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Interface-controlled magnetism and transport of ultrathin manganite films

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We report ferromagnetic, $T_C = 240$ K, and metallic, $T_{MI} = 250$ K, behaviors of a three unit cell thick interface engineered lanthanum manganite film, grown by metalorganic aerosol deposition technique on $SrTiO_3(100)$ substrates. Atomically resolved electron microscopy and chemical analysis show that ultrathin manganite films start to grow with La-O layer on a strongly Mn/Ti-intermixed interface, engineered by an additional deposition of 2 u.c. of Sr-Mn-O. Such interface engineering results in a hole-doped manganite layer and stabilizes ferromagnetism and metallic conductivity down to the thickness of d = 3 u.c. The films with $d = 8$ u.c. demonstrate a bulk-like transport behavior with $T_{MI} \sim T_C = 310-330$ K. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795422]

Recent fundamental and technological interest for ultrathin films of correlated oxides, like perovskite manganites, aluminates, titanites, and cuprates, with the thickness of only a few unit cells (u.c.) is basically determined by the two attractive possibilities: (1) to stabilize bulk-like properties (magnetism, metallicity, and ferroelectricity) in ultrathin films, thus making use of the advantages of half-metallic manganites for tunneling magnetoresistance (TMR) and/or multiferroic tunnel junctions, and (2) to create new interface-originated properties not akin to the bulk phases, like 2D-like metallic conductivity in ultrathin $LaAlO_3$ films grown on $SrTiO_3(100)$ (STO) substrates.[1] The main question, both research strategies address for, is how the interfaces can influence (control) the properties of ultrathin films. Concerning doped manganites, like $La_{1-x}B_xMnO_3$ (B = Sr or La-vacancy), it is well known that symmetry breaking interfaces (substrate/film and film/vacuum) strongly suppress spin polarization and ferromagnetic metallic (FMM) state in the vicinity of the interface.[2,3] The resulting insulating and antiferromagnetic interfacial layer, dubbed as dead layer, limits the critical thickness of a FMM manganate films, grown by pulsed laser deposition (PLD) technique, down to $d_c = 7-13$ u.c.. This thickness was found to be almost independent whether STO, MgO, $NdGaO_3$, or $LaAlO_3$ single crystals were used as substrates. For an optimally doped single $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/STO(100) film grown by PLD,[2] the metal-insulator (MI) transition survives down to $d_c = 8$ u.c. and a FM ground state with, however, strongly reduced Curie temperature, $T_C \sim 80-100$ K, was detected for $d = 5$ u.c. For short-period (LSMO/STO) superlattices, Kourkoutis *et al.*[4] have demonstrated FMM behavior for $d \geq 5$ u.c. with $T_{MI} = T_C \sim 280$ K, i.e., close to room temperature. Note that even with PLD, which is the mostly elaborated oxide film growth technique; the properties of ultrathin films are very sensitive to the growth parameters, like laser fluence.[5] Although a detailed mechanism of the formation of a "dead" layer is still not known, the symmetry-breaking-induced orbital ordering and related changes in the lattice structure,[6,7] accompanied by electronic modifications, seem to play an important role. To preserve the FM behavior close to the interface, Yamada *et al.*[8] suggested an "interface engineering" approach, which employs a deposition of 2 u.c. of $LaMnO_3$ (LMO) at each interface in the LSMO/STO superlattice structure. Considering LMO having one e_g-electron per Mn ion, the interface engineering can be viewed as an electron doping effect, which compensates the interface-induced hole overdoping.[9] Very recently, another engineering recipe, i.e., LMO-SMO buffering on a STO substrate,[6] was shown to enhance FM properties of an 8 u.c. thick LSMO film as compared to the unbuffered LSMO/STO(100) film. Here, we report the growth of ultrathin, $d = 3$–8 u.c., LMO and LSMO films on STO(100) substrates by a vacuum-free metalorganic aerosol deposition (MAD) technique and show that the FMM ground state can be stabilized down to a thickness of $d \sim 3$ u.c., by forming a strongly intermixed $(La, Sr)(Mn/Ti)O_3$ layer at the manganite/STO interface.

LMO and LSMO films were prepared and interface engineered by MAD technique, which is assumed to provide an exact oxygen stoichiometry in the grown manganite layers due to a high ($P_{O_2} \sim 0.21$ atm) gas pressure.[10] The films were prepared by spraying aerosols of organic solutions, containing metalorganic precursors, i.e., La-, Sr-, and Mn-acetylacetonates, onto a TiO_2-terminated STO(100) substrates, heated to $T_{sub} = 900-950$ °C. A monolayer accuracy was achieved by calibration of the precursor dosing units while depositing a thicker LMO and LSMO films with thicknesses, $d = 10$–30 nm, measured *ex-situ* by small angle X-ray scattering. To engineer the interfaces, 2 u.c. SMO were deposited onto the STO substrate as well as onto the surface of the grown LMO film, capped additionally by a

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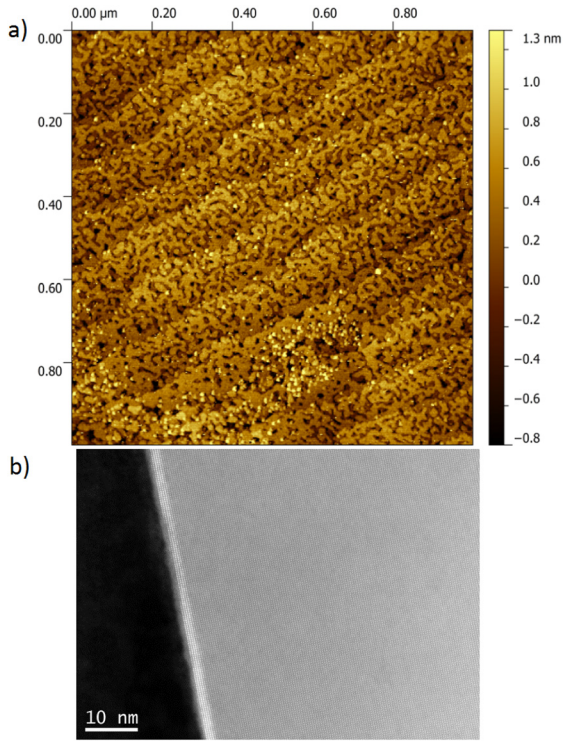


FIG. 1. STM morphology (a) and TEM low magnification image (b) of a 3 u.c. thick manganite film on the STO(001) substrate. The inset in the top image shows the line profile across the atomic terraces.

$La-O/TiO_2$ bi-layer. The nominal structure of the films is $SMO_{2\,u.c.}/LMO_n/SMO_{2\,u.c.}$ with $n = 3$–8 u.c. Considering the used feeding rate of the precursor solution $20\mu l/s$ and the precursor volumes $15\mu l(SMO)/30\mu l(LMO)/15\mu l(SMO)$, the total deposition time of the trilayer consists of about 3–5 s. After deposition, the films were cooled down to room temperature in 5 min. The structure was characterized by scanning tunneling microscopy (STM) and scanning transmission electron microscopy (STEM), equipped with a high annular angle dark-field detector (HAADF) and electron energy loss spectrometer (EELS). Four-probe electron transport and magnetization were measured as a function of temperature, $T = 2$–400 K, and magnetic field, $\mu_0 H = 0-5$ T, using commercial Physical Property Measurement System (PPMS) and SQUID (Magnetic Property Measurement System (MPMS)), respectively.

A STM image of a 3 u.c. thick LMO film, shown in Fig. 1(a), clearly demonstrates atomic terraces of about 150 nm width, originated from the STO(100) substrate, evidencing a layer-by-layer growth of the manganite film. The step height, $h \sim 0.4$ nm, agrees with the c-axis lattice parameter of the manganite. The measured mean square roughness of the film, $RMS = 0.2$ nm, is mainly due to the incompletely filled last perovskite layer. The cross-section low magnification TEM image (Fig. 1(b)) together with the STM picture in Fig. 1(a) basically confirm continuity, flatness and single crystal character of ultrathin films, although some thickness fluctuations of 2–4 u.c. as well as some indications of the surface damage due to sample preparation via ion beam milling (FIB) can be seen. A detailed structure of the film at the atomic scale was obtained by HAADF and EELS analyses. The high resolution HAADF image in Fig. 2(a) reveals a perfect epitaxy and coherent growth of the manganite film on the STO substrate. The distribution of La, Mn, and Ti elements obtained by EELS analysis at the atomic scale (see Fig. 2(b)) reveals the chemical composition and the structure of the engineered interface. The chemical map for Sr was not possible to obtain Ref. 4. One can see that the deposition of 2 u.c. of SMO on the TiO_2-terminated STO surface results in the formation of a mixed perovskite $La-O/(Mn,Ti)-O_2$ layer at the interface. Note that, interfacial intermixing region of the A-site cations (La and, likely, Sr) consists of about 2 u.c. and is larger than that for B-site cations (Mn and Ti), i.e., ~1 u.c.. For the 8 u.c. thick manganite film (not shown), the La-transition region consists of about 4 u.c., while the Mn-regions remain the same ~1 u.c. The growth of the manganite layer starts with a La–O atomic layer as one can reveal from the shift of La-associated peaks, marked by green color, with respect to those originating from Mn (blue); this shift occurs into the direction of the substrate (Fig. 2(c)). The body of the film can be viewed as three atomic layers of $Mn-O_2$ interpenetrated in between four layers of La–O. The growth of a manganite film according to the scheme: $A-O/B-O_2//A-O$ can be more preferable[11] as that of $A-O/B-O_2//B-O_2$.[12]

Transport properties of ultrathin LMO films with a thickness of 3 and 8 u.c. are shown in Fig. 3(b). Both films demonstrate a classical CMR behavior, well-known for the doped manganites. The MI transition temperature for the thinnest film consists of $T_{MI} = 250$ K and down to the lowest temperature, $T = 2$ K, the conductivity was of metallic type, i.e., $dR/dT > 0$. Relatively high residual resistivity of the 3 u.c. thick film, $\rho_0 \sim 2 * 10^{-3}\,\Omega$ cm, might be caused by thickness fluctuations and not completely filled top La–O layer. The film with the thickness of 8 u.c. shows bulk-like properties with $T_{MI} \sim 320$ K and residual resistivity, $\rho_0 \sim 2 * 10^{-4}\,\Omega$ cm. The value of T_Cs of ultrathin films, determined from the

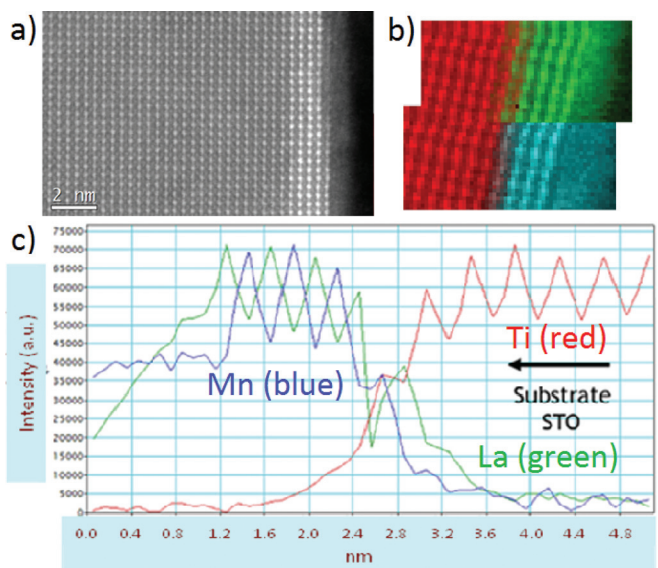


FIG. 2. Atomically resolved structure of a 3 u.c. thick film: (a) HAADF overview image; (b) elemental map of the Ti L2,3 (red), La M4,5 (green) and Mn L2,3 (blue); and (c) EELS signal profiles for these ions across the film/substrate interface.

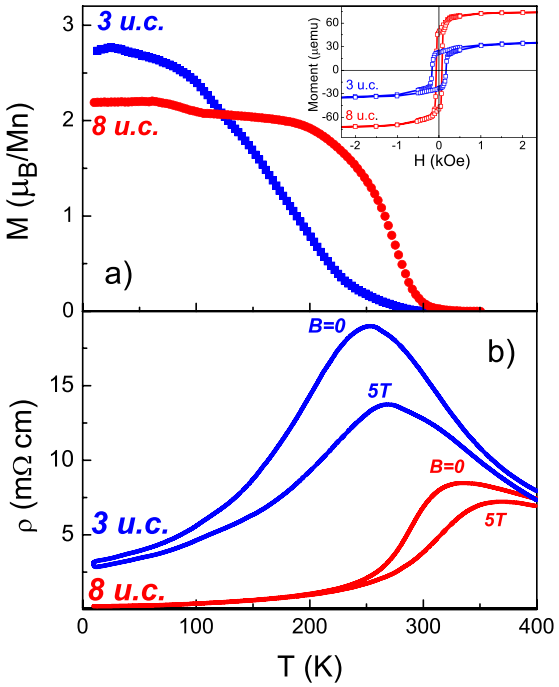


FIG. 3. Temperature dependence of the magnetization (a) and of the resistivity (b) of ultrathin manganite films with thickness of 3 (blue), and 8 (red) unit cells. Magnetization was measured in an external field of $H = 1$ kOe. The inset in (a) shows magnetization loops measured at $T = 10$ K.

temperature dependences of the magnetization, $M(T)$, as the minimum of the function $TCM = (1/M) * (dM/dT)$, correlates well with the values of T_{MI}, e.g., $T_C = 240$ K (3 u.c.) and $T_C = 310$ K (8 u.c.). Relatively low values of coercive field, $H_C = 70$ Oe and 170 Oe, measured at $T = 10$ K for 3 u.c. and 8 u.c. thick films, respectively, indicate magnetic homogeneity of the films and the absence of defects (strong pinning centers). Magnetization close to saturation, normalized on the number of Mn ions, consists of 2.75 μ_B/Mn for the 3 u.c. thick film and exceeds significantly the corresponding values obtained for the optimally doped manganite films with the same thicknesses.[2,6]

Thus, the measured magnetotransport indicates that the double-exchange mechanism responsible for the FMM state in doped manganites can survive in ultrathin manganite films down to a thickness ~3 u.c. We believe that the formation of a unique film/substrate as well as of film/vacuum interfaces with strongly intermixed B-site cations (Mn and Ti) plays a crucial role for the stabilization of FMM ground state in ultrathin films. Usually, an intermixing of cations at the interface is either ignored, assuming that intermixing within 2–3 monolayers represents itself as a sharp interface, or through the intermixing one can explain the degradation of magnetic and electron transport properties of the films.[4] In our case, to grow a polar $LaMnO_3$ film on the non-polar STO substrate at relatively high temperatures (950 °C), the cation intermixing at the interface[13] rather than an electronic reconstruction seems to be a more preferable mechanism to avoid the "polar catastrophe." Under high oxygen partial pressure, the intermixing of B-site cations can be difficult because of the absence of O_2 vacancies in between B-sites.[14] However, the treatment of a TiO_2-terminated STO(100) surface by the precursor flow, containing both Sr- and Mn-precursors, leads to a strongly intermixed layer with the ratio $Ti/Mn \sim 1$. It is this $(Ti, Mn) - O_2$ layer which changes the orbital and electronic structure in the adjacent to the interface manganite layers. Note that this mechanism can be active under high O_2 partial pressure, whereas under O_2 deficiency the vacancies by creating Mn^{4+} ions would change the structure and electronic properties of manganites,[15] probably following an electronic type of interface reconstruction to prevent the "polar catastrophe." A hole doping of the ultrathin LMO layer might be achieved both by gradient of the Sr distribution across the film thickness and/or by means of La-deficiency if one considers the observed La-rich regions close to the interface. Note that the observed magnetotransport in our ultrathin films is similar to the properties of the underdoped ($x \sim 0.1$) and La-deficient LSMO/STO films.[16] Relatively high values of the saturation magnetization, $\sim 3\mu_B$/Mn, could be related to the less distorted structure of the underdoped manganite close to the interface, due to practically strain-free state of the film, i.e., $a_{LMO} = a_{STO} \sim 0.390$ nm.[17]

In summary, the MAD engineered interfaces with strongly intermixed $(La, Sr)(Mn, Ti)O_3$ layers allow one to decrease the critical thickness of ferromagnetic metallic manganite film down to 3 u.c. We would like to point out the importance of oxygen stoichiometry and cation intermixing at the interface to preserve ferromagnetic metallic state close to the interface.

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