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Dependence of the critical temperature on n in $(BaCuO_2)_2/(CaCuO_2)_n$ superlattices

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$(BaCuO_2)_2/(CaCuO_2)_n$ superconducting superlattices have been grown by pulsed laser deposition for n ranging from 1 to 6. The critical temperature was found to depend strongly on the growth conditions. A maximum T_c value of about 80 K (zero resistance temperature) was found for superlattices grown at high oxygen pressure ($P_{O_2} \simeq 0.8$ mbar) and relatively high temperature ($T_g \simeq 600$ °C). The dependence of T_c on the number n of $CaCuO_2$ layers (for superlattices grown exactly in the same conditions) was investigated. T_c versus n showed the expected behavior with a maximum T_c value of 80 K for $n = 2-3$. However, such value is somewhat lower than that expected for a cuprate structure containing 3–4 CuO_2 planes and having an optimum carrier concentration. Two possible explanations for this effect can be envisaged. The first one deals with the chemistry of the "charge reservoir" block, the second one with the special role of interelectron interaction in these highly disordered artificial structures. Finally, it is shown that, taking into account the degree of disorder, a shift of T_c of about 20 K relative to the *bulk* value T_{c_0}, consistent with the microscopic parameters of these materials, can be foreseen. [S0163-1829(98)51334-3]

Layer by layer growth techniques of epitaxial thin films have opened new perspectives for the atomic engineering of artificially layered cuprate superconductors.[1] Such man-tailored materials allow us to study the dependence of the superconducting properties on some specific structural features. In this paper we report on the study of the critical temperature dependence on the thickness of the Ca-Cu-O layer in $(BaCuO_2)_2/(CaCuO_2)_n$ superlattices.

Starting from epitaxial films of the "infinite layers" (IL) (Ca, Sr, Ba)CuO_2 compounds,[2,3] several superlattices have been obtained by stacking in a sequence IL layers having different compositions. Most interesting, from the point of view of the superconducting properties, is the case of superlattices containing $BaCuO_2$ layers.

The Ba-based IL structure is very unstable.[4] It can easily include excess oxygen ($BaCuO_{2+\delta}$), thereby acting as a charge reservoir (CR) block for the second constituent IL layer $(Ca_{1-x}Sr_x)CuO_2$. Superconductivity has been reported by several authors for the $BaCuO_{2+\delta}$/(Ca, Sr)CuO_2 superlattices[5,6] with transition temperatures as high as about 70 K (zero resistance temperature).[7,8]

In Refs. 8 and 9 it was shown that high quality $(BaCuO_2)_{n_1}/(CaCuO_2)_{n_2}$ superlattices can be grown for $n_1 = 2$ and n_2 ranging from 1 to 6 (see, for instance, Fig. 1 of Ref. 9). It was also shown that these superlattices have a superconducting transition when grown at relatively high pressure of molecular oxygen (0.2 mbar) and that the best results are obtained for molecular oxygen pressures of about 0.8 mbar and high growth temperatures (about 600 °C). Unfortunately, the high oxygen pressure required for the growth of superconducting superlattices makes impossible the use *in situ* of the reflection high energy electron diffraction (RHEED) diagnostic. Therefore a structural analysis of the superlattice can be obtained only afterward by x-ray diffraction.

Superlattices with n varying from 1 to 6 were grown by pulsed laser deposition (PLD). Details on the growth technique and on the procedure used to calibrate the growth rate of the individual layers were given in Ref. 10. Superlattices with different values of n_2 were grown exactly at the same conditions. The transition temperature of these superlattices was studied as a function of the thickness of the Ca-Cu-O layer.

In Fig. 1 the diffraction spectra of four different $(BaCuO_{2+\delta})_2/(CaCuO_2)_{n_2}$ superlattices are shown. The spectra refer to superlattices grown leaving unchanged the thickness of the $BaCuO_{2+\delta}$ layer and increasing gradually the thickness of the $CaCuO_2$ layer. Peaks are indexed using the standard convention for superlattices. The period Λ of the $(BaCuO_2)_2/(CaCuO_2)_{n_2}$ superlattice [$\Lambda = 2c_1 + n_2 c_2$, where c_1 and c_2 represent respectively the thickness of a single ($BaCuO_{2+\delta}$) layer in the CR block, and the thickness of a single ($CaCuO_2$) layer in the IL block] can be calculated from the angular distance between the zeroth order peak (SL_0) and the first order satellite peaks (SL_{-1} and SL_{+1}) using the formula $\Lambda = \lambda/2|\sin\vartheta_{(\pm 1)} - \sin\vartheta_0|$, where λ is the x-ray wavelength (Cu $K\alpha$ radiation in the present case), $\vartheta_{(\pm 1)}$ and ϑ_0 are respectively the diffraction angles of the first order satellite peaks and of the zeroth order peak. The average lattice parameter $\overline{c}$ [$= (2c_1 + n_2 c_2)/(2 + n_2)$] can be estimated from the angular position of the zeroth order peaks [$SL_0(001)$ and $SL_0(002)$]. In the case of the (a) and (d) spectra the ratio $\Lambda/\overline{c}$ yields an integer number, respectively, 4 and 5. This result indicates that these superlattices consist

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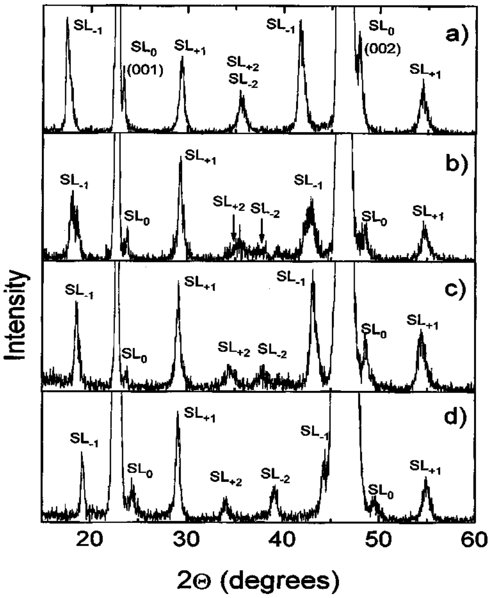

FIG. 1. X-ray diffraction spectra for four superlattices grown increasingly steadily from (a) to (d) the thickness of the Ca-Cu-O block. Peaks are indexed using the standard convention for superlattices: SL_0 indicate the zeroth order diffraction peaks, while $SL_{\pm N}$ the Nth order satellite peaks.

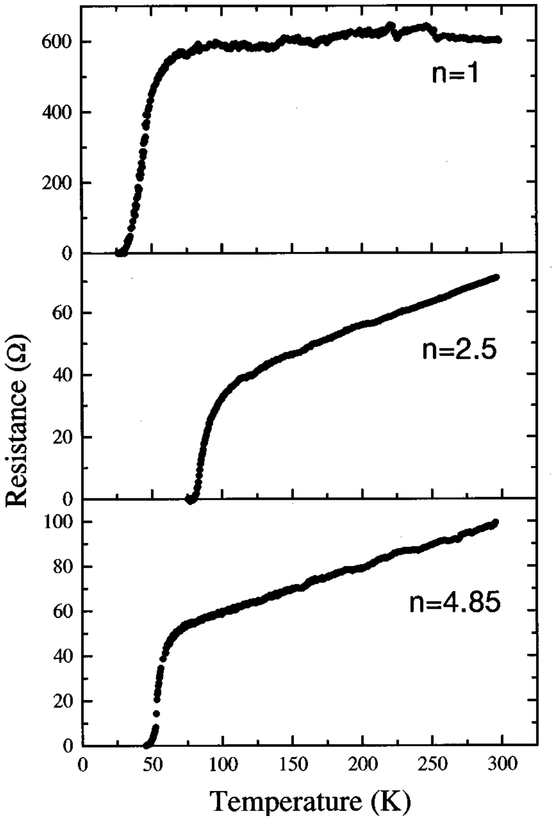

FIG. 2. Resistance vs temperature for three superlattices with different n (number of $CaCuO_2$ layers in the IL block).

of an exact integer number of individual layers and contain, respectively, two and three $CaCuO_2$ layers. On the other hand, the spectra (b) and (c) refer to intermediate situations where the thickness of the IL block does not correspond to an integer number of $CaCuO_2$ layers. Namely, using the above formulas, one obtains respectively $n_2 = 2.4$ and 2.7. Such incommensurability between the chemical period and the crystallographic structure is, to some degree, unavoidable when dealing with superlattices grown by pulsed laser deposition without *in situ* RHEED diagnostic for the layer by layer growth. The incommensurability between chemical and crystallographic structures possibly gives rise to a unit cell of mixed composition $[(Ca_{1-y}Ba_y)CuO_{2+\delta'}]$ at the interface between the $(BaCuO_{2+\delta})$ and $(CaCuO_2)$ crystallographic cells.

The occurrence of superconductivity in these superlattices is associated with the inclusion of extra oxygen ions in the $[BaCuO_2]_2$ block (CR block) due to the relatively high oxygen pressure during growth (about 0.8 mbar). In this case the layer stacking sequence (in a $2 \times n$ superlattice) should be $\ldots$-BaO_x-CuO_{2-y}-BaO_x-CuO_2-$[Ca\text{-}CuO_2]_n$-$\ldots$ $(2x - y > 0)$, so that the total number of CuO_2 planes in the IL block would be $m = n + 1$. Moreover, since the growth conditions are left unchanged when increasing n (number of $CaCuO_2$ layers in the superlattice), we do not expect any variation of the total excess oxygen content in the CR block. However, because of the increase of the number of CuO_2 planes, a decrease of the average content of charge carriers per single CuO_2 plane c_h is expected: $c_h \propto 1/m$. In Ref. 11 it was shown, by means of Hall effect measurements, that the concentration of electrical carriers in a $n = 2.4$ superlattice grown at the optimum conditions is about 0.6 hole per superlattice cell. Supposing that the hole content depends only on the nature of the CR block and is not affected by the number n of $CaCuO_2$ layers, and recalling that the optimal concentration of carriers in superconducting cuprates is about 0.15–0.20 hole per CuO_2 plane (see, for instance, Ref. 12), one can find that the maximum T_c should be reached for $n \simeq 3$ $(m \simeq 4)$ and that T_c should decrease both for $n > 3$ (underdoped samples) and $n < 3$ (overdoped samples). The behavior of resistance versus temperature was measured for a large number of superlattices grown in the identical experimental conditions but having IL layers of different thickness. Both commensurate and incommensurate structures were grown. In Fig. 2 are reported the resistance versus temperature curves for three relevant samples, namely, with $n = 1$, $n = 2.5$, and $n = 4.85$. The $n = 2.5$ and 4.85 superlattices have a metallic behavior with comparable values of the resistance and a T_c lower in the case of the $n = 4.85$ superlattice; on the other hand, the $n = 1$ curve shows a nonmetallic behavior with a resistance about one order of magnitude larger relative to the $n = 2.5$ and 4.85 superlattices. In Fig. 3 we report the results for a large number of superlattices grown in the same conditions. No difference can be noticed between the commensurate and the incommensurate structures: within the experimental error all T_c values lie on the same curve. According to Fig. 3, T_c versus n indeed follows qualitatively the expected behavior with a maximum T_c occurring for n between 2 and 3. Moreover, the decrease of T_c for $n \geqslant 3$ (underdoped region) can be explained qualitatively by the decrease of carrier concentration per CuO_2 plane: in Fig. 3 the dashed line indicates the expected decrease of $T_c(n)$ (T_c was

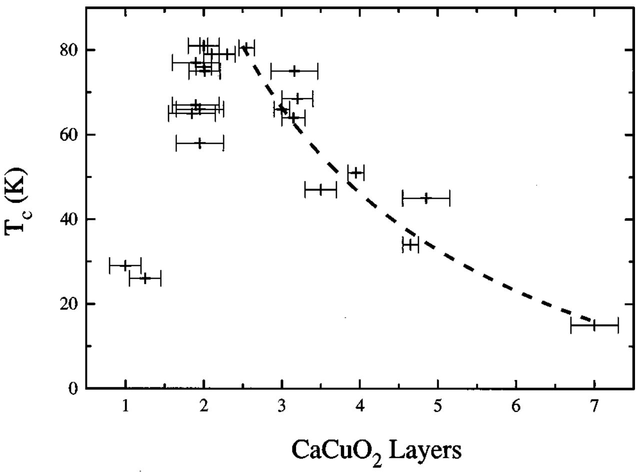

FIG. 3. Behavior of T_c vs n (number of $CaCuO_2$ layers in the IL block). The dashed line for n larger than 3 shows the expected decrease of T_c caused by the decrease of the effective concentration of electrical carriers per CuO_2 plane.

supposed to decrease linearly with c_h and to reach zero for $c_h \simeq 0.06$ hole per CuO_2 plane).

However, two major experimental findings cannot be explained according to the simple model proposed above:

(a) The maximum value of $T_c \simeq 80$ K, which occurs for $n=2,3$, is noticeably lower than that expected on the basis of the crystallographic structure of these superlattices. Namely, such structures contain 3–4 CuO_2 planes in the IL block and the expected transition temperature, for an optimized carrier concentration, should be above 100 K.

(b) For $n=1$, overdoped region, the resistivity of the superlattice is no longer metallic, with an absolute value at room temperature about one order of magnitude larger than that of the $n=2.5$ superlattice (see Fig. 2). This effect is completely unexpected because the $n=1$ sample should be strongly overdoped and then highly metallic.

The former feature could be readily explained if we suppose that the chemistry of the CR block is not yet optimized. However, this effect fails to explain the latter feature. On the other hand, a decrease of the transition temperature in superlattices with very thin constituent layers is not unexpected (at least in the case of conventional superconducting superlattices). For instance, in Ref. 13 it was shown that the T_c of Nb/Cu superlattices is strongly reduced (down to 2.8 K) for individual layer thicknesses smaller than 10 Å. Such a strong decrease of the transition temperature was ascribed to a decrease of the mean free path caused by the disorder at the interfaces in superlattices consisting of ultrathin individual layers.

A theoretical approach to the problem of the superconducting transition temperature in highly disordered or even amorphous films has been proposed in.[14–16] In the analysis of our data we followed the approach by Finkel'shtein.[16] We have estimated the surface resistivity $R_{\square} \simeq 3\,\mathrm{k}\Omega$ of a $n=2$ superlattice as ρ/t, where ρ is the bulk resistivity for $T \rightarrow 0$ K and t is the thickness of an individual superconducting $[CaCuO_2]_2$ layer in this superlattice ($t \simeq 6$ Å) (we have assumed no interaction among different $[CaCuO_2]_2$ layers). From this value and supposing a decrease of the transition temperature of the superlattice T_c, relative to the bulk value T_{c_0}, of about 20% ($T_c/T_{c0} \simeq 0.8$), we could estimate a value of the relaxation time τ of about $2-3\times10^{-15}$ s. Such a value of τ is about one order of magnitude smaller than that found in bulk high T_c superconductors[17] and corresponds to $\varepsilon_F \tau \sim 3$ [for a realistic value of $\epsilon_F \sim 0.5$ eV (Ref. 18)], i.e., close to the metal-insulator transition. Decreasing the number n of $CaCuO_2$ unit in the IL block from 2 to 1 the role of the disorder at the interfaces becomes overwhelming and the relaxation time τ is expected to decrease further, driving the system toward the insulating regime. Such an effect could then explain the high nonmetallic resistivity of the $n=1$ superlattices.

In this paper we have reported on the behavior of T_c in artificially layered cuprates where the thickness of the IL block was varied over a wide range. T_c versus n followed the expected behavior with a maximum value between 2 and 3. However, the maximum value of T_c was lower than expected and the behavior of resistivity versus temperature in superlattices having the thinnest Ca-Cu-O block ($n=1$) was nonmetallic, despite the highest carrier concentration. All these features could be explained considering the high degree of disorder in these artificial structures. Of course the not yet optimized chemistry of the CR layer could also play a role in causing a lowering of the critical temperature.

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