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Enhanced low field magnetoresistance in nanocrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ synthesized on MgO nanowires

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We report on the structure and transport properties of nanocrystalline manganite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) synthesized on nanowires-engineered MgO substrates by pulsed laser deposition, which is compared with reference samples deposited directly on flat MgO substrates. Such LSMO/MgO nanocomposites show enhanced low field magnetoresistance, especially at low temperature, due to the dominant spin-polarized intergrain tunneling. This work suggests that growing on nanoeengineered substrates is a viable route to achieve nanostructured materials with desired crystalline structure and physical properties. © 2010 American Institute of Physics.

Manganites are prominent members in the strongly correlated electron systems and have attracted lots of interest in the recent decades.1 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) is a stereotypical manganite with $T_C$ above room temperature. In manganites, applied magnetic field shifts the metal-insulator transition to higher temperature, leading to the well known colossal magnetoresistance (CMR).2 However, a high magnetic field ($>1$ T) is usually required to produce CMR, thus limiting the applications. Previous studies indicate that enhanced low field MR can be achieved at high frequencies or in polycrystalline manganites with small grains.3–5 In bulk ceramic synthesis, controlling the solid state reaction and the quenching process are often used to tailor the grain size,5 whereas in thin films the purpose is usually fulfilled by strain engineering or using polycrystal substrates.4,6 Recently, Moshnyaga et al.7 reported that the structural phase transition could be manipulated in epitaxial manganite/MgO nanocomposite films and large CMR was acquired at the percolation threshold.

In exploration of the emerging physics in complex materials, combining bottom-up nanomaterials growth with conventional thin film techniques has emerged as an effective approach to achieve hierarchically structured nanomaterials and functional devices.8,9 In conventional thin film growth, sufficient diffusion barrier can induce the transition from the two-dimensional (2D) layer-by-layer mode to the three-dimensional island-growth mode.10,11 The characteristics of diffusion and nucleation during growth can be significantly modified if the flat substrate surface is engineered with predesigned nanostructures, thus rich growth behaviors and resulting morphologies are expected. Recently, this paradigm of materials synthesis has received increasing attention. For example, Nagashima et al.11 deposited titanate on MgO nanowires (NWs) and studied in detail the growth behaviors. From the theoretical perspective, Wang et al.12 have analyzed the morphological stability of heterogeneous growth on NWs and found a growth regime analogous to the Stranski-Krastanow mode in conventional epilayers synthesis.

In this letter, we deposited LSMO on MgO NW arrays by using pulsed laser deposition (PLD) to achieve nanocrystalline films with uniform grain structure. Low field MR reaches $-32\%$ (5 kOe, 10 K) in these nanoeengineered LSMO thin films, which is among the highest reported values. This approach combining NW synthesis and thin film techniques posits as a viable route to produce nanocrystalline oxides with predesigned structural and physical properties. In typical experiments, MgO NW arrays were first grown on (100)-oriented MgO substrates via a vapor transport method at 900 °C in a tube furnace, and the details of the setup were given in previous reports.9,13 Catalyzed by Au nanoparticles, vertical MgO NWs were epitaxially grown on the substrates via the vapor-liquid-solid mechanism.14 This growth produces nanoeengineered MgO substrates with 2D arrays of MgO NWs with uniform diameter ($\sim 40$ nm), height ($\sim 300$ nm), and density ($\sim 10^{10}$ cm$^{-2}$). Then LSMO was deposited by PLD, as illustrated in Fig. 1(a). For comparison, LSMO thin film was also fabricated directly on flat MgO substrate as the “reference sample.” A nominal thickness of 300 nm was maintained in both cases. Au electrodes were sputter deposited for four-point transport measurements.

Insets in Fig. 1(a) show the scanning electron microscope (SEM) images of the well-aligned MgO NWs grown on MgO substrate. After PLD deposition, uniform nanocrystalline films with grain size $<40$ nm [Figs. 1(b) and 1(c)] were observed on the NWs. The NW density and the deposition rate were carefully chosen to produce uniform polycrystalline films. The growth morphology is in strong contrast to the reference sample deposited directly on flat MgO...
substrates, where no well-defined grain was observed [Fig. 1(d)] and the structural defects in the form of nanopits are presumably the result of large lattice mismatch (9%). As shown in Fig. 1(e), the x-ray diffraction (XRD) pattern of the LSMO/NW sample confirms the polycrystalline rhombohedral LSMO structure (a=5.50 Å and c=13.33 Å, JCPDS: 89-4466). In comparison, the reference sample is (012) oriented, suggesting different growth behavior. Transmission electron microscope (TEM) images in Figs. 2(a) and 2(b) indicate that the LSMO/NW sample comprises of crystalline LSMO nanograins. The selected area electron diffraction (SAED, inset in Fig. 2(b)) also suggests a polycrystalline nature. Energy-dispersive x-ray spectroscopy (EDS) element mappings (Figs. 2(c)−2(h)) confirm the composition of the LSMO/NW heterostructure and show Au catalyst nanoparticles remaining on top of the MgO NWs.

The magnetic hysteresis loops are shown in Fig. 3(b), also suggesting ferromagnetic order in the whole temperature range. In the tunneling process, the spin polarization of electrons is preserved, and the misalignment of the magnetic moments between the neighboring grains gives rise to the large tunneling resistance. The MR (defined as \( R(H) - R_{\text{max}} / R_{\text{max}} \)) versus magnetic field (\( MR-H \)) data were measured at various temperatures. As shown in Fig. 3(c), low field MR of \(-32\% \) (5 kOe, 10 K) was achieved, which is among the highest reported values. In the high field regime (>5 kOe), the increment of MR slows down (Fig. 3(b)), but no saturation was observed even as the field reaches 5 Tesla.

The \( R-T \) and \( MR-H \) characteristics of the reference LSMO thin film deposited on the normal flat MgO substrate were measured for comparison. As depicted in Fig. 4(a), this sample shows the typical metallic \( R-T \) behavior and its resistance is 4 to 5 orders lower than the nanocrystalline LSMO/NW sample. In addition, the MR of the reference sample is much smaller (~1.4% at 5 kOe and 300 K) and always proportional to the applied field (Fig. 4(b)).

The reduction of spin fluctuations by magnetic field should be responsible for the MR in the reference sample grown on flat MgO substrate.4 In contrast, the enhanced low field MR of the nanocrystalline LSMO/NW film arises from the dominant spin-polarized tunneling across the grain...
grown on NW-engineered MgO substrates by PLD. Enhancing the large MR.

It has been shown that the intergrain dipolar coupling can reduce the tunneling MR of magnetic composites containing magnetic grains due to the paramagnetic feature of this interaction. However, the gradients in the LSMO/NW sample are quite small, which weakens the inter-grain dipolar interaction and favors the enhancement of the low field MR. Another important factor is the broken symmetry at the grain boundaries and contribute to the high resistance at zero field. A magnetic field can align these disordered spins, thus reducing the tunneling barrier and giving the large MR.

In summary, nanocrystalline LSMO thin films were grown on NW-engineered MgO substrates by PLD. Enhanced low field MR, which reaches ~32% at 5 kOe and 10 K, was acquired due to the dominant spin-polarized intergrain tunneling. Our result suggests that growing thin films on nano-engineered substrates is a viable route to achieve desired crystalline structure and physical properties.

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