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Surface engineering with Ar⁺/O₂⁺ ion beam bombardment: Tuning the electronic and magnetic behavior of Ni₈₀Fe₂₀/La_{0.7}Sr_{0.3}MnO₃/SrTiO₃(001) junctions

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Abstract

The magnetic and magnetotransport properties of Ni₈₀Fe₂₀/La_{0.7}Sr_{0.3}MnO₃ (NiFe/LSMO) bilayers were investigated after bombarding the LSMO surface with low-energy Ar⁺ or O₂⁺/Ar⁺ ion beams before the growth of the top NiFe layer. A variety of magnetic properties are revealed, including an asymmetric two-stepped hysteresis loop with an exchange bias loop shift, and alternatively, a symmetric two-stepped hysteresis loop with an enhanced coercivity. Polarized neutron reflectometry measurements provide details of the magnetic depth profile and interface layer magnetism at different temperatures. The LSMO surface modifications determine a complex magnetic and electric NiFe/LSMO interface having a strong effect on the magnetoresistance of the bilayer. Surface engineering based on ion beam bombardment is presented as a promising technique for optimizing the electronic and magnetic properties of NiFe/LSMO junctions for future device applications.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Bergenti, I., Manna, P. K., Lin, C. H., Graziosi, P., Liu, X., Causer, G. L., Liscio, F., Ruotolo, A., Dediu, V. A., van Lierop, J., Klose, F. & Lin, K. W. (2018). Surface engineering with Ar⁺/O₂⁺ ion beam bombardment: Tuning the electronic and magnetic behavior of Ni₈₀Fe₂₀/La_{0.7}Sr_{0.3}MnO₃/SrTiO₃(001) junctions. *Journal of Applied Physics*, 124 (18), 183903-1-183903-1.

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Surface engineering with Ar^+/O_2^+ ion beam bombardment: Tuning the electronic and magnetic behavior of $\text{Ni}_{80}\text{Fe}_{20}/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3(001)$ junctions

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Citation: *Journal of Applied Physics* **124**, 183903 (2018); doi: 10.1063/1.5049235

View online: <https://doi.org/10.1063/1.5049235>

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(Received 20 July 2018; accepted 29 October 2018; published online 13 November 2018)

The magnetic and magnetotransport properties of $\text{Ni}_{80}\text{Fe}_{20}/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (NiFe/LSMO) bilayers were investigated after bombarding the LSMO surface with low-energy Ar^+ or O_2^+/Ar^+ ion beams before the growth of the top NiFe layer. A variety of magnetic properties are revealed, including an asymmetric two-stepped hysteresis loop with an exchange bias loop shift, and alternatively, a symmetric two-stepped hysteresis loop with an enhanced coercivity. Polarized neutron reflectometry measurements provide details of the magnetic depth profile and interface layer magnetism at different temperatures. The LSMO surface modifications determine a complex magnetic and electric NiFe/LSMO interface having a strong effect on the magnetoresistance of the bilayer. Surface engineering based on ion beam bombardment is presented as a promising technique for optimizing the electronic and magnetic properties of NiFe/LSMO junctions for future device applications. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5049235>

I. INTRODUCTION

Ferromagnetic (FM)/metallic manganese perovskites, such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO), are considered prototypical materials for the design and implementation of novel spintronic devices such as magnetic tunnel junctions (MTJs)¹ due to their large spin-polarization (nominally 100%) as well as good conductivity and thermal stability.^{2,3} The magnetotransport properties of manganese-based perovskites are nevertheless strongly sensitive to slight changes in bulk⁴ and surface⁵ stoichiometry, strain,⁶ and inter-grain structure.^{7,8} Critical features are also observed in the case of depositing metal contacts onto the LSMO surface, where both interface reactions and oxide reduction can impair LSMO performance critically⁹ leading to the formation of a non-magnetic and insulating layer.^{10,11} Controlling the formation of an intrinsic insulating layer on top of the LSMO layer allows one to exploit it as a tunnel barrier for the further development of high quality MTJ, thus avoiding the deposition of an additional tunneling layer. A way to induce a change in the surface layer has been proposed recently by using ion-beam bombardment techniques: both *in situ* bombardment with low-energy (~ 100 eV) Ar^+ or O_2^+/Ar^+ mixtures^{12–17} and

ex situ post-deposition irradiation with high-energy (~ 10 keV) O^{+18} have been successfully applied. In this work, we present the impact of low-energy *ex situ* Ar^+ and O_2^+ ion-beam bombardment on the LSMO surface, to etch and modify the stoichiometry of the native LSMO surface layer¹⁹ and how such an intrinsic layer can be exploited in $\text{Ni}_{80}\text{Fe}_{20}/\text{NiFe}/\text{LSMO}$ junctions to obtain a MTJ device. The NiFe/LSMO bilayers were structurally characterized by high-resolution X-ray diffraction (HR-XRD), transmission electron microscopy (TEM), and magnetically by SQUID magnetometry, magneto-transport, and polarized neutron reflectometry (PNR) to evidence the impact of LSMO bombardment on the overall magnetotransport properties of the junction. Our results indicate that the O_2^+/Ar^+ ion-beam bombardment is an effective way to induce an insulating tunneling layer on the LSMO surface.

II. EXPERIMENTAL METHODS

Epitaxial LSMO layers (~ 20 nm) were grown by the channel spark ablation (CSA) technique from a stoichiometric polycrystalline target in a partial oxygen pressure [$p(\text{O}_2) = 4 \times 10^{-2}$ mbar] at a substrate [$\text{SrTiO}_3(001)$ single crystal] temperature of 780°C .²⁰ A deposition rate of 0.1 ± 0.02 Å/pulse was used to ensure good film quality with low roughness. Our recent experimental and theoretical investigations of the LSMO surface composition using low-energy ion scattering (LEIS), X-ray photoelectron spectroscopy

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(XPS), and density functional theory (DFT) have shown that the topmost layer of an LSMO thin film consists of a Sr- and Mn-rich phase due to Sr segregation.⁵ LSMO films were then subjected to the ion bombardment technique following the procedure described in detail in Ref. 13. The Ar-bombarded (herein referred to as Ar-LSMO) and the O²⁺/Ar⁺ bombarded (herein referred to as O₂-Ar-LSMO) LSMO layer were obtained by treatment with argon (Ar) or a mixture of oxygen (O₂) and Ar gases (O₂/Ar ~35%) from an End-Hall ion source ($V_{EH}=70$ V, 500 mA)^{21,22} for 20 min each in order to etch away (etching rate ~0.3 nm/min) the outermost atomic layers of the LSMO surface.

To obtain the bilayer junction, the top polycrystalline NiFe layer (~10 nm) was grown using an ion-beam sputtering deposition technique with a DC Kaufman type ion source (800 V, 7.5 mA)^{15,23,24} to form NiFe/LSMO depending on the LSMO treatment [NiFe/(Ar-LSMO) and NiFe/(O₂-Ar-LSMO)]. A reference bilayer with a pristine LSMO layer was also obtained as the reference (NiFe/LSMO).

The crystallographic structure of the bilayers was investigated by high-resolution X-ray diffraction (HR-XRD) measurements using a Rigaku SmartLab diffractometer equipped with a rotating copper anode and a parabolic mirror with a 4-bounce Ge(220) crystal monochromator providing Cu-K α ($\lambda=1.54056$ Å) radiation in the incident beam. A 2-bounce Ge(220) analyzer crystal was placed in the diffracted beam before the scintillation detector.

A JEOL (JIB-4601F) focused ion beam (FIB) system was used for cross-sectional TEM sample preparation, and a JEOL (JEM-2100F) field emission transmission electron microscope (TEM) operating at 200 kV was used for the microstructural analysis. Magnetometry experiments (DC and AC) were performed using a Quantum Design SQUID magnetometer (MPMS-XL5). For hysteresis loop measurements, the films were field-cooled (FC) from 400 K to 10 K in an external magnetic field of 1 kOe applied along the film plane. The temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements was carried out in 100 Oe during warming up of the sample. The temperature dependence of the AC susceptibility measurements was performed in the frequency range of 10 Hz to 1 kHz using a 2.5 Oe driving field. Magnetoresistance measurements²⁵ were performed in a 4-point crossbar configuration using a Keithley 236 SMU in the temperature range of 10-300 K with a maximum applied field of 0.3 T. A bias was applied at the LSMO electrode, while the NiFe was kept at ground.

In order to elucidate the layer thicknesses, composition, interfacial roughness, and magnetization of the NiFe/LSMO bilayer before and after Ar⁺ bombardment, a combination of X-ray reflectometry (XRR) and polarized neutron reflectometry (PNR) experiments was performed.²⁶⁻²⁸ The XRR experiments were conducted at room temperature on a Panalytical X'Pert Pro X-ray reflectometer using Cu-K α radiation ($\lambda=1.54056$ Å). The structural depth profile of the layered sample is encoded in the reflectivity as a function of the scattering vector Q . PNR experiments were performed on the time-of-flight PLATYPUS reflectometer at the OPAL Research Reactor, Australia.^{15,21,29-31} The PNR samples were field-cooled in 10 kOe from 310 K to 110 K, and the

spin-dependent neutron reflectivity channels R^+ and R^- were measured at 110 K and upon warming to 310 K. The difference between the R^+ and R^- reflectivity channels gives the spin asymmetry $SA=(R^+-R^-)/(R^++R^-)$ of a sample as a function of the scattering vector Q . The depth-dependence of the sample's in-plane magnetic moment is encoded in the Q -dependence of the SA data. The SIMULREFLEC software package was used to fit the XRR and PNR data as a function of Q in order to construct structural X-ray scattering length density (XSLD), as well as the neutron scattering length density (NSLD) profiles of the spin up (R^+) and spin down (R^-) PNR data sets, respectively.^{31,32}

III. RESULTS AND DISCUSSION

A. Structural characterizations

The specular HR-XRD patterns of the three NiFe/LSMO structures representing different LSMO surface treatments are shown in Fig. 1(a). The LSMO film adopts the [001] orientation on the STO(001) surface as indicated by the LSMO (001), (002), and (003) reflections showing a lattice parameter of 0.3879 nm (LSMO bulk: 0.388 nm). The Laue fringes broaden and damp [as observed in the extended data range plotted in Fig. 1(b)] in the case of bilayers featuring LSMO surface treatment, in particular when O₂⁺/Ar⁺ mixture is used, compatible with a reduction in the out-of-plane coherence length of the LSMO layer. Moreover, LSMO (001), (002), and (003) Bragg peaks broaden regardless of the scattering wave vector Q [Fig. 1(b)], indicating that size effects rather than strain effects dominate the changes observed and suggest that ion bombardment simultaneously reduces the LSMO layer thickness. The top NiFe layer has no distinct reflection peaks as expected for ultra-thin layers (10 nm) with polycrystalline nature as confirmed by the high-resolution cross-sectional TEM images in Fig. 2 for the NiFe/LSMO bilayer. The same images clearly indicate the high quality epitaxial growth of the LSMO layer on STO. A thin layer with a thickness of ~1.3 nm separating the top polycrystalline Ni₈₀Fe₂₀ layer and the bottom LSMO layer is also clearly evident and does not features any Bragg diffraction peaks, as expected for short range crystalline order and/or structural disorder and defects. Images corresponding to the NiFe/(Ar-LSMO) bilayer and the NiFe/(O₂-Ar-LSMO) bilayer behave similarly (data not shown), except for a slight decrease of the LSMO layer thickness, probably due to ion-beam etching and again an interfacial disordered layer of thickness similar to that of a non-bombarded bilayer. More insight into the nature of the interfacial layer is presented in Secs. III B–III D.

B. DC and AC magnetization measurements

The temperature dependent low field magnetizations (susceptibilities) of the LSMO reference and the NiFe/LSMO bilayers are shown in Fig. 3. When warming the LSMO reference layer from 10 K, a maximum in the ZFC susceptibility is observed at ~50 K, which can be ascribed to the addition of enough thermal energy provided to the system to allow the LSMO nanocrystallites' magnetizations to

FIG. 1. (a) The HR-XRD patterns of the NiFe/LSMO (black), NiFe/(Ar-LSMO) (red), and NiFe/(O₂-Ar-LSMO) (blue) bilayers grown on a STO(100) substrate. (b) Magnified HR-XRD patterns of the (001), (002), and (003) LSMO diffraction peak regions. The STO substrate (green) is also shown for (002) peak.

align with the applied field. With further warming, the LSMO crystallites' magnetizations begin to fluctuate faster than the time scale of the measurement (~ 1 s), leading to a decrease in the susceptibility before it decreases to zero

with further warming, identifying the Curie temperature, T_C . The measured $T_C \sim 330$ K (Fig. 3) is in good agreement with our previous work.³³

When the LSMO layer is capped with NiFe, a non-zero magnetization (shown in Fig. 3) above the T_C of LSMO is observed which is attributed to the NiFe magnetization (NiFe $T_C \sim 860$ -870 K).³⁴ For the Ar⁺ and O₂⁺/Ar⁺ modified

FIG. 2. The high-resolution cross-sectional TEM micrograph of the NiFe/LSMO bilayer. The scale bar is 5 nm. White arrow indicates the NiFe/LSMO interfacial layer of thickness 1.3 nm.

FIG. 3. The temperature dependence of the ZFC and FC magnetizations of the reference LSMO film and the NiFe/LSMO bilayers measured in 100 Oe.

bilayers, a similar behavior of the LSMO magnetic transition from the FM to the paramagnetic phase is found near the T_C of LSMO, while the temperature dependence of the susceptibility is different. The susceptibility of NiFe/(Ar-LSMO) increases with decreasing temperature, whereas the susceptibility of the NiFe/(O₂-Ar-LSMO) bilayer exhibits a more pronounced temperature dependence (first increasing linearly and then remaining constant with cooling) with a higher susceptibility below ~ 240 K (divergence temperature of the ZFC and FC susceptibilities). These observations suggest the formation of different phases at the interface (e.g., antiferromagnetic vs. ferrimagnetic oxides) due to sputter etching (by Ar⁺) and/or oxidation (by O₂⁺).

The field dependent magnetizations (hysteresis loops) of the NiFe/LSMO bilayers and LSMO reference layer are shown in Fig. 4. The temperature dependence of the (a) coercivity and (b) exchange bias field of the LSMO layer and NiFe/LSMO bilayers is displayed in Fig. 5.

The NiFe/LSMO bilayer [Fig. 4(b)] exhibits an in-plane uniaxial anisotropy with low coercivity, $H_C \sim 5$ Oe at room temperature which is essentially identical to that of the LSMO reference film ($H_C \sim 3$ Oe) [Fig. 4(a)]. Due to similarities in the coercivities of LSMO and NiFe at room temperature,³⁵ the hysteresis loop of the NiFe/LSMO bilayer does

not present a two-stepped (or double) hysteresis loop. However, at 10 K, the NiFe/LSMO bilayer shows an enhanced $H_C \sim 80$ Oe [Fig. 4(b)] compared to $H_C \sim 65$ Oe observed for the LSMO reference film [Fig. 4(a)], indicating an increase of the effective anisotropy of the non-bombarded NiFe/LSMO bilayer. At 10 K, the feature of a two-stepped hysteresis loop was not observed in the NiFe/LSMO bilayer, indicating that the thinner intrinsic interfacial layer (~ 1.3 nm as observed by TEM) was not able to decouple the magnetizations of the NiFe and LSMO layers.³⁵ The observation of a smooth loop in the descending branch of the NiFe/LSMO bilayer is ascribed to magnetostatic “orange peel” coupling³⁵ that is likely to occur given the typical roughness values observed in such structures.²⁰

In contrast, a double hysteresis loop is exhibited by both Ar⁺ and O₂⁺/Ar⁺ bombarded bilayers, as shown in Figs. 4(c) and 4(d). For the NiFe/(Ar-LSMO) bilayer, a step is observed at 10 K in the field-dependent magnetization plot at ~ -100 Oe with a larger $H_C \sim 105$ Oe (vs. $H_C \sim 80$ Oe of the non-bombarded bilayer) and a hysteresis loop shift (exchange bias field, $H_{ex} \sim -20$ Oe, Fig. 5). This decoupled hysteresis loop identifies that an antiparallel magnetization configuration of the two layers is more evident in the NiFe/(O₂-Ar-LSMO) bilayer [Fig. 4(d)] with the largest

FIG. 4. Hysteresis loops of the (a) reference LSMO film, (b) NiFe/LSMO bilayer, (c) NiFe/(Ar-LSMO) bilayer, and (d) NiFe/(O₂-Ar-LSMO) bilayer, measured at 10, 100, 200, and 300 K. Insets show a magnified view of the low field regions.

FIG. 5. The temperature dependence of the (a) coercivity and the (b) exchange bias field of the reference LSMO layer and the NiFe/LSMO bilayers.

$H_C \sim 120$ Oe and distinct steps in both descending and ascending field branches. The presence of a non-zero exchange bias field, $|H_{ex}| \sim 20$ Oe, with enhanced H_C for the NiFe/(Ar-LSMO) bilayer (Fig. 5), but no loop-shift for the NiFe/(O₂-Ar-LSMO) bilayer [Fig. 4(d)] implies that the chemical composition and/or stoichiometry of the interfacial layers are different between the two bilayer samples (also different from the intrinsic interfacial layer on a non-bombarded NiFe/LSMO bilayer), depending on the ion species used (Ar⁺ or O₂⁺). The interfacial layer could be due to the formation of two-dimensional non-stoichiometric islands;¹⁹ and/or La-rich and Mn-rich oxide phases as reported previously.⁵ In the present case, the formation of interfacial antiferromagnetic phases, such as Mn, MnO, or NiO, could give rise to the observed H_{ex} , whereas the enhanced H_C could result due to the formation of harder ferrimagnetic phases like Mn₃O₄ or Fe₃O₄ or possible intermixed phases such as NiFeMn or NiFeO. X-ray and neutron scattering length density presented in Sec. III C better clarify the compositional profiles.

An indication of the formation of different interfacial phases having different magnetic ordering temperatures can be seen also for the temperature dependence of the AC-susceptibility measurements of the non-bombarded NiFe/LSMO and NiFe/(Ar-LSMO) bilayers (Fig. 6; representative figures). Both bilayers exhibit two characteristic peak temperatures in the real part of the susceptibility (χ') [~ 145 K, ~ 235 K for the NiFe/LSMO, and ~ 60 K, ~ 275 K for the NiFe/(Ar-LSMO) bilayer], indicating the formation

of different interfacial oxides. Based on the results of XRR and PNR, the peak temperatures (235 and 145 K) in χ' vs T of the NiFe/LSMO bilayers are assigned to the T_C of non-stoichiometric LSMO and T_N of NiO, respectively. For the NiFe/Ar-LSMO bilayer, these two characteristic temperatures are modified to 275 and 60 K, respectively. It can be noted that the observed magnetic ordering temperatures are less than the T_N of NiO (525 K in bulk form) and T_C of LSMO (330 K). We attribute this change of ordering temperatures to the differences in stoichiometries and thicknesses of LSMO and NiO layers present in the bombarded and non-bombarded bilayers. The peak temperatures did not show any frequency (10-1000 Hz) dependence that would indicate dynamical freezing of different spin configurations (e.g., domains of various sizes) which supports the ascribed ferromagnetism of the bilayers from the above measurements. Incorporating O₂⁺ (vs. Ar⁺ only) to bombard the LSMO surface has been proven to successfully create decoupled hysteresis loops with antiparallel spin configurations, which is a prerequisite for device applications based on spin-valve structures.³⁶

C. X-ray and polarized neutron reflectometry

To gain further insights into the interface quality and magnetic properties of the bilayers, depth-sensitive XRR and PNR measurements were carried out on two representative films. The non-bombarded NiFe/LSMO and NiFe/(Ar-LSMO) bilayer were selected for these experiments as they show the most distinct differences in their magnetization (Figs. 3–6) and their magnetoresistive characteristics (Fig. 9 — to be discussed in Sec. III D). The XRR datasets and best fits of these samples are shown in Fig. 7. The XRR profile of the NiFe/LSMO bilayer displays a set of oscillations with several characteristic periodicities, indicating a multilayer structure to the film. Typically, the largest period in Q-space is associated with the layer with the smallest thickness in real-space, while the smallest period of oscillation corresponds to the total thickness of the film. From fitting the reflectivity data and constructing the XSLD profile (inset Fig. 7), it is determined that the non-bombarded bilayer consists of a ~ 12 nm NiFe layer ($\text{XSLD} = 61.8 \times 10^{-6} \text{ \AA}^{-2}$) and a ~ 25 nm LSMO layer ($\text{XSLD} = 44.5 \times 10^{-6} \text{ \AA}^{-2}$). The fitted XSLD values of the NiFe and LSMO layers are in close agreement with their respective bulk values,³⁷ indicating fabrication of densely packed films. At the interface between the NiFe and LSMO layers, there exists a 2 nm reduced-XSLD layer, corresponding to an interfacial layer. This decreased XSLD indicates an off-stoichiometric effect at the LSMO surface due to a reduction in the density of heavy atom species (e.g., La or Mn). On the other hand, the XRR profile of the NiFe/(Ar-LSMO) bilayer displays a rapid decrease in reflectivity as a function of Q . From fitting the reflectivity data, this is found to be due to a large roughness (about 3 nm) on the surface of the NiFe layer. From the fits, the NiFe/(Ar-LSMO) bilayer has a similar XSLD to the NiFe/LSMO bilayer; however, LSMO has a reduced thickness of ~ 17 nm. This is believed to be due to the ablating power of the Ar⁺ beam during the bombardment process and it is in agreement with HR-XRD data.

FIG. 6. The temperature and frequency dependence of the real and imaginary parts of ac-susceptibilities of the [(a) and (b)] NiFe/LSMO and [(c) and (d)] NiFe/(Ar-LSMO) bilayers.

As a result, the XSLD at the LSMO/NiFe interface is quite complex. The Ar $^{+}$ bombardment seems to increase the XSLD in a range of ~ 1 nm toward the surface of the LSMO layer. The outer surface of the NiFe layer is found to be quite rough as observed from the systematic decrease in the XSLD of the layer beyond 23 nm from the STO substrate. The analysis of XRR results is consistent with the HR-TEM results which also showed an off-stoichiometry of the interfacial layer between LSMO and NiFe layers.

FIG. 7. Room-temperature X-ray reflectometry (XRR) data of NiFe/LSMO and NiFe/(Ar-LSMO) bilayers. The fitted X-ray scattering length density (XSLD) profiles of these two samples are shown in the inset.

The R^{+} and R^{-} PNR profiles of the NiFe/LSMO and NiFe/(Ar-LSMO) bilayers measured at 110 K and 310 K are shown in Fig. 8(a), plotted as a function of the scattering vector Q . All reflectivity channels exhibit clear oscillations resulting from the nuclear and magnetization potentials of each film. Unambiguous differences between the R^{+} and R^{-} channels are observed, indicating a FM component to each sample. To separate the nuclear and magnetic scattering components, the SA of each sample was also carefully analyzed - where SA is solely a magnetic response. As an example, the inset in Fig. 8(a) displays the SA data and SA fits of the non-bombarded bilayer at 110 K. From fitting the R^{+} and R^{-} data sets, together with the SA, the NSLD profiles of the NiFe/LSMO and NiFe/(Ar-LSMO) bilayers were constructed and the results are shown in Figs. 8(b) and 8(c), respectively. The nuclear density profiles of the samples established during the XRR fitting procedure were employed to constrain the PNR fitting parameters.

At a measurement temperature of 110 K, both the LSMO and NiFe layers of the non-bombarded NiFe/LSMO bilayer [Fig. 8(b)] are FM, as revealed by the splitting of the R^{+} and R^{-} NSLD profiles throughout each respective layer region. At 310 K, only the NSLD of the NiFe layer features a sizable splitting of the R^{+} and R^{-} channels. This is due to the higher T_C of NiFe ($T_C = 858\text{--}871$ K 34) with respect to the LSMO layer (with $T_C = 330$ K) which displays a significantly reduced splitting. Converting the splitting of the NSLDs into magnetization values, we note that from 110 K to 310 K,

FIG. 8. (a) Polarized neutron reflectivity data (R^+ and R^-) of NiFe/LSMO and NiFe/(Ar-LSMO) bilayers measured at 110 K and at 310 K (data sets are offset in the Y-scale for clarity). The spin asymmetry (SA) for the NiFe/LSMO bilayer measured at 110 K is shown in the inset. The corresponding neutron scattering length density (NSLD) profiles as a function of distance from the STO substrate are shown in (b) and (c), respectively.

the moment of the NiFe layer decreases only slightly from $\sim 0.9 \mu_B/\text{f.u.}$ to $\sim 0.8 \mu_B/\text{f.u.}$ This is in contrast to the moment of the LSMO layer, which decreases significantly from $\sim 2.8 \mu_B/\text{f.u.}$ at 100 K to $\sim 0.2 \mu_B/\text{f.u.}$ at 310 K, in proximity to the T_C of LSMO.

The non-bombarded NiFe/LSMO sample has a ~ 2 nm interface layer located toward the surface of the LSMO layer, indicated as TL1 in Fig. 8(b) (~ 25 nm from the STO substrate) which does not exhibit splitting between the NSLD R^+ and R^- channels at either measurement temperature. This indicates the formation of a non-magnetic interfacial LSMO-like layer. The NSLD of the interfacial layer is $\sim 4.0 \times 10^{-6} \text{ \AA}^{-2}$. In contrast to the XRR result, where a XSLD dip is observed throughout the interfacial region, the NSLD of the interface is found to be slightly higher than that of the LSMO layer ($\sim 3.5 \times 10^{-6} \text{ \AA}^{-2}$). This evidences that the LSMO-like interfacial layer TL1 could result from Mn vacancies on the surface of the LSMO layer, because Mn^{3+} has a large and positive X-ray scattering length [b_{Mn} ($\text{Cu } K_\alpha \text{ X-ray}$) = 64.8 fm], while having a negative neutron scattering length [b_{Mn} (neutron) = -3.73 fm]. Our analysis reveals further that there is a second interfacial layer [indicated by TL2 in Fig. 8(b)] which is on the NiFe side and has a thickness of ~ 0.9 nm. TL2 carries a net in-plane magnetic moment, is located in close proximity to the NiFe layer and has a NSLD only slightly smaller than NiFe. This NiFe-like layer is attributed to the formation of intermixed phases with LSMO which occurred during the deposition of the NiFe layer. As a final point, a surface oxide

layer (mainly NiO_x , ~ 1.7 nm) is visible on the very surface, for which the NSLD is determined to be $\sim 6.7 \times 10^{-6} \text{ \AA}^{-2}$, about $\sim 80\%$ of bulk NiO.

For the NiFe/(Ar-LSMO), the thickness of the LSMO layer is reduced to ~ 19 nm, as shown by the NSLD profile of Fig. 8(c). This sample also shows two distinct interface layers between LSMO and NiFe (note that this is consistent with the XRR derived fit profile shown in Fig. 7), even though the LSMO surface layer observed for the non-bombarded bilayer (TL1) had been completely removed by Ar^+ bombardment prior to the deposition of the NiFe layer. The first interface layer is LSMO-like in terms of NSLD [indicated by IL1 in Fig. 8(c)] and located on the LSMO-near side of the interface. It has a thickness of 3 nm and is found to be non-magnetic at 310 K. It is noted that even though the magnetization of the LSMO surface layer at 110 K is greatly reduced in comparison to that of the majority of the LSMO layer, a non-zero moment in this layer is favored in fitting, in contrast to the non-bombarded NiFe/LSMO bilayer where a zero moment is clearly preferred. The second interface layer is a distinct ~ 1 nm NiFe-like layer toward the NiFe side of the interface [indicated by IL2 in Fig. 8(c)]. It has a NSLD similar to TL2. However, in contrast to the NiFe/LSMO bilayer, where the interfacial layer TL2 near the NiFe is magnetic at both 310 K and 110 K, IL2 is found to be non-magnetic at both temperatures. For both XRR and PNR, this layer has a slightly smaller structural SLD than the NiFe layer. Due to its non-ferromagnetic nature, the

IL2 layer is therefore likely to be antiferromagnetic NiO, which could lead to the exchange bias effects observed by magnetometry via coupling to the neighboring FM NiFe layer.

For the case of the NiFe/(Ar-LSMO), it is demonstrated that the finite magnetization of the LSMO-like interface layer at 110 K may play an important role in coupling the magnetizations of the LSMO with NiFe layer and could explain the differences in magnetization and magnetotransport (to be discussed in Sec. III D) properties of NiFe/(Ar-LSMO) as compared to the NiFe/LSMO. Further PNR measurements performed on the NiFe/(O₂-Ar-LSMO) bilayer may provide magnetic and electronic depth-profile information which could be used to account for the differences in magnetization reversal mechanisms between these bilayers (not within the scope of this paper).

D. Magnetoresistance measurements

Magnetoresistance (MR) results of the NiFe/LSMO bilayers depending on LSMO surface treatments are shown in Fig. 9, together with the MR of the LSMO reference layer. The low MR ratio ($\sim 0.2\%$) of a LSMO reference layer at 100 K [Fig. 9(a)] indicates an anisotropic MR (AMR) behavior and the high epitaxial quality of the film (as confirmed by the cross-sectional TEM image in Fig. 2, and in good agreement with our previous work).^{19,20} However, the non-bombarded NiFe/LSMO bilayer exhibits quite a

different shape of MR in which the two peaks are more separated with a symmetric step in each branch, as shown in Fig. 9(b). This behavior indicates that the magnetoresistive response is dominated by the interfacial layer or the interfacial phases (as determined from the XRR and PNR measurements) which act as the effective barrier with different magnetic properties compared to bulk NiFe and LSMO layers, as evidenced by different switching fields in the magnetoresistance curve with respect to coercive fields deduced by magnetization measurements.

In contrast, when Ar⁺ was used to bombard the LSMO surface in the NiFe/(Ar-LSMO) bilayer [Fig. 9(c)], the MR ratio follows the AMR of the LSMO reference layer with the typical change of sign due to the change of the film orientation in the external field. The overall device behavior is dominated by that of the pristine LSMO layer indicating that, differently from the non-bombarded bilayer [Fig. 9(b)], the barrier is not effective and the MR is ascribed to the AMR of the FM LSMO reference layer. Two reasons can be envisaged: the presence of non-continuous/inhomogeneous barrier formed after Ar⁺ bombardment and subsequent creation of short circuits between electrodes, and/or to the local variation of stoichiometry of the interfacial layer (as evident from the XRR and PNR results) generating a pseudo-metallic barrier. In addition, the observed asymmetry in the MR curve [Fig. 9(c)] agrees with the magnetometry hysteresis loop [Fig. 4(c)].

Instead, when replacing Ar⁺ with O₂⁺/Ar⁺, the MR curve presents decoupled peaks not following the MR of single

FIG. 9. The magnetoresistance curves of the (a) reference LSMO film (100 K), (b) NiFe/LSMO bilayer (100 K), (c) NiFe/(Ar-LSMO) bilayer (100 K), and (d) NiFe/(O₂-Ar-LSMO) bilayer (15 K).

NiFe and LSMO layers, as shown in Fig. 9(d). For this film, the measurements were performed at 15 K to improve the signal-to-noise ratio and in order to compare the MR results with the magnetization measurements in Fig. 3(d). The MR shape depends on the geometrical configuration between the current and the external field (current perpendicular to plane). Here, a clear MR signal indicates that the interfacial layer, as a barrier via O_2^+ bombardment/passivation, is again effective and consistent with the observed steps in the hysteresis loop [Fig. 4(d)]. Moreover, compared to the broad peak and symmetric steps in the non-bombarded NiFe/LSMO bilayer [Fig. 9(b)], the distinct peaks in the NiFe/(O_2 -Ar-LSMO) film [Fig. 4(d)] imply a sharper magnetic transition between the top NiFe and bottom LSMO layers, which is modulated by the interface layer with different composition/stoichiometry.⁵ The variations of (1) hysteresis loops (enhanced coercivity and/or exchange bias loop shift) and (2) MR behavior signify that the low energy Ar^+/O_2^+ bombardment on the interface layer of the LSMO is an effective method to modify the magnetic and MR properties of NiFe/LSMO bilayers.

IV. CONCLUSIONS

In conclusion, we have investigated the magnetic and magnetotransport properties of NiFe/LSMO bilayers using a combination of HR-XRD, TEM (microstructures), magnetometry, XRR, and PNR (nuclear and magnetic depth profiling) techniques. We have demonstrated successfully that low-energy ion-beam bombardment can be used as a surface engineering method to effectively tune the outmost LSMO layer conditions [compositions and/or structures depending on the gas/ion species used (Ar^+ or O_2^+)] and thus affect the respective magnetic and magnetotransport properties. Pure Ar^+ ion-beam bombardment on the LSMO surface resulted in an exchange bias loop shift (accompanied with an asymmetric step) in a NiFe/(Ar-LSMO) bilayer. The density profiles deduced by XRR and PNR indicate the formation of a magnetic interfacial layer ascribed to both an off-stoichiometry of the LSMO layer in which the Mn^{3+}/Mn^{4+} valence is not optimal and an antiferromagnetic NiO layer. The magnetic nature of such an interfacial layer prevents the LSMO and NiFe electrodes from being decoupled and as such is not effective as a tunneling barrier, resulting in a short-circuited device. However, after incorporating O_2 into the Ar beam, a largely enhanced coercivity (with symmetric steps in the hysteresis loop) was observed in the NiFe/(O_2 /Ar-LSMO) bilayer. These results indicate that the composition and stoichiometry at the LSMO layer surface can be modified by O_2^+/Ar^+ , leading to decoupled magnetic LSMO and NiFe electrodes. The O_2 inclusion in the LSMO surface is known to modify the electronic phase of manganite films³⁸ inducing a metal-to-insulator transition. This is reflected in the MR results confirming that the $Ar-O_2^+$ ion-beam is more effective in modifying the LSMO interfacial layer, which can be used as a spacer-less barrier for device applications (as revealed by the distinct peaks in magnetoresistance curves and in agreement with the hysteresis loops measured by magnetometry). In future experiments, an optimization of the O_2^+

ion-beam contents would be useful to facilitate high MR ratios for actual device applications.

ACKNOWLEDGMENTS

The research was supported by CNR, Italy; NSERC, Canada; ANSTO, Australia; and MOST, Taiwan. I.B. acknowledges Dr. E. Lunedei and Dr. A. Riminucci for the support during MR measurements. P.G. acknowledges financial support from MIUR through PRIN project QCNaMos. G.L.C. acknowledges the support from the Australian Institute of Nuclear Science and Engineering (AINSE) Postgraduate Research Award (Award No. ALNSTU12030). X.L. appreciates the hospitality and support from ANSTO during his stay as an Asia-Oceania Neutron Scattering Association (AONSA) Young Research Fellow. K.-W.L. acknowledges support from ANSTO during a sabbatical leave.

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