Anisotropic strains, metal-insulator transition, and magnetoresistance of La$_{0.7}$Ca$_{0.3}$MnO$_3$ films

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Abstract

Thin films of perovskite manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$ were grown epitaxially on various substrates by either the pulsed laser deposition method or laser molecular beam epitaxy. The substrates change both the volume and symmetry of the unit cell of the films. It is revealed that the symmetry as well as the volume of the unit cell have strong influence on the metal-insulator transition temperature and the size of magnetoresistance.

Key words: anisotropic strains, metal-insulator transition, magnetoresistance

The perovskite compound La$_{1-x}$Ca$_x$MnO$_3$ with $x \approx 0.3$ (LCMO) shows a simultaneous appearance of metallic conduction and ferromagnetism below a certain ordering temperature [1,2]. It has attracted renewed attention due to its anomalously large magnetoresistance (MR) [3]. Considering numerous potential applications of large MR materials in thin film form, it would be of value to carefully examine their properties as a function of lattice strain [4].

Here we briefly describe our systematic investigations on the strain effects on $T_p$, the temperature at which a maximum resistance at zero field occurs, and MR of LCMO. By exploiting the fact that the lattice parameters of films can be varied by depositing films on various substrates, we were able to vary the lattice symmetry and constants of LCMO. Two methods of film preparation were used, pulsed laser deposition (PLD) and laser molecular beam epitaxy (LMBE). PLD and LMBE are similar in that high power pulsed laser is used as an energy source. However, there exist crucial differences in growth rate

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and growth mode; in PLD the typical growth rate is approximately 3 Å/s and films grow in the 3 dimensional island mode, while the growth rate of LMBE is about 0.1 Å/s and films grow in the layer-by-layer mode. The layer-by-layer mode for LMBE is ascertained by in-situ monitoring with reflective high energy electron diffraction; the details of the LMBE method will be described elsewhere [5].

A set of LCMO films with thickness 1000 Å were grown by PLD on SrTiO$_3$(100), MgO(100), and LaAlO$_3$(100) substrates (designated as the PLD films), and another set of thin films with thickness 400 Å were deposited by LMBE on SrTiO$_3$(100), NdGaO$_3$(100), and LaAlO$_3$(100) substrates (LMBE films). We first turn our attention to the results of four probe resistance measurements. In Fig. 1(a) plotted is the resistance $R$ of the the PLD films at $B = 0$ and 1 T versus $T$; Fig. 1(b) is the plot of the resistance of the LMBE films. It is striking that $T_p$, the maximum resistance temperature, varies enormously even within the set of the films prepared by the same method. This indicates that the strains in the films on various substrates vary and thus cause a variation in $T_p$ despite the fact that the processing conditions are exactly the same within a given set of films. High resolution 4-circle x-ray diffraction was carried out at room temperature to determine the strains, and the in-plane and surface-normal lattice parameters of the LCMO films are designated as $a$ and $c$, respectively. It should be noted here that the lattice parameters of ultra-thin films such as those under discussion may vary as a function of distance from the substrate [6], and if this is the case, then the lattice parameters measured may be regarded as the averaged ones.

For the PLD films, it is found that the film on SrTiO$_3$ possesses the largest unit cell volume ($V_c$) and the one on LaAlO$_3$ does the smallest. In addition, the lattice symmetry of the films changes from negative tetragonal (the SrTiO$_3$ case, $a=3.921$ Å, $c=3.845$ Å) to nearly cubic (the MgO case, $a=3.885$ Å, $c=3.891$ Å) and to positive or elongated tetragonal one (the LaAlO$_3$ case, $a=3.842$ Å, $c=3.878$ Å) as unit cell volume decreases. To expose the correlation between the lattice structure and $T_p$ and MR of LCMO, we plot $T_p$ and the maximum MR values against unit cell volume. Fig. 2(a) clearly illustrates that the samples with cubic symmetry (open symbols) show lower values of maximum MR than the noncubic ones (filled symbols) do. Fig. 2(b) shows that $T_p$ also varies nonmonotonically. This distinctive $T_p$ behavior may be interpreted as a superposition of two differing tendencies: one tendency is related to the volume effect favoring the monotonic increase of $T_p$ as the volume of unit cell is reduced. The other tendency is due to the symmetry effect, in accord with the MR behavior, favoring the maximum $T_p$ for cubic samples.

It is noted that the volume effect resembles that of a bulk under a hydrostatic pressure where the reduction in unit cell volume gives rise to a monotonic $T_p$ rise and an associated decrease of maximum MR [7,8]. However, the sym-
metry effect cannot be probed with isotropic hydrostatic pressure. To further shed light on the symmetry effect, we examined the LMBE films, i.e., the films grown in the layer-by-layer mode on SrTiO$_3$, NdGaO$_3$, and LaAlO$_3$ substrates. From the x-ray diffraction measurements, it was found that the unit cell volume variation in the LMBE films is within 0.8%, about four times less than that of the PLD films. X-ray diffraction also showed that the lattice symmetry of the films again changes from negative tetragonal (the SrTiO$_3$ case, \(a=3.893\ \text{Å}, \ c=3.827\ \text{Å}\)) to nearly cubic (the NdGaO$_3$ case, \(a=3.865\ \text{Å}, \ c=3.874\ \text{Å}\)) and to positive tetragonal one (the LaAlO$_3$ case, \(a=3.838\ \text{Å}, \ c=3.903\ \text{Å}\)). Fig. 3 is the plot of \(T_p\) against the teragonality. The figure clearly reveals the symmetry effect; a deviation from the cubic symmetry leads to a reduction in the transition temperature. It is of value to point out that the negative tetragonality is more effective in reducing \(T_p\) than the positive one. This, we believe, is related to the Mn d-orbital ordering induced by the imposed strains, and will be the topic of future publications.

References

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Fig. 1. Plotted as a function of temperature ($T$) is resistivity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films: (a) films deposited on SrTiO$_3$, MgO, and LaAlO$_3$ by the PLD method, and (b) films deposited on SrTiO$_3$, NdGaO$_3$, and LaAlO$_3$ by LMBE. Resistivity of each sample is normalized to the value at $T = 317$ K and zero field.
Fig. 2. MR (≡ [R(0) − R(B)]/R(0)) and $T_p$ of the films grown by the PLD method on SrTiO$_3$ (filled circle), MgO (open circle), and LaAlO$_3$ (filled square). The open square denotes the bulk values. (a) The maximum MR at $B = 0.5$ and 1 T, and (b) $T_p$ at zero field are plotted against the unit cell volume $V_c$. The lines are guide for the eye.
Fig. 3. $T_p$ of the films grown by LMBE is plotted as a function of tetragonality $(c-a)/a$ where $c$ and $a$ indicate the normal and in-plane lattice constants, respectively. Different symbols indicates the substrates: SrTiO$_3$ (open square), NdGaO$_3$ (filled square), and LaAlO$_3$ (open circle). The line is guide for the eye.