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Multiferroic studies on $(BiFeO_3)_m(BaTiO_3)_n$ superlattice structures

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ABSTRACT

$BiFeO_3$ has been studied extensively due to its room temperature multiferroic features and has been proven as a promising candidate for device applications. But $BiFeO_3$ possesses some drawbacks like high leakage current and complicated magnetic ordering, giving rise to a canted antiferromagnetic behavior. Hence, a superlattice approach of $BiFeO_3$ and $BaTiO_3$ with a good lattice matching was fabricated and the room temperature ferroelectric and ferromagnetic properties were studied. The macroscopic and local probe studies reveal a ferroelectric nature at room temperature, and most importantly a weak ferromagnetic like behavior was observed. The ferromagnetic behavior is expected to arise due to the variation introduced in the spin modulation of single $BiFeO_3$ layer due to the superstructure formation.

Materials that possess simultaneous coexistence of more than one ferroic order parameter have gained more interest in recent years due to both the technological application and the fundamental understanding of such materials [1]. Among the various applications put forth for the multiferroic materials like magnetic sensors, magnetic read write heads, etc., the four state memory device is the most highlighted application [1,2]. In recent years, numerous efforts have been dedicated to explore the multiferroic features of various materials in thin films and to manipulate the properties of the materials that naturally possess magnetic and electric order parameters [3]. $BiFeO_3$(BFO) is one among the multiferroic materials that possess room temperature multiferroicity with a complex spin cycloid magnetic ordering giving rise to a canted antiferromagnetic ordering with $T_N=650$ K and ferroelectric (FE) ordering with $T_C=1105$ K [4,5].

In spite of the interesting multiferroic features exhibited by BFO, there were other difficulties involved, like high leakage current and complex magnetic ordering [6,7]. There have been voluminous studies dedicated towards the reduction of leakage current in BFO in both bulk and thin film forms [8–10]. In the case of magnetic studies, there have been enormous studies dedicated to understand the magnetic ordering, anisotropy, and the coupling between ferroelectric polarization and magnetic ordering [7,11]. In the process of the optimization of magnetic properties of BFO, various theoretical calculations and experiments with B-site cationic substitution have been studied [12,13]. However, there have been practical difficulties in realizing a finite saturation magnetization, due to the complex magnetic ordering with a canted antiferromagnetic behavior [9,10]. In BFO the spin moment arising from the Fe cation is known to have a cycloidal arrangement in the (1 1 1) plane with the modulation vector pointing towards the ⟨1 1 1⟩ direction with a modulation period of 60 nm, effectively giving rise to a canted antiferromagnetism [6,7,14]. In the process of altering the magnetic modulation and simultaneously to make use of the ferroelectric polarization, an artificial superlattice structure comprising alternate layers of BFO and $BaTiO_3$ (BTO) was fabricated and the possibilities of utilizing the room temperature magnetization and ferroelectric polarization are studied. Utilization of $SrTiO_3$, a low temperature incipient FE, along with BFO to form a superlattice has been studied and reported elsewhere [8,15,16]. It is known that BTO provides a good lattice matching with BFO and also could provide an opportunity to alter the dipolar correlation among the TiO_6 and FeO_6 octahedra, with polarization along the ⟨0 0 1⟩ [17] and the ⟨1 1 1⟩ [5–7] directions, respectively.

In this work, a series of artificial superlattice structures made of $BiFeO_3$ (BFO) and $BaTiO_3$ (BTO) layers were fabricated using the pulsed laser deposition technique. The room temperature ferroelectricity and the magnetic behavior of $(BiFeO_3)_m(BaTiO_3)_n$ (m n—number of unit cells) superlattices and their periodicity dependence are studied. Remnant polarization and leakage current density displays an optimum for a periodicity range of ~20–60 Å and a possible mechanism of the leakage current in these superlattice structures is proposed.

Thin films of $BiFeO_3$ and $BaTiO_3$ and their superlattices were grown on the (0 0 1) oriented $SrTiO_3$ substrates at 700 °C in an oxygen ambient of 20 mTorr using a multitarget pulsed laser ablation and deposition technique. A pulsed KrF excimer laser ($\lambda=248$ nm) was fired onto the ceramic targets at a repetition rate of 3 Hz. The deposition rates (typically ~0.1 Å/pulse) of $BiFeO_3$ and $BaTiO_3$ were calibrated individually for each laser pulse of energy density ~1.5 J/cm^2. The superlattice structures were

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synthesized by repeating several times the bilayer consisting of '*m*' unit cells thick BFO layer and '*n*' unit cells thick BTO layer, with *m* and *n* taking integer values from 2 to 12, keeping a constant total thickness of the superlattice equal to 1200 Å. A series of superlattices with periodicity ranging from ~8to 90 Å were fabricated. Prior to the growth of superlattice, a bottom electrode of $LaNiO_3$ (800 Å) was deposited at 700 °C in oxygen ambient of 300 mTorr. Gold pads of size $400 \times 400\ \mu m^2$ (physical mask) were sputtered on top of the superlattice structures and on top of $LaNiO_3$ regions unexposed to the superlattice deposition. The fabricated heterostructures were characterized in the metal–insulator–metal (MIM) configuration to study their electrical properties. Ferroelectric polarization hysteresis (P–E) of the superlattice structures were performed using radiant technology high precision loop tester. The surface morphology, ferroelectric polarization switching, and piezo electric behavior of the super-structures were studied using a modified commercial atomic force microscope (AFM) (multimode, nanoscope IIIa, digital Instruments). Local piezo phase measurements were performed to highlight the direction of polarization on reversal of applied electric field. The magnetic characterization was performed using a vibrating sample magnetometer (VSM) attached with a quantum design physical property measurement system (PPMS).

Fig. 1 shows the XRD pattern of a $(BFO)_m(BTO)_n$ superstructure with a periodicity of Λ ~65 Å. The satellite reflections observed around the central average peak clearly reveal the formation of a superstructure. No impurity phases like bismuth oxide or iron oxide were detected in the X-ray studies of all superlattice structures. The periodicity of the superstructures was calculated from the conventional θ–2θ scan [8]. A pseudo-cubic out-of-plane lattice parameter of 4.003 Å was observed on a single layer BFO and an in-plane lattice parameter of 3.866 Å through cross-sectional electron microscopy studies (not shown). In the case of BTO the out-of-plane lattice parameter was observed to be around 4.020 Å and an in-plane lattice parameter of 4.006 Å. The average out-of-plane lattice spacing observed for the superstructures, given in Fig. 1(b), clearly reveals that the layers comprising the superlattice suffer an in-plane compressive strain and an out-of-plane tensile strain.

Fig. 2(a–c) shows the room temperature FE polarization of the $(BFO)_m(BTO)_n$ superlattice structure of periodicity Λ ~92 Å. Fig. 2(a) shows the macroscopic ferroelectric polarization measured using a radiant precision loop tester. The electric coercive field and the remnant polarization hysteresis observed exhibited a frequency and applied field independent behavior, indicating the true FE behavior and not any artifacts arising due to any leakage current. To further confirm the FE nature of the grains comprising the superstructure of BFO and BTO layers, local probe piezo measurements were performed. Fig. 2(b) shows the variation of phase difference between the applied signal and the tip deflection with respect to applied field, which indicates a clear hysteretic behavior and 180° degree switching with respect to reversal of applied electric field. Fig. 2(c) shows the hysteretic behavior of the piezo response of the superstructure with an applied electric field. The ferroelectric measurements performed on both the macroscopic and the microscopic scale clearly indicates the presence of switchable remnant polarization at room temperature. The macroscopic remnant polarization was found to be close to the value of single layer BTO (~2 $\mu C/cm^2$) rather than single layer BFO (~60 $\mu C/cm^2$), which could be due to the difference in the easy axis of polarization ⟨1 1 1⟩ and ⟨0 0 1⟩ for BFO and BTO, respectively, and mechanical strain experienced by both layers in the superstructure.

Fig. 3(a–c) shows the magnetic hysteresis of a $(BFO)_m(BTO)_n$ superlattice structure measured at 10 K. The magnetic measurements of the fabricated superlattice structures revealed

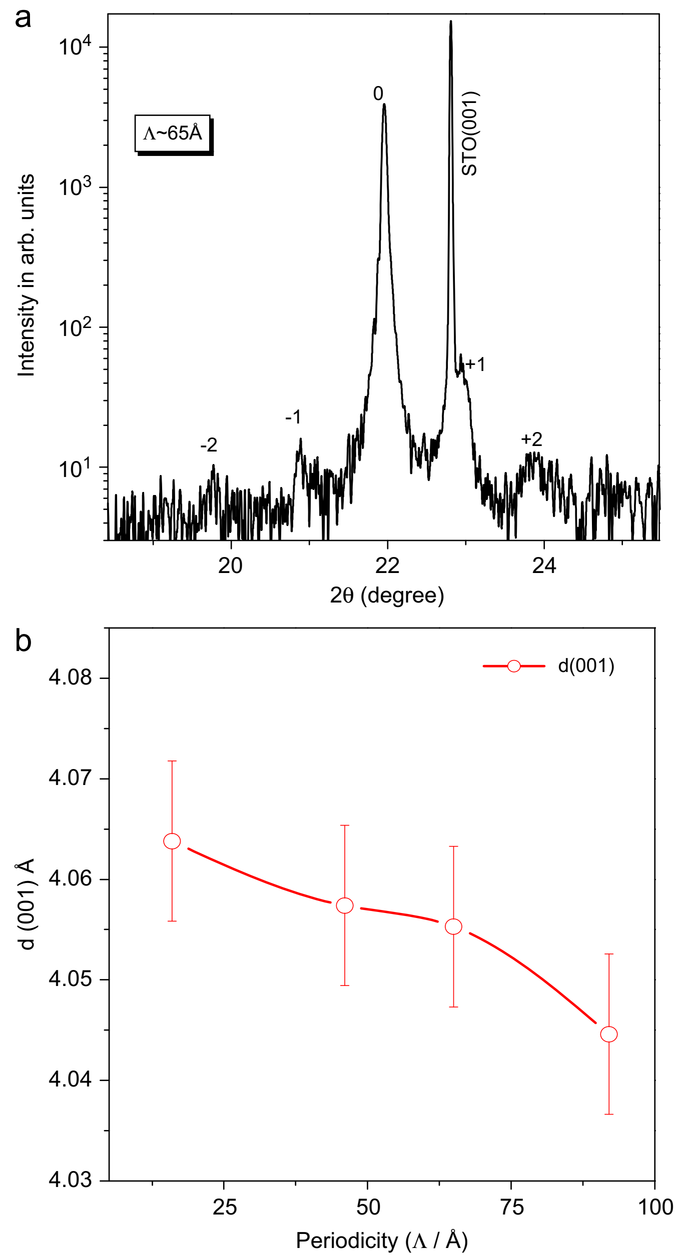

Fig. 1. (a). X-ray diffraction pattern of a $(BFO)_m(BTO)_n$ superlattice structure with a periodicity of Λ~65 Å. (b) The variation of the out-of-plane lattice parameter (d⟨0 0 1⟩) of the $(BFO)_m(BTO)_n$ superlattice structures with periodicity.

a weak ferromagnetic behavior up to 300 K. The weak ferromagnetic behavior is expected to arise as a result of the variation in the modulated spin structure of BFO along the ⟨1 1 1⟩ direction and the compressive strain introduced by the BTO layer. Fig. 3(d) shows the variation of the μ_B/super-cell formed by BFO and BTO and the variation of μ_B/Fe site in the total superlattice structure. The values of the μ_B/Fe site are comparable with the single layer BFO thin films (0.014 μ_B/Fe) of the same total thickness. The aforementioned electrical and magnetic studies clearly reveal the presence of two energetically identical stable states, in case both of FE and FM behavior. Hence, the $(BFO)_m(BTO)_n$ shows promise of overcoming the hindrances experienced in utilizing the individual BFO single layer thin films.

In summary, superlattice structures comprising $BiFeO_3$ and $BaTiO_3$ layers were fabricated using pulsed laser ablation and their room temperature ferroelectric and magnetic behavior was