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Thickness dependent magnetic and ferroelectric properties of $LaNiO_3$ buffered $BiFeO_3$ thin films

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ABSTRACT

$BiFeO_3$ (BFO) thin films with thickness increasing from 40 to 480 nm were successfully grown on $LaNiO_3$ (LNO) buffered $Pt/Ti/SiO_2/Si(100)$ substrate and the effects of thickness evolution on magnetic and ferroelectric properties are investigated. The LNO buffer layer promotes the growth and crystallization of BFO thin films. Highly (100) orientation is induced for all BFO films regardless of the film thickness together with the dense microstructure. All BFO films exhibited weak ferromagnetic response at room temperature and saturation magnetization is found to decrease with increase in film thickness. Well saturated ferroelectric hysteresis loops were obtained for thicker films; however, the leakage current dominated the ferroelectric properties in thinner films. The leakage current density decreased by three orders of magnitude for 335 nm film compared to 40 nm film, giving rise to enhanced ferroelectric properties for thicker films. The mechanisms for the evolution of ferromagnetic and ferroelectric characteristics are discussed.

1. Introduction

$BiFeO_3$ (BFO) has attracted great deal of attention after the discovery that it exhibit intrinsic large polarization (100 $\mu C/cm^2$) along [111] direction [1–3]. To date BFO is still the only known single-phase room temperature multiferroic material with Curie temperature (T_{CE}) of ~1103 K and Néel temperature (T_N) of ~643 K [4,5]. The direct coupling between ferroelectric and magnetic ordering parameters would offer the possibility of electric field controllable magnetism which paves the way for bridging electronic and spintronics industries [6–8]. However despite a number and variety of efforts in this direction [9–13], a number of unresolved issues remain as an obstacle to the practical utilization of BFO as a multiferroic device material [14,15].

The lattice structure of BFO is rhombohedrally distorted perovskite with the space group $R3c$. The lattice parameters of bulk BFO in rhombohedral unit cell are $a_{rh} = 5.634$ Å and $\alpha_{rh} = 59.348°$ and can be represented as a pseudocubic perovskite with lattice constant $a = 3.965$ Å and $\alpha = 89.46°$ between pseudocubic <100> axis [16,17] Fe^{3+} ions are responsible for the magnetism in this system whose d^5 electronic configuration [18] (5 unpaired spin electrons) provides an effective magnetic moment of ~5.9 μ_B while the ferroelectric properties arise from the stereochemical activity of Bi^{3+} cations with $6s^2$ lone pair electrons [3]. It has been established through neutron-scattering experiments that spin-up and spin-down sublattices are not exactly antiparallel rather they are slightly canted thereby resulting in weak ferromagnetism [19,20]. However a cycloid type spatial spin modulation superimposed to the antiferromagnetic spin ordering prevents the observation of net magnetization in bulk [21].

Origin of magnetism and hence the saturation magnetization of BFO thin films has been reported to be different by various groups. For example, Bea et al. [22] studied neutron diffraction data for BFO thin films and reported that the cycloid spin structure observed in bulk is absent in thin films which results in a net magnetic moment. Zhao et al. [23] reported a magnetic moment of 8–10 emu/cm^3 and they interpreted the observed moment to the canting of the antiferromagnetic sublattice. Wang et al. found a very large M_s ~150 emu/cm^3 and they attributed it to a strong compressive in-plane stress imposed by the bottom structure ($SrRuO_3/SrTiO_3$) [24]. However, recently, Eerenstein et al. [25] observed that compressive epitaxial strain does not enhance the magnetization and they interpreted that the co-existence of Fe in +2 and +3 state is responsible for the observed enhance magnetization. However it

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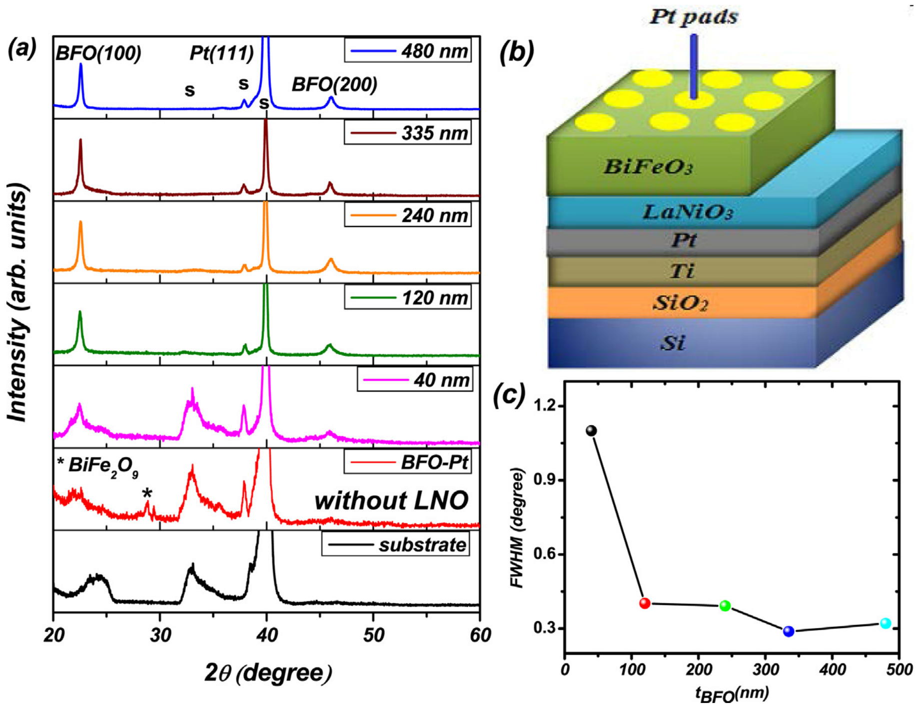

Fig. 1. (a) XRD patterns of LNO buffered BFO thin films with different thicknesses in the range between 40 and 480 nm. Substrate response and the BFO thin film deposited without LNO buffer layer is also shown (b) Schematic diagram showing the arrangement of different layers, and (c) Full width at half maximum (FWHM) as a function of film thickness (t_{BFO}).

has also been reported that the large moment may come from impurity phases such as γ-Fe_2O_3 [26]. Hence, to date mixed reports, including reports of enhanced magnetism in thin films of BFO as well as observation of samples exhibiting no such enhancement have been presented. It is thus fair to say that this issue remains unresolved in a rigorous sense and questions still remain concerning the magnetic properties of BFO films.

In spite of the multiferroic nature of BFO, the high unwanted leakage current limits the performance of multiferroic BFO thin films. The major contributors to the leakage current are chemical fluctuations and poor film texture [27]. The defects in the metallic electrode/ferroelectric usually have a dominant role in the observed degradation in ferroelectric behaviors. Therefore the surface chemistry of BFO films deserves more attention. In recent years, considerable efforts have been focused to fabricate BFO thin films with the most desirable texture and reproducible electrical behavior. In this regard, several thin film deposition techniques have been employed on various substrates [24,28–30]. Pt/Ti/SiO_2/Si(100) substrate is mostly used to fabricate ferroelectric thin films as sintering temperatures typically reach 650 °C to 850 °C. However for BFO films deposited on Pt/Ti/SiO_2/Si(100) substrate the interfacial diffusion of charge defects to electrode takes place, resulting in poor ferroelectric–electrode interface which restricts the intrinsic ferroelectric behavior of BFO films [31]. To avoid this problem, it is recommended to use a conducting oxide as a buffer layer. Due to the similar crystal structure of the conducting oxide and the ferroelectric film much better affinity is expected that will provide better interfacial properties. $LaNiO_3$ (LNO) is good candidate in this regard as it has a low resistivity and a perovskite structure with a lattice parameter of 3.84 Å compatible with that of BFO (3.94 Å). The presence of LNO effectively eliminates the interfacial charge defects at the interface between LNO and BFO and decreases the leakage current [32,33].

The incorporation of multifunctional films into practical devices alongside the constraint of size reduction has triggered a fundamental question concerning thickness dependence of magnetic and ferroelectric properties. The technological importance of these multifunctional films depends on their maintaining stable multiferroic behaviors as devices continue to be miniaturized. It is therefore essential to study the thickness dependent multiferroic properties of BFO thin films. Another point which we would like to mention here is that in most of the published work on BFO thin films, either the magnetic properties or the ferroelectric properties have been reported separately. Some papers describe the basic leakage mechanisms in BFO [34–37]. However no correlation between all properties viz. morphological, magnetic, ferroelectric and leakage current properties has been drawn. In the present study, these various aspects (morphological, magnetic, ferroelectric and leakage current properties) have been discussed and a co-relation between various properties has been drawn. With this general perspective, in the current study we report the growth and thickness dependent multiferroic properties of BFO thin films deposited on LNO buffered Pt/Ti/SiO_2/Si(100) substrate grown by radio frequency (rf) sputtering. The BFO films were deposited with and without LNO buffer layer to study the effect of LNO buffer layer on film growth and crystallinity. The thickness of the films was varied in the range between 40 and 480 nm to understand the effect of thickness variation on crystal structure, ferroelectric and magnetic properties.

2. Experimental procedure

A ceramic target with a nominal composition of $Bi_{1.1}FeO_3$ was prepared by sintering the constituent oxide mixture of Bi_2O_3 and Fe_2O_3 at 820 °C for 6 h. A 10% excess Bi was used in the target to compensate the loss of Bi during heat treatment. Prior to the deposition of BFO thin films, LNO buffer layer with a thickness of ~90 nm was sputtered on Pt/Ti/SiO_2/Si(100) substrate at 350 °C and then the BFO thin films with thickness in the range between 40 and 480 nm were sputtered at 570 °C. All the BFO thin films were