

Epitaxial growth of “infinite layer” thin films and multilayers by rf magnetron sputtering

L. Fàbrega^{a)} E. Koller, J. M. Triscone, and Ø. Fischer

Département de Physique de la Matière Condensée, Université de Genève, 24 quai Ernest Ansermet, 1211 Genève, Switzerland

(Received 28 October 1996; accepted 20 October 1997)

We report on the preparation and characterization of epitaxial $ACuO_2$ ($A = Sr, Ca, Ba$) thin films and multilayers with the so-called infinite layer (IL) structure, by rf magnetron sputtering. Films and multilayers without Ba have a remarkable crystal quality, whereas those containing this large ion are often multiphased and unstable. In spite of the excellent crystalline quality of these samples, obtaining thin films having both IL structure and displaying superconducting properties has not succeeded; our pure IL samples display semiconducting behavior, and the different procedures tried in order to dope them—annealings, introduction of disorder or cation vacancies, artificial layering—have failed. These results support that the pure IL structure $ACuO_2$ ($A =$ alkaline earth) cannot superconduct.

I. INTRODUCTION

Copper oxides $ACuO_2$ ($A =$ alkaline earth) with the so-called “infinite layer” (IL) structure,¹ consisting of an infinite stacking of A and CuO_2 planes, have aroused in the past years a live interest, because of two main reasons. First, this is the simplest possible structure containing Cu–O planes, which are known to be essential to the occurrence of high temperature superconductivity.² Second, the report of high temperature superconductivity, presumably of p -type, in bulk samples having this structure [(Ba, Sr) CuO_2 , with $T_c \approx 45$ –60 K³ and (Sr_{0.7}Ca_{0.3})_{1-y} CuO_2 , with $T_c \approx 110$ K⁴] indicated that the IL structure might be doped with both holes and electrons, as n -type superconductivity ($T_c \approx 40$ K) was also observed in the IL compounds Sr_{1-x}L_x CuO_2 ($L = La, Nd, Pr^5$); in addition, this result would break down the idea that apical oxygens are needed to have hole-doped high temperature superconductors (HTS). Finally, HTS with this structure would be specially interesting for future applications, since a very moderate anisotropy is expected from their crystal structure, and it is well known that the layered character of HTS is one of their main constraints for their technological use.

The study of the physical properties of IL materials has been, however, very poor because of the difficulties in their preparation. With the exception of the first reported IL phase, of composition Sr_{0.14}Ca_{0.86} CuO_2 ,¹ this structure is metastable or unstable; bulk samples with the compositions of interest can thus only be obtained by high pressure synthesis.⁶ These are polycrystalline and often multiphased, or contain structural defects.^{3,4,7,8}

These features, together with the usually reported low superconducting fractions, had in fact raised questions concerning whether the reported superconducting properties of these samples were really due to the IL phase or to some minor impurity phase, with structure likely related to those of the other p -type HTS. Azuma and co-workers^{3,4} detected defect layers in bulk superconducting (Sr_{1-x}Ca_x)_{1-y} CuO_2 samples and argued that they might provide charge carriers to the neighboring Cu–O planes and thus lead to a localized, inhomogeneous superconductivity; recently, a study by Shaked *et al.*⁹ on samples with different fractions of IL phase lead the authors to the conclusion that the IL structure is not superconducting.

Thin film techniques, allowing the growth of phases out of the equilibrium, seemed to constitute an excellent alternative way to obtain epitaxial IL samples with a good control of the structure. Indeed, investigations in the past years have led to the fabrication of high quality IL thin films and multilayers by sputtering,^{10–15} laser ablation,^{16–20} and MBE²¹ techniques. Moreover, the research in this area has opened the path to the design of new (superconducting) materials, because of the possibility of growing heterostructures with very short wavelengths.

Unfortunately, the IL thin films and multilayers have added confusion to the existing questions regarding the occurrence of superconductivity in the IL structure (with the exception of the electron-doped Sr_{1-x}L_x CuO_2 , $L = La, Pr, Nd$). The obtaining of thin films both having this structure and displaying superconducting properties turned out to be very difficult.^{10–25} Furthermore, the possibility of the presence of apical oxygens may not be disregarded in the very few superconducting thin films²³ and multilayers^{19,24} with presumed IL structure. It should be specially remarked here that, within the

^{a)}Present address: Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., 08193 Bellaterra, Spain.

variety of reported IL multilayers with different alkaline earth cations (Ca, Sr_{1-x}Ca_x, Sr, Ba),^{15,19,20,24,25} only those containing Ba^{19,24} display superconducting behavior, and this is precisely the alkaline earth ion considered too large to stabilize the IL structure; it has been argued,^{6,19} however, that the presence of apical oxygens might stabilize this phase and give rise to superconductivity. On the other hand, superconducting oxycarbonate thin films have been recently obtained^{26,27} by the incorporation of C present in the deposition atmosphere or as impurity in the targets; these compounds may be regarded as IL blocks with an ordered partial substitution of CuO₂ by carbonate groups CO₃²⁻, resulting in a modulation of the IL structure. Remarkably, the *c*-axis parameter of the structure appears rather insensitive to the C incorporation. Because of this, the presence of C is difficult to detect; it has been observed by Rutherford Back Scattering (RBS), and it has been claimed to be detected by TEM.^{26,27} As a small amount of C seems to have dramatic effects on the appearance of superconductivity, and because targets are usually made from carbonates, it is experimentally difficult to rule out the possibility of C traces in any thin film.

We report here on the epitaxial growth of IL thin films and multilayers by rf planar magnetron sputtering, in the on- and off-axis configurations. The samples have been mainly characterized by x-ray diffraction (XRD) and also by AFM and electrical resistivity measurements. The ACuO₂ thin films and multilayers (A = Sr, Ca, Sr_{1-x}Ca_x) reveal a high crystalline quality, likely because of the very small lattice mismatch with the substrate [(100) SrTiO₃]. This work confirms thus the possibility of controlling the growth of these copper oxides in the scale of a few Ångström by the sputtering technique. Indeed, we have been able to obtain heterostructures with a periodicity down to 20 Å, the shortest ever reported with this technique, to our knowledge. The control of modulation at such an essentially atomic level demonstrates the capability of sputtering for an atomic construction of oxide materials.

All the obtained IL samples are semiconducting in the temperature range where superconductivity might be expected, though their resistivities may differ by several orders of magnitude depending on their composition. We have explored different routes of doping (annealings, introduction of disorder by alloying or artificial layering, cation deficiencies, introduction of carbonate groups). The persistent semiconducting behavior and high resistance values, observed for all the grown samples with clear IL structure, are indicative of the difficulties to introduce free charge carriers in these compounds.

On the other hand, high quality thin films and multilayers with barium, more difficult to stabilize, can be obtained only when CO₂ is present in the sputtering

atmosphere. It turns out that these films have a more complex structure, Ba₂CuO₂(CO₃), different from the IL, as discussed in Refs. 32 and 33.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

A. Sr_{1-x}Ca_xCuO₂ thin films (0 ≤ *x* ≤ 1)

Sr_{1-x}Ca_xCuO₂ (SCCO) thin films with IL structure were grown by single target planar rf magnetron sputtering on (100) SrTiO₃ substrates, at temperatures between 550 °C and 620 °C, in a mixture of Ar and O₂ gases, as previously reported.^{13,14} Both the on- and off-axis configurations, in which the sample and the target are face to face and at 90°, respectively, have been used. The total pressure in the UHV deposition chamber was of 0.7 Pa (10 Pa) in the on-axis (off-axis) depositions; the oxygen partial pressure was of about 10–20%. The output power to the targets (∅ = 55 mm) was $P \approx 100$ W. Three homemade targets of composition $x = 0, 0.3,$ and 1 were used, prepared from SrCO₃, CaCO₃, and CuO powders. The thickness of the films was between 250 and 2000 Å.

The films so obtained have the *c*-axis of the IL structure parallel to the growth direction. The *c* parameters extracted from the position of the (001) peak in the XRD are, respectively, 3.45 Å, 3.33 Å, and 3.18 Å for the compositions $x = 0, 0.3,$ and 1. Off-angle scans for the (101) reflection indicate that the films are epitaxial, with the *a*, *b* axes oriented along the *a*, *b* axes of the substrate. These features may be appreciated in Fig. 1, displaying the θ - 2θ and ϕ scans for a SrCuO₂/CaCuO₂ (SCO/CCO) bilayer grown in the off-axis configuration. This figure also reveals the epitaxial growth of CCO on SCO, with cell parameters similar to those of the individual thin films of each compound.

The narrowness of the peaks and the rocking curves [full-width at half-maximum (FWHM) of about 0.10°] reveals the excellent crystalline quality of the samples. Indeed, an intensity modulation around the main reflections is observed in very thin films, as a result of finite thickness effects (see Fig. 2). This feature allows for an accurate determination of the deposition rates, which are about 60 Å/min and 10 Å/min, respectively, for the on- and off-axis depositions; the number of deposited unit cells (u.c.) per unit of time slightly increases with the cation size.

B. ACuO₂/BCuO₂ multilayers (A = Sr; B = Sr_{1-x}Ca_x; *x* = 1, 0.3)

ACuO₂/BCuO₂ multilayers (A = Sr; B = Sr_{1-x}Ca_x; $x = 1, 0.3$) with periodicities $20 \text{ \AA} \leq \Lambda \leq 180 \text{ \AA}$ have been obtained with the same deposition conditions as the thin films described in Sec. A. Sequential depositions

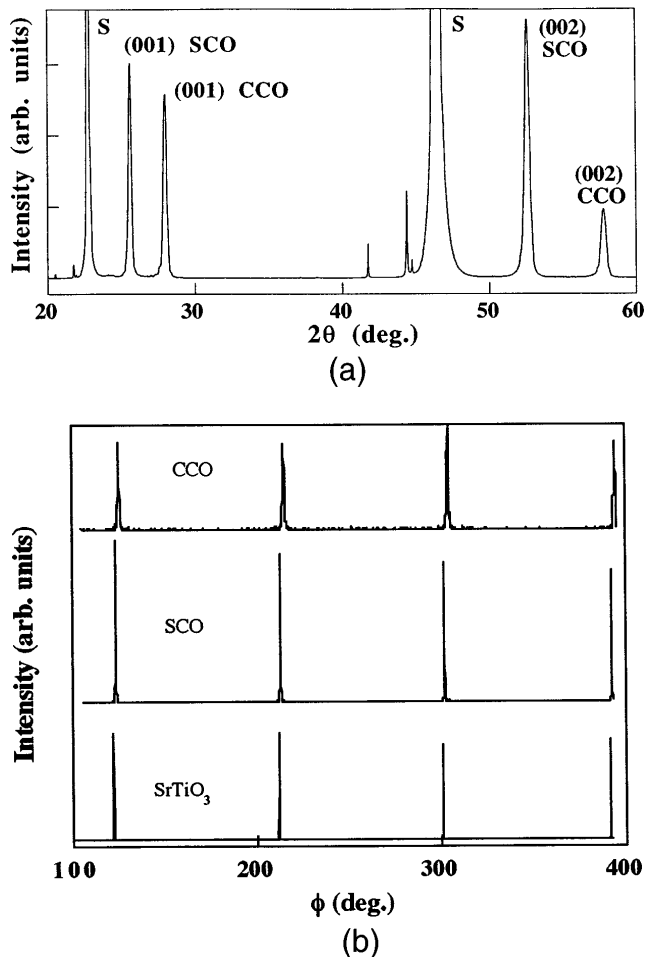


FIG. 1. (a) θ - 2θ scan of a SCO/CCO bilayer with IL structure, grown in the off-axis configuration. All the unindexed peaks belong to the substrate. (b) ϕ -scans along the (101) reflections of the substrate and the SCO and CCO layers. The presence of the four reflections at the same position indicates that the IL films grow epitaxially, axis-on-axis on the substrate.

under the two rf guns containing the ACuO₂ and BCuO₂ targets were carried out by using a computer-controlled step motor to rotate the sample holder. A buffer layer of SCO or SCCO of about 300–400 Å deposited on the (100) SrTiO₃ substrate has often been used to improve the quality of the multilayers, which have a total thickness between 900 and 2000 Å. The satellite peaks in the XRD have confirmed the modulated IL structure, as shown in Fig. 3; the splitting of the peaks in this figure is due to the separation of the $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections. This fact indicates the very good structural quality of the sample, also revealed by the narrow rocking curves (FWHM \approx 0.12 Å).

The periodicities Λ obtained from the position of the satellite peaks are in agreement with the deposition rates of each of the components, extracted from finite size effects in very thin films. The evolution of the satellite positions compares well to theoretical calculations

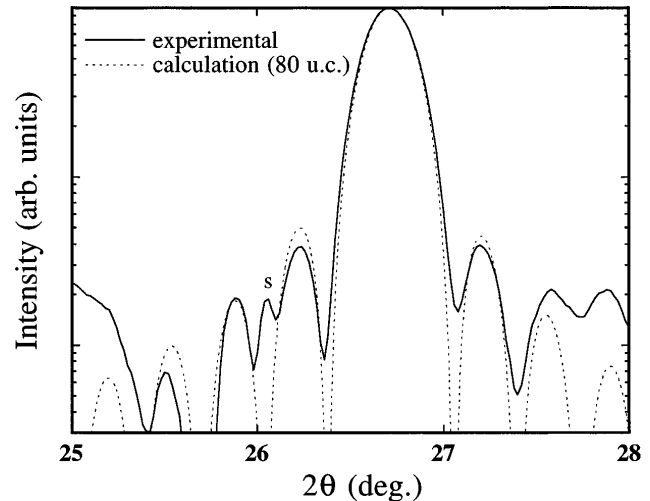


FIG. 2. Modulated intensity around the (001) peak of an epitaxial SCCO film, as a result of its finite thickness ($d = 268$ Å). The dashed line corresponds to the theoretical XRD pattern, assuming $c = 3.334$ Å.

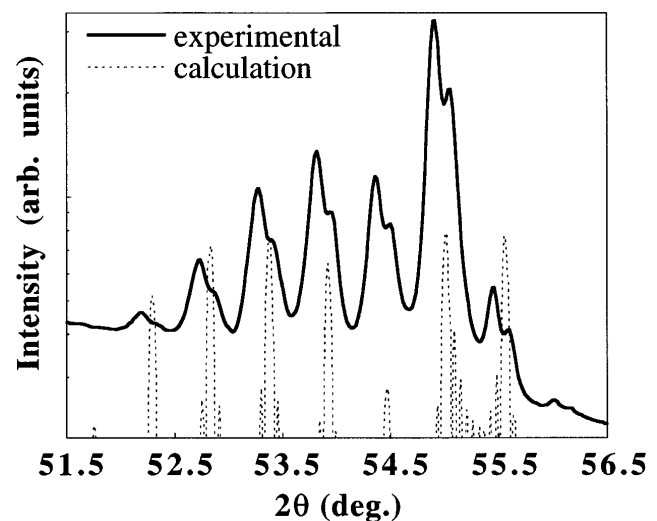


FIG. 3. θ - 2θ scan of a SCCO/SCO (36/18 u.c.) multilayer with $\Lambda = 182$ Å. The satellite peaks around the (002) peak of the pure IL structure reveal the artificial modulation, perfectly matching the theoretical calculation. The splitting of the peaks, corresponding to the $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections, reveals the excellent quality of the sample.

assuming an ideal IL structure with abrupt interfaces, as shown in Fig. 3; the relative intensities between the satellites differ, however.

Experimentally, satellite peaks in SCO/CCO multilayers disappear for $\Lambda \leq 26.3$ Å, corresponding to 4×4 u.c., and are substituted by a single peak. The theoretical calculations reveal that this is indeed the position for the main reflection of the short period multilayers, but it might also correspond to an alloy with the IL structure and the Sr/Ca ratio of the multilayers. Although satellite peaks for these short periodicities

are expected to be weak, and some of them might be hidden by substrate peaks, we must thus consider the possibility of cationic interdiffusion (thermal or related to the growth mechanism), which might lead to the formation of an alloy for these short wavelengths. The existence of low angle reflections for $\Lambda \geq 20.2 \text{ \AA}$ (2×4 u.c.), as shown in Fig. 4, indicates the presence of a certain chemical modulation at these length scales and therefore sets an upper limit to the extent of the interdiffusion. These low angle peaks are not present any more for the shortest wavelength tried, $\Lambda 13.5 \text{ \AA}$, corresponding to 2×2 u.c.

Cationic interdiffusion may in fact account for the different in the relative intensities of satellite peaks of theory and experiment (Fig. 3). A first step toward the analysis of the extent of this effect has been thus made by incorporating the presence of an interface with finite thickness in our XRD simulations. In Fig. 5 we display the experimental pattern for the $\Lambda = 140 \text{ \AA}$ multilayer together with the calculations corresponding to an abrupt—without strain—interface between SCO and CCO [Fig. 5(a)], and an interface extending up to 2 u.c. because of cationic interdiffusion [Fig. 5(b)]. Comparison of both do not allow us to conclude whether or not interdiffusion is important; more sophisticated models, taking into account strain and dislocations, should be used to better describe our diffraction patterns and extract a definitive conclusion in that sense.

We would like to emphasize that, in spite of the limitations imposed by the possible interfaces with finite thickness, the shortest modulations of the multilayers

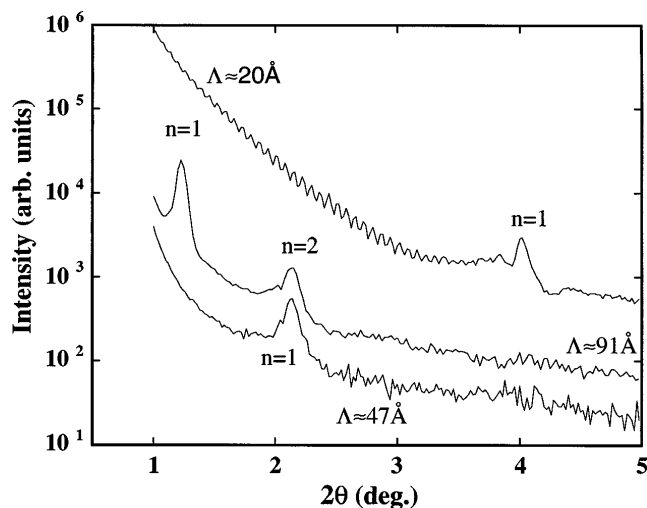


FIG. 4. Low angle θ - 2θ scans of three SCO/SCCO multilayers with periodicities $\Lambda = 20 \text{ \AA}$, 47 \AA , and 91 \AA . The peaks correspond to the first reflection of the artificially modulated structures, and indicate thus their chemical modulation. Note also the short-period modulated intensity for the $\Lambda = 20 \text{ \AA}$ (3×3 u.c.) sample, indicative of its extremely flat surfaces.

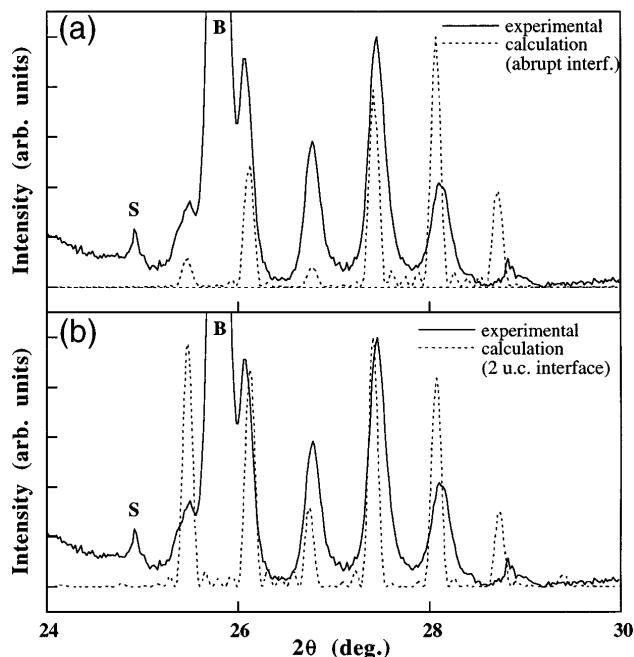


FIG. 5. Comparison of the experimental XRD pattern of a SCO/CCO multilayer of $\Lambda = 139.8 \text{ \AA}$ with the theoretical calculations assuming (a) a perfect (abrupt) interface or (b) an incoherent interface extending to 2 u.c., as a result of cationic interdiffusion. The peaks denoted by *S* and *B* in the experimental pattern belong to the substrate and to the SCO buffer layer, respectively.

obtained in this work are in the scale of the nanometer. To our knowledge, these are the shortest periodicities ever obtained by sputtering in oxide materials and indicate that this deposition technique can be used to build (design) new structures with a control within the atomic level. Besides, we draw the attention to the *high quality* of these heterostructures, evidenced, for instance, by the short period modulations of the low angle XRD patterns displayed in Fig. 4. They correspond to the finite thickness effect of the overall multilayer, and therefore indicate that its surface is very smooth. This fact was confirmed by the AFM analysis of several films, revealing a very smooth surface background. Finite thickness effects are commonly observed in our thinner samples.

C. BaCuO₂ thin films

Growth of IL thin films with composition BaCuO₂ appears much more delicate than for the other (smaller) alkaline earth cations. This difficulty is thought to be related both to the size of the Ba²⁺ ion, considered too large to stabilize the IL structure,⁶ and to the existence of a highly stable cubic phase ($a = 18.28 \text{ \AA}$) for this compound. In fact, the IL BaCuO₂ compound has not been obtained in bulk form, to our knowledge.

We obtain the stable cubic structure in films prepared in a very wide range of deposition conditions and on

different substrates (LaAlO₃, MgO, SrTiO₃). However, a second phase has been identified in samples grown on (100) SrTiO₃ in the on-axis configuration, for a very narrow window of parameters [$P \approx 50$ W, $T_s = 620$ °C, $p(\text{O}_2)/p(\text{Ar}) = 2$, $p = 0.7$ Pa]. This phase has a lattice parameter of about 8.2 Å, as shown in the θ - 2θ scan of Fig. 6(a). It is rather unstable and coexists always with the highly stable one. These two facts, together with the poor crystal quality, have prevented deeper analysis of its structure, which might be related to the IL, as reported by Adachi *et al.*²⁷; it might be a modulation of the IL structure, as a result of the ordered incorporation of either some impurity carbonate groups or apical oxygens in the IL structure, which would contribute to its stabilization, as discussed above. The second possibility is supported by the fact that the sputtering gas required to obtain this phase has a much higher oxygen content than the atmosphere used to grow epitaxial IL SCCO thin films. We note that this fact is in contrast with the reports by other groups, who have succeeded in obtaining the BCO in IL or related structures by using almost identical deposition conditions to those for the other alkaline earth cations (Sr, Ca).

Following the work by Adachi *et al.*,²⁷ we have recently analyzed the effect of introducing CO₂ in the sputtering atmosphere. For a very wide range of tempera-

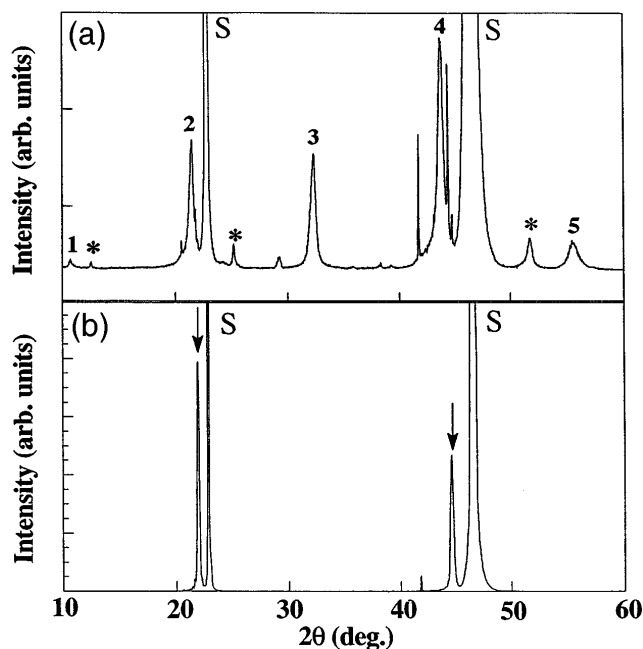


FIG. 6. θ - 2θ scans of two BCO thin films grown on (100) SrTiO₃ substrates, without (a) and with (b) CO₂ ($T \sim 560$ °C). The arrows in (b) indicate the positions of the (001) and (002) peaks of a tetragonal lattice with $c \approx 4.1$ Å. The numbers in (a) indicate the (00 n) peaks of a lattice with parameter $c \approx 8.2$ Å, may be a double modulation of the structure of (b); # denotes the position of both the (600) reflection of the cubic BCO phase and a weak peak of the sample holder; stars indicate unidentified peaks.

tures and CO₂ partial pressures, and with the other conditions similar to the above one ($p \approx 0.7$ Pa, $P = 50$ W, O₂/Ar = 2), we obtain high quality films containing a single stable phase with $c \approx 4.06 \pm 0.04$ Å on the (100) SrTiO₃ substrates. ϕ -scans along the (101) and (111) directions indicate that this phase has tetragonal crystal symmetry, with an in-plane parameter $a \approx 3.96$ Å, as one would expect for the IL structure. The θ - 2θ scans of films grown at temperatures $T \sim 560$ °C do not show any evidence of the modulation observed in samples obtained without CO₂, as may be appreciated in Fig. 6(b). However, as the deposition temperature is increased, a low angle peak corresponding to an interplanar distance of about $2c$ develops, and attains its maximum intensity at $T \approx 660$ °C. A deep analysis of the structure of *all* these films indicates that they have, in fact, a more complex, larger unit cell, with structure *different* from the IL and formula Ba₂CuO₂(CO₃). A correlation between the intensity of the mentioned low angle peak and a resistance decrease has been observed. Some of the high quality, single phased Ba₂CuO₂(CO₃) films, grown on SrTiO₃ with CO₂, are even metallic and superconducting, after annealing. Details on the structural and physical properties of these oxycarbonate samples will be published elsewhere.^{32,33} The minor phase observed in samples grown without CO₂ might have this same structure and formula, as a result of the presence of carbon impurities, in either the target or the sputtering chamber.

D. SCCO/BCO multilayers

Finally, we have also grown—in the on-axis configuration—heterostructures constituted by very thin layers of BaCuO₂ (1 or 2 u.c.) sandwiched between SCCO layers of different thickness $d(\text{SCCO})$, using deposition conditions close to those of the individual SCCO films. The existence of satellite and low angle peaks for $d(\text{SCCO}) \geq 30$ Å reveals a structural and chemical periodicity close to the designed one; we cannot tell, however, the crystal structure of the Ba–Cu–O layers. For shorter wavelengths, the satellites are substituted by a single broad peak, indicative of the deterioration of the structure. The crystalline quality of these heterostructures is poorer than that of the multilayers without Ba.

III. TRANSPORT PROPERTIES

Resistivity measurements have been systematically carried out on the thin films and multilayers by the standard four probe method, using dc currents between 1 and 50 μ A. Figure 7 displays the characteristic temperature dependence of the resistivity of the different types of IL films and multilayers we have grown.

Our IL films exhibit usually semiconductor-like behavior, indicative of the localization of the charge car-

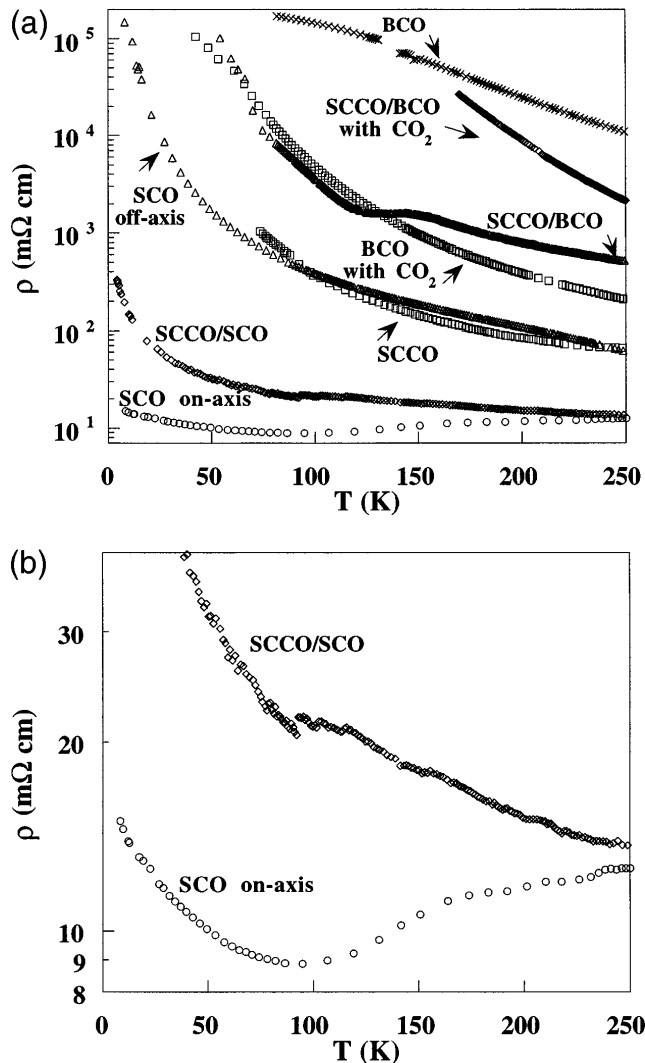


FIG. 7. (a) Temperature dependence of the resistivity of several thin films and multilayers grown in on-axis configuration; (b) low resistance part of (a).

riers. On-axis SCO films have the lowest resistivities, which are similar to those commonly reported in Sr-deficient SCO films with IL structure.^{28,29} These films display also an anomaly in the $R(T)$ curves, as shown in Fig. 7(b); at a temperature $T_a \approx 160$ K there is a sudden resistance drop, which may be of 30% ρ , followed by a semiconducting behavior at lower temperatures; above T_a the resistivity is weakly dependent on T , and sometimes metallic. This anomaly has been previously observed in Sr-deficient films,^{13,28,29} and its origin has not been clarified yet. Both the existence of the anomaly and the lower resistivity values of our SCO thin films grown in on-axis configuration, as compared to those obtained for off-axis films, seem to indicate a stoichiometry deviation (Sr loss) in the on-axis samples. This is indeed likely, due to the selective back sputtering produced by

the normal-incident, high energy ions which arrive at the film surface in this growth configuration.

SCCO and off-axis SCO films have higher resistivities; the similarity of their value and T -dependences might indeed indicate that these are characteristic of the stoichiometric IL phase. We note that the resistivities of our SCCO thin films are lower than those reported by Wong *et al.*, even after oxygen implantation.³⁰ The $R(T)$ curves of these SCCO and SCO films do not display any anomaly but are a monotonous function of temperature, which may be described by a variable range hopping dependence, $\rho \sim \exp[-(T_o/T)^m]$, with exponent $m \approx 1/4-1/3$. From the fits to the $m = 1/4$ law, an estimate of the density of states n can be obtained by assuming a certain tunneling length L between localized states. Taking $L \sim 10$ Å provides a rather high value $n \sim 2 \times 10^{20}$ cm⁻³, similar to that obtained for SrCuO₂ films by Ahn *et al.*³¹

The $R(T)$ curves of IL multilayers are also semiconducting-like with, usually, resistivity values between those of their two components; no systematics with Λ has been observed. Some of the samples evidence anomalies (flattenings) in the $R(T)$ curves.

We have carried out a series of *in situ* annealings in the above thin films and multilayers, during the cooling down process, in different atmospheres (oxidizing and reducing) and at different plateau temperatures ($250 \leq T \leq 500$ °C) and times ($15' \leq \Delta t \leq 90'$). These annealings have very little or negative effect on the values and temperature dependence of ρ , unless at temperature close to those of the formation of the phase; a degradation of the crystallinity and a clear resistivity increase are observed in the latter case.

Thin films and multilayers containing BCO and deposited without CO₂ have higher resistances than all the other compounds we have grown. BCO thin films with the presumed surmodulated IL phase are strongly insulating, but with somewhat lower resistance than those of the single-phased cubic BCO films; this resistance can be further lowered in the heterostructures containing thin BCO layers between thick SCCO layers, as shown in Fig. 7. It is difficult to tell, though, if these lower resistivities correspond to the overall heterostructure or arise from the less resistive individual SCCO layers.

IV. CONCLUSIONS

In summary, we have grown a wide variety of ACuO₂ thin films and multilayers, with different cations and periodicities. Structural characterization has been mostly restricted to XRD, due to the samples' instability and sensibility to humidity.

Films and multilayers without Ba have the IL structure, display an excellent crystal quality, and are stable if stored in a dry atmosphere. These results are indicative

of the ability of thin film techniques, like sputtering, to obtain these metastable phases with good structure control. On the contrary, films containing Ba are of less evident crystalline structure and quality, and usually degrade very fast, as it could be expected from the large size of this ion, which has been reported to make the IL structure highly unstable. When CO₂ is introduced in the sputtering atmosphere, BCO films become more stable. They display, however, a larger and more complex unit cell, resulting from a modulation of the IL structure; these films, rather than having the IL structure, may be considered as oxycarbonates with formula Ba₂CuO₂(CO₃).

All the obtained samples are semiconducting, with the only remarkable exception of the Ba₂CuO₂(CO₃) films; these latter are the only ones not having the IL structure, and can be made metallic and superconducting by annealing, as reported in Ref. 32. From the XRD and resistance measurements, a relationship between crystal quality of IL compounds and their electric properties may be drawn; samples with better crystallinity have higher resistivities, whereas those which are likely to contain a certain amount of defects or impurities have lower resistivity values, and may become eventually superconducting. Further studies of the microstructure of these samples—by TEM, for instance³—would help to confirm this conclusion but they have been hindered up to now because of the films' degradation.

ACKNOWLEDGMENTS

We would like to thank Mme Schnellmann for target preparation. This work was supported by the Fonds National Suisse de la Recherche Scientifique. Financial support from the Spanish Ministerio de Educación y Ciencia (L.F.) is acknowledged.

REFERENCES

1. T. Siegrist, S. M. Zahurac, D. W. Murphy, and R. S. Roth, *Nature (London)* **334**, 231 (1994).
2. R. J. Cava, *Nature (London)* **351**, 518 (1991).
3. M. Takano, M. Azuma, Z. Hiroi, Y. Bando, and Y. Takeda, *Physica C* **176**, 441 (1991).
4. M. Azuma, Z. Hiroi, M. Takano, Y. Bando, and Y. Takeda, *Nature (London)* **356**, 775 (1992).
5. M. G. Smith *et al.*, *Letters to Nature* **351**, 549 (1991).
6. M. Takano *et al.*, *Physica C* **159** 375 (1989).
7. Z. Hiroi, M. Azuma, M. Takano, Y. Bando, and Y. Takeda, *Physica C* **208**, 286 (1993).
8. X. Zhou, J. Li, F. Wu, B. Yin, S. Jia, Y. Yao, and Z. Zhao, *Physica C* **223**, 30 (1994); X. Zhou, F. Wu, B. Yin, W. Liu, Ch. Dong, J. Li, W. Zhu, S. Jia, Y. Yao, and Z. Zhao, *Physica C* **233**, 311 (1994).
9. Shaked, Y. Shimakawa, B. A. Hunter, R. L. Hitterman, J. D. Jorgensen and P. D. Han, and D. A. Payne, *Phys. Rev. B* **51**, 11 784 (1985).
10. I. Yazawa, N. Terada, K. Matsutani, R. Sugise, M. Ja, and H. Ihara, *Jpn. J. Appl. Phys.* **29**, L566 (1990).
11. Y. Terashima, R. Sato, S. Takeno, S. Nakamura, and T. Miura, *Jpn. J. Appl. Phys.* **32**, L48 (1993).
12. J. G. Wen, H. Yakabe, A. Kume, Y. Shiomara, N. Koshizuka, and S. Tanaka, *Physica C* **228**, 279 (1994).
13. E. Koller *et al.*, *J. Alloys and Compounds* **195**, 303 (1993).
14. E. Koller, L. Miéville, L. Fàbrega, J.-M. Triscone, and Ø. Fischer, *Physica C* **235–240**, 707 (1994).
15. T. Satoh, H. Adachi, Y. Ichikawa, K. Setsune, and K. Wasa, *J. Mater. Res.* **9**, 1961 (1994).
16. M. Kanai, T. Kawai, and S. Kawai, *Appl. Phys. Lett.* **58**, 771 (1991).
17. M. Yoshimoto *et al.*, *Physica C* **185–189**, 2085 (1991).
18. Q. Y. Ma, P. Dosanjh, I. Enten, R. Liang, and J. F. Carolan, *J. Appl. Phys.* **75**, 3089 (1994).
19. D. Norton, B. C. Chakoumakos, J. D. Budai, D. H. Lowndes, B. C. Sales, J. R. Thompson, and D. K. Christen, *Science* **265**, 2074 (1994).
20. D. P. Norton, J. D. Budai, D. H. Lowndes, and B. C. Chakoumakos, *Appl. Phys. Lett.* **65**, 2869 (1994).
21. H. S. Wang, W. Dietsche, L. Viczian, and X. Q. Pan, *Physica C* **235–240**, 977 (1994).
22. X. Li *et al.*, *Jpn. J. Appl. Phys.* **31**, L217 (1992).
23. R. Feenstra, X. Li, M. Kanai, T. Kawai, S. Kawai, J. D. Budai, E. C. Jones, Y. R. Sun, J. R. Thompson, S. J. Pennycook, and D. K. Christen, *Physica C* **224**, 300 (1994).
24. X. Li, M. Kanai, and T. Kawai, *Jpn. J. Appl. Phys.* **33**, L18 (1994).
25. A. Gupta, T. M. Shaw, M. Y. Chern, B. W. Hussey, A. M. Guloy, and B. C. Scott, *J. Solid State Chem.* **114**, 190 (1995).
26. J. L. Allen, B. Mercey, W. Orellier, J. F. Hamet, M. Hervieu, and B. Raveau, *Physica C* **241**, 158 (1995).
27. H. Adachi, M. Sakai, T. Satoh, and K. Setsune, *Physica C* **244**, 282 (1995).
28. X. Li, T. Kawai, and S. Kawai, *Jpn. J. Appl. Phys.* **31**, L934 (1992).
29. D. P. Norton, B. C. Chakoumakos, E. C. Jones, D. K. Christen, and D. H. Lowndes, *Physica C* **217**, 146 (1993).
30. A. S. Wong, Q. Y. Ma, P. Dosanjh, J. F. Carolan, and W. N. Hardy, *J. Appl. Phys.* **78**, 1382 (1995).
31. C. Ahn, J.-M. Triscone, N. Archibald, M. Decroux, R. H. Hammond, T. Geballe, Ø. Fischer and M. R. Beasley, *Science* **269**, 373 (1995).
32. E. Koller, L. Fàbrega, J.-M. Triscone and Ø. Fischer, *J. Low Temp. Phys.* **105**, 1325 (1996).
33. E. Koller, L. Fàbrega, J.-M. Triscone and Ø. Fischer, unpublished.