Synthesis of $Bi_2Sr_2CaCu_2O_8/Bi_2Sr_2CuO_6$ Superlattices with a T_c Enhancement Effect

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$Bi_2Sr_2CaCu_2O_8$(2212)/$Bi_2Sr_2CuO_6$(2201) superlattices epitaxially grown *in situ* by reactive rf magnetron sputtering on heated MgO substrates were studied by x-ray diffraction methods and resistive measurements. The highest $T_c(R=0)$ of 94 K, notably higher than that of single phase 2212 films prepared in the same conditions ($T_c=75$–80 K), was obtained for $(2212)_m/(2201)_n$ superlattices where the numbers m of c-axis half-unit cells are close to unity. We attribute this fact to the metallic nature of the intervening 2201 layer favoring in such a situation an optimal O_2 doping of the 2212 layers.

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An important method for understanding the mechanism of high T_c superconductors is the study of artificial superlattice structures, in which the high T_c superconducting layers are separated by insulating or by lower T_c superconducting layers. These superlattices including $YBa_2Cu_3O_7$(YBCO)/$PrBa_2Cu_3O_7$(PrBCO), the most extensively studied system, and $Bi_2Sr_2CaCu_2O_8$(2212)/$Bi_2Sr_2CuO_6$(2201) have been prepared by sputtering [1–3], laser ablation [4–6], and molecular beam epitaxy (MBE) [7–9] methods. The influence of the coupling between the neighboring CuO_2 planes on electrical transport properties of high T_c materials has been particularly investigated in YBCO/PrBCO superlattices [2,4,5]. For instance, Triscone *et al.* [2] first varied the coupling between ultrathin YBCO layers by interposing PrBCO layers of increasing thickness in YBCO/PrBCO superlattices and studied the consequences of decoupling 12 Å YBCO unit cells on the superconducting properties of the superlattice. They found a broadening of the superconducting transition and a decrease of the critical temperature. Thus T_c(midpoint) of a 12 Å/12 Å superlattice was only 55 K. On the other hand, concerning the 2212/2201 superlattices, in most cases, T_c values much less than 77 K have been reported. However, more recently, Bozovic *et al.* [7] synthesized by MBE a series of such superlattices in which ultrathin layers of 2212 alternate with up to five layers of 2201 phase. They found T_c of their superlattices to be essentially equal to that of the 2212 phase itself, and inferred that it was not reduced at heterostructure interfaces. The critical temperature of superlattices in all these reported works was *lower* (or at most equal [7]) to that of the high T_c phase, which was present in the superlattices. In fact, the oxygen content, electronic structure (hole carrier density), and crystallization of high T_c layers are influenced by the neighboring insulating or lower superconducting layers. These effects could play a role in determining the critical temperature of high T_c layers and consequently affect the superconductivity of the superlattices. By systematically varying the hole concentration of the barrier layers used to isolate ultrathin YBCO layers, Norton *et al.* [10] showed that the superconducting transition width depends on the carrier density in the barrier layer.

In this Letter, we report first how we have synthesized *in situ* 2212/2201 superlattices by rf magnetron sputtering. Then we describe the results of the characterization of the multilayer structure by x-ray diffraction analysis and of their superconducting properties by resistance measurement. We show for the first time that the superconductivity of such superlattices can be in some cases significantly enhanced compared to that of a 2212 single layer prepared in the same conditions.

Our sputtering deposition technique is described in Refs. [11] and [12]. Briefly to prepare 2212/2201 superlattices, 2201 and 2212 films are deposited sequentially onto heated MgO(100) substrates by reactive rf magnetron sputtering using a single target of each phase. A computer controlled rotating table sequentially positions the heated substrate holder (725 °C) in front of the desired target for a given time. The deposition rate is -0.3 Å/s. In the 2212/2201 superlattices considered here, the deposition sequence started with the 2201 layer followed by the 2212 layer and was repeated up to 30 times. The numbers of c-axis half-unit cells was varied from 1 to 10 for 2212 phase layers and 1 to 8 for 2201 phase ones. In addition 2212 and 2201 single phase films were also prepared under the same conditions (using sequential deposition) as for the superlattices except that only the desired target was activated. Under these conditions, the critical temperatures, $T_c(R=0)$, of 2201 and 2212 films were 5 K (in the oxygen overdoped region [11]) and 75–80 K, respectively.

X-ray diffraction (XRD) patterns of these 2212 and 2201 films show that they are single phase, c-axis oriented. This indicates that the deposition conditions used for the superlattices are suitable for preparing both kinds of single phase films. The c-axis lattice constants of these 2212 and 2201 films were $c_2=30.79(2)$ and $c_1=24.65(2)$ Å, respectively.

Figure 1 shows the XRD patterns of $(2212)_1/(2201)_2$ and $(2212)_2/(2201)_6$ multilayers. Following Ref. [8], we describe the superlattices using the notation $(2212)_m/(2201)_n$, where m and n are the numbers of 2212 and 2201 c-axis half-unit cells per multilayer period. Addi-

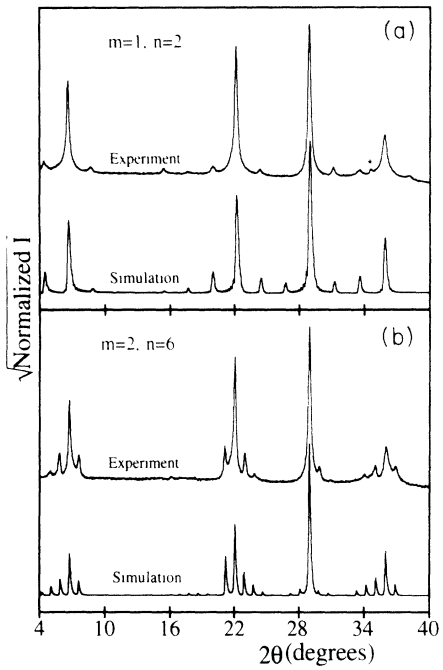

FIG. 1. X-ray diffraction patterns of superlattices $(2212)_m/(2201)_n$: (a) $m=1$, $n=2$; (b) $m=2$, $n=6$. The asterisk indicates a small peak due to sample holder. (Cu $K\alpha$ radiation, Ge III monochromator, position sensitive detector for data acquisition).

tional peaks are present in the x-ray diffraction patterns of multilayers compared to those of the single oriented 2212 or 2201 phases. These peaks are the signature of multilayer structures [13]. The full width at half maximum (FWHM) measured from the rocking curve of the strongest (00l) reflection is about 0.2° and is then comparable to that of 2201 single phase film [11]. The deduced superlattice period Λ for the multilayers of Fig. 1 are equal to 40.03(4) and 104.9(2) Å, respectively. These values are very close to the "ideal" values: 40.05 and 104.74 Å, obtained using the cell parameters determined from the pure phases according to $\Lambda=(nc_1+mc_2)/2$, with $m=1,n=2$ and $m=2,n=6$, respectively. To confirm the above simple m and n determinations we used, as a first step, a structural model with *perfect* $(2212)_m/(2201)_n$ layers. The results are shown in Fig. 1 as simulation curves. Detailed x-ray spectrum analysis of 2212/2201 multilayers will be published later. The relatively good agreement between observed and calculated diagrams, is of particular interest, as the model only considers abrupt interfaces. Indeed further higher resolution diagrams are in progress and already show persisting oscillations around main reflections at 2θ angles as high as 30° which attests to the high quality layering.

The calculated spectrums are obviously very sensitive to the choice of m and n, because this acts strongly on the peak positions. It is clearly possible to discriminate from the peak positions between the two situations $(2212)_1/(2201)_2$ or $(2212)_2/(2201)_1$. In the latter case, $\Lambda=43.11$ Å leads to discrepancies on the peak positions as large as several tenths of a degree, whereas in the former case, where Λ is equal to 40.03 Å, the discrepancies are reduced to a few hundredths of a degree. Therefore it appears that the sputtering technique allows us to grow multilayers with layers as thin as *half a unit cell.*

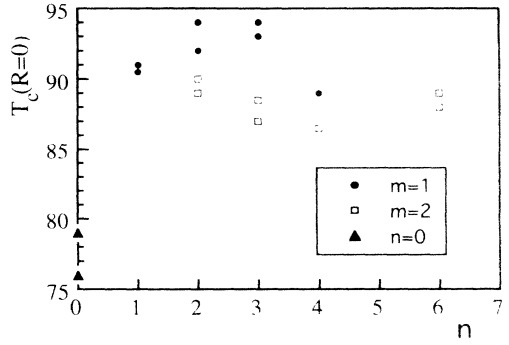

FIG. 2. $T_c(R=0)$ for two series of as-prepared superlattices: (●) $(2212)_1/(2201)_n$ and (□) $(2212)_2/(2201)_n$, as a function of n (see text); (▲) T_c range for single phase 2212 films prepared under the same conditions. The chosen experimental points give the width of the T_c distribution across several samples for multilayers with identical m and n values. The small dispersion may be related to a slightly different oxidation state of the samples.

Superconducting critical temperatures T_c of single phase films and $(2212)_m/(2201)_n$ superlattices were measured resistively by the standard four probe method. As indicated already above, single phase 2212 and 2201 films prepared under the same conditions as the multilayers presented in this Letter have critical temperatures T_c equal to 75–80 K and 5 K, respectively.

Figure 2 displays the zero resistance transition temperature values T_c of as-prepared $(2212)_1/(2201)_n$ and $(2212)_2/(2201)_n$ superlattices as a function of n ($n=1$–6). Two important results should be noted in this figure. One is the fact that for the first time, the critical temperature $T_c(R=0)$ of a multilayer with a short period value can be significantly higher than that of 2212 single phase films prepared under the same conditions (see triangles in Fig. 2). The other remarkable feature is the fact that the critical temperature T_c of a 15 Å thick 2212 layer is not degraded by the presence of a 50 Å thick 2201 layer. This latter point is in agreement with the results of Bozovic *et al.* [7]. Our highest $T_c(R=0)$ value was 94 K and was observed reproducibly for several $(2212)_1/(2201)_2$ multilayers. Figure 3 displays the curve representing the temperature dependence of the resistance of a $(2212)_1/(2201)_2$ multilayer. Transport experiments [14] under parallel magnetic fields ($H\|ab$) up to 20 T show no degradation of superconductivity in this multilayer, proving that superconductivity is indeed confined in the 15 Å thick 2212 layers.

Before discussing the origin of this T_c enhancement

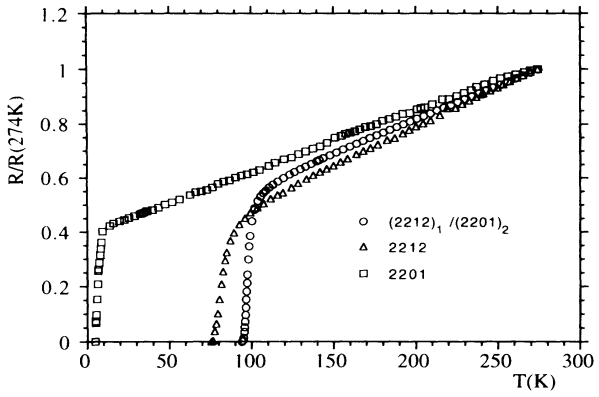

FIG. 3. Variation of the normalized resistance as a function of temperature for a $(2212)_1/(2201)_2$ superlattice and for single phase 2212 and 2201 films prepared under the same conditions as the superlattices.

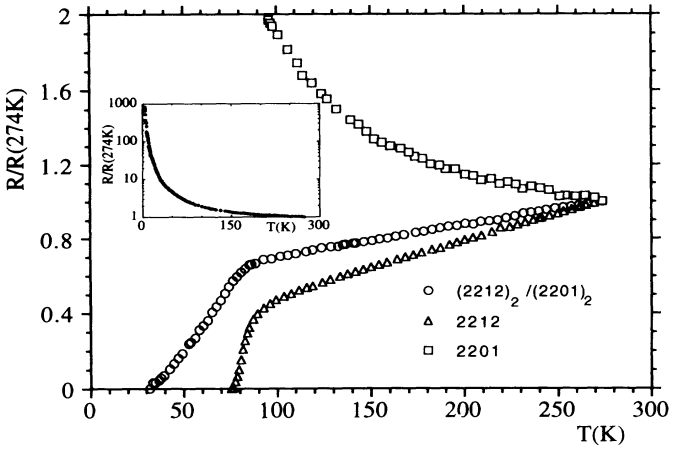

FIG. 4. Variation of the normalized resistance as a function of temperature for a $(2212)_2/(2201)_2$ insulating [20] superlattice and for single phase 2212 and 2201 films prepared under the same conditions as the superlattices. The inset displays the whole $R(T)$ curve for the insulating 2201 film.

effect, some remarks can be made concerning the *structure* of these multilayers. First, it is quite unlikely that this high T_c value is due to the 2223 phase because the presence of the 2223 phase in the superlattice as an impurity phase might have manifested itself in the form of an anomaly at 110 K in the $R(T)$ curve, a method which has proved to be more sensitive than XRD in this respect [15–17]. We do not see any hint of such an effect. Second, such a rather sharp transition (no tailing effect) would not be observed for a disordered system. This implies that the microstructure of the multilayers and in particular of the superconducting 2212 layers is not too much disturbed by structural defects. It correlates well with XRD analysis which demonstrates that our multilayering technique works well for ultrathin (half a unit cell) layers. It can be further remarked that 2212/2201 multilayering is favorable to obtain good quality ultrathin 2212 layers: The crystallization of 2212 layers may be improved by the 2201 intervening layers because the lattice mismatch between these two phases is much smaller than that existing between the 2212 phase and MgO substrate. In some respect, the 2201 layer can play the role of a buffer layer improving epitaxial growth and limiting the interdiffusion between the MgO substrate and 2212 layer.

Let us discuss now the *physical* origin of this T_c enhancement. It is well known that in these oxide superconductors, T_c is depending on their oxygen content. We have shown [11] that T_c in epitaxial 2201 thin films is strongly dependent on oxygen content, these films becoming metallic upon increasing O_2 doping. For the 2212 phase there is also a dependence of T_c on oxygen doping. For instance, it has been shown in earlier studies on ceramics [18,19] and textured films [20] that by adjusting their O_2 content, it is possible to reach T_c values as high as 92 K in the 2212 phase. This observation leads us to propose as the most plausible explanation that our multilayering method results in optimum O_2 doping of 2212 layers, that is to say to an optimum carrier concentration of the 2212 layers favored by a charge transfer from the O_2 overdoped intervening 2201 layers. If it is the case, this peculiar doping effect should depend (a) for a given 2201 layer, on the thickness of the 2212 layer; (b) —and this is the main argument—it should depend on the *nature* of the 2201 layer (metallic or insulating), i.e., on its carrier concentration. Experimental proofs are observed for both situations. Concerning point (a), we found that by increasing for a given n the 2212 layer thickness (i.e., m), T_c decreases progressively towards the ones of as-prepared 2212 films ($T_c \sim 80$ K). Moreover, as shown in this paper, it is for the layering with the smallest values of m that we observe the largest T_c increase: Since the superconducting properties of the 2212/2201 superlattices are mostly determined by the 2212 layers, the effect of the charge transfer becomes maximum when the thickness of the 2212 layer comprises only half a unit cell, i.e., only two CuO_2 planes. Concerning point (b), in order to study the influence of the *nature* of the 2201 layer on the T_c of 2212/2201 superlattices, we have recently grown 2212/2201 superlattices, where the spacing layers 2201 had an *insulating* behavior [21]. The superconducting temperature T_c of this kind of superlattice was always lower than that of 2212 single phase films and the transitions were *broadened* (Fig. 4). For instance, in the case of $(2212)_4/(2201)_2$ and $(2212)_2/(2201)_2$, $T_c(R=0)$ decreased to about 60 and 30 K, respectively, suggesting that the 2212 layers are underdoped or carrier depleted due to the neighboring insulating 2201 layers. A detailed comparison of the influence of the nature of the spacing layers on the electrical properties of 2212/2201 superlattices is proceeding and will be published elsewhere [21].

In conclusion, by growing ultrathin 2212/2201 multi-

layers with metallic 2201 layers, we have obtained values of T_c higher than those of the initial constituents. XRD studies confirm the multilayering for very small periods. Thus $(2212)_1/(2201)_2$ multilayers exhibit a $T_c(R=0)$ of 94 K and the XRD diagram is in good agreement with the perfect superlattice simulation. We ascribe this high T_c value to an optimal O_2 doping and related carrier concentration of the 2212 layer favored by the intervening *metallic* 2201 layers.

This explanation allows us to understand *a posteriori* the different results already published on 2212/2201 multilayers. Except in Ref. [7] in which the spacing 2201 layers were superconducting, the reported T_c of such multilayers was rather low. In spite of the fact that the T_c of 2212 single layers was lower than 70 K, the low T_c values of the multilayers in Refs. [3,6] may be ascribed also to the fact that the 2201 layers were *semiconducting*.

Turning to the case of YBCO/PrBCO multilayers, several mechanisms have been proposed in various theoretical models to account for the observed T_c suppression, including spin polarons and hole filling mechanism [22], Kosterlitz-Thouless (KT) transition, and charge transfer (CT) [23], proximity effect, and charge transfer effect [24]. Among them the only mechanism which explains directly either a T_c decrease (with insulating 2201 layers) or an increase (metallic 2201) as a function of the carrier charge concentration of the 2201 layer is the CT mechanism. Our results lead us to suggest that charge transfer may be the dominant mechanism in this system [25]. In that case, would it mean that it could be possible to observe, in one unit cell layer, superconductivity at a temperature as high as in the bulk material, if the optimum doping conditions were fulfilled? This might be obtained with overdoped intervening layers as appears to be the case in 2212/2201 multilayers.

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