Structure and magnetic properties of three-dimensional (La, Sr)MnO$_3$ nanofilms on ZnO nanorod arrays

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Three-dimensional (3D) cubic perovskite (La, Sr)MnO$_3$ (LSMO) nanofilms have been deposited on ZnO nanorod arrays with controlled dimensionality and crystallinity by radio frequency (rf) magnetron sputtering and post thermal annealing. Compared to the two-dimensional (2D) LSMO nanofilm on flat Si, the structure and magnetic properties of 3D LSMO nanofilms on ZnO nanorod arrays have a strong anisotropic morphology and thickness dependence. Ferromagnetic property has been observed in both 2D and 3D LSMO nanofilms while a ferromagnetic–superparamagnetic transition was revealed in 3D LSMO nanofilms on ZnO nanorod array with decreasing nanofilm thickness, due to a large surface dispersion effect. The LSMO/ZnO nanofilm/nanorod structures could open up new avenues for intriguing magnetic properties studies and applications of nanoscale perovskites. © 2011 American Institute of Physics.

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When lanthanum ions (La$^{3+}$) in lanthanum manganese oxide (LaMnO$_3$) are partially substituted with divalent ions like Sr$^{2+}$, a mixed valence state of Mn$^{3+}$/Mn$^{4+}$ is generated, leading to a number of spectacular physical properties, such as insulating to metal transition, colossal magnetoresistance, and paramagnetic to ferromagnetic transition. The electrical and magnetic characteristics of (La, Sr)MnO$_3$ (LSMO) can be tuned per device requirements by changing Sr dopant concentration in LSMO. As a result, LSMO has potential applications in various magnetic devices including magnetic field sensors and recording devices. Usually LSMO are grown in the form of two-dimensional (2D) flat films on single crystal oxide substrates, such as SrTiO$_3$ (STO), MgO, or LaAlO$_3$ (LAO). However, perovskite-type LSMO has been rarely studied in the form of three-dimensional (3D) nanostructure arrays although the nanostructured or nanopatterned substrates could provide a viable route to achieve nanomaterials with desired crystalline structure and physical properties.

In this letter, the anisotropic structure and magnetic properties of LSMO thin films has been observed on 3D ZnO nanorod arrays compared to the LSMO nanofilm on 2D flat Si. It has been found that the magnetic properties of LSMO nanofilm are highly dependent on the morphologies and thicknesses in terms of intensity and anisotropy of magnetization. LSMO nanofilms were deposited on both Si substrate and ZnO nanorod arrays simultaneously by a rf magnetron sputter using a stoichiometric La$_{0.8}$Sr$_{0.2}$MnO$_3$ target (99.999%, Kurt J. Lesker Co.), with the film thickness on Si substrate as the reference “sample thickness.” ZnO nanorod arrays were grown on Si (100) substrate by hydrothermal method using the aqueous solutions of zinc acetate (Zn(AC)$_2$) and hexamethylenetetramine as precursors, which has been reported elsewhere. The LSMO films were sputtered in 1.2×10$^{-2}$ Torr of argon (Ar) plasma, followed by postannealing at 800 °C for crystallization. The thicknesses of sputtered LSMO films range from 12.5 nm, 25 nm, to 50 nm. An Asylum Scientific atomic force microscope (AFM), a JEOL 6335F field emission scanning electron microscope (SEM) and a FEI Tecnai T12 transmission electron microscope (TEM) attached with an energy-dispersive x-ray spectrometer (EDXS) were used to investigate the morphologies, structures, and compositions of ZnO nanorods and LSMO nanofilms. The structure of LSMO nanofilm was characterized by a BRUKER AXS D5005 (Cu $\lambda$ radiation) x-ray diffractometer (XRD). A vibrating sample magnetometer attached with the physical property measurement system (Quantum Design) was employed to collect magnetic (magnetization versus magnetic field, M-H) hysteresis curves of LSMO at temperatures from 80 to 300 K.

A typical XRD pattern of 50 nm LSMO thin films on Si (100) substrate is shown in Fig. 1. A major peak at $\sim$32.9° was identified as (110) atomic plane of cubic perovskite La$_{0.8}$Sr$_{0.2}$MnO$_3$ (JCPDS# 04–006-9331, SG: $Pm\bar{3}m$ (221), a=3.86 Å), with (400) planes corresponding to Si substrate, indicating that the LSMO film are mainly (110)-oriented. The inset shows a typical AFM topography image of LSMO nanofilm on flat Si substrate, revealing a rather smooth LSMO film with a root-mean-square roughness as small as 3.8 Å.

Structure and morphologies of the 3D LSMO nanofilm on ZnO nanorod arrays substrate are displayed in Fig. 2. In Fig. 2(a), the large area LSMO/ZnO nanofilm/nanorod arrays have similar morphologies to those of ZnO nanorod arrays, indicating a well-retained array structure after sputtering and post annealing processes. With a uniform hexagonal cross section [inset, Fig. 2(a)], the LSMO/ZnO nanorods are predominantly aligned perpendicular to the substrate despite a little randomness [Fig. 2(b)]. The width of individual nanofilm/nanorod composite decreases from nanorod tip to
its bottom with the width of ZnO nanorod core kept uniform. This is caused by the directional sputtering process from the top of ZnO nanorod arrays. The average thickness of 3D LSMO nanofilm is much smaller than 50 nm due to the larger deposition surface area of ZnO nanorod arrays than the flat Si substrate. The XRD patterns collected from LSMO/ZnO samples were presented in Fig. 2(c), where the ~34.8° peak corresponds to (0002) planes of ZnO nanorods with wurtzite structure. Inset in Fig. 2(c) shows the XRD pattern with logarithm (Log) intensity. A major (110) diffraction peak of the cubic perovskite LSMO was clearly identified at ~32.9° as pointed by an arrow; although the peak is not very strong due to a much smaller thickness of LSMO nanofilm compared to that of ZnO nanorods. TEM investigation was performed to unravel the detailed structural characteristics of LSMO/ZnO as displayed in Fig. 2(d). The grainy surface of LSMO nanofilms on the ZnO nanorod was clearly revealed [Fig. 2(d) and the inset in Fig. 2(b)]. The upper right inset is the corresponding selected area electron diffraction pattern, revealing the polycrystalline nature of LSMO nanofilm. The EDX spectrum of the annealed LSMO/ZnO nanofilm/nanorod is displayed in the bottom left inset, where the Cu and C peaks come from the TEM grid, while the contents of O, Zn, La, Sr, and Mn are about 24.36 at. %, 14.71 at. %, 1.74 at. %, 0.58 at. %, and 1.89 at. %, respectively. Therefore ~25 at. % of Sr dopant was achieved within the LMO lattices, which is close to the Sr content in the target (~20 at. %).

Figure 3(a) shows the magnetic (M-H) hysteresis curves of 50 nm LSMO nanofilm on flat Si substrate with field applied parallel to the film. The magnetization increases with increasing magnetic field at all temperatures until saturation is reached. A well-behaved M-H curve was observed for the LSMO nanofilm on Si substrate magnetized by an in-plane magnetic field at 150 and 80 K, which indicates a ferromagnetic behavior. The in-plane magnetization value was ~45 emu/g, ~100 emu/g, and ~108 emu/g for 300 K, 150 K, and 80 K, respectively, indicating the close relationship between the temperature and ferromagnetic properties. The in-plane coercive fields are 20 Oe, 170 Oe, and 240 Oe at 300 K, 150 K, and 80 K, respectively. Inset of Fig. 3(a) shows the M/Ms versus magnetic field plots of the film with field parallel and perpendicular to the films measured at 80 K. The enhanced in-plane magnetization of LSMO film can be clearly seen in the inset as compared with the out-of-plane counterpart, indicating the presence of an anisotropic demagnetization effect. Fig. 3(b) shows the field-dependent magnetization of the LSMO nanofilms on ZnO nanorod arrays deposited together with 50 nm LSMO on flat Si at 80 K, 150 K, and 300 K with magnetic field applied parallel to the sample. The hysteresis curves show that the area of the curve decreases with an increase in temperature and is nearly zero at 300 K [Figs. 3(a) and 3(b)], indicating a transition from paramagnetic behavior to ferromagnetic behavior of LSMO in both films with decreasing temperature. At low temperature, both the saturated magnetization and coercive field of LSMO nanofilm on ZnO are lower than those on flat Si substrates.

It is worth noting that the magnetic disorder at the surface has been suggested to be considerably larger than in the bulk. In perovskite material, the cubic symmetry lacks at surfaces and charge is transferred from the bulk to the surface layers, leading to the formation of Mn2+, which implies the dominance of antiferromagnetic interactions between the Mn spins at the surface. On the other hand, nonferromagnetic Mn2+ ions can form at the LSMO surface. Since the LSMO nanofilm surface area on ZnO nanorod arrays is much larger than that on flat Si, the larger surface dispersion effect will lead to smaller saturated magnetization and coercive fields. From the inset of the Fig. 3(b), which presents the M/Ms versus H plots at 80 K with the magnetic field applied parallel and perpendicular to the substrate.

![FIG. 1. XRD pattern of LSMO 2D nanofilms deposited on flat Si (100) substrate. Inset: an AFM topography image of LSMO 2D nanofilm on flat Si substrate.](image1)

![FIG. 2. (Color online) Characterizations of the LSMO/ZnO nanofilm/nanorod arrays: (a) a top view SEM image; (b) a cross-sectional view SEM image; inset in (b) shows the TEM image of the as-deposited LSMO/ZnO nanofilm/nanorod. (c) XRD pattern; Inset in (c) the XRD pattern with Logarithm intensity. (d) TEM images of a typical LSMO/ZnO nanofilm/nanorod. Upper right inset in (d): the corresponding electron diffraction patterns. Bottom left inset in (d): the corresponding EDXS.](image2)
sample, it was observed that the two plots are nearly identical. The magnetic anisotropy behavior depends on the structure and morphology of the film, which in turn is related to the substrate used. Clearly, unlike the anisotropic magnetization behavior in LSMO 2D nanofilm on flat Si, the LSMO 3D nanofilm deposited on ZnO nanorod arrays might have become magnetization isotropic.

Magnetic property of LSMO has been suggested to be morphology and thickness dependent, including magnetoresistance and magnetization. To investigate the thickness dependence of magnetization, 3D LSMO nanofilms with various thicknesses have been studied on ZnO nanorod arrays. Figure 3(c) shows the M-H hysteresis curve of LSMO nanofilm on ZnO nanorods with various thicknesses represented on flat Si. It is clear that the magnetization increases with the increasing magnetic field for LSMO with all thicknesses until saturation is reached. While the saturation magnetizations decrease with the increasing thickness of LSMO nanofilm, the thinnest film has the largest saturation magnetization. Early report has suggested that, if nanoparticles of LSMO are small enough, the single magnetic domains will interact with each other and lead to the superparamagnetism. Here 12.5 nm is the thickness of LSMO on flat Si deposited at the same time. The real thickness of LSMO nanofilm on ZnO nanorod side surfaces is much smaller due to the increased surface area. Therefore, the ultrathin nanofilm of LSMO on 3D ZnO nanorod arrays shows the superparamagnetic property. The inset shows the detailed M-H hysteresis curves at low magnetic field. The hysteresis curves show that the curve area is nearly zero for the thinner LSMO nanofilms. When the thickness increases, the total surface area of LSMO on ZnO nanorods decreases, so a well-behaved M-H curve was observed for the thickest LSMO nanofilm on ZnO nanorods revealing a ferromagnetic behavior, as a result of the maintained bulk ferromagnetic property.

In summary, homogeneous 3D LSMO film on oriented ZnO nanorod arrays has been fabricated with controlled dimensionality, crystallinity, and crystal structures, which is different from that on flat Si substrate in terms of the intensity and anisotropic magnetization. The large surface area effect of LSMO nanofilm on ZnO nanorod arrays and the thickness dependent ferromagnetic–superparamagnetic transition in ultrathin nanofilm of LSMO is observed. The nanofilm engineered on the 3D nanostructured surface may bring up a viable route to design and fabricate high quality tunable magnetic devices such as magnetic sensors and memories.

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