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Correlation between structural and transport properties in epitaxial films of $Nd_{2-x}Ce_xCuO_{4\pm\delta}$

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A B S T R A C T

We present here a study on the influence of the oxygen reduction process on the structural and transport properties of epitaxial thin films of the electron-doped cuprate $Nd_{2-x}Ce_xCuO_{4\pm\delta}$. As is well known, the gradual removal from as-grown samples of a tiny percentage of excess oxygen ions leads to a drastic improvement of the metallic character of this system, which eventually becomes superconducting for suitable values of the cerium concentration, with a maximal critical temperature $T_c \simeq 25$ K. We find that the oxygen loss occurring in thermal treatments in the temperature range 500–850 °C leads to a reduction of the disorder hindering conductance processes, but is insufficient to make the system become superconducting. On the other hand, as soon as the annealing temperature is raised above 850 °C, superconductivity appears, and at the same time a systematic variation of the length of the unit cell along the *c*-axis direction is detected. This is a clear indication that the transition to the superconducting phase is always accompanied by a structural modification. A further salient feature characterizing samples annealed at high temperatures is the emergence of a linear contribution in the normal-state resistivity, which superimposes to the quadratic one already present in samples which are oxygen-reduced below 850 °C. This contribution is probably associated with the formation of hole-like carriers located at hole pockets developing at the Fermi energy along the nodal direction in the Brillouin zone. We conjecture that the evolution of the electronic states with oxygen removal for a given cerium concentration close to optimal doping, is similar to the one taking place in optimally annealed samples where cerium concentration is raised from the underdoped to the lightly overdoped regime value.

1. Introduction

The majority of the high-temperature superconductors (HTS) discovered so far are antiferromagnetic Mott insulators with perovskitic structure doped with hole-like charge carriers injected in the CuO_2 planes. However, as first shown in 1989 [1], a small number of other perovskitic cuprates can become superconducting, though with lower critical temperatures, when doping is made with electrons rather than with holes. The most relevant of these systems are those denoted by the chemical formula $RE_{2-x}Ce_xCuO_{4+\delta}$ (RE-CCO), where RE denotes a trivalent lanthanide rare earth element (RE = Nd, Pr, Sm, Eu) whose partial substitution with tetravalent cerium leads, for suitable values of x, δ and the temperature T, to the superconducting transition thanks to the related injection of electron-like charged carriers. Though in the last two decades the attention has predominantly been devoted to hole-doped cuprates, the electron-doped ones have received a renewed interest in recent years [2] since it has been realized that a powerful route towards the understanding of the physics of HTS may come through a careful analysis of the analogies and the differences between the superconducting phases induced by the two kinds of doping [3].

Electron-doped materials belonging to the RE-CCO family crystallize in the so-called T′ structure, which is characterized by the absence of oxygen ions in the apical position. Compared with hole-doped systems such as $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_4$, which crystallize in the T structure where apical sites are instead occupied, RE-CCO compounds exhibit a larger anisotropy in the transport properties corresponding to a more pronounced quasi two-dimensional character. Superconductivity occurs in a narrow range of Ce doping, going approximately from $x = 0.12$ to $x = 0.22$ [4], with the highest critical temperature T_c (≈ 25 K) occurring at a doping level of about 0.15. A comparison with the results obtained on hole-doped cuprates underlines a number of other differences between the two families of cuprates, among which of special relevance are the much larger robustness of the antiferromagnetic phase against electron doping and the apparently different *d*-wave character of the superconducting order parameter. A further peculiarity of the electron doped compounds not shared by the hole-doped ones, is that they require a careful annealing in a reducing atmosphere to achieve superconductivity. This thermal treatment leads to the removal of a very small fraction of the oxygen atoms, usually ranging around 1%, which is essential for the transition to the superconducting phase to occur. The effect of this reduction process is still not fully understood at a microscopic level, though it is clear that it must be considered as additional with respect to cerium doping,

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since an oxygen removal insufficient to generate superconductivity can by no means be compensated by a corresponding increase of cerium concentration.

A large amount of work has been devoted to the understanding of how the removal of a tiny percentage of oxygen ions drastically changes the transport properties of the electron-doped cuprates [5–7]. Iodometric titration and thermogravimetric analysis (TGA) performed on as-grown samples have allowed to detect an oxygen stoichiometry slightly exceeding the nominal value of 4. This extra oxygen tends to balance the effect of the tetravalent Ce^{4+} substitution and therefore increases with cerium doping. Despite the smallness of the amount of oxygen removed during the annealing (~ 1%), a strong influence is observed on the electric and magnetic properties of the samples, which at suitably low temperatures change from antiferromagnetic insulators into metallic superconductors.

The physical properties of the *n*-type cuprates have mainly been analyzed on bulk and single crystal samples. Investigations on thin films are instead rather limited, since their fabrication is made difficult by the high sensitivity of the properties of the samples on both the cerium and the oxygen content. High-quality thin films are important not only for experiments devoted to the understanding of fundamental properties of HTS, but also in the field of microelectronics research. In this context, superconducting devices based on hetero-epitaxial samples with high quality *p*–*n* interfaces require well-controlled and highly reproducible fabrication processes. In particular, most of the $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ (NCCO) thin films have so far been fabricated by pulsed laser deposition [8–13], molecular beam epitaxy [14,15], magnetron sputtering [16,17] and pulsed electron deposition [18].

In this paper we report on a highly reproducible fabrication method of growth of epitaxial superconducting NCCO thin films, based on the use of a computerized dc diode sputtering. As-grown non-superconducting as well as superconducting samples have been fabricated in order to systematically investigate the structural and transport properties of the NCCO films as a function of the oxygen content varied in the reduction process. In particular, samples reduced in a temperature range going from 500 °C to 850 °C have been used for a combined analysis of X-ray diffraction and resistivity versus temperature data. We find that the effect of the oxygen loss during treatments in the above mentioned temperature range amounts to a reduction of the disorder, as seen from the decrease in magnitude of the resistivity at any temperature, but no trace of superconductivity as well as no structural change is ever observed. In particular, a crossover from a metal-like to an insulator-like behavior emerges from the resistivity data, which is usually explained in terms either of 2D weak localization effects or of Kondo-like scattering from magnetic ions. On the other hand, when the annealing is performed at temperatures higher than 850 °C, our approach combining high resolution X-ray diffraction and temperature-dependent resistivity measurements, clearly shows that the appearance of superconductivity is systematically accompanied by a structural change of the *c*-axis lattice parameter. The detection of this effect, which has never been observed before, was most probably possible thanks to the high degree of epitaxial growth of our samples which the peculiar growth technique presented here allows to achieve. This result points out the crucial importance of the oxygen reduction performed above 850 °C, establishing a close relation between the occurrence of superconductivity and a subtle structural modification induced by the annealing treatment. This implies that the drastic change in the transport properties underlying the superconducting transition is essentially triggered by a structural modification rather than by the continuous reduction of disorder induced by the annealing.

2. Experimental details

The NCCO films were grown on (001)-oriented $SrTiO_3$ (STO) substrates by dc sputtering technique in on-axis configuration [19]. In a limited number of cases the X-ray diffractogram of the substrate showed low-intensity reflections associated with orientations different from the (001) one. These features, however, never affected the transport and the superconducting properties of the films. A single stoichiometric $Nd_{1.85}Ce_{0.15}CuO_4$ target, homemade prepared by standard solid-state reaction, was used as sputtering source [20]. The samples were deposited at 850 °C in a mixed atmosphere of Ar and O_2 with ratio O_2/Ar ~1% at a total pressure of 170 Pa. After deposition at a power equal to 12 W, the samples were annealed in vacuum for about 30′ at the same growth temperature. Whereas these steps were all realized in situ, the additional heat treatment needed to induce superconductivity via further reduction of the oxygen content was performed ex-situ in ambient atmosphere of Ar above 850 °C. A precise measurement of the oxygen concentration in the samples unfortunately was not possible due to intrinsic difficulties of making this kind of estimate in electron-doped cuprates, here further enhanced by the presence of oxygen in the substrate.

By using the technique described above, films with a thickness of 2500 Å were obtained at a growth rate of 12 Å/min. Film quality was monitored by X-ray diffraction (XRD) measurements, scanning electron microscopy and wavelength dispersive spectroscopy (WDS). XRD data were collected by means of a Philips X'Pert-MRD high resolution diffractometer equipped with a four circle cradle. The incident beam is generated by X-ray tube focusing Cu $K\alpha_1$ wavelength on the sample by an asymmetric four crystal Ge(220) Bartels monochromator followed by a graded parabolic Guttman mirror. The diffracted beam reaches the detector with an angular divergence of 12 arcsec crossing a triple axis attachment and undergoing three (002) reflections within a channel cut Ge Crystal. The scanning electron microscope LEO EVO50 used in this work is equipped with a wavelength dispersive spectrometer, Oxford Wave 700, which performs the compositional analysis of the samples and collects the X-ray spectrum starting from elements with $Z \geq 4$. It acquires a spectrum of wavelengths (a chemical element at a time) with a high resolution, ranging from 2 to 20 eV, depending on the element. The resistivity was measured as a function of the temperature in a standard four-probe configuration.

3. Compositional and structural characterization

It is widely known that crystal structure distortions may have large effects on the properties of HTS. It is therefore of great interest to analyze possible structural changes induced in the *n*-type superconductors by the oxygen reduction process. Neutron powder diffraction data used to investigate the local structure of overdoped superconducting NCCO samples gave indications of appreciable deviations from the ideal T' lattice structure in which electron-doped cuprates are known to crystallize. In particular, a salient feature is considered to be the spatial inhomogeneity of the CuO_2 planes which are not flat, but rather consist of domains of tilted and strained CuO_4 plaquettes induced by oxygen displacements and regions of flat, undistorted CuO_4 plaquettes [21]. This lattice distortion, which appears to be an intrinsic property of the crystal structure, has been supposed to be responsible of the formation of lattice-induced hole states which for cerium concentrations close to optimal doping participate in the charge transport together with electron-like carriers [22].

A systematic analysis of the compositional and structural properties of our samples as a function of the growth conditions as well as of the post-deposition annealing has been performed. In particular, for the latter a temperature range extending from 500 °C to 950 °C has been explored, with a regular step $\Delta T = 50$ °C. The composition has been studied by WDS on several sample areas of ~100 μm^2, making a comparison of the results obtained before and after the thermal treatment needed to obtain the superconductivity. The possible presence of some spurious elements was checked by WDS scans on the whole surface, lasting approximately 10 h per sample in a range of wavelengths going from 1.14 to 175 Å. The results obtained on one of the samples are shown in Fig. 1 for a reduced wavelength range, extending from 1.14 to 24 Å. In this range all the peaks can be