure film was successfully obtained used by Pulsed Laser Deposition on LaNiO$_3$ (LNO) coated SrTiO$_3$ (STO) substrate. XRD was utilized to determine the growth condition in which phase separates. Accordingly, the strain of CFO phase is analyzed to arise from restrict of BFO due to the mismatch of two different kinds of structure. Furthermore, SEM image gives a further visualized confirmation of phase separation.

2. Experimental

The film BCFO was grown on the LNO coated STO (100) substrate by Pulsed Laser (KrF excimer). Due to the volatility of Bi, a 15% Bi excess ceramic target was used in the conventional sintering process with molar ratio (0.67) BFO-(0.33) CFO. During the deposition process, the pulse laser energy is 250mJ with repetition rate of 5Hz. The oxygen partial pressure is 50mTorr, and the deposition
temperature varies at 550°C and 700°C. In order to investigate the annealing influence, post-annealing is operated in the oven at different temperature 650°C, 700°C, 750°C for 1h after the in-situ growth.

The crystal structure of the film was examined by x-ray diffraction (Philips PW1710 diffractometer) with a Cu Kα radiation source. The morphology of the film was obtained by the field emission scanning electron microscope (SEM, JEOL JSM-6700F).

3. Results and Discussion

Our BCFO films were deposited at different temperature and the related crystalline properties were analyzed by XRD as shown in Figure 1. Compared with the film at different growth temperature 550°C and 700°C, the lower growth temperature 550°C will just prefer formation of BFO phase, while higher growth temperature 700°C only have the presence of CFO phase, in which cases both do not have the phase separation. However, for the sample deposited at 550°C, post-anneal at 650°C will induce the growth of CFO phase, and this phase has somewhat texture with (l00) and (l10) orientation. The low growth temperature of 550°C is believed to form supersaturated perovskite type phase due to the kinetic limitation, thus lacking of phase-separation. The high growth temperature 700°C is too high for the BFO formation, similar with other’s report.

Influence of annealing temperature on the crystalline structure was investigated using XRD in Figure 2. The BCFO film annealed at three temperatures 650°C, 700°C and 750°C all display well phase separation with (l00) oriented BFO and (l10) & (l00) oriented CFO. Focusing on change in the range 43°-49° schematically in the inset of Figure 2, LNO (200) peak position shifts towards to lower value with increasing annealing temperature, expecting a lattice parameter close to the bulk value. In the meanwhile, BFO (200) peak also have approaching lattice parameter of bulk value as increasing annealing temperature. This indicates the strain relaxation occurring in LNO and BFO phase due to annealing treatment. In the case of CFO, the (400) peak position at around 2θ ≈ 43.4° remains almost the same for all three annealing temperature, with a little smaller lattice parameter a=0.833 nm than bulk value 0.839 nm. This will accompany with a stable compressive out-of-plane strain of CFO, regardless of annealing treatment and the strain change both of LNO and BFO. These further provide another conformation that strain of CFO in such nanocomposite system stems from mismatch of BFO, not form the substrate.

Figures
Figure 1. XRD pattern of BCFO film at different growth temperature (550°C, 700°C) and annealed film grown at 550°C. The 1st bottom is the XRD pattern of LNO coated (100) STO substrate.

Figure 2. XRD pattern of BCFO film at different annealing temperature. The 1st bottom black one is for sample annealed at 650°C, the 2nd bottom red one is at 700°C, the 3rd blue one is at 750°C. The inset is the XRD pattern between 43°–49°.

Figure 3 (a). The plan-view SEM picture of BCFO film annealed at 650°C with a low magnification of 20k.

Figure 3 (b). The plane-view SEM picture of BCFO film with a high magnification of 100k.
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