Intracell Changes in Epitaxially Strained $YBa_2Cu_3O_{7-x}$ Ultrathin Layers in $YBa_2Cu_3O_{7-x}/PrBa_2Cu_3O_7$ Superlattices

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The structure of high quality $[YBCO_N/PBCO_M]_{1000\ Å}$ superlattices, with N ranging between 1 and 12 unit cells and $M = 5$ unit cells, grown by high oxygen pressure sputtering, is analyzed. Intracell atomic structure of the layers along the c axis and disorder at interfaces is investigated using an x-ray refinement technique. Negligible roughness, step disorder, and interdiffusion are found at the interfaces. Epitaxial mismatch strain results in a surprising reorganization of interatomic distances for the thinnest YBCO layers, which seems to correlated with the decrease in the critical temperature. Intracell structure is invoked as an additional source of T_c changes in very thin YBCO layers.

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Since the discovery of the high T_c superconductivity, structure has been recognized to play a crucial role towards the understanding of its nature and mechanisms. It has been known for years that distortions arising from cation substitution can produce significant changes in T_c [1], and recent experiments on doped La_2CuO_4 superconductors at constant carrier concentration show a clear dependence of T_c on lattice strains [2]. A great effort has been put in structure determination under hydrostatic pressure [3]. Epitaxial stress in thin films offers a simple way to arrive at a strain pattern not attainable under hydrostatic pressure [4]: According to the Poisson effect, film growth on a substrate with slightly smaller (larger) in-plane lattice parameters may lead to a compression (expansion) in the *ab* plane that can result in an expansion (contraction) in the out-of-plane direction. Uniaxial epitaxial strain, together with Poisson's ratios, has been addressed before [5]. However, the general applicability of the Poisson effect to thin films is still doubtful [6], especially in these highly anisotropic materials. Anyway, Locquet *et al.* [7] have been able to double the critical temperature in the $La_{1.9}Sr_{0.1}CuO_4$ high T_c superconductor using mismatch strain. They show that compressive epitaxial strain in-plane can generate much larger increases in T_c than those obtained by comparable hydrostatic pressures, and their claim is that the distance relevant to the mechanism of the superconductivity being modified is the separation between consecutive CuO_2 planes. Mismatch strain constitutes an alternative way to change the intracell distances which may be "relevant" to the mechanism of superconductivity, but a *quantitative* structure analysis of strained films is necessary. X-ray diffraction is a widely used technique to analyze structure, which supplies structural information averaged over a length scale (structural coherence length) which may be around a hundred angstroms. The extraction of quantitative information requires the fit of the diffraction pattern to a structure model containing a large number of parameters in these complex materials, and, therefore, results may not be very reliable for single epitaxial films, which usually show a reduced number of diffraction peaks. Artificial superlattices are very adequate systems to study the structural implications of strained growth for two central reasons. First, a modulated structural strain profile can be obtained varying the relative thicknesses of the components. Second, the structural modulation introduced by the artificial periodicity results in a feature rich diffraction pattern which makes the confidence factor of the fit, χ^2, highly sensitive to the values of the fitting parameters. The refinement of superlattice x-ray spectra was first developed by Schuller and co-workers and has been successfully extended to high T_c materials in the pioneering study of interface disorder and interdiffusion [8].

In this Letter, we revisit an already widely studied system $[YBaCu_3O_{7-x}/PrBa_2Cu_3O_7$ (YBCO/PBCO)] superlattices which, due to the good chemical compatibility of both compounds is very adequate to the study of the epitaxial strain resulting from lattice mismatch. We show that intralayer epitaxial strain is responsible for pronounced nonuniform changes in intracell distances of the YBCO. We propose that, besides dimensionality or proximity effects, these structural changes may be responsible for the changes in the critical temperature resulting from modifications of the electronic structure, and may add information to the long debated question of the superconductivity of ultrathin layers [9,10].

The samples for this study were epitaxial YBCO/PBCO superlattices grown on (100) $SrTiO_3$ using a high pressure (3.6 mbar pure oxygen) multitarget sputtering system. High pressure oxygen atmosphere yields a very thermalized growth at a very slow rate, 8 Å/min for YBCO, which allows an accurate control of film

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thickness. The thickness of the PBCO layer was fixed at five unit cells (≈60 Å) to keep coupling between YBCO layers constant. The number of YBCO cells was changed between 1 and 12 and repeated up to a total thickness of 1000 Å. Rocking curves around the (005) peak, showing FWHM as small as 0.1°–0.2°, point to a very small mosaic spread in the superlattices. Φ scans indicated perfect in-plane matching not allowing to resolve in-plane lattice parameters for both YBCO and PBCO. Low angle x-ray diffraction spectra showed finite size oscillations indicating a surface planitude of the order of 1 unit cell. High angle spectra were analyzed using the SUPREX9 [11] refinement program, which allows one to obtain not only fractional unit cell positions of the different elements in the c direction, but also disorder related parameters such as step disorder, interdiffusion, interface strain, etc. [8].

Figure 1 shows the high angle diffraction spectrum and the fit for a typical sample. Fitting results were tested to exclude local minima in the multidimensional space of solutions, and the sensitivity of the confidence factor, χ^2, to small changes in parameter values was also checked. This was done by manually displacing single parameters from the final value in both directions monitoring the increase in χ^2; the inset of Fig. 1 shows the sensitivity of χ^2 for various intracell distances. The structural coherence length determined from the width of the superlattice diffraction peaks was in the range 500–800 Å. Interestingly, we have found negligible small interdiffusion (<5% in the first layer) and step disorder, showing that high pressure oxygen growth promotes sharp interfaces over length scales of the order of the structural coherence length (which is certainly not true for macroscopic length scales). In the absence of large interface disorder, interface mismatch strain may play a major role in determining the structural details as far as layer thickness is below the critical value for stress relaxation.

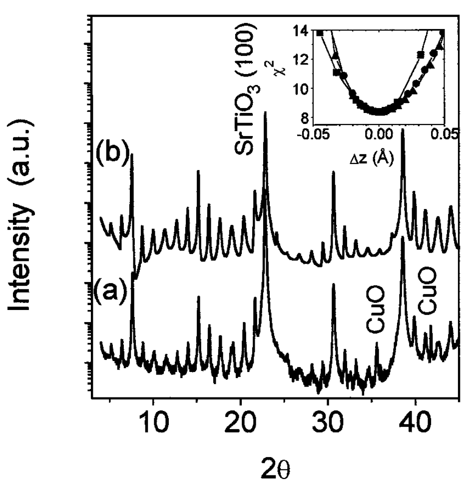

FIG. 1. θ-2θ spectrum for a $[YBCO_1/PBCO_5]_{1000\ Å}$ superlattice (a) together with the superlattice fit, vertically displaced two decades for clarity (b). Extra peaks due to CuO precipitates present in the sample are marked, together with the (100) substrate peak. Inset: Chi-squared versus relative departures of interatomic distances from the refinement minima. Sensitivity has been computed by changing distances manually. Squares: Vertical distance from the CuO chain (Cu1) to the Ba ion. Circles: Vertical distance from the Ba ion to planar Cu (Cu2). Up triangles: Vertical distance from the planar Cu (Cu2) to the Y ion.

Samples were superconducting with a critical temperature decreasing with the number of YBCO unit cells as depicted in Fig. 2. The critical temperature (T_c) was determined using the zero resistance criterium. T_c values agree with previously reported data on similar superlattices [8,12]. The T_c dependence on YBCO thickness has been reported previously in trilayer samples and single films [10,13,14]. We found a systematic and monotonous increase of the c parameter when YBCO layer thickness increases from 1 to 12 unit cells approaching the value reported for single 1000 Å thick films (see Fig. 2); PBCO lattice parameter, however, remained practically unchanged. In-plane PBCO lattice parameters are larger than those of YBCO by about 1% [$(b_{YBCO} - b_{PBCO})/b_{YBCO} = -0.011$ and $(a_{YBCO} - a_{PBCO})/a_{YBCO} = -0.007$] therefore, thin YBCO layers sandwiched in between may show certain in-plane expansion and eventually out-of-plane compression. In-plane expansion of YBCO up to four unit cells due to lattice mismatch has been recently established in $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_{3-x}Ga_xO_7$ from high resolution x-ray analysis [15]. Increasing YBCO thickness would relax epitaxial stress when the critical thickness, four unit cells from Fig. 2, is exceeded and YBCO would tend to recover single film lattice parameters (dotted lines in the figure are lattice parameters of typical 1000 Å thick films). From the observation of Fig. 2, the changes in T_c seem to correlate with those of the c lattice parameter, and it may be then tempting to explain the effect of epitaxial stress in terms of the results of hydrostatic pressure or uniaxial

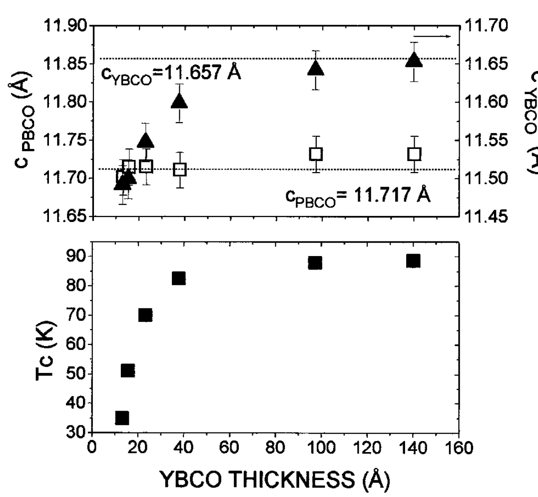

FIG. 2. Dependence of T_c and c parameters on YBCO layer thickness, being PBCO thickness fixed in 60 Å (five unit cells). Dotted lines represent the typical 1000 Å thin film values (triangles: YBCO lattice parameter; squares: PBCO lattice parameter).

strain experiments. It is well known that YBCO shows an anomalously low T_c dependence under pressure, probably owing to the opposite dependencies on uniaxial stress in a and b directions in-plane, $dT_c/d\varepsilon_a = +212$ K and $dT_c/d\varepsilon_b = -244$ K (Ref. [16] and references therein). We can use these uniaxial strain dependencies of T_c to estimate roughly the T_c changes expected from the observed strains. Assuming that the structural changes for the one unit cell YBCO superlattice would occur as a result of an in-plane expansion $\varepsilon_a = 0.007$ and $\varepsilon_b = 0.011$ due to matching with PBCO, the expected decrease of T_c would be of 1.2 K. Concerning the 1.42% decrease in the c lattice parameter, since $dT_c/d\varepsilon_c = -8$ K, a very small increase is expected on the base of uniaxial strains. It is clear, therefore, that the superposition of the equivalent uniaxial strains of the lattice parameters due to epitaxial stress can be ruled out as a possible source of the changes in T_c when the YBCO thickness is reduced. However, it is worth stressing that in-plane and out-of-plane strains have different signs, a situation impossible to achieve under hydrostatic pressure. Another point of interest is whether the Poisson effect holds in this system as a result of epitaxial stress. Since there are no external forces applied to the superlattice, the perpendicular components of stress σ_{cc} must vanish. The equilibrium condition should then be $\varepsilon_c = -(C_{ca}\varepsilon_a + C_{cb}\varepsilon_b)/C_{cc}$. If both ε_a and ε_b are tensile, a compressive effect is expected in ε_c, according to the Poisson effect. An estimate can be done using the elastic moduli determined by Lei *et al.* [17] ($C_{ca} = 89$ GPa, $C_{cb} = 93$ GPa, and $C_{cc} = 138$ GPa). If we again assume that for the one unit cell YBCO sample ε_a and ε_b are those expected from the lattice mismatch to the PBCO, a value for the c lattice parameter of 11.51 Å is obtained, which is close enough to the 11.49 Å obtained from the x-ray fits. It turns out that, although the Poisson effect may hold for lattice parameters as a result of in-plane lattice mismatch between YBCO and PBCO, its effect is not strong enough to account for the drastic decrease observed in T_c when the thickness of YBCO is reduced.

However, aside from changes in the lattice parameters, the overall stress pattern gives rise to very significant and nonuniform changes in the intracell distances, which might be responsible in their own for the changes in the superconducting properties. Figure 3 gathers the changes in some significant intracell distances in the c direction. Error bars describe the range over which the goodness of the fit did not significantly change, i.e., the width of the χ^2 minimum at a 3% increase. The important new result is that epitaxial stress causes very nonhomogeneous strain in the YBCO cell when the thickness of this layer is reduced up to one unit cell: The distance between CuO_2 planes decreases (3.8%) when the thickness is reduced and the barium approaches the chains (4%) and moves away from the planes (3%). Meanwhile, the change in the c lattice parameter is only of 1.42%. When the thickness of the YBCO layer is increased, intracell distances get close to bulk material values. In fact, the fractional atomic positions in the unit cell in the thicker YBCO $[YBCO_8/PBCO_5]_{1000\ Å}$ and $[YBCO_{12}/PBCO_5]_{1000\ Å}$ superlattices were in agreement, within 0.5%, with those reported for bulk samples. While separation between CuO_2 planes and the distance between the barium and the chains become smaller under epitaxial stress, as qualitatively (but not quantitatively) expected from the Poisson effect, the opposite happens to the distance from the barium to the planes. It is worth remarking that, although quite large, structural changes are not unrealistic.

(i) According to the values of the elastic moduli [17], the 1.42% change in the c lattice parameter is the one expected

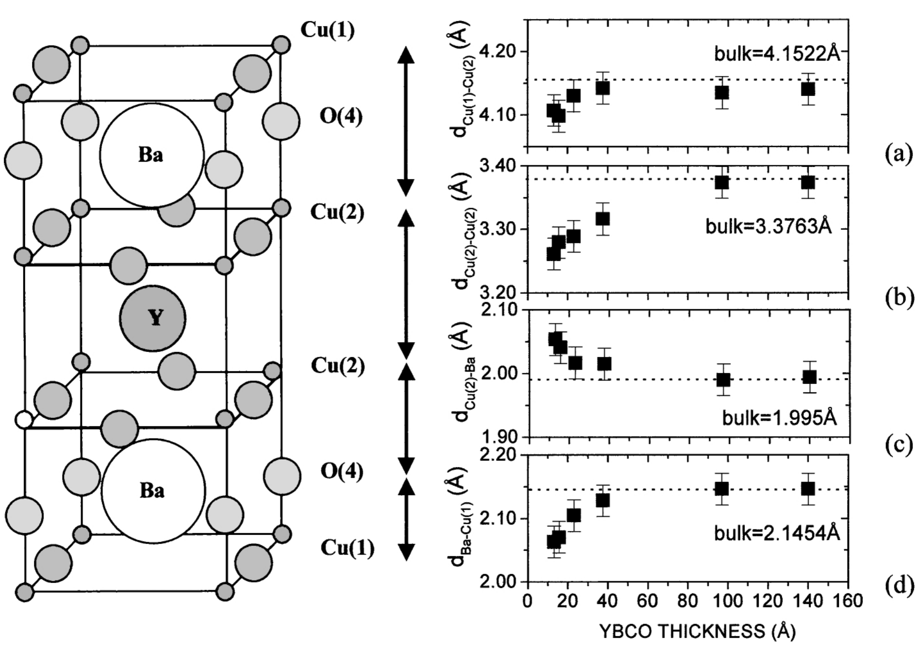

FIG. 3. Changes in the main YBCO intracell distances along the c axis when changing YBCO layer thickness. (a) Distance from planes to chains [Cu(2)-Cu(1)]. (b) Distance between neighboring CuO_2 planes [Cu(2)-Cu(2)]. (c) Plane to barium [Cu(2)-Ba]. (d) Barium to the chain [Ba-Cu(1)]. Dotted lines are the corresponding bulk values after Ref. [18].

for a uniaxial stress in the order of only 2 GPa along this direction.

(ii) Concerning the distance between consecutive CuO_2 planes which decreases by 3.8% when the YBCO thickness is reduced, it increases by 4.9% when the rare earth is substituted from Y to Nd, increasing the ionic radius by a factor of 1.088 [18].

(iii) The distance between the CuO chains and the barium, decreasing by 4%, is also known to show a large change when oxygen content is reduced. In fact, this distance increases by 5% in going from the fully oxygenated YBCO to the antiferromagnetic insulator $YBa_2Cu_3O_6$ [19].

In some sense, epitaxial stress may be complementary of pressure or cation substitution in producing internal strains affecting superconductivity. Cation substitution, depending on its valence, may change carrier concentration aside from cell distances; however, it has been recently shown that lattice distortions at a constant doping level cause significant T_c changes [2]. As far as pressure is concerned, the enhancement of T_c observed in some optimally doped superconductors under pressure points also to other effects besides doping [16]. In this respect, it is important to remark that the change in intracell distances may have drastic effects on the electronic structure affecting carrier concentration (doping or chain to plane charge transfer) or causing charge rearrangements in-plane which may influence coupling strength to spin fluctuations, charge fluctuations, or phonons [16]. In this complicated scenario, it is very difficult to ascribe the changes in T_c to the changes in any particular interatomic distance. However, it is clear that these changes are directly implicated in important theories, calculations, and experimental findings. We can say, for example, that, as far as the CuO_2 planes are concerned, we observe a reduction of the distance between planes along with a decrease in T_c in agreement with Locquet *et al.* [7]. The situation in the field, however, is controversial; recently, experimental evidence has been presented for T_c being independent of planes separation in bismuth based superconductors suggesting a 2D nature of high T_c superconductivity [20] in disagreement with theoretical models based on the Josephson coupling between consecutive planes [21]. The important changes in the position of the large Ba ion may affect the apical oxygen bond length. A number of studies have stressed the importance of the CuO_2 plane to apical oxygen interatomic distance in determining Madelung potentials [22] or bond valence sums [23] and their correlations with the superconducting properties of high T_c compounds. Additionally, changes in this bond length will change the overlap integrals directly affecting the charge transfer mechanisms.

In summary, we have shown that superlattice x-ray fitting allows obtaining precise information about epitaxial strain in YBCO layers. Intracell strain increases continuously when YBCO thickness is reduced down to one unit cell. Deep nonuniform changes in some interatomic distances have been found, which seem to correlate with the decrease of T_c when thickness is reduced. Although at present it is not possible to conclude on a direct effect on the superconductivity mechanism, the important changes in the intracell distances have to be taken into account, besides dimensionality (Kosterlitz-Thouless transition), as extrinsic factors to explain the decrease in the critical temperature of ultrathin YBCO films.

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