Oleg I. Lebedev, Gustaaf van Tendeloo
EMAT, University of Antwerp, Antwerp, Belgium

Phase transitions: an alternative for stress accommodation in CMR manganate films

Thin films of perovskite-based material, exhibiting colossal magnetoresistance properties have been structurally characterized. The lattice mismatch with the substrate and the associated stress can induce different types of distortions in the film, resulting in different crystal structures. This opens the possibility to design new structures with predictable physical properties. The structure of epitaxial La$_{0.97}$Sr$_{0.03}$MnO$_3$ on a (100) SrTiO$_3$ substrate and of the epitaxial composite (La$_{0.65}$Ca$_{0.35}$MnO$_3$)$_{1-x}$ (MgO)$_x$ films on a (100)MgO substrate have been investigated by electron microscopy. Novel mechanisms for misfit accommodation in epitaxial films have been detected. For the La$_{0.97}$Sr$_{0.03}$MnO$_3$/SrTiO$_3$ film, where there is only a small mismatch ($\alpha \simeq \alpha_0$), the formation of periodic microtwins is observed. For the composite (La$_{0.65}$Ca$_{0.35}$MnO$_3$)$_{1-x}$ (MgO)$_x$/MgO films under a 3D stress (mismatch $\simeq 8\%$), a phase transition from low to high symmetry is detected.

Keywords: Structure; Phase transition; HREM; TEM; Thin film

1. Introduction

The discovery of "colossal magnetoresistance" (CMR) in perovskite-based rare-earth manganates of the type Ln$_{1-x}$A$_x$MnO$_3$ (Ln rare-earth, A divalent cation) has caused intense research activities over the last few years [1]. One of the main directions to develop new materials with better CMR properties is to modify the basic (A$_{1-x}$A'$_x$BO$_3$) structure. This can be done by adopting different A rare-earth cations, by doping with A' cations and/or by altering the oxygen stoichiometry. This will alter the internal strain, leading to rotation and/or distortion of the vertex-sharing MnO$_6$ octahedra.

Thin (perovskite-based) films on a substrate will always exhibit a lattice mismatch with the perovskite substrate. This misfit can induce different types of perovskite distortions depending on the stress (compressive or tensile). Changing the substrate, i.e., changing the misfit, opens the possibility to design new thin-film structures with predictable physical properties [2–5]. The structural changes with respect to the bulk are usually small and can vary locally. Therefore, transmission electron microscopy (TEM) and, in particular, high-resolution electron microscopy (HREM) is the better technique to study these subtle structural changes.

We will present our results for thin films of La$_{0.97}$Sr$_{0.03}$MnO$_3$ (LSMO) on a (100) SrTiO$_3$ (STO) substrate with a minimal misfit ($\alpha \simeq \alpha_0$) [6], and composite

Fig. 1. Low-magnification and HREM cross-sectional images of LSMO/STO films of different thickness: (a) 9 nm; (b), (c), (d) 100 nm. The electron diffraction pattern in (c) corresponds to the microtwinned region in Fig. (b).

© Carl Hanser Verlag, München Z. Metallkd. 95 (2004) 4
(La_{0.67}Ca_{0.33}MnO_{3})_{1-x}:(MgO)_x films grown on a (100)MgO substrate (misfit = 8%) [7].

For epitaxial LSMO films, grown by pulsed laser deposition on a STO(100) substrate, the small misfit ($\alpha_{\text{STO}} = \alpha_{\text{MgO}}$) is accommodated either purely elastically (for very thin films) or by the formation of periodic microtwins (for thicker films). The TEM observations for a LSMO film on a STO(100) substrate can consistently be interpreted on the assumption that misfit stresses influence the structure and the microstructure of the epitaxial film. The LSMO/STO system is particularly suited to demonstrate this effect, especially if the composition is chosen close to the phase boundary between two different structures (rhombohedral versus orthorhombic). These two structures are topologically similar but differ in features that are sensitive to the applied stress, such as the tilt angle and tilt axis or the shape of the oxygen octahedra. These film/substrate interfaces are found to be perfectly coherent, thus free of interfacial dislocations.

Different film thickness, i.e., different stress pattern, leads to a different rhombohedral deformation. The thinner films (9 nm) are found to be rhombohedral ($R\bar{3}c$) without any planar defects (Fig. 1a). The thicker films (50–100 nm) also have a rhombohedral structure but are periodically microtwinned. This is evident from the cross-sectional image (Figs. 1b and d) and the corresponding spot splitting in the electron diffraction pattern (Fig. 1c). The width of the twins is around 50–60 nm; close to predicted separation for dislocations at the critical thickness for LSMO [8]. Fine-scale microtwinning is suggested to be a way to accommodate misfit in epitaxial growth [6], minimizing also the transformation strain energy. Periodic microtwinning is, therefore, a novel mechanism to accommodate misfit [6]. Stress-free (i.e., thick, free-standing) films are found to exhibit a domain structure of the orthorhombic (Pnma) O' phase [6].

Thin-film composites seem to be promising for the realization of a low-field magnetoresistance material. In these composites, a chemical phase separation results in a corresponding electronic (metal–insulator) or/and magnetic (ferromagnetic–antiferromagnetic) phase separation [5]. The parameters of such an “electronic phase separation” can be controlled by the processing conditions on the scale of a few nanometers [7, 9]. The magnetotransport in this system can be compared with that recently observed in ferromagnetic metal/antiferromagnetic insulator phase-segregated systems [10].

Composite (La_{0.67}Ca_{0.33}MnO_{3})_{1-x}:(MgO)_x films were prepared by metalorganic aerosol deposition on a (100)MgO substrate for different concentrations of the MgO phase (0 ≤ x ≤ 0.8). For x ≈ 0.3, a percolation threshold in conductivity is reached, at which an insulating MgO cluster forms around the LCMO grains. This yields a drastic increase of the electrical resistance for films with x > 0.3 [5].

The microstructure and magnetotransport properties of (La_{0.67}Ca_{0.33}MnO_{3})_{1-x}:(MgO)_x films on (100)MgO depend on the MgO concentration. Films are epitaxial at all MgO concentrations and exhibit sharp, well-defined film/substrate interfaces. Diffraction patterns from cross-sectional specimens clearly show a variation of the film structure with increasing MgO content (Fig. 2). All patterns can be indexed as a superposition of LCMO and MgO. The electron diffraction pattern obtained from the pure LCMO film (x = 0) (Fig. 2a) can be indexed with respect to an orthorhombic lattice (Pnma, $a_0 = c = a_0\sqrt{2}$, $b_0 = 2a_0$). The reciprocal rows, indicated by white arrows in Fig. 2a, however, disappear for x = 0.33 (Fig. 2b). This suggests a phase transition to a different structure with space group $R\bar{3}c$.

The films exhibit a remarkable microstructure consisting of domains of LCMO surrounded by an epitaxially intergrown MgO thin layer. A HREM image taken across the interface shows that the LCMO film (x = 0) grows epitaxially and is coherent across the interface as well as across the low-angle grain boundary (GB) in Fig. 3a. Increasing the MgO concentration (x = 0.33–0.5) leads to buckling of the film/substrate interface (Fig. 3b), induced by the epitaxial growth of MgO islands on the MgO substrate surface. The MgO layers start from the interface, grow along the original domain boundaries, and extend all the way through the film up to the surface. This MgO layer creates a wall around the LCMO domains and, as a result, a uniform 3D stress is built up (for more details see [7]).

A new type of 3D stress accommodation through a phase transition from a low symmetry to a high symmetry is, therefore, proposed [7]. Our experimental observations, and in particular the EELS and HREM data, suggest that only the internal pressure, resulting from the epitaxial intergrowth of the MgO columns within the LCMO film, cause the Pnma to $R\bar{3}c$ phase transition in La_{0.67}Ca_{0.33}MnO_{3}.

This work was performed within the framework of IAP V.I.
Fig. 3. Cross-sectional HREM images of the interface (LCMO)$_{1-x}$:
(MgO)$_x$/MgO for a sample with (a) $x = 0$ and (b) $x = 0.5$.

References


(Received October 21, 2003; accepted February 9, 2004)

Correspondence address

Dr. O.I. Lebedev
EMAT
University of Antwerp
Groenenborgerlaan 171, B-2020 Antwerp, Belgium
Tel.: +32 3 265 3261
Fax: +32 3 265 3257
E-mail: oleg.lebedev@ua.ac.be