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Microstructure tuning and magnetism switching of ferroelectric barium titanate

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ABSTRACT

Single-crystal and polycrystal $BaTiO_3$ (BTO) materials synthesized by the physical and chemical methods, respectively, have been studied based on microstructural characterizations and magnetic measurements. The results of X-ray diffraction and Raman scatting spectra show that a single crystal tetragonal to polycrystalline pseudo-cubic structure transformation occurs in BTO ferroelectrics, dependent of growth conditions and interface effects. High-resolution transmission electron microscope data indicate that the as-prepared BTO/$SrTiO_3$ (001) and BTO/$SrRuO_3$/$SrTiO_3$ (001) heterostructures are highly *c*-axis oriented with atomic sharp interfaces. Lattice defects (i.e., edge-type misfit dislocations and stacking faults) in the heterostructures could be identified clearly and showed tunable with the variations of interface strain. Furthermore, the effects of vacancy defects on magnetic properties of BTO are discussed, which shows a diamagnetism–ferromagnetism switching as intrinsic vacancies increase. This work opens up a possible avenue to prepare magnetic BTO ferroelectrics.

1. Introduction

Multiferroic materials, which can exhibit simultaneous effects of ferroelectricity and ferromagnetism, have attracted considerable attention for both fundamental scientific understanding and their potential applications in devices based on the mutual controls of magnetic and electric fields [1,2]. However, the intrinsic multiferroics are particularly rare as the formal d^0 configuration of conventional ferroelectrics (FE) is contradictory with partially filled *d*-states of ferromagnetism (FM) [3]. A lot of efforts on single-phase multiferroics concentrate on the Bi-based perovskites such as $BiFeO_3$ and $BiMnO_3$, where the ferroelectricity mainly arises from the lone pair of 6*s* electrons [4,5]. However, none of these multiferroics combine large and robust electric and magnetic polarizations at room temperature (RT) [2]. Therefore, it is expected that magnetism can be gained in prototypical perovskite ferroelectrics (PPFE) such as $BaTiO_3$ (BTO), $PbTiO_3$ (PTO), and $KNbO_3$ which have high electrical permittivity and large spontaneous polarization.

For many years, a number of methods have been attempted in order to provide possible avenues of the observed magnetism in PPFE. Only two approaches are currently prevalent for achieving magnetism in these FE perovskites: (1) transition metal elements TM (TM = Fe, Mn, Co, etc) doped FE perovskites [6–8]; and (2) FE—FM multilayered composite structures [2]. TM-doped ferroelectric oxides have been studied extensively, but even low doping concentration would induce exterior impurity and the second phase limits their further application in device design. Although FE–FM multilayered composites show an excellent feature of coupling magnetic and electric fields, the structures are too complex to be well integrated for functional applications.

To better address the above issues, some recent experimental studies suggested that magnetism can be induced by the intrinsic vacancy in undoped nonmagnetic oxides, and RT FM can be observed in undoped metal oxides, such as HfO_2, ZnO, TiO_2, and PTO [9–12]. It makes a possibility to realize the coexistence of ferroelectricity and magnetism in conventional FE. Importantly, the intrinsic defects-induced magnetism does not bring exterior impurities, which contributes to the performance and life of the device. It is thus of interest to investigate the effect of vacancies in PPFE and explore the potential magnetism in such materials. BTO is one of the most extensively studied ABO_3 perovskite materials. In a previous theoretical study, Bahoosh et al. have reported that oxygen vacancies can induce RT FM in nanosized BTO perovskite [13]. Compared with the nanopowders, high-performance nanolayered FE occupy more important position in the field of actual device preparations [14]. In addition, it is also easy to produce the vacancy defects during the BTO growth process in a non-vacuum system and the coupling of the surface effect and vacancy defects may lead to more intriguing electrical and magnetic properties in BTO crystals. However, few experiments on magnetism in such BTO material with vacancies have been conducted so far. We hope that our work

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will inspire more experimental explorations and that the same mechanism can be used for other PPFE.

In this study, we have prepared phase-pure BTO materials on $SrTiO_3$ (STO) (001) substrate and on heteroepitaxial $SrRuO_3$ (SRO)/STO (001) substrate by laser molecular-beam epitaxy, which are labeled BTO-1 and BTO-2, respectively. Assuming that lattice mismatch between the BTO layer and substrate could introduce strain giving rise to local structural distortion and lattice defects, the physical properties of the crystals may consequently be modified. To generate more intrinsic defects to induce magnetism in BTO, we also grew BTO on fused quartz substrates by a sol–gel technique (abbreviated as BTO-3). In this case, the mismatch between the two sets of lattices is amplified and the oxygen loss exists commonly during the deposition in atmosphere. Our characterization shows that FE loops are present at RT, and scanning transmission electron microscopy (STEM) images confirm the lattice distortion and defects induced by the interface effect. Meanwhile, magnetic measurement results reveal that both BTO-1 and BTO-2 show no FM whereas BTO-3 exhibits well RT FM, which is indicative of vacancy dependence of magnetic properties in BTO materials.

2. Experimental

2.1. Preparations of BTO materials

Multilayered BTO/SRO was grown on STO (001) substrate by laser molecular-beam epitaxy. Single-phase pure SRO and BTO targets were ablated sequentially in the same chamber using the radiation of a KrF excimer laser ($\lambda = 248$ nm). Before deposition, the STO substrate used in this study was treated with mechanical polishing and growth repairing in order to get well-defined vicinal surfaces. Subsequently, a SRO layer (3.6 nm) was prepared under 100 mTorr and 2 Hz. Finally, BTO deposition was carried out under oxygen pressure of 75 mTorr at a substrate temperature of 700 °C. The energy density and pulse frequency were 2 J/cm^2 and 5 Hz, respectively. Once completed, the samples were cooled naturally to ambient temperature. Meanwhile, the BTO was also deposited directly on STO (001) under the same growth condition. Furthermore, for comparison, BTO was grown on fused quartz substrate by a sol–gel method. Barium acetate [$Ba(CH_3COO)_2$] and tetrabutyl titanate [$Ti(OC_4H_9)_4$] were used as the starting materials. Acetic acid (CH_3COOH) and acetylacetone ($CH_3COCH_2COCH_3$) were used as the solvent and the chemical modifier, respectively. The concentration of the final solutions was ~0.25 mol/L and the pH value was adjusted to 3–4. The precursor solution was spin-coated on fused quartz substrate, to then be dried at 180 °C for 120 s and finally annealed at the optimum temperature 800 °C for 300 s for crystallization in a rapid thermal processor.

2.2. Characterizations

Detailed structural and morphology analyses of the growth of BTO materials based on X-ray diffraction (XRD), reflection high energy electron diffraction (RHEED), and STEM images were provided and discussed. For measuring the ferroelectric hysteresis loops, a metal layer of Pt was deposited on the epitaxial BTO/SRO heterostructures as the top electrode. A FE analyzer was employed to characterize the FE properties (FE hysteresis loops). Additionally, the lattice dynamics of BTO-3 were investigated by means of Raman scattering using a micro-Raman spectrometer (Renishaw plc InVia plus, 514.5 nm). Its surface micrograph and chemical composition were further measured by scanning electron microscopy (SEM, Philips XL30FEG) with an energy dispersive X-ray spectroscopy (EDX) analyzer. The magnetic properties were investigated with a vibrating sample magnetometer in a physical property measurement system (Quantum Design). All measurements of the BTO samples were performed at room temperature.

3. Results and discussion

3.1. Structure and purity

Typical RT XRD patterns for BTO-1 and BTO-2 are shown in Fig. 1(a), respectively. Only (00 l) peaks appear in the θ–2θ scans for BTO-1 and BTO-2, indicating that BTO perovskites have grown with c-axis perpendicular to the plane of the substrates. No evidence of additional phases or interfacial reaction products was observed within the limit of XRD. BTO is tetragonal phase ($a = 3.994$ Å, $c = 4.038$ Å, $c/a = 1.011$) and STO is cubic phase ($a = 3.905$ Å) at RT, thus the lattice mismatch between BTO layer and STO substrate is 2.28% in (001) plane based on theoretical consideration. The SRO lattice ($a = 3.930$ Å) is between those of STO and BTO, which can decrease the lattice mismatch and alleviate interfacial stress as well as dislocations to better favor epitaxial growth of BTO-2 compared to BTO-1. This is consistent with the following STEM results. Fig. 1(b) shows the XRD pattern of BTO-3 sample. XRD pattern of the fused quartz substrate was included for comparison. The broad peak near 23° comes from the fused quartz substrate. The sample is a polycrystalline perovskite structure, at least within the detection limits of the instrument, and no impurity phases are observed. This indicates that 800 °C is high enough for the BTO-3 to be well crystallized. It is notable that the splitting of the doublet characteristics of the tetragonal structure is not observed in our BTO-3 sample, differing from common tetragonal-phase BTO in many reports possibly due to strong interface strain leading to a high degree of (110) preferred orientation [15]. From the XRD spectra, the lattice parameter and cell volume of BTO-3 were calculated to be $a = 4.013$ Å and $V = 64.626$ Å^3, respectively. Meanwhile, the structural characterization was further studied by

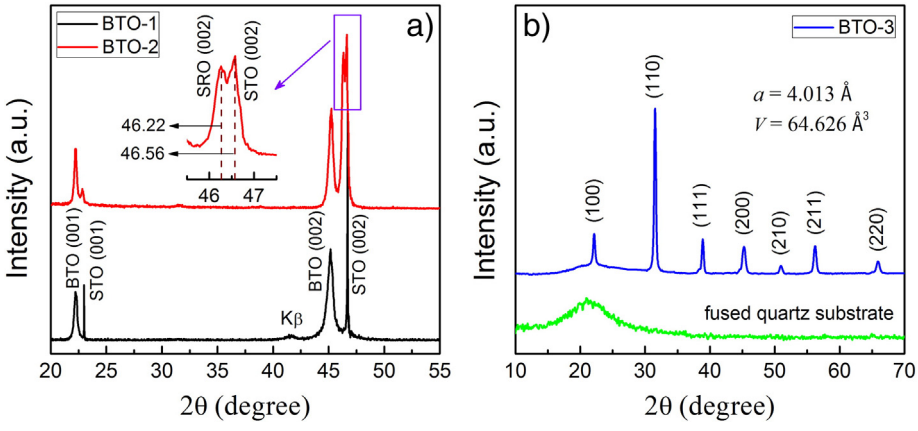

Fig. 1. XRD patterns of the samples: (a) BTO-1, BTO-2, and (b) BTO-3.