Magnetic-Electric Behaviors and Physical Properties of The Thin Films on ITO-Glass Substrate

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Abstract. Polycrystalline BiFeO₃ thin films on ITO glass substrates were prepared by radio frequency magnetron sputtering using a Bi₁₋ₓFeO₃ target. The samples which were annealed with different annealing conditions are pure without impurities. We measured the magnetic properties and ferroelectricity of the BiFeO₃ films. The measurement results show that the magnetic and electrical properties of the BiFeO₃ films are significantly different under different annealing conditions.

Keywords: BiFeO₃ films, oxygen vacancy, annealing, ferroelectricity.

1. Introduction

Recently, single multifunctional materials with magnetic and electric orders coexisting have been extensively studied. The kind of multiferroic material is not only promising in designing multifunctional devices, but the physics is also interesting. The kind of instances contains manganese-based oxides (HoMnO₃, TbMnO₃, and YMnO₃) [1-3] and Bi based ferroelectrics. Multiferroic research was difficult to develop in the century, mainly because the magnetic and ferroelectric properties of most materials were mutually exclusive. Until 2003, another interest in multiferroic materials is the discovery of giant ferroelectric polarization in BiFeO₃ (BFO) films and magnetically controlled ferroelectric polarization in perovskite manganite TbMnO₃ crystals. Now, multiferroics have become a hot research field. More and more multiferroic-materials appear, and the explanation of the physical mechanism is gradually advancing. At present, there have been many experimental confirmed multiferroic materials, mostly transition-metal-oxides. According to Khomskii’s study, the origin of ferroelectric polarization in type-II multiferroic materials (or magnetic multiferroic materials) is related to certain specific magnetic profiles, while the origin of polarization in type-I multiferroic materials is almost independent of magnetism. In most type-I multiferroics, the magnetoelectric coupling is usually weak [4-6]. However, the type-II multiferroics exhibit more stronger intrinsic magnetoelectric coupling. Its ferroelectric polarization can be more pronounced by tuning magnetism. From this perspective, type-II multiferroic materials will be very important in future application [7,8].

At present, the most studied multiferroic materials are the Bi which are the biggest cations in the structure. BiFeO₃ is widely studied as perovskite structure. At room temperature, it has rhombohedral distorted perovskite structure of R3c space group, and has significant multiferroic (ferroelectric, antiferromagnetic), and latent value in storage and logic equipment. In the bulk BFO, ferroelectricity is generated by the relative Bi–O shift caused by the stereochemical characters of the lone-pair
electron located on the Bi cation with smaller polarization. The high Curie temperature (~820 °C), high Neél temperature (~370 °C) and large polarization of BFO make it have broad application prospects in high temperature electronics and ferroelectric nonvolatile memory. The magnetic ordering structure is G-type antiferromagnetism, and the Fe magnetic moment is ferromagnetically coupled in the pseudocubic (111) planes and antiferromagnetically between adjacent crystal planes. However, disappearance of macroscopic magnetization due to long-wavelength (62 nm) incoherent helical modulation. [2]

BFO has become widely studied perovskite structure due to its significant multifunctionality, room temperature optical characteristics and possible applications in memory devices. More and more people are interested in multifunctional materials with ferroelectric and magnetic properties. The preparation and properties of BFO single crystal and films have been extensively studied. These studies show that BFO has many interesting properties, which offer a chance for the preparation of multi-function equipment based on BFO. However, one of the main obstacles to potential applications is the relatively high leak current density of BFO thin films.

Many studies have been done on how to lower the leak current of BFO thin films [9,10]. Otherwise, the leak current caused by oxygen vacancies in BFO also exhibits lots of interesting characters, such as photovoltaic properties. The conduction of current through high impedance materials has been shown new physics. For instance, various rectifier current-density-voltage characteristics are encountered in the study of resistance switches pursued by resistance-random access memory. Rectification effect is due to asymmetric interfaces with semiconductor-metal contact, and the resistance switch is due to the surface. While studies have shown that the origin is the bulk effect. Choi et al. lately published a switchable diode effect in BFO single crystal, which was attributed to the bulk effects.

Since naturally generated oxygen vacancies are donor impurities, BFO films are usually regarded as n-type semiconductors. Dawber and Scott proposed the model, under the action of AC electric field, the oxygen vacancy is likely to migrate to the electrode interface and aggregate to form a two-dimensional array. Jiang et al. pointed out that the switchable diode effect using BFO thin film capacitor is by reason of the accumulation of oxygen vacancies near the electrode. And Lee et al. reported that the switchable diode effect is related to the oxygen-vacancy-rich defective layer. Although a lot of research has been done in this area, the source of the switchable diode effect in BFO is yet not interpreted. There is little consensus on whether the diode effect is the interface source or the bulk source, and how the oxygen vacancy affects the effect.

In this work, we have proposed optimized conditions for the preparation of pure perovskite BFO films by magnetic controlling sputtering method. In many preparation conditions of sputtering, the oxygen partial pressure and the substrate temperature during the deposition process were carefully studied to find the stoichiometric BFO films. And we measured the magnetic properties and ferroelectricity of the BFO films.

2. Experiments

Polycrystalline BiFeO₃ films were prepared on the glass with ~180 nm-thick conductive ITO buffer layer (ITO/glass) using a Bi₁₁₋ₓFeO₃ target by radio frequency magnetron sputtering. The overmuch Bi in sputtering target was to compensate for the loss of Bi in process. During magnetron sputtering, the Ar/O₂ ratio was maintained at 4:1, the BFO thin films were prepared at 650 °C and 1 Pa pressure, and in-situ annealed in oxygen atmosphere for 2.5 h. The thickness of polycrystalline BFO films was measured by a Dektak 6M surface profiler as ~150 nm. The conductive substrate can be used as bottom electrode for electrical measurement, such as oxide electrodes. ITO/glass shows metallic behaviors, which is used as substrate and bottom electrode with high conductivity for polycrystalline growth. The circle Ag top electrodes with about 100 µm in diameter were deposited onto the surface of the BFO films applying a shadow mask by magnetron sputtering.

The structural characteristics of the thin films were verified by Cu Kα radiation X-ray diffraction, including ϕ scanning, θ-2θ scanning and pole figure scanning. The morphology of the films was
characterized by scanning electron microscopy. The ratio of Bi and Fe in the sample was examined by energy-dispersive X-ray spectroscopy, and the chemical state was analyzed by X-ray photoelectron spectroscopy. Quantum Design magnetic property measurement system and physical property measurement system were used to measure magnetic properties, and TF analyzer 2000 (aixACCT) was used to measure ferroelectric properties at room temperature.

![XRD patterns of polycrystalline BFO thin films deposited on ITO glass with different in situ annealing conditions](image)

**Figure. 1** XRD patterns of polycrystalline BFO thin films deposited on ITO glass 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.

### 3. Results and Discussion

We adjust density of oxygen vacancies by annealing BFO films under different deposited conditions. The polycrystalline BFO film on ITO/glass substrates was annealed under various in situ annealing conditions with Ar/O\(_2\) ratios of 0:0, 1:0, 4:1, 1:1 and 0:1 at 1 Pa. As shown in Fig. 1, the main diffraction peaks of the XRD patterns are in accordance with the rhombohedral distorted perovskite structure BiFeO\(_3\) (a=3.96 Å) (001), (110), (111), (002), (120) and (121). The surface morphology of BFO films annealed in different oxygen partial pressures was characterized by scanning electron microscopy. As shown in Fig. 2, the surface of BFO film annealed in vacuum condition is rougher and less dense. As the oxygen partial pressure increasing, the compactness of the BFO film becomes better. The Bi and Fe contents by EDX in the samples were consistent with the relationship of Bi: Fe~1:1.
Figure 2 The morphology of polycrystalline BFO thin films deposited on ITO glass with different in situ annealing conditions (a) Vacuum; (b) Ar/O$_2$~1:0; (c) Ar/O$_2$~4:1; (d) Ar/O$_2$~0:1.

Magnetization of the BFO thin films is measured by SQUID–VSM with a higher sensitivity of ~10$^{-7}$ emu. Fig. 3 gives the room-temperature magnetization loops of polycrystalline BFO thin films under various in situ annealing conditions. The oxygen–pressure–dependent magnetization changes within the range of 4 emu/cm$^3$ (0.026 $\mu_B$/Fe) to 15 emu/cm$^3$ (0.1 $\mu_B$/Fe). It can be seen that the saturation magnetization of the BFO films gradually increases, as the oxygen partial pressure increasing. It shows that the magnetic properties of the film are also affected and gradually enhanced while the oxygen vacancies are supplemented by annealing the BFO film. During the process, the measurement temperature has no significant effect on the magnetic properties of the BFO films.

In order to study the ferroelectricity of the BFO film, we prepared the BFO films with the thickness of 100 nm on the conductive ITO substrates which serve as the bottom electrode. The silver films were deposited on the surface as the upper electrode. The leak current is measured at room temperature by scanning the top electrode of the as-grown BFO capacitance at the switching triangular voltage. A positive bias applied to the film is defined as the current flowing into the BFO film from the top electrode Ag. The bias was conducted in the direction 0→+$V_{max}$→0→$-V_{max}$→0. Fig. 4 gives the ferroelectric polarization versus voltage ($P$–$V$) curves of the films at room temperature without electrical training. The remnant polarization (Pr) is small for the high oxygen vacancy density. Obviously, at lower oxygen pressure, more oxygen–vacancy forms, therefore the $P$–$V$ curves are shown in round shapes. Investigations of the magnetic and ferroelectric properties have confirmed that weak ferromagnetism and spontaneous polarization coexist in these BFO samples at room temperature. Moreover, it can be seen from the shape of the pattern that the BFO film annealed under pure oxygen has better ferroelectricity.
Figure 3. Room-temperature magnetization curves of the polycrystalline BFO films with different \textit{in situ} annealing conditions (a) Ar/O$_2$~1:0; (b) Ar/O$_2$~4:1; (c) Ar/O$_2$~1:1; (d) Ar/O$_2$~0:1.

Figure 4. Room-temperature ferroelectric hysteresis loops of the polycrystalline BFO films with different \textit{in situ} annealing conditions (a) Vacumm; (b) Ar/O$_2$~1:0; (c) Ar/O$_2$~1:1; (d) Ar/O$_2$~0:1.
4. Conclusions
We have prepared polycrystalline BFO thin films with various preparation environments on ITO glass substrates with and without post-annealing treatment. The composition of BFO films remains pure phases in different oxygen partial pressures. Under the same magnetic measurement conditions, the polycrystalline BFO films in different annealing environments show different saturation magnetization. And the BFO film annealed under pure oxygen has better ferroelectricity.

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