Role of interface on La$_{0.7}$Sr$_{0.3}$MnO$_3$ - Si junction properties

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(Received 21 November, 2014; accepted 18 February, 2015; published 01 April, 2015)

We present the structural, interface, surface morphological and transport characteristics of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) thin film on Si (001) substrate. X-ray reflectivity of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin film confirms the presence of silicon oxide at the interface and a dead layer below the LSMO film layer. Reflectivity data also supports the granular growth of La$_{0.7}$Sr$_{0.3}$MnO$_3$ islands, causing voids in the Si at the interface and a dead layer below the LSMO film surface as observed from atomic force microscopy studies. From current-voltage measurements, Shottky behaviour is observed for La$_{0.7}$Sr$_{0.3}$MnO$_3$ on Si (001) substrate. In comparison to La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin film on Si (001), normal p-n junction behaviour is observed when SiO$_2$ is introduced in between La$_{0.7}$Sr$_{0.3}$MnO$_3$ layer and Si (001) substrate. Observed transport properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ on Si are discussed phenomenologically in the presence of intermediate layers.

Keywords: Manganites, X-ray reflectivity, p-n junctions, atomic force microscopy.

INTRODUCTION

Over past years, perovskite manganites with general formula La$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr, Ba, and Pb) exhibiting colossal magnetoresistance (CMR) effect had extensively attracted interest of researchers to carry out theoretical and experimental investigations, not only because of rich physical properties of these materials but also because of their potential applications in various devices [1-6]. Amongst them La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) is an optimally doped, typical double exchange system with a high Curie temperature (~370 K), and has been considered to be one of the best choice for the device applications [7]. In particular manganite-based p-n junctions have intensively been studied due to the possible approaches to integrate artificially designed structures on various technologically viable substrates and are found to be sensitive to external magnetic and electric fields [8-12]. Manganite-based p-n junctions are promising candidates particularly when integrated with silicon substrates, and becomes compatible with the main stream of semiconducting industry. Though there are already some studies of manganites on Si substrates [13], there are many issues to be resolved. Various factors affect the growth, when Si substrates are used for perovskite manganite thin films: e.g. large difference in the thermal expansion coefficient, lattice mismatch and severe chemical reaction between Si and the deposited film layers. Serious studies about the growth, interface and properties of these films on silicon substrates are the present issue. The present study is focused to x-ray reflectivity (XRR) studies of LSMO thin films on Si (001) substrate, performed at 3rd generation synchrotron source. XRR is an efficient and nondestructive tool to probe the microstructures of the thin films, such as to laterally average electron density profile perpendicular to the surface which gives access to characteristic parameters such as thicknesses, densities, and interfacial roughness of single and multilayered systems. Detailed investigations of LSMO-Si junction, using XRR, atomic force microscopy (AFM), and rectifying current-voltage (I-V) characteristics have been carried out. Results obtained from the different methods mentioned above complement well to each other.

EXPERIMENTAL

Pulsed laser deposition system was used to deposit thin films of LSMO on oriented Si (001) substrate. The single phased LSMO target used for the deposition was synthesized using citrate gel route, details are presented elsewhere [14]. Prior to mounting the Si (001) substrates into the deposition chamber, they were degreased ultrasonically, first in CCl4, then in acetone, and finally in methanol for 5 min each. The substrate was partially masked for the purpose of transport measurements and then the LSMO film was deposited at 1173 K in the oxygen partial pressure of 400 mTorr. The deposited samples were cooled to room temperature in 500 Torr oxygen ambient. The laser energy density and pulse frequency was 2 J/cm$^2$ and 10 Hz, respectively. Using tally step profilometer, the nominal film thickness was found to be ~1000 Å. Details of synthesis of LSMO-SiO$_2$ bilayer on Si substrate used as a reference for transport characteristics in this study is provided elsewhere [15]. The XRR measurements on the LSMO-Si (001) thin film were performed at the high resolution X-ray diffraction beamline P08 at PETRA III, DESY, Hamburg. Beamline P08 uses a Si (111) double crystal monochromator in addition a Si (511) double crystal large offset monochromator which also serves as high resolution element and suppresses higher harmonics. It is equipped with a high precision six-circle diffractometer (Kohzu NZD-3). The energy of the X-rays during the measurements was 21.692 keV with a beam size of 0.1 mm vertically and 1 mm horizontally. The detector was a Mythen linear position sensitive detector [16] with 1280 channels.

Surface morphology and surface roughness of the films at nanometric scale was investigated by AFM (Digital Instruments NanoScope E of ‘Digital Instruments, USA, contact mode with a Si$_3$N$_4$ 100 µm cantilever, spring constant of 0.58 N/M). For transport
measurements, contacts were made in geometry perpendicular to the film plane, with contacts on either regions of the film measured using standard four probe method (c.f. inset of Fig. 3). Current was passed through the extreme electrodes and voltage between the middle two electrodes was noted to get the transport characteristics. The typical current value was 1 μA for all the samples and the estimated error in the measurements is less than 3%.

RESULTS AND DISCUSSION

The x-ray diffraction (XRD) (not shown here) pattern revealed polycrystalline growth of LSMO films on Si (001) substrate, all the peaks could be indexed either with the bulk LSMO as the perovskite-type manganite with pseudo-cubic structure or with the substrate. Fig. 1 shows the measured XRR intensity (open circles) and best fitted calculated intensity (solid circles) of LSMO films grown on Si (001) substrate. To get accurate results from the XRR measurements, the film thickness (d), roughness (σ), and electronic density (ρ), of each layer were obtained based on least squares minimization using the dynamical (optical) formalism of Parratt [17]. Fitting of the reflectivity data, assuming a trivial trilayer system of a known Si substrate, native oxide (SiO2) and LSMO layer does not produce the observed pattern and unphysical values of fitting parameters are returned. However, assuming an additional thin layer in between the LSMO and SiO2 layer, along with the LSMO island layer above the LSMO film layer (conjectured from the atomic force microscopy results as discussed later) results to best fit. As stated, presence of additional thin layer between the LSMO and SiO2 layer can be estimated by looking at the broad oscillations in the Fig. 1, between q values 0.1-0.25 Å⁻¹. And it is to be mentioned that the fitted electronic density (~1.37 x 10²⁴ cm⁻³) for this layer is close to the value of bulk LSMO (~1.69 x 10²⁴ cm⁻³). This layer trivially may be similar to what has already been reported in many other studies on manganite’s and transition metal oxides thin films [18, 19]. In literature this very layer, below the manganite thin films, has been identified as magnetic “dead” layer and often it is claimed to appear due to chemical interdiffusion [18]. Tunneling electron microscopy (TEM) images directly showing presence of dead layer in similar system is already published [20]. However, the scanning transmission electron microscopy and high spatial resolution electron energy loss spectroscopy results have shown that there is no actual chemical intermixing [21]. Nevertheless, until now, one thing which is clear is the existence of the magnetic “dead” layer in these systems but the quandary about origin still remains unsolved [21-23]. Some studies, focused to conductance measurements of manganite thin films of different thicknesses have shown that these magnetic “dead” layers are actually highly strained like wetting layers [19,24,25]. Importantly, this layer does not found to have any impeding influence on electrical properties. This dead layer serves as a semiconductor layer with LSMO together and does not affect to the transport properties as shown by others [25]. Thickness of this layer depends on both substrate and composition of film. Here, using the XRR fitting, we observed that the thickness of this thin layer is ~ 3.57 nm. Apart from thickness and roughness, electron density is the very crucial parameter in the analysis of reflectivity data, which has the capability of probing the element specific properties of thin layer systems. The electronic densities are related to the number of electrons per particle (Nₑ) and density ρ of the material, through ρₑ = NₑNₐ/M₀, where Nₑ is the Avogadro’s number and M₀ the molar mass. So to start with, the calculated electron density of LSMO bulk ceramic (ρₑ ~1.69 x 10²⁴ cm⁻³) has been used. According to the fitting, the observed density of the LSMO layer (ρₑ ~1.72x 10²⁴ cm⁻³) is slightly higher than the above mentioned bulk value. Whereas, the LSMO island layer is found to have a relatively low electron density (ρₑ~1.64x 10²⁴ cm⁻³). Two effects may contribute to the low values of electron density of LSMO island layer. First, due to the voids present in the island layers the averaged density is decreased, second, increased oxidation due to increased surface area would also decrease the density.
The higher electron density of the LSMO layer may be attributed to the under oxidation of the film layer, during pulsed laser deposition, as already explained by I. T. Gomes et al. [26] According to I. T. Gomes et al., under oxidation of LSMO formulates the increased participation of other comparably heavier elements (La, Sr, and Mn) contributing more electrons in the layer and thereby more electron density. Growth of LSMO islands and presence of voids on the LSMO layer can also be visualized from the values of the thin films obtained from the fitted result. The fitted values of layer thickness contributes more electrons in the layer and thereby more electron participation of other comparably heavier elements (La, Sr, and Mn)

The discrepancies in the mentioned values (roughness from AFM & reflectivity) may be due to the fact that the depth of the valley height in the AFM images depends on the size of the tip used. Hereby, it can be confirmed that the reflectivity data provides fairly similar trend in roughness values as well as the presence of islands and voids in comparable limits with that of the AFM measurements.

Hence, presence of islands and voids in comparable limits with that of the LSMO island layer on top of LSMO-Si layer system. The granular islands as seen from the AFM figures are of size ~ 200 - 313 nm and the peak to valley surface roughness by AFM data is ~ 13.14 nm. The roughness of the AFM data corresponds to the average height of the islands which roughly corresponds to the roughness of the LSMO layer from XRR fitting which is 26.3 nm. The discrepancies in the mentioned values (roughness from AFM & reflectivity) may be due to the fact that the depth of the valley height in the AFM images depends on the size of the tip used. Hereby, it can be confirmed that the reflectivity data provides fairly similar trend in roughness values as well as the presence of islands and voids in comparable limits with that of the AFM measurements.

The surface morphology of the film was probed by AFM in contact mode. Fig. 2 shows the 2D AFM images of LSMO on Si (001) substrate. For clarity images are shown with different scales (5 μm x 5 μm & 1 μm x 1 μm). AFM micrographs clearly show that the film bears largely rough granular structures at the surface. Analysis of the AFM image yield approximately 60% coverage of the surface by island structures. XRR fitting also confirms the presence of these islands in the form of LSMO island layer on top of LSMO-Si layer system. The granular islands as seen from the AFM figures are of size ~ 200 - 313 nm and the peak to valley surface roughness by AFM data is ~ 13.14 nm. The roughness of the AFM data corresponds to the average height of the islands which roughly corresponds to the roughness of the LSMO layer from XRR fitting which is 26.3 nm. The discrepancies in the mentioned values (roughness from AFM & reflectivity) may be due to the fact that the depth of the valley height in the AFM images depends on the size of the tip used. Hereby, it can be confirmed that the reflectivity data provides fairly similar trend in roughness values as well as the presence of islands and voids in comparable limits with that of the AFM measurements.

Fig. 3 shows the I-V characteristics of (a) LSMO - Si and (b) LSMO-SnO2-Si i.e. with SnO2 intermediate layer. Inset of both the figures demonstrate the contact geometries adopted for I-V measurement. These measurements have been done for current applied perpendicular to the film surface with a typical junction area of 0.04 cm² using four-probe technique at room temperature. It is noteworthy that the current density vs. voltage curves of the LSMO-Si junction, showed typical Shottky type rectifying properties, as shown in Fig. 3 (a). According to the Schottky model, I under the forward bias is expressed as a function of V using following relation

\[ I = I_o \exp \left( \frac{eV}{kT} \right) \]

where,

\[ I_o = \frac{S \exp \left( \frac{e \phi_0}{kT} \right)}{A*} \]

Here, \( e \) is the electronic charge, \( n \) an ideality factor, \( k_0 \) Boltzmann’s constant, \( T \) the temperature, \( S \) the junction area, \( A* Richardson’s constant, and \( \Phi_0 \) the Schottky barrier height. This equation indicates that \( I \) increases exponentially with \( V \) under the forward bias. In general, the Shottky behavior is observed when metal-semiconductor junction is realized. However, in the present case if we assume the absence of native oxide (SiO2), LSMO (room temperature resistivity ~ 10³ Ω cm) and Si (room temperature resistivity ~ 10² - 10⁴ Ω cm) has roughly comparable and semiconducting range of conductivity, which does not fulfill the criterion for the Schottky behavior. Whereas, considering SiO2: intermediate layer, which has the very high and broad range of room temperature resistivity ~ 10⁸ - 10¹⁶ Ω cm, presents a simpler explanation for observed Shottky behavior observed in LSMO-Si junction. Presence of SiO2 in between the LSMO and the Si layer increases the difference of conductivity and makes an analog to metal-semiconductor bilayer, requirement for Shottky effect. In the above explanation, presence of “dead” layer is ignored due to
similar electrical properties to LSMO. At this point it is important to mention that insertion of an extra semiconductor layer between LSMO and Si may establish the true manganite-semiconductor p-n junction. So, we have chosen SnO$_2$ because of its n type conductivity and tunable band-gap, and it is suitable for making a perfect manganite-semiconductor p-n junction with p type LSMO. Fig. 3 (b) shows the plot of I-V characteristics of LSMO-SnO$_2$-Si junction. The I-V curve shows as expected good rectifying behavior for LSMO-SnO$_2$-Si. Asymmetry in I-V curves under forward and reverse bias conditions can clearly be seen. It is very similar to that of p-n junction made of conventional semiconductors and nearly independent on temperature except for the variance of diffusion potential. From this curve we found the diffusion potential for LSMO-SnO$_2$ heterostructure to be 0.5 V at 300 K.

At the end, we would like to emphasize that interface in case of LSMO-Si junction has a crucial role in determining the rectifying/transport properties. Data presented in this paper clearly demonstrates that LSMO on Si prepared using PLD technique cannot be assumed to be a true manganite-semiconductor p-n junction. At the same time presence of intermediately native oxide (SiO$_2$) layers induces the Shottky behavior with very low forward barrier potential (~ 0.02 V), and proper tunability of the same may establish an unconventional way of synthesizing the Shottky diodes. Very low forward barrier potential of these unconventional Shottky diodes indicates that these may be used for very fast electronic switching application purposes and suitable for device working at low potential.

CONCLUSION

In summary, a study on LSMO thin film grown on Si (001) substrate using a pulsed excimer laser is presented. From specular reflectivity measurements, presence of intermediate SiO$_2$ layer, magnetic “dead” layer and formation of LSMO islands on the films surface are observed and well supported/explained using AFM and I-V characteristics. Good rectifying characteristics are observed for LSMO-SnO$_2$-Si; however for LSMO-Si it showed a Shottky effect due to the presence of native SiO$_2$ at the interface between LSMO and Si (001). Nonetheless very low forward barrier potential observed for LSMO-Si Shottky diodes is fascinating from application point of view.

ACKNOWLEDGMENTS

The authors thank scientists of UGC DAE CSR, Indore for help in performing AFM and I-V measurements. J. Mona would like to thank DESY, Helmholtz society, Hamburg, Germany, for financial support.

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BIOGRAPHY

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