Polarized neutron reflectivity studies on epitaxial BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ heterostructure integrated with Si (100)

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This work reports polarized neutron reflectivity (PNR) measurements performed using the Magnetism Reflectometer at Oak Ridge National Laboratory on epitaxial BiFeO$_3$(BFO)/La$_{0.7}$Sr$_{0.3}$MnO$_3$(LSMO)/SrTiO$_3$(STO)/MgO/TiN heterostructure deposited on Si (100) substrates. By measuring the angular dependence of neutrons reflected from the sample, PNR can provide insights on interface magnetic spin structure, chemical composition and magnetic depth profiles with a nanometer resolution. Our first analysis of nuclear scattering length density (NSLD) and magnetic scattering length density (MSLD) depth profiles measured at 4 K has successfully reproduced most of the expected features of this heterostructure, such as the NSLD for the Si, TiN, MgO, STO, LSMO layers and remanent magnetization (2.28 µB/Mn) of bulk LSMO. However, the SLD of the BFO is decreased by about 30% from the expected value. When 5 V was applied across the BFO/LSMO interface, we found that the magnetic moment of the LSMO layer could be varied by about 15-20% at 6 K. Several mechanisms such as redistribution of oxygen vacancies, interface strain, charge screening and valence state change at the interface could be at play. Work is in progress to gain an improved in-depth understanding of these effects using MOKE and STEM-Z interface specific measurements. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5006473

I. INTRODUCTION

Recently, there have been significant efforts in condensed matter physics$^{1-3}$ devoted towards exploring novel physical phenomenon such as metalliccy, ferromagnetism and superconductivity in artificially fabricated oxide heterointerfaces. These material systems can be envisaged for potential applications as magnetic memory, sensors and spintronics. Best of all, the transition metal oxides which have 3d electrons such as cuprates, manganites, and more recently, multiferroics present an ideal test bed for exploring the complex interactions that exist between charge, spin and orbital degrees of freedom operating at heterointerfaces.

Of particular interest, a great deal of research$^{4-6}$ has been directed toward the investigation of BiFeO$_3$ (BFO), a room-temperature multiferroic. In particular, there has been widespread interest in utilizing the ferroelectric-antiferromagnetic (FE-AFM) couplings present in the BFO and

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ferromagnetic (FM) exchange coupled systems to achieve voltage-induced magnetic moment switching of the ferromagnetic over layer. Interfacial effects are crucial in the development of exchange bias. In particular, the role of uncompensated interfacial spins in the BFO layer is important. However, because the interface is buried, these uncompensated spins can be difficult to measure using conventional magnetometric techniques, e.g. superconducting quantum interference device (SQUID). These techniques probe the overall magnetic response of the sample. It is hard to separately resolve the contributions arising from the bulk and interfacial spin components. In contrast, polarized neutron reflectometry (PNR)\(^7\) can provide magnetic depth profiles with nanometer resolution, which should be able to directly extract data on the magnetic moments at interfaces. Both pinned and unpinned contributions to the magnetization can be measured, thus providing details regarding the exchange bias mechanism unobtainable by any other means. PNR has been used previously to explore FM-AFM interactions\(^8\)–\(^11\) in heterostructures. For example, Bea and co-authors\(^12\) have used PNR measurements to study the uncompensated spins at CoFeB/BFO. In another work, Singh and co-workers\(^13\) have used PNR to study the magnetic nature at the interface between LSMO/BFO superlattices. Spurgeon and co-authors\(^14\) have employed PNR to better understand the magnetic properties of LSMO/PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) heterostructures. However, all the above heterostructures were deposited on insulating oxide substrate STO, which is not suitable for next generation microelectronic devices.

The main purpose of this PNR study is to look at the BFO/LSMO heterostructure deposited on silicon substrates under various thermomagnetic conditions to determine the interface magnetic structure and to better understand the anomalous magnetic features observed in our previous work\(^15\),\(^16\). To the best of our knowledge, these are the first PNR measurements of BFO/LSMO heterostructure integrated on CMOS compatible silicon substrates. As such, it is expected to have high scientific impact with direct technological implications.

II. EXPERIMENTAL METHODS

Pulsed laser deposition (PLD) was used\(^15\)–\(^20\) to epitaxially grow BiFeO\(_3\) (BFO)/La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) (LSMO)/SrTiO\(_3\) (STO)/MgO/TiN heterostructure on Si (100) substrate. A Rigaku SmartLab X-ray diffractometer with a Bragg Brentano Goniometer (copper X-ray anode, K\(_\alpha\) radiation, \(\lambda = 0.154 \text{ nm}\)) was used to perform 0-20 x-ray diffraction scans to determine the structure, crystallinity and out-of-plane orientation of the films. Microstructural studies were carried out employing JEOL 2010F high-resolution/analytical transmission electron microscope (TEM), operated at 200 KV, with a point-to-point resolution of 1.8 Å. SPECS-made XPS spectrometer with Al/Mg anode source was used for the surface elemental analysis and to identify the Fe valence state. To probe ferroelectric characteristics at room temperature, we have used switching spectroscopy piezo-response force microscopy (SSPFM) technique. For this purpose, the commercial scanning probe microscope (Cypher, Asylum Research) equipped with a Pt-coated conducting tip (AC240TM, Olympus) was operated at the resonance frequency of about 260 kHz and the ac bias amplitude of 2 V. The same setup was augmented to carry out advanced SSPFM measurements. The temperature- and magnetic-field dependent magnetization measurements were carried out using Quantum design SQUID magnetometer with the sensitivity \(\leq 10^{-8} \text{ emu at 0 Tesla}\). It should be noted that TiN, MgO and STO buffer layers are all non-magnetic, and hence, are not expected to contribute to the magnetic properties of BFO/LSMO heterostructure reported in this work. The deposition parameters have been kept the same to maintain the same thicknesses of TiN, MgO, STO, and LSMO (250 nm) layers. In all the measurements reported here, the magnetic field is applied parallel to the film plane.

PNR experiments were performed on the Magnetism Reflectometer at the Spallation Neutron Source at Oak Ridge National Laboratory.\(^21\) Neutrons with wavelengths \(\lambda\) within a band of 2–8 Å and with a high polarization of 99% to 98.5% were used. Measurements were performed in a closed cycle refrigerator (Advanced Research System CCR) with an applied external magnetic field by using a Bruker electromagnet with a maximum magnetic field of 1.15 T. Using the time-of-flight method, a collimated polychromatic beam of polarized neutrons with the wavelength band \(\Delta \lambda\) of 3 Å impinges on the film at a grazing incidence angle \(\theta\), where it interacts with atomic nuclei and the spins of unpaired electrons. The reflected intensity is measured as a function of momentum transfer,
Q = 4πsin(θ)/λ, for two neutron polarizations R⁺ and R⁻, with the neutron spin parallel (+) or antiparallel (−) to the direction of the external field, H_{ext}. Here, θ is the angle between the incident wave vector and the sample surface. To separate the nuclear from the magnetic scattering, the data is presented as the spin-asymmetry (SA) ratio \( SA = (R_+ (Q) - R_- (Q))/(R_+ (Q) + R_- (Q)) \). A value of \( SA = 0 \) designates no magnetic moment in the system. Being electrically neutral, spin-polarized neutrons penetrate the entire multilayer structures and probe magnetic and structural composition of the film through the buried interfaces down to the substrate. PNR data were measured when the sample was cooled under the absence and presence (2000 Oe) of magnetic field down to 4 K and 100 K, separately. For electric field induced measurements, the sample was cooled under the presence of 2000 Oe magnetic field down to the measuring temperature; and then the electric field was applied. It should be mentioned that the sample was not cooled under the electric field.

III. RESULTS AND DISCUSSION

In our previous work,\(^{15,16}\) we have reported on the epitaxial growth of BFO-LSMO heterostructures by PLD. Epitaxial growth on Si (100) was achieved by introducing an epitaxial buffer layer of STO/MgO/TiN. X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, X-ray photo absorption spectroscopy, atomic force microscopy and piezo-force microscopy were employed to fully characterize the samples. Bright field TEM image shows BFO/LSMO interface is relatively sharp with little or no evidence of mixing between the Fe\(^{3+}\) in the BFO and the multivalent Mn\(^{3+}/Mn^{4+}\) transition metal ions in the LSMO layer. In addition, we investigated the magnetic behavior of this five-layer heterostructure using SQUID magnetization measurements. When BFO layer is in contact with LSMO layer, we observed an unexpected enhancement in the saturation magnetization of BFO/LSMO, when it was cooled under 2000 Oe magnetic field. On the other hand, the magnetization of LSMO layer remains constant under the field (2000 Oe) cooled as well as zero-field conditions. We also observed a stronger temperature dependence of the exchange bias when the polarity of field cooling is negative as compared to positive. We believe such an enhancement in magnetic moment and magnetic coupling is likely directly related to an electronic orbital reconstruction at the interface which involves a complex interplay between orbital and spin degrees of freedom. To shed some light on the BFO/LSMO interface magnetic spin structure, we conducted PNR studies as a function of magnetic field, temperature and voltage.

PNR measurements were conducted under both zero field cooled (ZFC) and field cooled (FC) conditions over a temperature range of 4-400 K. We kept the LSMO layer thickness constant at 250 nm and BFO layer thickness at 100 nm. The main panel of the Fig. 1 plots the reflectivity versus Q (0.01 to 0.1 Å\(^{-1}\)) for parallel and antiparallel neutron-beam spin configurations, measured at 4 K and 100 K. The solid curves are the fits to the experimental data. Most importantly, the finite difference (though not large) between the parallel and anti-parallel spin reflectivity curves at both measurement temperatures clearly show the ferromagnetic nature of the sample being studied, consistent with our conventional magnetization measurements reported previously.\(^{15,16}\) It should be pointed that the reflectivity damping in the reflectivity curves are believed to be due to the unavoidable roughness on the film interfaces and surface, diffusive nature of interfaces, and stresses resulting from the mismatch in the thermal expansion coefficient between the oxides and the silicon substrate\(^{17}\) generated during cooldown following the high temperature deposition process. Although we have some intrinsic difficulties in extracting the accurate geometrical details (such as surface roughness, interlayer diffusion) of our heterostructure, the observed reflectivity curves generally reproduced the expected features of the sample. The inset in Fig. 1 shows the corresponding spin asymmetry determined as a function of Q.

Two models were used to try to capture the experimental observations shown in Fig. 2. Based on our previous work,\(^{21}\) in model 1, the thickness of each layer is taken as BFO ~ 100 nm, LSMO ~ 250 nm, STO ~ 30 nm, MgO ~ 20 nm, TiN ~ 40 nm. In addition, model 1 considers that there is a significant inter-diffusion (1-3 nm) across the BFO/LSMO and LSMO/STO interfaces, and the surface of the film is rougher (~ 2 nm). Whereas model 2 takes into account that the surface is relatively smoother (< 1 nm) and interfaces are sharper as inferred from our previous work,\(^{15}\) in which the
FIG. 1. Polarized neutron reflectivity for a BFO (100 nm)/LSMO (250 nm)/STO/MgO/TiN/Si (100). The data were measured at 4 K as well as at 100 K. The curve is generated by fitting the data with a model. The dots represent the experimental data for neutron with spin parallel (+) and antiparallel (−) to the magnetic field. Solid lines are the best fit to the experimental data. The inset shows the deduced spin asymmetry at both the temperatures measured.

thickness of each layer is the same as that of model 1. Model 1 clearly provided the best fit to the data, in which, we had to consider the significant interdiffusion and surface roughness. As shown in Fig. 3, the nuclear and magnetic depth (z) profile scattering length density (SLD) was measured at 4 K and 100 K. Since Si, TiN, MgO, STO layers are non-magnetic, they are not expected to contribute to the total magnetic depth profile. However, they will contribute to nuclear depth profile. Our first analysis of the data has successfully reproduced most of the expected features such as nuclear scattering length density for the Si, TiN, MgO, STO, LSMO layers and remanent magnetization (2.28µB/Mn) of bulk LSMO. However, the SLD of BFO is decreased by about 30% from the expected value, and the variations (crests and troughs) in the magnetic profile particularly in the region of the LSMO/BFO interface is not currently understood. We believe that a sign inversion between 4 K and 100 K could be
due to the diminishing of exchange interactions about the blocking temperature 50 K of LSMO/BFO. This information can be extracted from our previous work on the same sample, where we see no exchange bias at 100 K (see, Fig. 5b, in ref. 15). In addition to unacceptable surface roughness and interface diffusion, we believe that several other atomistic mechanisms such as redistribution of oxygen vacancies, interface strain, charge screening and valence state change at the interface could be at play.

PNR measurements were repeated on this sample with both a positive and negative 5 V electric potential applied across the BFO/LSMO interface using soldered indium contacts to the top Pt and bottom LSMO electrodes. The experiments were performed at 6 K under various cooling fields ranging from 150-350 G. Spin asymmetry was determined as a function of Q. The magnetization was

![FIG. 3. Nuclear and magnetic scattering length density (SLD) profiles of BFO (100 nm)/LSMO (250 nm)/STO/MgO/TiN/Si (100), measured at 4 K as well as at 100 K, in the remanent state.](image1)

![FIG. 4. Voltage (±5V) induced variation in magnetic moment as a function of field cooling measured at 6 K. The voltage was applied across BFO/LSMO interface. We have used LSMO as a bottom electrode and Pt as a top electrode to make a capacitor structure. The resistance of BFO layer is 0.1 MΩ at 6 K, and indium was used in soldering the external connections.](image2)
estimated at each cooling field. Insulating and non-leaky behavior of the BFO layer was observed with a resistance of 0.1 MΩ. Figure 4 shows the variation of magnetization as a function of cooling field collected at 6 K, when the electric potential of 5 V was applied in both directions across BFO/LSMO interface. As it can be clearly noticed, when ±5 V were applied across the BFO layer, the magnetic moment of the LSMO layer reproducibly varied by about 15-20% at low temperatures (6 K). Additional work is in progress to gain deeper understanding of this effect. To really gain a proper atomistic magnetic interface spin structure and to fully understand the previously observed magnetic behavior of these heterostructure, one must further optimize the thin film deposition conditions, and reduce the number of buffer layers to obtain an atomically smooth surface and interfaces.

IV. CONCLUSIONS

Polarized neutron reflectivity measurements were performed using the Magnetism Reflectometer at Oak Ridge National Laboratory to probe the interface magnetic spin structure of exchange-coupled BFO-LSMO heterostructure epitaxially deposited on silicon substrate. Preliminary analysis of nuclear and magnetic scattering length density depth profiles (NSLD and MSLD, respectively) measured at 4 K and 100 K have successfully reproduced most of the expected features such as the NSLD for the Si, TiN, MgO, STO, LSMO layers and remanent magnetization (2.28µB/Mn) of bulk LSMO. However, the SLD of BFO is decreased by about 30% from the expected value. When 5V was applied across the BFO layer at low temperature, we found that the magnetic moment of the LSMO layer could be varied by about 15-20%. Mechanisms such as redistribution of oxygen vacancies, interface strain, charge screening and valence state change at the interface could be at play. Effort is in progress to shed light on these effects using magneto optical Kerr effect (MOKE) and scanning transmission electron microscopy (STEM-Z) interface specific measurements.

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