Phase Transition of BiFe$_{1-x}$Al$_x$O$_3$ Films Prepared by Chemical Solution Deposition

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Abstract
BiFe$_{1-x}$Al$_x$O$_3$ thin films with rhombohedral (R3c), monoclinic (Cm) and tetragonal (T)-like symmetry were obtained by the chemical solution deposition (CSD) and rapid thermal annealing (RTA). The T-like phase is formed under high temperature and high Al concentration. While the Cm phase is stable in the region of low temperature and high Al concentration. The phase transition is suggested to be arisen from strain induced in the film formation.

Key Words: BiFeO$_3$, Aluminum substitution, Phase transition

I. INTRODUCTION
BiFeO$_3$ (BFO), a typical multiferroic material, exhibits antiferromagnetism and ferroelectricity properties at room temperature, offering a range of potential applications in energy and data-storage fields.\cite{1,2} Recently, the contribution of B-site ions on the ferroelectric polarization has been recognized. Zhang et al.\cite{3} indicated that a large Fe-ion displacement from the relative negative charge center induced by epitaxy was the mechanism for the large polarization in the tetragonal(T)-like BFO phase. Researches on polar perovskite-type crystal, such as BiMO$_3$ (M=Al, Ga, In, and Co) have been intensively done.\cite{4-6} Belik et al.\cite{7} reported that a large family of polar materials with R3c and Cm symmetries was found for solid solution of BiFe$_{1-x}$Al$_x$O$_3$ under high-pressure and high-temperature. However, there is no such study focused on Al doped BFO. Theoretical studies on BiAlO$_3$ predicted that they could be high-performance piezoelectrics and ferroelectrics with a very large spontaneous polarization (75.6 \( \mu \)C cm\(^{-2} \) along the [111] direction).\cite{8} However, high-pressure and high-temperature synthesis is required for preparation of these materials and the measurement of ferroelectric properties is failed. In this paper, we will report for the first time that BiFe$_{1-x}$Al$_x$O$_3$ thin films with R3c, Cm and T-like phase can be simply obtained using the chemical solution deposition (CSD) method. The sketchy phase diagram for BFAO system is displayed.

II. EXPERIMENT

The BiFe$_{1-x}$Al$_x$O$_3$ (x=0, 0.1, 0.2, 0.3 and 0.4, BF1-xAxO) thin films were prepared via CSD method. The starting reagents were bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O, 99.5%), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O, 99%) and aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, 99.5%). They were dissolved in acetic acid (C$_2$H$_4$O$_2$, 99.7%) by stirring under heating. An appropriate amount of acetylacetone (C$_3$H$_5$O$_2$, 99%) was added into the solution as a chelating agent. The concentration of precursor solutions was 0.2mol L\(^{-1} \). The solution was spin-coated onto glass substrate or Si (100) substrate, followed by pre-heating at 180 °C and heating at 380 °C for 3 min to remove the solvent and decompose the nitrates, respectively. These steps were repeated for 5 times. Finally, the films were annealed at a range of temperature for crystallization using rapid thermal annealing (RTA, temperature rise up in 1 min and keep 10 min). X-ray diffraction measurement was used to characterize structure properties at room temperature (Cu Ka radiation, Rigaku-Smartlab).

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of BFAO deposited on glass substrate and annealed at different temperatures. The synthesized pure BFO thin films keep a perovskite structure with rhombohedral distortion. Especially the sample annealed at 600 °C shows obvious split peaks of (104) and (110) which are considered as characteristic for R3c BFO. However, Al substitution gives additional peaks around 24°, 30° and 34° for low temperature annealing as shown in Fig. 2(b)-(d). These peaks become more clear and remain up to higher annealing temperature when Al amount is increased. From the peak positions in Fig. 2(c) showing clear additional peaks and similarity to the reported X-ray pattern of BiFe$_{1-x}$Al$_x$O$_3$ with Cm symmetry,\cite{7} we judged that the additional peaks are most likely due to creation of the phase with Cm symmetry. However, the Cm phase is unstable at high temperate. With increasing annealing temperature to 600 °C, pure R3c phase
appears. With increasing Al concentration to 0.3, the stable region for Cm phase extends. BF0.7A0.3O sample annealed at 650 °C shows mixture phase of R3c and Cm.

In order to detect the crystallization property of BFAO at temperature higher than 650 °C, thin films were deposited on Si (100) substrate which can be heated at higher temperature. Pure BFO is not stable at high temperature known from Fig. 2(a). Thin film which is heated up to 700 °C shows major other phase of Bi2Fe5O11. Subsequently, γ- Bi2O3 and α-Fe2O3 phases appear with increasing annealing temperature due to decomposition of BFO.

There are many compelling changes in XRD patterns after doping Al. BF0.9A0.1O shows oriented Fe2O3 phase at high temperature as a result of decomposition (Fig. 2(b)). For BF0.8A0.2O (Fig. 2(c)), R3c phase still remains even at 700°C while fully changes to other crystalline phases above 800°C. In particular, it is of interest that new two peaks which located in 38 ° and 59 ° are observed for 900 °C. The positions and relative intensity of these peaks are similar to those of (002) and (003) peaks calculated for tetragonal BFO (T-BFO) with \( a=b=0.361 \text{ nm} \) and \( c=0.471 \text{ nm} \) (we call a phase showing their peaks T-like phase below). With increasing amount of doping Al, the relative intensity of their peaks further increased (Fig. 2(d) and (e)). When \( x=0.4 \), the phase turns to be the major phase for BF0.6A0.4O. However, there is no directed evidence at present that these observed peaks are due to creation of BFAO with tetragonal symmetry. Further careful investigations are required.

Based on the above results, we summarized the phases observed for BiFe1-xAlxO3 films as a function of the Al doping concentration (x) and RTA annealing temperature. R3c phase, which is the ground phase of BFO, is stable at low temperature (550-650 °C) and low Al concentration (x≤0.2). Cm phase appears at lower temperature (500-550 °C) and higher Al concentration (x≥0.2) compared with R phase. There is an obvious co-existence region for R3c and Cm phase. The T-like phase is formed under high temperature (900 °C) and high Al concentration (x≥0.2). However, T-like phase is obtained passing an amorphous intermediate region and there is no co-existence region for T-like phase with the other phases.

The formation of Cm and T-like phases is likely associated with strain induced in the film formation. The strain is derived from the difference of thermal expansion coefficient between film (10.9×10^-6 °C^-1 for BFO\(^{[9]}\)) and substrate (3.17×10^-6 °C^-1).
for glass and $3 \times 10^{-6} \text{°C}^{-1}$ for Si), reaching an order of GPa by estimated assuming thermal expansion coefficient and typical values of Young modulus (~195 GPa) and Poisson’s ratio (~0.3) for ferrite.\textsuperscript{[10]} The film suffers in-plane tensile stress from the substrate that has a smaller thermal expansion coefficient. This tensile stress expands the lattice volume and lowers formation energy of crystal phase that has larger unit cell volume. Thus, it is natural that the tensile stress assists the transition from $R3c$ to $Cm$ and $T$-like phases. Moreover, the doped Al can supply the chemical pressure to crystal structure, promoting the phase transition as an alternative way of strain.\textsuperscript{[2]} And it is reported that monoclinic is the ground phase for tetragonal.\textsuperscript{[11]} As a result of that the formation energy of $T$-like phase is larger than that of $Cm$ phase, resulting in the crystallization of $T$-like phase at higher temperature and higher Al concentration.

**Fig. 2** XRD patterns of (a) BFO, (b) BF0.9A0.1O, (c) BF0.8A0.2O, (d) BF0.7A0.3O, (e) BF0.6A0.4O deposited on Si (100) substrate and (f) sketchy phase diagram for BiFe$_{1-x}$Al$_x$O$_3$ system.

**IV. CONCLUSIONS**

BiFe$_{1-x}$Al$_x$O$_3$ thin films with $R3c$, $Cm$ and $T$-like phase can be simply obtained using the chemical solution deposition (CSD) method. It is the first time to obtain $T$-like BFO via CSD method, under high temperature (900 °C) and high Al concentration. The $Cm$ phase is likely to appear in the region of low temperature (500-600 °C) and high Al concentration. The phase transition is associated with strain induced in the film formation.

**REFERENCES**


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