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Control of the surface roughening in the epitaxial growth of manganite films

F. Sánchez *, I.C. Infante, Ll. Abad, U. Lüders, Ll. Balcells, B. Martínez, J. Fontcuberta

Institut de Ciència de Materials de Barcelona, CSIC, Campus UAB, 08193 Bellaterra, Spain

Abstract

To fabricate magnetic tunnel junctions the morphology of the films is a key issue, and two dimensional (2D) growth and very smooth film surfaces are required. In the epitaxy of manganites like $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) above a relatively low thickness a roughening transition is frequently found: growth starts by a layer-by-layer mode, but roughness increases fast as three-dimensional islands form on the surface. We have analyzed the morphology of LCMO epitaxial films and here we report on the roughening process and methods to suppress it. We show that the roughening is due to the formation of multilayered islands. Initially, there are 2D islands on the surface, but before the full coverage of the layer is reached, new 2D islands nucleate and grow on the surface of the existing islands. As new 2D layered islands grow, multilayered mounds are formed. We demonstrate that mounds do not appear if the growth is by step flow mechanism, although there is a marked step meandering. These findings get insight on the epitaxy of complex oxides and provide rules to control the morphology in manganites.

Keywords: Manganite films; Surface roughening; Mounds; Layer-by-layer growth

1. Introduction

Within the complex oxides with perovskite structure, a great variety of functional properties is found. Considering, for instance, electrical properties they can be superconducting, metallic, semiconducting, insulating or even ferroelectric. They can also exhibit a variety of magnetic properties going from antiferromagnetism, the most common, to ferromagnetism. Indeed, the materials displaying the largest magnetoresistance are some ferromagnetic manganites [1]. On the other hand, the interest in biferroic materials has been renewed after recent findings in some oxides [2].

The variety of properties that these materials can present is a consequence of their complexity. But this complexity can also make difficult to control their properties. For example, in thin films slight structural distortions induced by epitaxial stress can dramatically modify the superconductivity [3], the ferroelectricity [4] or the ferromagnetism [5]. On the other hand, growth mechanisms in epitaxy of oxides are not well known yet and can differ from those involving semiconductors and metals [6–9]. Clearly, progress in the understanding of oxides' epitaxy is necessary to reach control on the micro(nano)structure of the films and, in turn, their properties. Also, the control of the film morphology is important, and it constitutes a critical issue in the case of heterostructures.

In the epitaxy of ferromagnetic manganites, morphology is certainly critical since their main interest is to be used as electrodes in magnetic tunnel junctions. High quality epitaxial films have been reported with either atomically smooth [10–13] or rough grain-like [14–17] surfaces. Although the growth process was not investigated in detail, it seems that films tend to be rougher increasing thickness [17–19]. We have recently investigated the surface roughening in the epitaxy of ferromagnetic $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) [20]. We found that with increasing thickness multilayered mounds are formed due to anisotropy in the adatom current. Here we report on the control of the morphology by using vicinal substrates. We demonstrate that mound formation is suppressed in step flow growth mode, although the anisotropy in the adatom current induces pronounced step meandering.

2. Experimental

$La_{0.67}Ca_{0.33}MnO_3$ films were grown on $SrTiO_3(001)$ substrates of controlled vicinality (<0.1°, ~0.15°, and ~0.5°) by rf magnetron sputtering of a stoichiometric ceramic target. The deposition pressure was 33 Pa (80%Ar–20%O_2), and the

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* Corresponding author. Tel.: +34 935801853; fax: +34 935805729.
E-mail address: fsanchez@icmab.es (F. Sánchez).

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substrate temperature was 800 °C. Films with varied thickness were prepared at a growth rate around 0.2 nm/min by varying the sputtering time. The thickness (t) of the films discussed here was 30 and 80 nm, as determined from X-ray reflectometry measurements; given the number of intensity oscillations, the accuracy of these measurements is of about 1 nm. The crystal structure was investigated by X-ray diffractometry (XRD) with Cu Kα radiation in a four-circle diffractometer. The surface morphology was characterized by atomic force microscopy (AFM) working in tapping mode, being the scan rate 1 line/second and using silicon tips having a nominal radius of 5 nm. Image processing and analysis were done using the WSxM software [21]. Additional details on structure and magnetotransport properties can be found elsewhere [22].

3. Results and discussion

XRD characterization (not shown here) revealed a high crystalline quality of the films. Films are epitaxial, having a cube-on-cube epitaxial relationship with the substrate. The rocking curves of the (002) symmetrical reflection have a full-width at half-maximum (FWHM) of 0.17°, while the FWHM of the substrate peaks 0.13° wide. From reciprocal space maps around asymmetrical reflections it was determined that the films have an in-plane lattice parameter of 0.3905 nm, coincident with the lattice parameter of the substrate. The full strained state was found even in the $t=80$ nm films. In contrast with the high crystal quality, the surface of the films is not smooth but granular. A typical morphology is shown in Fig. 1a. It corresponds to a $t=30$ nm film grown on a $<0.1°$ miscut substrate. The morphology is clearly grain-like, with a submicron grain size. Concerning the height data, the histogram has a FWHM of 1.5 nm, whereas the root-mean-square (rms) roughness is 0.65 nm. More details of the morphology can be observed in the topographic image of a 1×1 μm^2 scan (panel b). The grains appear to have an elliptical base contour, with dimensions of the order of 100 nm. The uniformity in the separation between grains is confirmed with the analysis of two dimensional (2D) Fast Fourier Transform (FFT) (panel c). The maximum intensity points in the 2D-FFT are found to be uniformly distributed around an elliptical ring (marked in the image with the dashed line). The uniformity in the intensity implies that there is not long-range ordering along specific directions, whereas the existence of maximum intensity on an elliptical ring means that intergrain separation is quite uniform (i.e., there is uniformity in their size) and also

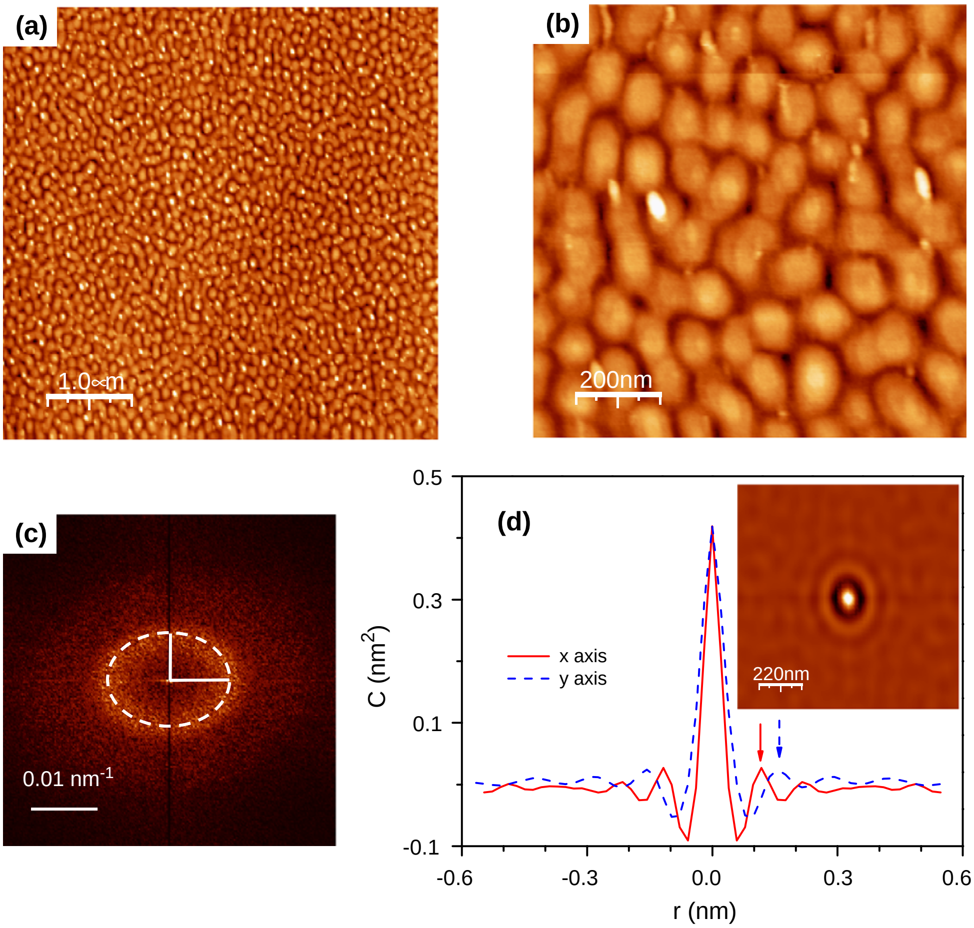

Fig. 1. (a) Topographic atomic force microscopy image (5×5 μm^2) of a $t=30$ nm LCMO film grown on a $<0.1°$ miscut SrTiO$_3$(001) substrate; (b) Image from a 1×1 μm^2 scan size; (c) Two dimensional Fast Fourier Transform of topographic data (from the 5×5 μm^2 scan). The ellipse (dashed line) marks the highest intensity points. Half major and half minor axes are marked by continuous lines; (d) Intensity profiles of the autocorrelation function (from the 5×5 μm^2 scan) along the horizontal and vertical directions. Inset: zoom of the autocorrelation.