Electron-beam evaporated bismuth ferrite (BiFeO₃) thin films and characterization

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Abstract
The BiFeO₃ (BFO) thin films made by the electron beam evaporator are systematically investigated. As the most difficult part of this work, the preparation process is repeated until the optimal deposition power and elemental composition of BFO are obtained. With the help of X-ray diffraction and Raman spectroscopy, we specify precisely that the sample annealed at the temperature of 650°C is the purest BFO phase with rhombohedral R3c structure. The Scanning Electron Microscopy images provide the surface morphology and cross-sectional thickness of each sample for the further performance analysis. With the aim of understanding the changes in the chemical bond structure of BFO samples at the different annealing temperatures, we applied X-ray photoelectron spectroscopy and the result indicates that the absorption of oxygen is increasing with the raising of the annealing temperature. Finally, we measured the magnetic property and resistivity of BFO samples to explore their applications. The saturation magnetization measurement shows the correlation between the magnetization of BFO and microstructures such as phase structure, grain size. Meanwhile, the electronic resistivity explains the close relationship between the resistivity and surface morphology.

1. Introduction

Material technology is being better developed with the emergence of new functional materials such as multiferroics. Multiferroic materials are particularly appealing not only because they have the properties of two or more ferroic phenomena [1], but also because interactions between the magnetic and electric polarizations lead to additional functionalities such as electric field–controlled magnetic data storage [2]. That fascinating properties of the multiferroic materials make them the key to reducing manufacturing costs and thereby obtaining more profits [3].

BiFeO₃ (BFO) is the only single-phase multiferroic that has both magnetic and ferroelectric orders at room temperature, which leads to being considered a good choice for the applications in information storage technology [1, 4]. BFO also has environmental suitability due to its narrow band gap, and exhibits excellent visible light-induced photocatalytic performance [5, 6]. In addition, recent research results indicate that BFO has more extended applications including photo-detectors [7], energy harvesting [8], and microwave absorption [9], which makes BFO an attractive promising material for the research and development.

The deposition process is the basic step in the manufacture of BFO thin films. As one of the physical vapor deposition (PVD) method, electron beam (e-beam) evaporation technology achieves the cleanest film deposition at the lowest pressure [10]. Its adjustable high voltage not only evaporates high melting point materials, but also provides a wide range of possibilities for controlling variations in the structure and composition of the processed materials [11]. Besides, smooth surface, stable coating conditions, low operating cost and no residual pollution [12] are the reasons why the e-beam evaporation can be used widely for the thin film deposition.
In fact, there are a lot of studies on deposition of metal oxides and perovskites by e-beam evaporation technique [13–18], but to the best of our knowledge, there is rare work has been done on the deposition of BFO thin films by e-beam evaporation. Although there are many methods for preparing BFO thin films, such as sol-gel method, hydrothermal method and magnetron sputtering method, etc [19], the films made by these methods have a low purity and a rough surface in comparison with the films deposited by e-beam evaporation. In this work, we aim to obtain a BFO film with an improved elemental ratio under a suitable depositing power and vacuum pressure. BFO films will have higher purity and a smooth surface with the using e-beam evaporator, so that it can expand its application for various fields.

2. Experiment

The BFO films are deposited on a well-cleaned SiO₂ layer with a thickness of 300 nm on top of the silicon substrate (with BFO/SiO₂/Si structure). In this work, an e-beam evaporation system using 270° double guns co-evaporates Fe (99.95% pure) and Bi₂O₃ (99.99% pure) pellet (2–3 mm) under the vacuum pressure of 1.0 × 10⁻⁴ Pa. The evaporation chamber is pumped down to 2.1 × 10⁻⁵ Pa before exposure and no carried any gas flow during whole deposition process, which provides a clean coating environment. By fixing the voltage at 8.16 kV for each gun with currents of 0.43 A for Fe and 0.56 A for Bi₂O₃, we were able to get a deposition speed of about 8 Å s⁻¹. For the purpose of obtaining a smoother surface, we set the distance between the substrate and the evaporation target to 17 cm and kept the substrate rotating in clockwise.

BFO film deposition is started after 10 min of pre-evaporation, and the entire coating process is performed for 20 min without heating the substrate. The thermal annealing is performed in an air environment and the temperature range is selected from 450 °C to 750 °C. The heating rate of the muffle furnace is 23 °C min⁻¹, after the temperature of each sample reaches the target temperature, keeping the sample for 20 min and then cool down to room temperature naturally.

The grazing incidence X-ray diffraction (GIXRD, Bruker D8 ADVANCE, Germany) with an incident angle of 1.5° and the 2θ range of 10° to 90° and Raman spectrometer (Horiba Scientific LabRAM HR Evolution, France) are used to determine the crystal structure and phase composition of the BFO thin film. The surface morphologies and thickness are characterized by the cold field emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). To validate the chemical bonds on the surface of the BFO film, we performed X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALAB 250Xi, USA) measurement. Then the magnetic property and electric resistivity of the BFO thin film are tested on the super-conducting quantum interference...
device (SUQID, MPMS-SQUID-XL USA) and Ultra-high resistance micro current tester (ST2643, Suzhou Jingge Electronics, China) respectively.

3. Results and discussions

The GIXRD patterns of BFO thin films are shown in figure 1, it can be seen a corresponding phase transformation which occurs as follows the increasing of the annealing temperature. Due to the thin film thickness or the large X-ray incidence angle, the samples annealed at each temperature contains the peak of the substrate SiO$_2$ (040) [20]. For the as-deposited sample, there are four peaks of Bi$_2$O$_3$ (111) [21], Bi (014), Bi (113) [22], Fe (110) [23] and two of the substrate peaks [20, 24] that indicating there is a less chemical reaction between iron and bismuth. As the annealing temperature rises to 450 °C, the BFO peak begins to be visible, and detects

![Raman scattering spectra for BFO thin films.](image)

**Figure 2.** Raman scattering spectra for BFO thin films.

**Table 1.** Comparison of Raman mode positions (cm$^{-1}$) from the present study and the literatures.

| Raman modes | As-deposited | 450 °C | 550 °C | 650 °C | 750 °C | Reference [39] | Reference [33] | Reference [40] |
|-------------|--------------|--------|--------|--------|--------|----------------|----------------|----------------|
| E-1         | 77           | 78     | 74     | 77     | 82     | 71             | —              | —              |
| E-2         | 106          | 114    | 104    | 115    | 118    | 98             | —              | —              |
| A$_1$-1     | 147          | 151    | 141    | 140    | 148    | 135            | 136            | 152.6          |
| A$_1$-2     | —            | —      | 166    | 165    | —      | 167            | 168            | 177.5          |
| A$_1$-3     | 231          | —      | 220    | 217    | 223    | 218            | 211            | 224.2          |
| E-3         | 259          | 250    | 267    | 262    | 241    | 255            | 275            | 270            |
| E-4         | 283          | —      | —      | 289    | 283    | 335            | 298.8          |
| E-5         | 302          | 299    | 304    | 301    | 301    | 321            | —              | —              |
| E-6         | 323          | 330    | 338    | —      | —      | —              | —              | —              |
| E-7         | 364          | 372    | 369    | 369    | 373    | 352            | 365            | 354.9          |
| A$_1$-4     | 425          | 426    | 426    | 435    | —      | 430            | 425            | 473.3          |
| E-8         | —            | —      | —      | —      | —      | 526            | 549            | 554.3          |
| E-9         | 618          | 620    | 641    | 628    | 608    | 598            | 597            | 618.3          |
the corresponding BFO (110) phase at $2\theta = 31.8^\circ$ [25]. Because the reaction temperature is not high enough, there are also formed partly crystallized Bi$_2$O$_3$ (223) and (621) oriented phase [26]. When the temperature is increased to 550 °C, the number of BFO peaks [25] increases to compare with the case of 450 °C, which shows that the improved preferred orientation of BFO. There is also a strong Fe$_3$O$_4$ (422) peak in the GIXRD spectra, this may be due to the excess iron produced easily in a short reaction time and reacts with oxygen in the air [27].

The sample annealed at 650 °C is the best BFO structure we ever get, which has a single-phase rhombohedral structure with space group of R3c [25, 28]. At 750 °C, there is the same peak of Fe$_3$O$_4$ as the case of 550 °C, and there are other peaks that indicate a chemical reaction between BFO and the substrate [29], because high temperature affects the thermodynamic stability of BFO [30, 31].

In order to understanding of the microstructure of BFO, further exploration carries out by Raman spectroscopy in the frequency range of 50–900 cm$^{-1}$ by the Laser light source with a wavelength of 514 nm. Due to the surface effect is relatively large or the crystal structures has low similarity [32], this allows us to subtract the background data and then apply a Gaussian fit to each spectrum to assign the Raman activation modes, the results are as shown in figure 2 and table 1. Group theory infers 13 Raman activation modes ($\Gamma = 4A_1 + 9E$ [33, 34]) for the rhombohedral BFO with R3c space group. As the annealing temperature rises up 650°C, the intensity and number of vibration modes increase, and the regularity is broken as annealing temperature is reached the 750 °C. The as-deposited sample shows a peak at
569 cm$^{-1}$, which we speculated corresponding to Bi$_2$O$_3$ [35]. The height and width of the peaks for the sample annealed at the temperature of 750 °C show some disorders compared with other samples, and there are two peaks located at 408 cm$^{-1}$ and 671 cm$^{-1}$ where E$_g$ and A$_{1g}$ vibration modes are related to Fe$_3$O$_4$ [36, 37]. Due to the thinner thickness of the film, each sample has a substrate peak near at the 520 cm$^{-1}$, possibly covering an E mode [38]. According to the four A modes and the most fully-appearing part of the E modes, we ascertain that the samples annealed at the temperature of 650 °C and 550 °C are the closest to the rhombohedral R3c structure.

The surface morphologies and cross-sectional image of the BFO thin films are shown in figure 3. We can see that crystal grains and large blocks of different sizes are formed on the surface of the film, but the large blocks become smaller as the temperature rises, which may be due to the effect of temperature on the completeness of the reaction [41]. Figure 4 shows that the variation trends of grain size with annealing temperature both for the values estimated from the FE-SEM image and calculated from the GIXRD [42] are consistent with each other. Moreover, the grain size is obviously larger at 750 °C, due to the secondary phases as shown in GIXRD result [43]. Figure 3(f) shows a typical FE-SEM cross-sectional microstructure of the BFO thin film for 650 °C, and the suggesting thickness is about 200 nm.

Figure 5 shows the XPS survey spectra and Gaussian–Lorentzian fitting diagrams for the elements in BFO thin films. The survey spectrum (figure 5(a)) of BFO sample contains the elements of Bi, Fe, O and C. The C 1s line (284.9 eV) corresponding Carbon contamination is used to compensate for charging effects on calibration.
The bonding state of Bi 4f at each annealing temperature is shown in figure 5(b), the Bi 4f7/2,5/2 core level binding energy peaks are observed at 158.8 and 164.1 eV, and the energy difference is about 5.3 eV [46]. Because of the high temperature volatilization of Bi element, the lower atomic percentage of Bi leads to a slight right shift in the binding energy for the sample annealed at the temperature of 750 °C. The photoemission spectrum of Fe is shown in figure 5(c), there are two main peaks at 710.4 eV and 724.0 eV corresponding to the Fe 2p3/2,1/2 and two satellite peaks in the range of the binding energy from 700 eV to 740 eV [47, 48]. From the results of Gaussian fitting, there are mainly Fe2+ and Fe3+ contributions [49], which are marked with the different colors in the figures. Among them, the content of Fe3+ in the samples with annealing temperatures of 550 °C and 750 °C is relatively high. It is known in the literature that as Fe content increases, the height of the Fe3+ peak increases [50]. Similarly, in the samples annealed at the temperature of 750 °C and 550 °C, the content of Fe is relatively high, which may be related to the Fe3O4 proposed by the GIXRD results. The fitting results of O 1s binding state ranging from 525 eV to 540 eV are shown in figure 5(d) [51, 52] and there are three peaks corresponding to the oxygen metal binding at 529.5 eV, O1− ion contribution at 531.0 eV and the surface oxygen adsorption at 532.5 eV [53]. We can confirm that the metal binding energy of the oxygen for the samples annealed at 450 °C, 550 °C and 650 °C slightly left shifts as compared to the samples of as-deposited and annealed at 750 °C, which means that the O2− content in the samples of as-deposited and annealed at 750 °C is
relatively small. It can also be known, the films with annealed at the temperature of 450 °C to 650 °C is more ionic than the other two films [34]. The O¹⁻ bonds are more abundant in the sample with annealed at the temperature of 750 °C and as-deposited sample because the atoms are more electronegative [35]. As the annealing temperature increases (650 °C and 750 °C), the amount of adsorbed oxygen on the surface increases because the high temperature accelerates the oxygen diffusion [36].

Magnetism is a very important property of BFO that we have to measure. The room temperature magnetic hysteresis curves of 2 × 2 mm BFO films are shown in figure 6. It can be seen that even though the magnetic field is very weak, the magnetization curve of all the samples reaches saturation. The magnetization strength increases with the raising of the annealing temperature [57], however the highest magnetization occurs in the sample annealed at the temperature of 550 °C. This probably related to the effect of grain size and Fe₃O₄ content [58], which is consistent with the FE-SEM and GIXRD results. In this study, the relationship between magnetism and annealing temperature is basically consistent with the literature [59], but we have got the opposite result from the relationship between magnetism and grain size [60], which may be caused by the inconsistency of the film phase at different annealing temperatures.

Furthermore, we applied electric resistivity measurement for better understanding the electric property of BFO annealed at different temperatures, and the result is shown in figure 7. We can see that the resistivity increases as follows the raising of annealing temperature except for the sample annealed at the temperature of 650 °C. As the annealing temperature rises at 750 °C, the BFO thin film changed into isolating state with the high electrical resistivity. Interestingly, the variation trend of the resistivity with the annealing temperature is agreed well with the result of grain size trend with the annealing temperature as shown in figure 2, indicating that electrical resistivity is closely related to the grain size. It is well known that the resistivity is determined by the carrier concentration, mobility, impurity, defects and temperature [61]. According to the FE-SEM result and the resistivity formula: \( \rho = \frac{1}{ne\mu_e} \) (where the \( n \) is charge carriers, \( e \) and \( \mu_e \) are charge and mobility of electron, respectively), we mainly summarized that the uneven grain size produces different block size and distinct preferred orientations, which affects the carrier concentration and mobility of electrons, leads to the changing of the resistivity with the annealing temperature.

4. Conclusion

In this study, we tried to use e-beam evaporation method to deposit BFO thin films and characterize their performances. We systematically characterize the crystal structure, chemical bond structure, surface morphology, magnetic property and resistivity of BFO thin films. The results provide a single crystal R3c rhombohedral BFO sample which is obtained at an annealing temperature of 650 °C. The tendency of the grain size with annealing temperature is consistent both for the GIXRD calculation and the FE-SEM estimation, and the appearance of uneven grains might be the source of changes in saturated magnetization and electronic resistivity. Present work mainly focuses on the preparation method and annealing process of BFO. However, it is hardly avoiding the shortcomings of BFO thin film deposition by the e-beam evaporation, therefore further work is needed to improve the deposition process.

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Data availability statement

All the data that support the findings of this study are included within the article (and any supplementary files).

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