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Research Report

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Abstract

Using a molecular beam epitaxy deposition technique, c-axis oriented $La_{2-x}Sr_xCuO_{4-\delta}$ very thin films were prepared on (001) $SrTiO_3$ substrates. Structural properties were analyzed by x-ray diffraction (XRD) and transmission electron microscopy, and reveal the existence of a distortion of the film unit cell with respect to the bulk material. This distortion is induced by the significant film–substrate mismatch. Intensity analysis of XRD peaks suggests a modification of the relative position of the apical oxygen, which could be responsible for the reduction of the critical temperature in thin films.

I. INTRODUCTION

Since the discovery of superconducting properties in the '214' phase upon doping with Ba or Sr [1], this system has been actively studied. One reason for this is its simple crystal structure with a single copper-oxide plane per half-unit cell. By studying very thin epitaxial $La_{2-x}Sr_xCuO_{4-\delta}$ (LSCO) films, we hope to evidence the role of this plane on superconducting properties. Three series of films with different thicknesses (390, 520 and 2100 Å) were grown on (001) $SrTiO_3$ substrates using sequential molecular beam epitaxy (MBE) deposition. For each series, the Sr content, x, was varied between 0.10 and 0.25.

While the normal-state properties are similar to those of single crystals, the critical temperature T_c of our films is strongly reduced with thickness (see Fig. 1), in agreement with other work (for example [2,3]).

C-axis compression, as reported in [2], was also observed in our thin films (see Fig. 2), suggesting that epitaxial strain might be related to the lowering of T_c.

In this contribution, we present results from transmission electron microscopy (TEM) and x-ray diffraction (XRD) analysis which reveal the existence of a distortion of the film unit cell (UC) with respect to the bulk material, induced by the in-plane epitaxial stress due to the large lattice mismatch between substrate and film.

The main effect of this distortion might be to modify the related position along the c-axis direction of the apical oxygen which could be responsible for the reduction of T_c. The displacement of apical oxygen in the interior of the UC is induced by a relatively small variation of both in-plane and vertical lattice spacings. We explain this fact by invoking the known structural instability of the '214' system, in particular the compressed apical La–O bond.

II. RESULTS AND DISCUSSION

A good crystallographic c-axis structure and single phase material was obtained for these films. These results along with experimental details have been published elsewhere [6].

The c-axis in LSCO thin films grown on $SrTiO_3$ is compressed by about 0.3% compared to bulk values (see Fig. 2).

Influence of a buffer layer

In order to compensate for the mismatch, a buffer layer of undoped material was inserted between substrate and thin film. For film thicknesses of less than 300 Å, the presence of a buffer layer improves T_c. For thicker films, its influence is negligible, and T_c values remain lower than for single crystals [6].

RHEED spectra analysis

Recently, we performed a detailed analysis of *in-situ* RHEED spectra recorded during the deposition of an undoped thin LCO film on $SrTiO_3$ at 750 °C. A more detailed report of this method and the analysis of the data will be given elsewhere [10]. The evolution of the [100] lattice parameter as a function of the number of deposited UCs is shown in Fig. 3.

For the first UC, the in-plane lattice parameter is very close to that of the substrate. For larger thicknesses, a decrease of the lattice parameter is observed, but, even at the maximum thickness studied here (30 UCs), there is no saturation, and the $d_{[100]}$ lattice parameter is still larger than that of the bulk, suggesting that stress is not completely relieved.

TEM results [8]

TEM investigations reveal a network of misfit dislocations lying close the film/substrate interface. This means that the films have relaxed most of the misfit strain, in good agreement with the RHEED analysis (showing that relaxation begins after 10 UCs). If the dislocations nucleate at the deposition temperature and both lattices have the same thermal expansion coefficient, then the misfit dislocation spacing can be calculated for a completely relaxed film: i.e., 14.5 nm for $x = 0$ and 11.1 nm for $x = 0.2$. In fact, the spacing observed is $\approx 14 \pm 2$ nm, independent of x. Possible explanations for this invariance could be differences in the thermal expansion coefficients as a function of x or that the dislocation network cannot be further compressed owing to interaction between dislocations. The observed c-axis lattice parameter compression suggests that the in-plane lattice parameter is slightly increased leaving a residual stress within the total thickness.

XRD results

A detailed analysis has been made of the ratio of XRD intensities as a function of x and will be published elsewhere [9]. Briefly, standard XR diffractograms taken on carefully aligned samples provide structural information over four orders of diffraction. Using the relative peak intensities, we compute the relative positions of the different atomic planes in the UC. Together with the c-axis values given by the peak positions, we estimate the atomic distances in the c-axis direction. Unfortunately, the relative weight of the apical oxygen planes in the UC structure factor is too small to obtain an accurate estimation of its deviation. However, this procedure reveals a clear trend suggesting the compression (a few %) of the apical Cu–O bond (d_2). Since the total compressions of both the c-axis and the Cu–La bond (d_1) are small, it follows that the distance La–O (d_3) is correspondingly expanded. In the limits of our analysis, this behavior seems to be independent of doping as well as of thickness. This distortion is schematically depicted in Fig. 4. From the structural point of view, in the bulk material, the apical La–O bond (d_3) is strongly compressed (2.35 Å) with respect to the value expected from the ionic radii, while the eight remaining bonds are weakly expanded (average 2.69 Å) [11]. This competition ensures the crystal cohesion. At the same time, it leads to a corrugation of the LaO plane ($d_2 > d_1$). On the contrary, in epitaxial thin films, the stress induced by the substrate slightly expands the in-plane lattice parameter and allows a relaxation of the apical distance d_3.

III. CONCLUSIONS

We have carried out several experiments in order to understand the possible correlation between the c-axis compression and the lowering of T_c. The results on samples containing a buffer layer together with the *in-situ* RHEED spectra (at 750 °C) show that thin films need about 10 to 20 UCs to allow relaxation of the stress imposed by the $SrTiO_3$ substrate. Nevertheless, for thicker films, the influence of the buffer layer is negligible.
A possible answer may come from both TEM and XRD analysis. First of all, the presence of a misfit dislocation network confirms the partial relaxation of misfit stress in these films. Secondly, the dislocation lattice spacing is unexpectedly independent of doping. In addition, in the limits of our analysis, the calculated compression of the distance between apical O and Cu does not show any evidence of doping or thickness dependence.

Two complementary mechanisms can be invoked to explain the above observations. On the one hand, one may argue that strongly repulsive interactions between dislocation lines or a difference in thermal expansion coefficient hinders further relaxation of the stress field. Then, a residual stress in the in-plane lattice parameter remains, distorting the UC. On the other hand, our calculations suggest that the vertical displacement of the oxygen atoms is relatively large (a few %) in comparison with the displacement of the remaining atoms in the cell and the global deformation of the UC itself ($\approx 0.3\%$). If true, such a distortion is far from a usual elastic uniaxial strain. In other words, the in-plane-induced expansion allows the apical La–O bond to relax, reaching a more stable configuration. This new stability could underlie the observed invariance of the misfit dislocation network.

If the effect of the differential thermal expansivity can be ignored, then a complete explanation could be given in terms of a competition between nucleation energy of the misfit dislocations and elastic deformation energy in this 'new' equilibrium state.

Anyway, one important consequence of this distortion is the compression of the apical Cu–O bond that could be related to the decrease of T_c. Other manifestations of the instability of the UC have been observed, for example under hydrostatic pressure [12] or upon Nd substitution [13], leading to structural transformation in which the c-axis is expected to induce a quite different structural response.

N.B.: First results from thin films grown on $SrLaAlO_3$ substrates which have a lower but inverse mismatch show an expansion of the c-axis as expected and correspondingly a higher T_c for the same film thickness.

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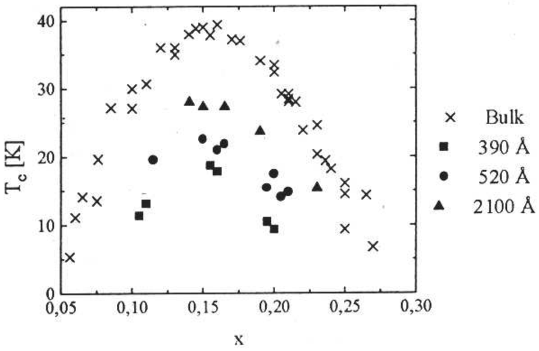

FIG. 1. Critical temperature T_c as a function of doping x for three films with different thicknesses (390, 520 and 2100 Å) and for bulk samples (powder and single crystal (Refs. [4,5])).

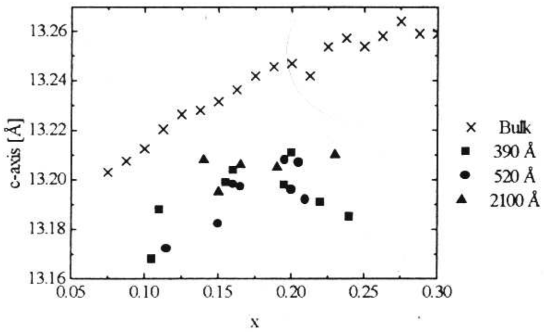

FIG. 2. c-axis lattice constant as a function of doping x for single crystals of LSCO [7] and for three series of films with different thicknesses (390, 520 and 2100 Å) at 295 K.

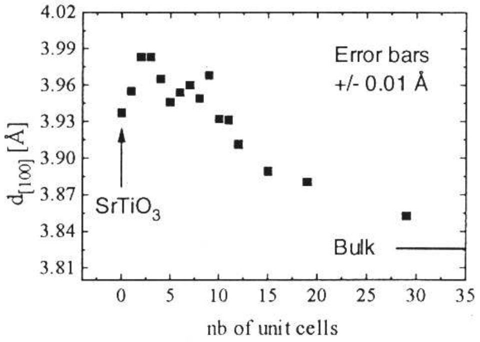

FIG. 3. Evolution of the in-plane $d_{[100]}$ lattice parameter of LCO as a function of the number of UCs for an undoped film measured at 750 °C from RHEED. The extrapolated bulk value is indicated by the short line.

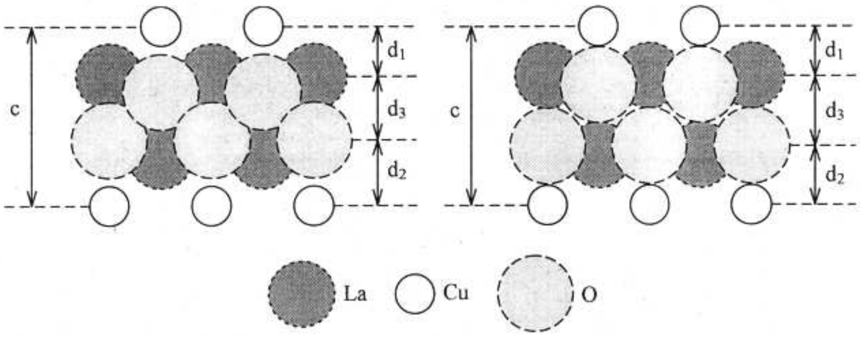

FIG. 4. Schematic view of the (110) plane of the half-unit cell for relaxed material (left) and strained film (right). The sphere radii are proportional to the classical ionic radii, d_1 corresponds to the distance La–CuO_2 plane, d_2 to the Cu–O bond, and d_3 to the La–O bond. In the right picture, the d_2 (and hence d_3) value corresponds to the upper limit of our estimations.