Polycrystalline BiFeO$_3$ thin films prepared by magnetic controlling sputtering method

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Abstract. Polycrystalline BiFeO$_3$ films were fabricated by radio frequency magnetron sputtering using a Bi$_{1.1}$FeO$_3$ target onto the glass and Si/SiO$_2$/Ti/Pt substrates respectively. The samples which were annealed with different annealing conditions are pure without impurities. Our results indicate that there are relatively wider growth conditions for pure polycrystalline BFO phases.

1. Introduction

Extensive researches have recently focused on studying the coexistence of magnetic and electric orders within a single multifunction material. In addition to the fact that such multiferroics are promising materials for the design of multifunctional device applications, the physics is interesting in this class of materials. Such examples include manganese-based oxides (TbMnO$_3$, YMnO$_3$, and HoMnO$_3$) and Bi-based magnetic ferroelectrics. For classic condensed matter physics, magnetism and ferroelectricity in many materials are mutually exclusive, which blocked the development of multiferroicity research in the last century. Till 2003, two milestones, i.e. the discovery of magnetic-field-controllable ferroelectric polarization in perovskite manganite TbMnO$_3$ crystals and giant ferroelectric polarization in BiFeO$_3$ films, revived the aggressive interests on multiferroicity. Since then, multiferroics have become a flourishing research area. A rapidly growing number of multiferroic materials have been discovered and synthesized, while the understanding of underlying physical mechanisms has also been pushed forward gradually. To date, there are already many experimentally verified multiferroic materials, most of which are transition metal oxides although there are also some exceptions, e.g. some fluorides and organic tetrathiafulvalene-p-bromanil. According to Chomsky’s classification, some of these materials belong to type-II multiferroics (or so-called magnetic multiferroics), in which the origins of ferroelectric polarization are relevant to some particular magnetic profiles, while in type-I multiferroics the origins of polarization are nearly irrelevant of magnetism. The type-II multiferroics exhibit strong intrinsic magneto electric couplings, or more precisely. Their ferroelectric polarizations can be significantly affected by tuning their magnetism, while in most type-I multiferroics, the magneto electric couplings are usually weak. In this sense, type-II multiferroics are more interesting to physics, and will be also important in future applications. The promising multiferroic materials are those where Bi is the largest cation in the structure. BiFeO$_3$(BFO) is one of the most extensively investigated perovskite oxide materials because of its remarkable multiferroic (ferroelectric, antiferromagnetic), optical properties at room temperature and potential applications in memory and logic devices. It has been shown to possess a rhombohedral distorted perovskite structure with space group R3c at room temperature. Its
large polarization, high Curie temperature (~820°C), and high Néel temperature (~370°C) make it appealing for applications in ferroelectric nonvolatile memories and high temperature electronics. In bulk BFO, ferroelectricity is known to originate from a relative Bi–O displacement that results from the stereo chemical activity of the lone electron pair located on the Bi cation, but the polarization shows smaller. The magnetic structure is essentially G-type antiferromagnetic which the Fe magnetic moments are coupled ferromagnetically within the pseudo cubic (111) planes and antiferromagnetic ally between adjacent planes. However, a long-wavelength (62 nm) incommensurate spiral modulation leads to a vanishing macroscopic magnetization.

The severe leakage problem and large coercive field of BFO films may hinder its future application in devices. A lot of efforts have been made to decrease the leakage current of BFO film. It is difficult to observe the ferroelectric hysteresis loops in the bulk BFO ceramic, as well as in the BFO films, prepared by using common solid state reactions. Although rhombohedral BFO has been studied extensively since first discovery in 1960s, the films with high defect density and poor sample quality5-7 were usually prepared may be due to uncertain oxygen stoichiometry. In order to understand the properties of multiferroic BFO, it is very important that the fabrication procedure of pure BFO phase should be established. If temperature and oxygen partial pressure were not controlled accurately during crystallization of the BFO phase, the kinetics of phase formation always lead to other impurity phases in Bi-Fe-O system, such as Bi3Fe5O15, Bi4O2,75, and Bi3Fe2O7,6, 8, 9 BFO films deposited on Pt or some conductive oxide bottom electrodes by chemical solution deposition method usually showed a lower polarization with a large leakage current at room temperature6, 7. And the leakage current is mainly dominated by electrode effects, such as Schottky barrier formation if one uses materials with a high work function such as Pt. While the high leakage current in the BFO thin film arises due to intrinsic low resistivity of the thin film, which is attributed to the presence of Fe2+ and O vacancies.8 In recent years, more attentions were focused on the preparation of BFO films since they allow direct integration of the material into the semiconductor technology. In order to improve ferroelectric properties of BFO, significant works have been done to prepare BFO thin films by using different methods, such as pulsed-laser deposition (PLD) chemical solution deposition (CSD) and rf-sputtering. Sputtered BFO thin films need the relative complexity of the preparation conditions. However, the sputtering method has some advantages, such as well-known specifications and well-controlled stoichiometry with dense and uniform films.

In this paper, we present the optimizing conditions for the fabrication of pure perovskite BFO films by magnetic controlling sputtering method. Among many preparation conditions for sputtering, the partial pressure of reactive oxygen gas and the substrate temperature during the deposition were carefully investigated for finding stoichiometric BFO thin films.

2. Experiments
Polycrystalline BiFeO3 thin films were fabricated by radio frequency magnetron sputtering using a Bi1.1FeO3 target onto the glass and Si/SiO2/Ti/Pt substrates respectively. The excess Bi in target was for compensation of Bi loss during the preparation. The BFO thin films were deposited on glass substrates at different temperatures by magnetron sputtering. And on Si/SiO2/Ti/Pt substrates, the Ar/O2 ratio was kept at 4:1, the BFO thin films were deposited at 650°C with 1 Pa pressure and annealed for 2.5 h in situ in oxygen atmosphere. The thickness of films determined by a Dektak 6M surface profiler for polycrystalline BFO layers.

The structure of the films was determined by x-ray diffraction (XRD) with Cu Kα radiation, including normal θ–2θ scan, θ scan and pole figure scan. The morphology was observed by scanning electron microscopy (SEM). The chemical state was analysed using x-ray photoelectron spectroscopy (XPS).

3. Results and Discussion
In order to prepare the pure BFO phases, the BFO films were deposited on glass substrates at different substrate temperatures, 500°C, 600°C, 650°C, 700°C respectively. As shown in fig. 1, the only
diffraction peaks of the XRD patterns ($\theta$-2$\theta$ scan) is consistent with the rhombohedral distorted perovskite–like structure BiFeO$_3$ (a=3.96 Å) (110) at the 31.77 degree when the substrate temperature at 500°C or 600°C. However, the main diffraction peaks of the XRD patterns ($\theta$-2$\theta$ scan) which are consistent with the rhombohedral distorted perovskite–like structure BiFeO$_3$ (a=3.96 Å) (001), (111), (002), (220) and (230) corresponding to the degrees 22.50, 38.95, 45.75, 66.40 and 88.60 respectively are appeared when the substrate temperature rising above 650°C. And the intensity of these peaks increases.

The results show that the crystallinity of BFO films will be affected when the substrate temperature is too low. It can be seen from the XRD patterns that the impurity phases increase as the temperature increasing. It may be caused by Si content in glass which easily reacts with the elements in the BFO films to form new impurity phases at higher temperatures.

![XRD patterns of the polycrystalline BFO films grown on glass under different temperature](image)

**Figure 1.** XRD patterns of the polycrystalline BFO films grown on glass under different temperature (The black dots represent the impurity phases).
In addition, the key factors are suitable sputtering rate, oxygen content and annealing environment in the process of preparing BFO films, because oxygen vacancies are easily formed during the high temperature deposition. In the preparation process, we have prepared the pure BFO phase by repeated attempts and optimization of experimental conditions.

We further choose to prepare BFO films on Si/SiO$_2$/Ti/Pt substrates due to the poorer heat resistance of ordinary glass. In order to control oxygen vacancies density, the BFO films were annealed under different annealing conditions. For polycrystalline BFO, the films were annealed under different in situ annealing conditions with Ar/O$_2$ ratios of 0:0, 1:0, 4:1, 1:1 and 0:1 at 1 Pa. The main diffraction peaks of the XRD patterns (θ–2θ scan) are consistent with the rhombohedral distorted perovskite–like structure BiFeO$_3$ (a=3.96 Å) (001), (110), (111), (002), (120) and (121). As shown in fig. 2, the relative intensity and half-width of the diffraction peaks of the BFO films show significant changes in different annealing environments, such as the peak of BFO (001), the half-width decreased from 0.28 to 0.23 compared with the pure argon or pure oxygen environment. And the intensity of the peak is also enhanced significantly.

Similarly, the BFO films were deposited on the ITO glass under the same preparation conditions as on Si/SiO$_2$/Ti/Pt substrates. And the pure BFO phases were also grown which were annealed in situ under different oxygen partial pressure environments. The main diffraction peaks of the XRD patterns (θ–2θ scan) are consistent with the rhombohedral distorted perovskite–like structure BiFeO$_3$. The results indicate that the pure polycrystalline BFO films can be grown on different substrates. And the phase structures of BFO films are not affected.

The surface morphology of BFO films annealed under different oxygen partial pressures on ITO glass substrates was observed by scanning electron microscopy. The results show that the surface of polycrystalline BFO films annealed under vacuum conditions is rough and poorly compact. As the partial pressure of oxygen increases, the compactness of the film increases. In addition, the relative contents of Bi and Fe in the sample were analysed by X-ray energy dispersive spectroscopy. The results show that the atomic ratio of positive ions in BFO film is closer to Bi: Fe~1:1 annealed in oxygen-containing annealing environment. It is indicated that the pure BFO films are more easily prepared under the oxygen annealing environment.

**Figure 2.** XRD patterns of the polycrystalline BFO films grown on Si/SiO$_2$/Ti/Pt substrates with different in situ annealing conditions (a) Ar/O$_2$~0:1; (b) Ar/O$_2$~1:1; (c) Ar/O$_2$~4:1; (d) Ar/O$_2$~1:0; (e) Vacuum; (f) Si/SiO$_2$/Ti/Pt substrate.
The results indicate that the crystallinity of the BFO films is changed by adjusting the oxygen vacancies in different annealing environments. However, the adjustment of oxygen partial pressure does not affect the composition of the BFO phases, and no other impurity phases is formed in the annealing environments.

4. Conclusion
We have prepared pure BFO films with different in situ annealing conditions by radio frequency magnetron sputtering using a Bi$_{1.1}$FeO$_3$ target onto the glass and Si/SiO$_2$/Ti/Pt substrates respectively. There are relatively wider growth conditions for pure polycrystalline BFO phases. The composition of BFO films remain pure phases in different oxygen partial pressure. The pure polycrystalline BFO films can be grown on different substrates, and the phase structures of BFO films are not affected.

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