Epitaxial growth of colossal magnetoresistive films onto Si(100)

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We report the growth of colossal magnetoresistive (CMR) films $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.9}Ba_{0.1}MnO_3$ (LBMO) onto Si (100) using a simple pulsed-laser deposition technique. To avoid oxidation of the Si surface, an initial growth of $SrTiO_3$ of a few atomic layers was carried out. We found that epitaxial growth of LCMO and LBMO films on Si can be realized by optimizing the deposition process. The obtained LCMO and LBMO films show ferromagnetic nature and the resulted LCMO/Si and LBMO/Si heterojunctions exhibit good rectifying behavior with magnetically tunable characteristics. © *2008 American Institute of Physics*.
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It is known that colossal magnetoresistance (CMR) manganites exhibit polaronic semiconducting behavior. Silicon (Si) is a conventional material in semiconductor industry. To deposit CMR manganites on Si and obtain magnetically tunable heterojunctions would be of high significance not only for developing novel devices but also for the basic studies on spintronics and the physics of CMR manganites. Although numerous investigations on the rectifying heterojunctions composed of various perovskite oxides were carried out,[1–6] reports on the junctions constructed with CMR manganites and Si are very limited. A primary reason is that such heterojunctions with high quality are difficult to made because of the easily oxidized surface of Si. Interfacing perovskite oxide with Si has been a challenge for a long time. Various buffer layers were tried to be placed at the interface between perovskite oxide and Si, and the resulted films were found to pose various orientations, crucially depending on the details of the introduced buffer.[7–12]

Recently, we systematically investigated the growth of CMR perovskites on Si and the transport properties of the resulted heterojunctions. Our studies revealed that CMR perovskites can be well grown on Si by introducing an ultrathin STO film of a few atomic layers. It was found that $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) poses a clean (110) orientation, and $La_{0.9}Ba_{0.1}MnO_3$ films could pose two orientations of (110) and (111) or a single (110), crucially depending on the specific growing processes. The orientations of the CMR films can be well controlled by carefully adjusting the growing conditions. The resulted LCMO/Si and LBMO/Si heterojunctions exhibit good rectifying behavior with magnetically tunable characteristics.

The growth of LCMO and LBMO films on Si(100) was performed using the conventional pulsed-laser deposition (PLD) technique. To form junctions with rectifying characteristics, *n*-type single crystal Si(100) with resistance of 6 Ω cm are adopted as substrates considering the *p*-type conductive nature of LCMO and LBMO films. To avoid oxidation of the Si surface, an initial growth of STO was carried out under a low O_2 pressure of 2.0×10^{-3} mbar for 20 s at 750 °C. The evaluated thickness of the STO buffer is of several atomic layers based on the deposition time. As soon as the STO deposition is finished, the oxygen pressure was increased to 0.5 mbar and the deposition of LCMO or LBMO films was immediately performed at the same temperature, 750 °C. The growing process was halted when the thickness of the LCMO or LBMO film reached about 80 nm.

Our repeated experiments indicated that the substrate temperature plays a key role in altering the orientations of the CMR films. If the deposition of the STO buffer is immediately performed when the substrate temperature is raised to 750 °C, coexistence of (110) and (111) orientations tends to form. However, if the substrate temperature is raised to a higher temperature such as 820 °C and maintained for a short while, such as 1 min, prior to deposition of STO buffer at 750 °C, the (111) orientation tends to disappear and the films pose a clean (110) orientation. Our repeated experiments confirmed that both LCMO and LBMO films can be epitaxially grown on Si(100) by carefully adjusting the substrate temperature before deposition. Figure 1(a) displays X-ray diffraction (XRD) pattern of $La_{0.9}Ba_{0.1}MnO_3$ films grown on Si(100) by using the former process (denoted as LBMO-1 thereafter). Strong (110) and (111) diffraction peaks from perovskite structure are identified in addition to the reflection from Si (100) substrate. These peaks should come from the LBMO films rather than the STO buffer because the STO layer of a few atomic layers is too thin to be detected by XRD. The resulted out-of-plane lattice parameter of LBMO films is 3.875 Å. Figure 1(b) shows the XRD patterns of $La_{0.9}Ba_{0.1}MnO_3$ (denoted as LBMO-2 thereafter) and $La_{0.7}Ca_{0.3}MnO_3$ films deposited on Si (100) by employing the mentioned latter process. One can find that the (111) orientation disappears. Besides the reflection from Si(100) and the (110) peaks of the CMR perovskites, no other peaks are visible, demonstrating that the grown films are of single phase and well epitaxially grown on Si.

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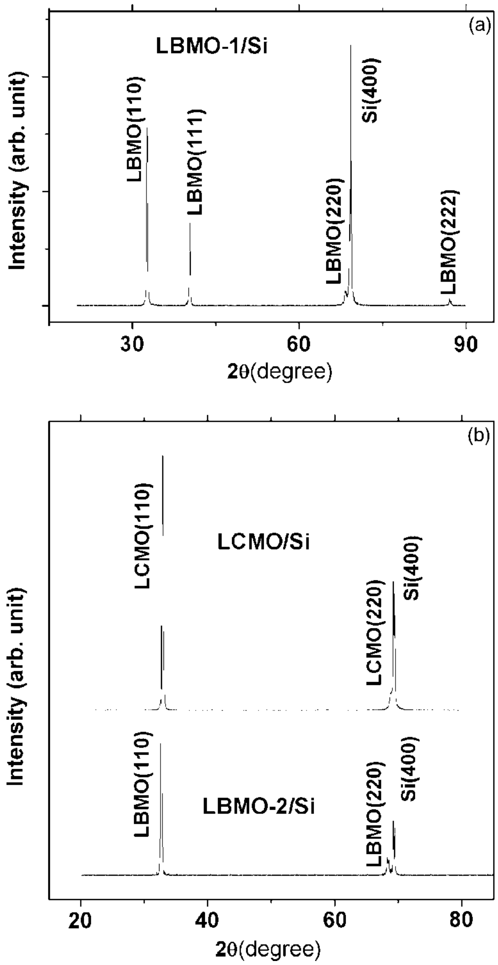

FIG. 1. X-ray diffraction spectra of (a) LBMO-1/Si, (b) LBMO-2/Si, and LCMO/Si heterojunctions.

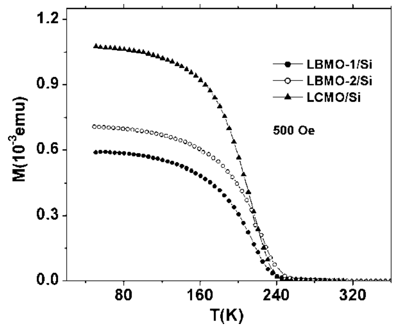

FIG. 2. Temperature dependent magnetization of LBMO-1/Si, LBMO-2/Si, and LCMO/Si heterojunctions measured under a field of 500 Oe.

LCMO, LBMO, and STO take on perovskite structure, while Si with cubic diamond structure. The lattice parameters of bulk LCMO, LBMO, STO, and Si are 3.867, 3.880, 3.905 and 5.429 Å, respectively. Obviously, the lattice mismatch is quite large between the perovskites and Si but small between LCMO (LBMO) and STO. Previous studies[10] showed that the orientation relationship between STO thin film and Si (001) substrate can be described as $(001)_{STO} \parallel (001)_{Si}$ and $\langle 100 \rangle_{STO} \parallel \langle 110 \rangle_{Si}$, which means that the STO lattice is rotated by 45° on the Si (001) surface. The lattice misfit between Si (110) (3.82 Å) and STO (3.905 Å) is reasonably small between the parallel interfaces and a little strain can be induced. Therefore, the STO (110) orientation is strongly favored on Si (100). In our experiments, when the substrate temperature is increased to a higher temperature, such as 820 °C, and maintained for a short while before deposition, the surface of Si substrates may be further cleaned by decomposing residual silicon oxide; thus, the epitaxial growth with clean (110) orientations is highly favorable. On the other hand, the films pose coexistent orientations of (111) and (110) if the deposition is immediately performed when the substrate is increased to the deposition temperature, 750 °C. Many evidences indicated that the orientations of the perovskite STO on Si (100) are crucially dependent on the specific details of the buffer layer.[8] Although no buffer was placed between STO and Si in this work, a formation of Sr silicate at the interface was suggested to stabilize the epitaxy of STO on Si.[9] The appearance of (111) orientation in the perovskite films might be related to a possible formation of a new phase at the interface caused by the residual oxide on Si surface. For detailed information, further careful investigations are required.

Shown in Fig. 2 is the temperature dependent magnetization for LCMO and LBMO films measured under a field of 500 Oe. One can notice that all films on Si exhibit ferromagnetic nature. The Curie temperatures T_C are at 240, 238, and 248 K for LCMO, LBMO-1, and LBMO-2, respectively. The LCMO films on Si show comparable T_C with that directly grown on STO. However, the T_C of LBMO films for both cases are somewhat lower than that of the samples directly grown on STO substrates.[13,14] The reported T_C of LBMO films on STO is ranging from 285 to 300 K. Detailed investigations[14] indicated that T_C of $La_{0.9}Ba_{0.1}MnO_3$ is crucially dependent on the lattice parameter. A tensile strain in $La_{0.9}Ba_{0.1}MnO_3$ makes T_C increase, which is different from the general case of CMR materials, where tensile strain usually reduces T_C and ferromagnetism. The abnormal increase of T_C in LBMO systems with tensile strain was interpreted by considering the strain-induced modification for the orbital stability of the conducting e_g electron.[14] In-plane lattice tends to adopt the same structure of substrate, and the out-of-plane parameter changes correspondingly to maintain unit cell volume. The out-of-plane lattice parameters for both LBMO-2 (3.869 Å) and LBMO-1 (3.875 Å) are smaller than that of the bulk LBMO (3.880 Å), indicating that a tensile strain occurs in the LBMO films on Si. However, the tensile strain in the present samples may be weaker than that appeared in the films directly grown on STO substrates, noting the fact that the out-of-plane lattice parameter of LBMO (3.865 Å) on STO is smaller than that of LBMO on Si. A smaller out-of-plane lattice parameter predicts a stronger tensile strain for in-plane lattice. This leads to the T_C of LBMO on Si larger than that of the bulk LBMO [185 K (Ref. 14)] but smaller than that of the films directly grown on STO substrates ($T_C \sim 285$ K). LBMO-2 shows a little higher T_C than that of LBMO-1, which is also consistent with the strain effect noting the fact that the out-of-plane lattice parameter of LBMO-2 is slightly smaller than that of LBMO-1.

The current-voltage characteristics (*I*-*V* curve) of the resulted heterojunctions were measured by tuning the applied

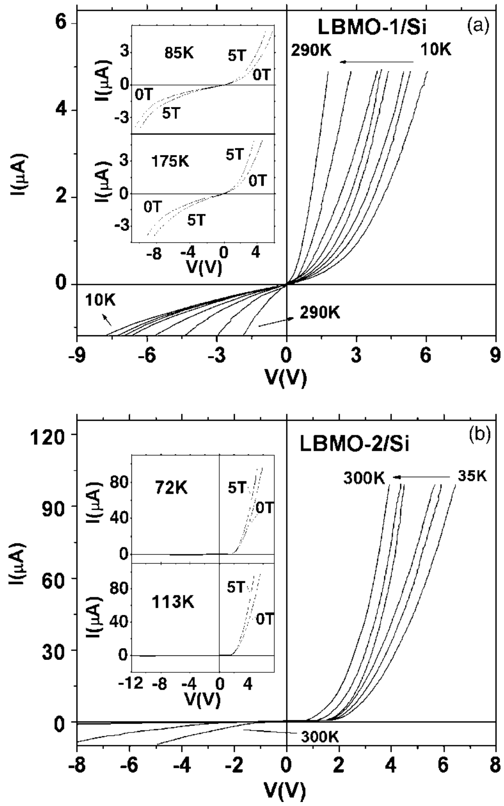

FIG. 3. Isothermal *I*-*V* curves of (a) LBMO-1/Si heterojunctions measured from 10 to 290 K with a step of 40 K and (b) LBMO-2/Si heterojunctions measured at 35, 72, 113, 160, 225, and 300 K. Insets show the response of *I*-*V* curves to magnetic field for the corresponding samples.

current. Typical results for LBMO-1/Si and LBMO-2/Si are presented in Figs. 3(a) and 3(b), respectively. One can find that both heterojunctions display asymmetric rectifying characteristics. LBMO-1/Si shows higher diffusion voltage and larger reverse leakage current than LBMO-2/Si, noting the different scale of the vertical axis. Such differences should be associated with the different interface structure. A possible complicated interface and interface defect probably appear in LBMO-1/Si junctions considering the growing specifics, which may lead to a thicker depletion layer, a higher diffusion voltage, and a larger reverse leakage compared with the case of LBMO-2/Si with clean interface. However, both junctions show similar dependent trends on temperature and magnetic field. The asymmetric transport behavior is strong at low temperatures and becomes weak with increasing temperature, which can be understood by considering the change of band gap in LBMO films. In the hole-doped LBMO manganites, three Mn 3*d* electrons occupy the localized t_{2g} band and the remaining electrons occupy the conducting e_g band. The e_g band further splits into two subbands of spin up and spin down under Hund's rule, and a band gap would show up. With increasing temperature, magnetic ions deviate from a fully ferromagnetic alignment and the energy cost for the e_g electron to reverse its direction would reduce,[2,15] resulting in a decrease of energy gap, a reduction of the diffusion voltage V_d, and a weakening of the rectifying ability of the junctions. Insets of Fig. 3 show the response of the *I*-*V* curves to external magnetic field for the corresponding samples. One can find that the magnetic field modifies the *I*-*V* relations. It bends the *I*-*V* curves, inclines them to *I* axis, and pushes V_d to lower voltages. Depletion layer may become thinner when the magnetic field makes LBMO film into a well metallic state, which reduces the diffusion voltage V_d and enhances the electron conductivity.

In summary, the growth of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.9}Ba_{0.1}MnO_3$ perovskites on Si (100) was systematically investigated. We found that LCMO and LBMO films can be well grown on Si(100) by introducing an ultrathin STO film of a few atomic layers. The orientations of the perovskite films are crucially dependent on the specific deposit processes. By carefully adjusting the substrate temperature prior to the deposition, a clean (110) orientation on Si(100) can be achieved for both LCMO and LBMO films. It has been revealed that the resulted heterojunctions show a good rectifying behavior and magnetically tunable characteristics. The possibility to control the rectifying behavior by a magnetic field may lead to new control methods for electric devices, and novel magnetically controllable functional electric devices based on conventional semiconductors Si could be created.

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