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Effect of oxygen pressure on the interface related magnetic and transport properties of $La_{0.7}Sr_{0.3}MnO_3/BaTiO_3$ superlattices

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Abstract

Superlattices of $[(La_{0.7}Sr_{0.3}MnO_3)_{10}/(BaTiO_3)_4]_{25}$ were grown on (001)-oriented $SrTiO_3$ using the pulsed laser deposition technique. The magnetic and transport properties were studied as a function of the oxygen pressure. The suppressed magnetism and associated transport properties are discussed. A high value of magnetoresistance at low temperature with more pronounced hysteretic behaviour is observed for the superlattice grown at low oxygen partial pressure. Our results clearly suggest the importance of controlling the oxygen stoichiometry during the growth of the oxide superlattice to minimize the interface related problems.

1. Introduction

In recent years, functional oxide (superconducting, ferroelectric, magnetic, etc) heteroepitaxial structures have attracted more interest for designing new systems with novel properties [1–3]. In particular, superlattice structures made from combinations of perovskite manganite with ferroelectric, and paraelectric insulator layers have yielded unusual magnetic, electronic and ferroelectric properties [3–9]. The heterostructures showed an enhancement in magnetoresistance (MR) over a wide range of temperature along with reduced magnetic properties such as saturation magnetization, Curie temperature, and metal–insulator transition temperature compared to their parent manganite film. The unusual physical properties of the superlattices were mostly attributed to the existence of various interesting physical phenomena occurring at the interfaces, such as spin exchange, charge transfer, magnetic inhomogeneities, and strain. For example, spin canting at the interfaces [3] and carrier confinement as well as the charge transfer at the $La_{0.6}Sr_{0.4}MnO_3/SrTiO_3$ multilayer interfaces manifests itself as a suppressed magnetization and huge MR existing to low temperature [6]. However, it is widely believed that the magnetic inhomogeneities due to the phase separated state of ferromagnetic metallic and less magnetically ordered insulating clusters in the $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$

multilayers are responsible for the systematic suppression of ferromagnetic order and metallic conductivity [7–9]. This explains the large MR in a wide range of temperature as well as the anomalous MR effect. However, the origin of such magnetic inhomogeneities is not clearly understood. Although strain is clearly implicated in this magnetic disorder [9], we have suggested that the strain alone could not be ascertained as being responsible for the magnetic inhomogeneities at the superlattice interfaces [10]. It is important to note that in oxides, the structural, transport and magnetic properties of the films are strongly dependent on the oxygen content [11–14]. Fath *et al* speculated that though the origin of phase separation in doped manganites is not clear, variations in the oxygen content could be one possibility [15]. However, the effect of oxygen pressure during the growth process, which eventually determines the oxygen content of the grown layers, on the transport and magnetic properties of the superlattice films has always been overlooked. In this paper, we report on the magneto-transport properties of superlattices made with ferromagnetic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and ferroelectric $BaTiO_3$ (BTO) layers prepared under different oxygen pressure conditions. The electric and magnetic transport properties of the films show a strong dependence on oxygen partial pressure. The sample grown at high oxygen pressure shows near bulk-like properties, whereas the one grown at low oxygen pressure shows suppressed magnetism with high MR over a wide range of temperature, suggestive of the presence of phase separation in the samples. Our results strongly indicate that magnetic inhomogeneities associated with the suppressed magnetism in manganite based superlattice structures could originate from oxygen non-stoichiometry in the layers.

2. Experimental details

The superlattices of $(LSMO_{10}/BTO_4)_{25}$ were deposited on (001)-oriented $SrTiO_3$ substrates by the pulsed laser deposition technique using 200 mJ laser power from a KrF laser (laser wavelength $\lambda = 248$ nm). The samples were grown at 720 °C under various oxygen partial pressures (pO_2) ranging from 50 to 400 mTorr. After deposition, the samples were cooled to room temperature under 300 Torr of oxygen pressure at the rate of 13 K min^{-1}. Earlier, the LSMO and BTO targets were prepared by standard solid state chemistry routes using stoichiometric ratios of La_2O_3, $SrCO_3$, MnO_2, $BaCO_3$ and TiO_2 as starting materials. A Seifert 3000P diffractometer (Cu Kα1, $\lambda = 1.5406$ Å) was used to analyse the structure of the samples. The resistance (R) and the magnetoresistance (MR) of the samples with respect to the temperature (T) were measured using a quantum design physical property measurement system. The magnetization (M) was measured as a function of temperature and magnetic field (H) using a superconducting quantum interference device magnetometer.

3. Results and discussion

3.1. Structural properties

The θ–2θ x-ray diffraction (XRD) patterns around the (002) fundamental peak of the superlattice films, grown at different pO_2, are shown in figure 1. The denoted number i indicates the ith satellite peak. The laser pulse numbers allowed the estimation of the layer thickness and thus the number of unit cells. Thus, the estimated layer thickness for LSMO and BTO in our superlattice was 10 and 4 unit cells, respectively. The samples grown at different oxygen pressures shown several well-defined high intensity diffraction peaks along with numerous satellite peaks, except the one grown at 10 mTorr. The chemical modulation of the multilayers usually results in satellite peaks in the superlattice structure, and the presence of numerous such satellite peaks in our samples confirms the formation of a well-defined

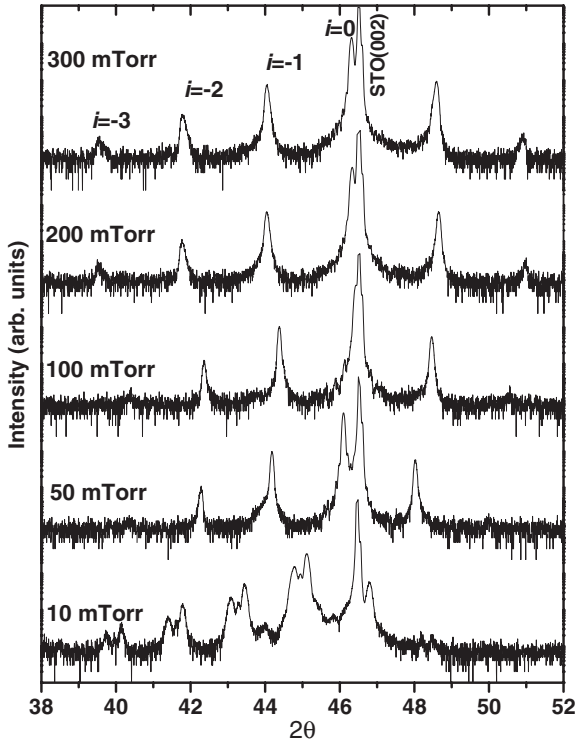

Figure 1. θ–2θ XRD scan recorded around the (002) reflection of $(LSMO_{10}/BTO_4)_{25}$ superlattices grown at different oxygen partial pressure.

superlattice structure. We have also carried out the XRD simulation of the superlattice structure using the DIFFAX program [16]. It was found that the experimentally measured peaks are in reasonably good agreement with the simulated one (not shown in the figure). The small difference in peak position among the samples grown at different oxygen partial pressure could be due to the difference in lattice parameter arising from oxygen non-stoichiometry in the manganite and ferroelectric layers [13, 17].

3.2. Magnetic properties

The magnetizations of the samples measured with respect to the temperature, from 380 K down to 5 K in a field of 100 Oe applied parallel to the plane of the sample, are shown in figure 2(a). A clear ferromagnetic transition temperature (T_C) in the range 200–300 K is observed. The inset of figure 2(a) shows an enlarged version of the graph for the sample grown at 100 mTorr. The respective plots of magnetization with applied magnetic field measured at 10 K are presented in figure 2(b).

From figure 2, it is noted that the superlattice samples show a systematic change in magnetic properties with growth pressure, pO_2. The magnetic moment and the T_C of the samples increase with increase in oxygen pressure. For example, we found 65, 225, 275, 280 and 290 K as the T_C value for the samples grown at 10, 100, 200, 300 and 400 mTorr pressure, respectively. However, the T_C values of the superlattices are always lower than that of the bulk LSMO sample, which is around 330 K. Although the reduced ferromagnetism

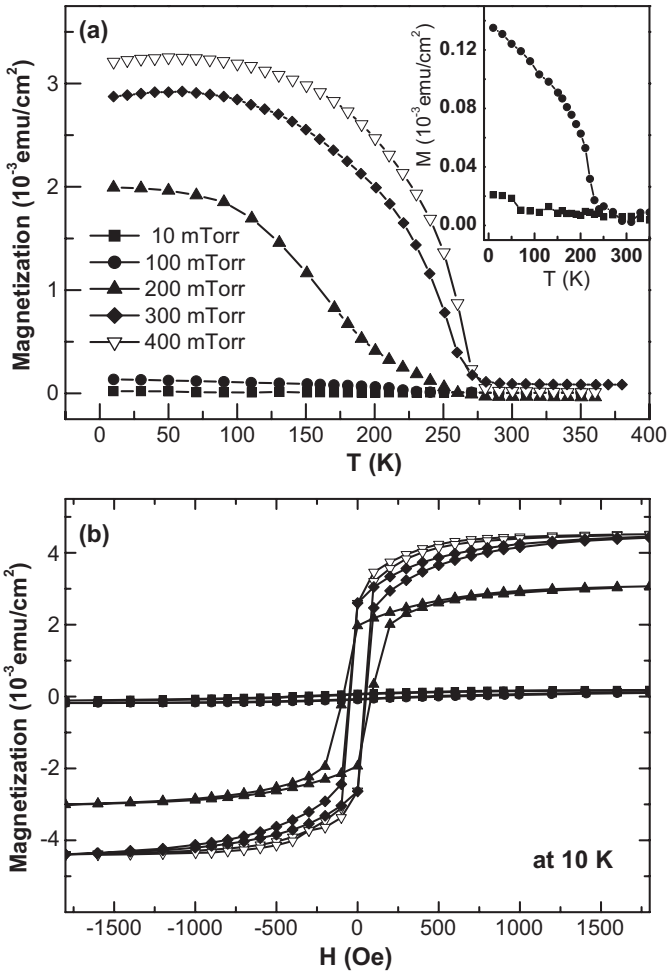

Figure 2. (a) The temperature dependent magnetization of $(LSMO_{10}/BTO_4)_{25}$ superlattices grown at different oxygen partial pressure. The inset shows an enlarged graph for the sample grown at 10 and 100 mTorr. (b) Magnetization hysteresis loop for the respective samples measured at 10 K.

in manganite films and superlattices has been attributed to the spin canting, phase separation and strain induced magnetic disorder in the film, it is believed that the presence of magnetic inhomogeneities plays a major role [6–10]. However, the origin of such inhomogeneities is not clearly understood. The increase in T_C of the superlattice samples toward the bulk LSMO value with increase in pO_2, inferred from figure 2, suggests that the origins of magnetic inhomogeneities in the superlattices might be related to the oxygen non-stoichiometry in the samples acquired during the sample growth at low pO_2.

3.3. Transport properties

For the transport properties, we have measured the resistance of the samples with temperature and magnetic field by applying the current within the plane of the substrate. Figure 3 shows resistance versus temperature plots of the samples with zero (closed symbols) and 3 T (open symbols) magnetic fields, grown at different oxygen pressure, pO_2. The respective percentage

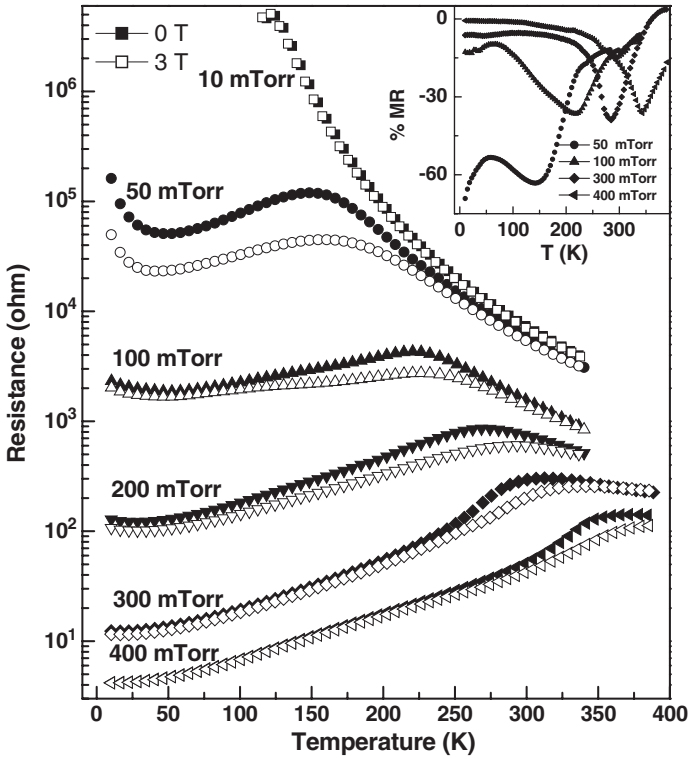

Figure 3. (a) The resistance measured as a function of temperature for $(LSMO_{10}/BTO_4)_{25}$ superlattices at 0 T (closed symbol) and 7 T (open symbol) field, grown at different oxygen partial pressure. The inset shows the respective %MR as a function of field.

magnetoresistance (MR) measured at 3 T field ($MR(\%) = 100 \times (R_H - R_0)/R_0$, where R_H and R_0 are the resistances measured with and without magnetic field, respectively) is shown as an inset in figure 3. The samples showed a metal-to-insulator-like transition (T_{MI}), except for the sample grown at 10 mTorr (an insulating behaviour is observed down to very low temperature). We are aware that the broad peaks do not correspond to a clear metal-to-insulator transition. However, a T_{MI} of 150, 225, 275, 302 and 350 K is found for samples grown at 50, 100, 200, 300 and 400 mTorr of pO_2, respectively. Figure 3 indicates that the superlattice samples exhibit several interesting features: (i) a systematic increase in T_{MI} with increase in pO_2, (ii) except for the sample grown at 400 mTorr, the T_{MI} of the samples was lower than that of the bulk LSMO, (iii) the T_{MI} of the samples grown at 300 and 400 mTorr was higher than their respective T_C value, (iv) high MR value in a wide range of temperature for the samples grown at low oxygen pressure (50 and 200 mT). As was shown in figure 3, the T_{MI} of the superlattice samples could be tuned to a value near the one of the bulk value by adjusting the oxygen partial pressure during the growth process.

The reduced magnetism and T_{MI} are mostly attributed to the presence of magnetic inhomogeneities in the superlattice samples. One of the origins of magnetic inhomogeneities could be oxygen non-stoichiometry of the superlattice layers. We believe that the oxygen non-stoichiometry in manganites could result in phase separation with regions of ordered spins (metallic region) separated by a matrix of disordered regions (insulating region). Hence, the ratio between the ordered and disordered region could vary with change in oxygen

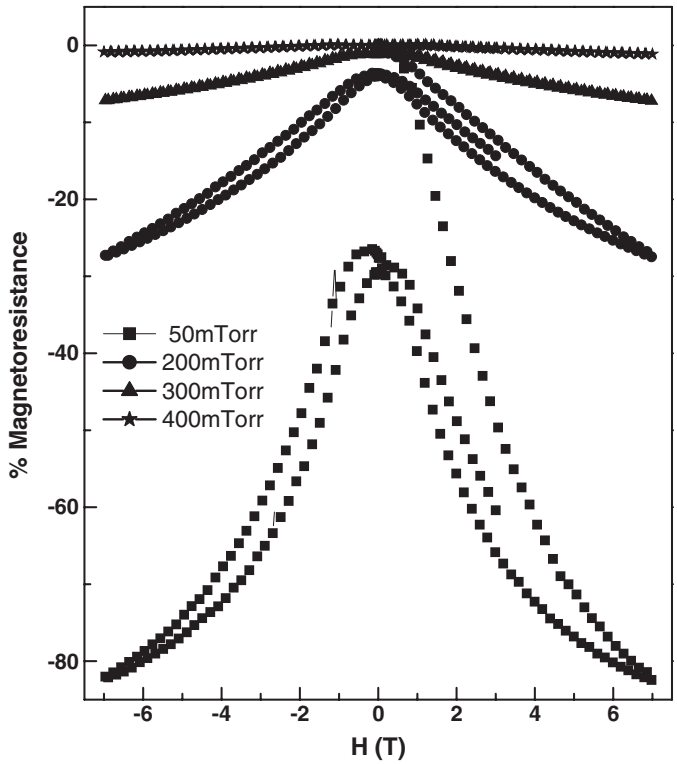

Figure 4. The magnetoresistance as a function of field for the $(LSMO_{10}/BTO_4)_{25}$ superlattices measured at 5 K.

stoichiometry. It is generally believed that the manganites grown at low oxygen partial pressure are compounds with an oxygen deficiency compared to the compounds grown at high oxygen partial pressure [11–13]. Thus the changes in T_C and T_{MI} with pO_2 could very well be attributed to the oxygen non-stoichiometry induced change in phase separated ordered and disordered spin regions. The high T_{MI} value compared to T_C shown in the samples grown at 300 and 400 mTorr could be understood in the following way: though the T_C of the sample was lowered by the dominance of disordered spin region, the presence of more ordered region compared to the disordered region for the sample grown at higher oxygen pressure will eventually leads to a good percolation conducting path, which could result in higher T_{MI} than the T_C. The increase in magnetoresistance in manganites with applied magnetic field was explained by alignment of the disordered spin region to the ordered region under applied magnetic field. This explains very well the high MR observed for the sample grown at low oxygen pressure (50 mTorr), which has more disordered region than ordered region.

The MR of the superlattice samples, grown at 50, 200, 300 and 400 mTorr, measured at 5 K up to 7 T field sweeping is shown in figure 4. The MR of the superlattices shows an increase with decrease in pO_2, with the highest value observed for the sample grown with a pO_2 of 50 mTorr. We observed 82, 27, 7, and 1% MR for the samples grown at 50, 200, 300 and 400 mTorr, respectively. Also, the samples grown at low oxygen pressure (50 and 200 mTorr) show hysteretic MR with applied field. The superlattice grown at 50 mTorr shows stronger hysteretic MR than the one grown at 200 mTorr. Recovering of percolation due to the field induced growth of clusters [7, 8] and the time dependent relaxation of the resistive state

follows a field change due to the presence of magnetic disorders. This could give a hysteretic MR with sharp resistance drop during the field sweeping [18]. The more pronounced hysteretic MR for the sample grown at low pO_2 and its absence for the one grown at high pO_2 provide further evidence of the presence of oxygen non-stoichiometry in the superlattices as the origin for magnetic inhomogeneities in our superlattices.

In a second step, it should be interesting to evaluate precisely the oxygen components of the samples (i.e. δ of $La_{0.7}Sr_{0.3}MnO_{3-\delta}$) based, for example, on the x-ray diffraction data. However, there are still some hurdles for such an experiment in the case of a thin film.

4. Conclusions

Several superlattices of $[(La_{0.7}Sr_{0.3}MnO_3)_{10}/(BaTiO_3)_4]_{25}$ were grown on $SrTiO_3(001)$ substrate with different oxygen partial pressure ranging from 10 to 400 mTorr. The samples show a systematic change in magnetic and transport properties with oxygen pressure, used as a parameter of change during the growth process. The ferromagnetic Curie temperature, T_C, and associated metal insulator transition, T_{MI}, show huge suppression compare to the bulk values. The reduction in T_C and T_{MI} in the superlattices could be attributed to the presence of magnetic inhomogeneities in the samples. The low value of T_C and T_{MI} for the sample grown at low oxygen partial pressure and their increasing trend toward the bulk value for the sample grown at high oxygen partial pressure clearly indicate that oxygen non-stoichiometry is one of the origins for the magnetic inhomogeneities in our superlattice samples. Moreover, a high MR value accompanied with hysteretic behaviour over a wide range of low temperature for the sample grown at low oxygen pressure compared to the one grown at high oxygen partial pressure provides further evidence for the presence of oxygen non-stoichiometry driven magnetic inhomogeneities in our superlattice samples. Our study elucidates the importance of oxygen stoichiometry playing a major role in controlling interface related problems in oxide superlattices.

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