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Materials

Comparison of room-temperature multiferroics in $Bi_4Fe_2TiO_{12}$ film and bulk

Jun Lu, Lijie Qiao, and Wuyang Chu

Department of Materials Physics, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

Abstract: It was reported that both dielectricity and magnetism at room temperature were appreciably improved in $Bi_4Fe_2TiO_{12}$ film compared with $Bi_4Fe_2TiO_{12}$ bulk. X-ray diffraction profiles reveal similar crystalline nature and random orientation of the two, but X-ray photoelectron spectroscopy (XPS) experiments indicate that it is 1.4 eV lower binding energy of core-state O1s in the film relative to that of the bulk, so the improvement of multiferroics in the film is attributed to oxygen vacancies and high fraction of interface. The results have promising applications in multifunctional integrated devices.

Key words: multiferroic film; X-ray photoelectron spectroscopy (XPS); oxygen vacancy; magnetism; dielectric property

1. Introduction

Multiferroics has become one of the time-honored issues in past years, where polarization and spin order coexist simultaneously in one entity [1-7]. Considerable progresses in single-phase materials include direct manipulation of polarization reversal by magnetic field in single-crystal $TbMn_2O_5$ [1], giant magnetodielectric in single-crystal $DyMnO_3$ [2], and colossal magnetodielectric effects in single-crystal $CdCr_2S_4$ [3]. However, so far, such strong multiferroic couplings have never been discovered at room temperature, although room-temperature strong coupling between magnetic field and polarization has been recently reported in $LuFe_2O_4$ single crystal, where the dielectric constant transiently decreases by only 20% [4]. Epitaxial $FeBiO_3$ thin films have been synthesized with remarkable spontaneous polarization, magnetism, and magnetoelectric output at room temperature [5]. The interaction between spontaneous polarization and external magnetic field in $Bi_{0.6}Tb_{0.3}La_{0.1}FeO_3$ single phase but thin film has also been suggested to be more pronounced with about 80% reduction of remanent polarization after magnetic-field treatment of 9 T as a consequence of magnetic-field-induced irreversible reorientation of grains [6]. However, the comparison between films and bulks in strong correlated multiferroic materials and uniqueness of multiferroics in films have rarely been discussed. This article presented room-temperature experimental results of enhanced dielectricity and magnetism in $Bi_4Fe_2TiO_{12}$ film in comparison with $Bi_4Fe_2TiO_{12}$ bulk, wherein the origin of improvement was interpreted by the evidences from X-ray diffraction (XRD) profiles and X-ray photoelectron spectroscopy (XPS).

2. Experiments

$Bi_4Fe_2TiO_{12}$ film was deposited by spin coating onto the platinized silicon layer by layer from chemical solution, and the single-phase polycrystalline film with a thickness of hundreds of nanometers was then obtained by rapid annealing. Before the electric measurement, which was carried out under the HP4194 dielectric spectra analyzer at room temperature, top electrodes were prepared *via* conventional mask technology. The measurement of magnetism is conducted in a superconducting quantum interference device (SQUID, by Quantum Design Inc.). The details of sample preparation have been published elsewhere [7].

3. Results and discussion

The structure of $Bi_4Fe_2TiO_{12}$ film is shown in Fig. 1 with comparison to $Bi_4Fe_2TiO_{12}$ ceramic bulk. The XRD pattern of $Bi_4Fe_2TiO_{12}$ ceramic, which agrees well with that of $Bi_4Ti_3O_{12}$ cited from JCPDS file 35-0795, is then indexed according to $Bi_4Ti_3O_{12}$ powder, which suggests its nature of single phase and bismuth-layered Aurivillius structure with *B2cb* space

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Corresponding author: Lijie Qiao, **E-mail:** lqiao@ustb.edu.cn

group [8]. Fe favors to share the Bi site with Ti in the center of a pseudo-perovskite cell when it is appropriate to substitute into this bismuth layered lattice [9]. By comparing the peak positions of $Bi_4Fe_2TiO_{12}$ film with those of $Bi_4Fe_2TiO_{12}$ ceramics, one can find good correspondence between the two except for peaks from the substrate, indicating the single-phase nature of $Bi_4Fe_2TiO_{12}$ film. It is understandable that $Bi_4Fe_2TiO_{12}$ polycrystalline film is random oriented since the intensity of corresponding peaks is the same order of magnitude with that of $Bi_4Fe_2TiO_{12}$ ceramics.

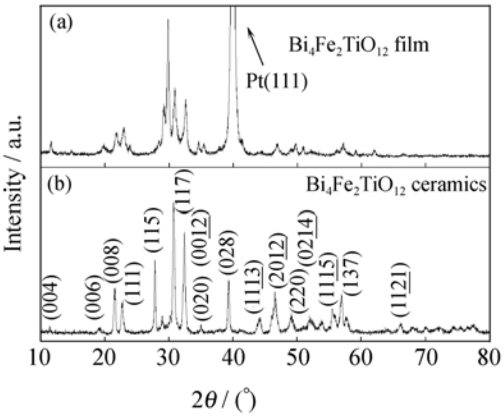

Fig. 1. X-ray diffraction profile of $Bi_4Fe_2TiO_{12}$ film and ceramic bulk.

The results of functional measurement of $Bi_4Fe_2TiO_{12}$ ceramic bulk and film have been shown in Fig. 2 and Fig. 3. In Fig. 2, the dielectric constant of $Bi_4Fe_2TiO_{12}$ film at room temperature is approximately twice as much as that of $Bi_4Fe_2TiO_{12}$ ceramics in the frequency range of 100 Hz-100 kHz. Meanwhile, the magnetization of $Bi_4Fe_2TiO_{12}$ film is remarkably larger than that of $Bi_4Fe_2TiO_{12}$ ceramics up to room temperature, as shown in Fig. 3, even though the scanning magnetic field of $Bi_4Fe_2TiO_{12}$ film in warming process is only 1/50 of that of $Bi_4Fe_2TiO_{12}$ ceramics. The clear peak of $Bi_4Fe_2TiO_{12}$ film at about 50 K in Fig. 3 implies a transition from antiferromagnetism to weak ferromagnetism when warming, as indicated in another publication [7].

To analyze the XPS data, all of the binding energies at various peaks were calibrated by using the binding energy of C 1s (284.6 eV) [10], as shown in Fig. 4 and Fig. 5. In Fig. 4, the 7/2 and 5/2 spin-orbit doublet components of Bi 4f core level photoemission are located at 158.9 and 164.2 eV, respectively, not only for $Bi_4Fe_2TiO_{12}$ film but also for $Bi_4Fe_2TiO_{12}$ ceramics when taking the error about 0.5 eV into account. These two peaks, as well as the 5.3 eV spin-orbit splitting of Bi 4f core level, are quite close to that of $Bi_4Ti_3O_{12}$ ceramics [11], suggesting the same chemical environment of $Bi_4Fe_2TiO_{12}$ film and ceramics to $Bi_4Ti_3O_{12}$ ceramics and uniform substitution of Fe at Ti sites in $Bi_4Fe_2TiO_{12}$ film and ceramics. In contrast, the O1s core level photoelectron energy of $Bi_4Fe_2TiO_{12}$ film is different from that of ceramics, as shown in Fig. 5, where the XPS peak of $Bi_4Fe_2TiO_{12}$ film are shifted to the lower-energy end by 1.4 eV in comparison with that of $Bi_4Fe_2TiO_{12}$ ceramics and furthermore a shoulder appears at about 532 eV on the higher energy side of $Bi_4Fe_2TiO_{12}$ film, which can be proved by splitting curves from fitting results of experimental XPS data. Intuitively, the decrease of O1s core-level binding energy is attributable to the screening effect, where emitted photoelectrons leave behind a positive-charged hole, which is screened by relaxation of surrounding atoms [12]. Strictly speaking, in the view of the band theory, the promotion of oxygen vacancies, which act as donors in oxides, causes an increase in surface conductivity and a band bending [13]. Another feature of the XPS plot of the presence of a side peak at about 532 eV in $Bi_4Fe_2TiO_{12}$ film should not be due to hydroxyl groups, or to any other impurities, but arises from the effect of oxygen vacancies [14]. The assignment of this O1s shoulder at 532 eV to O^{2-} anions located near to oxygen vacancy sites in the film has been also claimed by another separated group [15].

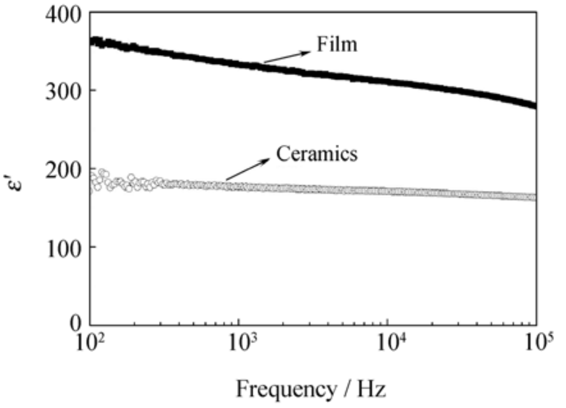

Fig. 2. Dielectric constant of $Bi_4Fe_2TiO_{12}$ film and ceramic bulk.

It was not unusual for the occurrence of a higher dielectric constant in perovskite-oxide film, compared with ceramics because of various factors such as stresses from the substrate and dielectric inhomogeneit like interface layers, grain boundaries, and porosity [16]. Actually, in bismuth layered materials, rotation of defect dipoles associating the oxygen vacancies toward the direction of applied electric field caused the majority of polarizability [17]. Hence, the increase of dielectric constant in Fig. 2 can be explained by the more oxygen vacancies in $Bi_4Fe_2TiO_{12}$ film, which is consistent with Fig. 5.

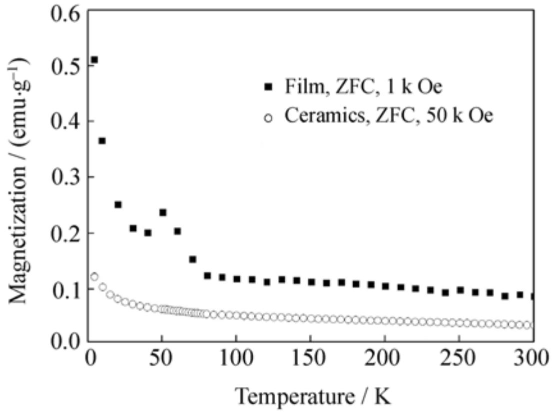

Fig. 3. **Magnetization *versus* temperature curves of $Bi_4Fe_2TiO_{12}$ film and ceramic bulk.**

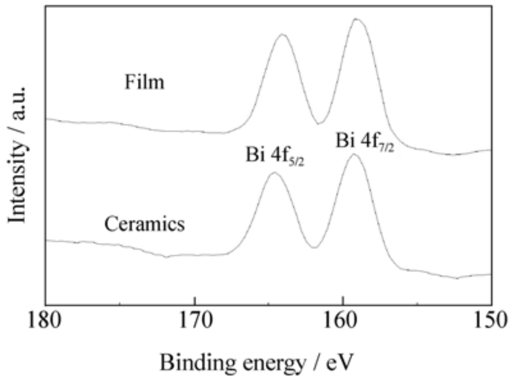

Fig. 4. **Core level photoelectron spectra of Bi 4f of $Bi_4Fe_2TiO_{12}$ film and ceramic bulk.**

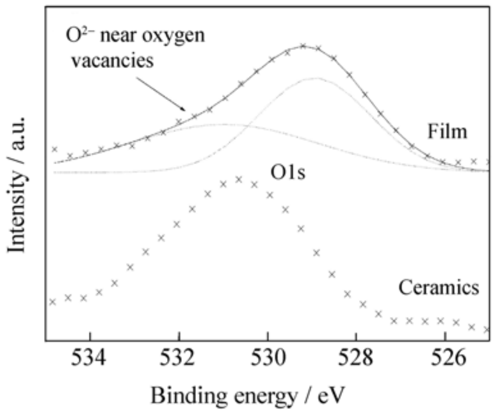

Fig. 5. **Core level photoelectron spectra of O1s of $Bi_4Fe_2TiO_{12}$ film and ceramics. The crosses denote experimental data, the solid line denotes the fitting XPS curve of the film, and the dotted profiles indicate the split peaks of the fitting curve.**

Intriguingly, the room-temperature striking improvement of magnetism in $Bi_4Fe_2TiO_{12}$ film, which is hardly due to the minor impurity or orientation effect in the film as shown in Fig. 3, can be understood by the unique room-temperature ferromagnetic phenomena in the film. Coey, *et al*. advocated that room-temperature ferromagnetism of film arose from shallow donor electrons that formed bound magnetic polarons, which overlapped to create a spin-split impurity band [18]. Therefore, we propose that the nontrivial room-temperature ferromagnetism $Bi_4Fe_2TiO_{12}$ film is also attributable to the number of oxygen vacancies, which is consistent not only with dielectric characterization in Fig. 2, but also with XPS results in Fig. 5.

4. Conclusion

In conclusion, we have synthesized $Bi_4Fe_2TiO_{12}$ film with appreciably promoted room-temperature dielectric constant and magnetism in comparison with $Bi_4Fe_2TiO_{12}$ bulk *via* a facile chemical deposition method. The presence and interaction of oxygen vacancies is speculated a critical feature in $Bi_4Fe_2TiO_{12}$ film to produce enhanced correlated properties. The reported materials and phenomena are promisingly applicable in integrated multifunctional devices.

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