Superconductivity in Nonsymmetric Epitaxial $YBa_2Cu_3O_{7-x}$/$PrBa_2Cu_3O_{7-x}$ Superlattices: The Superconducting Behavior of Cu-O Bilayers

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We have fabricated epitaxial, nonsymmetric $M \times N$ superlattices in which $YBa_2Cu_3O_{7-x}$ (YBCO) layers either $M = 1$, 2, 3, 4, or 8 c-axis unit cells thick are separated by insulating $PrBa_2Cu_3O_{7-x}$ (PrBCO) layers N unit cells thick ($N = 1$ to ~ 16). The zero-resistance transition temperature T_{c0} initially decreases rapidly with increasing PrBCO thickness but saturates at $T_{c0} \sim 19$ K or $T_{c0} \sim 54$ K for 1- and 2-cell-thick YBCO layers, respectively. We conclude that although intercell coupling may enhance T_{c0}, it is not necessary for superconductivity of single-cell-thick YBCO layers in a PrBCO matrix.

The layered structure of high-temperature superconductors (HTSC) and particularly the existence of closely spaced pairs of Cu-O planes is widely considered to be responsible for both their remarkable superconducting properties and their (as yet unidentified) superconducting pairing mechanism. The two Cu-O planes within a $YBa_2Cu_3O_{7-x}$ (YBCO) unit cell are separated by ~ 0.39 nm, while the Cu-O bilayers in successive cells are separated by $c \sim 1.17$ nm. Although the bilayer structure is responsible for the large anisotropy of HTSC properties, the fact that the zero-temperature superconducting coherence length $\xi_c(0)$ is comparable to these separations suggests that the Cu-O planes within a cell and in adjacent cells must be closely coupled. Conversely, additional quantum confinement effects might result if an isolated, single-cell-thick YBCO layer could be formed, so it is not clear whether its superconductivity would be two or three dimensional. In particular, it still is unresolved whether interactions are necessary between the Cu-O bilayers in adjacent unit cells for superconductivity to occur, or how T_c would vary with the number of interacting unit cells in a YBCO layer.

Transmission electron micrographs of epitaxial YBCO films on KTaO₃[1] and on SrTiO₃[2,3] show that there is a transition zone ~ 10 nm thick next to the substrate in which the film defect density rapidly decreases and the connectivity of the c-axis-perpendicular planes rapidly improves. Because $\xi_c(0)$ is so much smaller than this transition region, single-cell-thick films cannot be grown even on SrTiO₃ with any assurance that their properties are representative of isolated ultrathin YBCO. The most promising approach is to grow very thin YBCO films epitaxially on a lattice-matched nonsuperconducting M-1:2:3 material. We have used $PrBa_2Cu_3O_{7-x}$ (PrBCO) because it is not superconducting or even metallic, but is a room-temperature semiconductor ($\rho_{a-b} \sim 3$ mΩ cm) and a low-temperature insulator having a-b lattice constants within 1.5% of YBCO's and the same orthorhombic structure as superconducting YBCO.[4,5] Oxygen also diffuses readily through PrBCO so that fully oxidized YBCO/PrBCO superlattices can be formed by the same *in situ* process that is used for entirely superconducting M-1:2:3 materials.[4,5]

In this Letter we report the fabrication, structure, and superconducting properties of epitaxial, nonsymmetric, $M \times N$ superlattices in which YBCO layers $M = 1$, 2, 3, 4, or 8 unit cells thick are separated by insulating PrBCO layers N unit cells in thickness. By varying N from 1 to 16, we have systematically mapped out the dependence of T_c on YBCO layer thickness and interlayer separation, in a set of nearly lattice-matched periodic epitaxial structures that contain up to 60 layers (30 periods) of alternating composition. We find distinctly different superconducting properties for these compositionally periodic, layered materials than for random alloys of the same average composition. Most important, we find that T_c does *not* go to zero for isolated, single-cell-thick YBCO layers, in contrast to the result implied in a recent paper.[6]

Heteroepitaxial growth of thick PrBCO films on thick YBCO with the c axis normal to the substrate was first reported by Poppe et al.,[7] using dc sputtering. Triscone et al.[8] then demonstrated growth by dc magnetron sputtering of $YBa_2Cu_3O_{7-x}$/$DyBa_2Cu_3O_{7-x}$ superlattices (in which both layers are superconductors) with a modulation wavelength Λ as short as two c-axis unit cells (~ 2.34 nm), i.e., one YBCO unit cell alternating with one DyBCO cell. They found no degradation of the superconducting T_c due to the numerous interfaces, nor was the normal-state resistivity affected. Triscone et al. extended their work[6] to thin-film $Y_yPr_{1-y}Ba_2Cu_3O_{7-x}$ alloys and to YBCO/PrBCO superlattices on MgO substrates, which they used to study the effect of the interposed insulating PrBCO layers on the YBCO superconducting transition. They observed a linear decrease of T_c (defined in their case as 10% of the normal-state resistance) with increasing PrBCO layer thickness d_{Pr} in a series of superlattices having constant 1.2-nm (single-cell) YBCO layer thickness. They concluded that T_c extrapolated to zero in these structures for $d_{Pr} \sim 10$ nm, although the thickest PrBCO layer for which they showed data was $d_{Pr} = 7.2$ nm, for which their $T_c(10\%) \sim 13$ K. They pointed out that the most interesting possibility to explain this T_c reduction is that it reflects the intrinsic behavior of a single Cu-O double layer, and they suggested that "a small but finite coupling between the CuO

double layers is necessary in order to produce supercon-ductivity."[6]

Our superlattices were grown by an *in situ* pulsed-laser-ablation process that was described earlier.[9] Briefly, stoichiometric YBCO and PrBCO targets were mounted in a multitarget holder that permits target rota-tion and exchange. The pulsed KrF (248 nm) laser beam was brought to a line focus on the target; this line was scanned over the target in a direction perpendicular to its length to produce a region of only slowly varying film thickness. Epitaxially polished (100) SrTiO₃ sub-strates were bonded to the heater using silver paint. Su-perlattices were grown at a heater (substrate) tempera-ture of 730°C (~670°C) in 200-mTorr oxygen, at a deposition rate of 1.1 Hz and ≤ 0.1 nm per laser pulse. The superlattice periods measured directly by x-ray diffraction (XRD) agreed with those calculated from film-thickness/laser-shot measurements to within a few percent. Venkatesan *et al.*[10] and Wu *et al.*[11] also recent-ly used excimer-laser ablation to grow YBCO and PrBCO bilayers and trilayers, and $YBa_2Cu_3O_{7-x}/Y_yPr_{1-y}Ba_2Cu_3O_{7-x}$ superlattices with $y=0.0$ and 0.8, respectively, and showed that heterostructures having good crystallinity, compositional periodicity, and abrupt interfaces can be grown.[10,11]

Figure 1 shows XRD spectra for three different YBCO/PrBCO superlattices in which the YBCO layers are approximately 1 unit cell thick. The two large peaks (truncated) in each scan correspond to the superlattice (005) and the SrTiO₃ (002) plus superlattice (006) peaks. XRD θ-2θ scans revealed only (00l) diffraction peaks, indicating that the only crystalline phase present
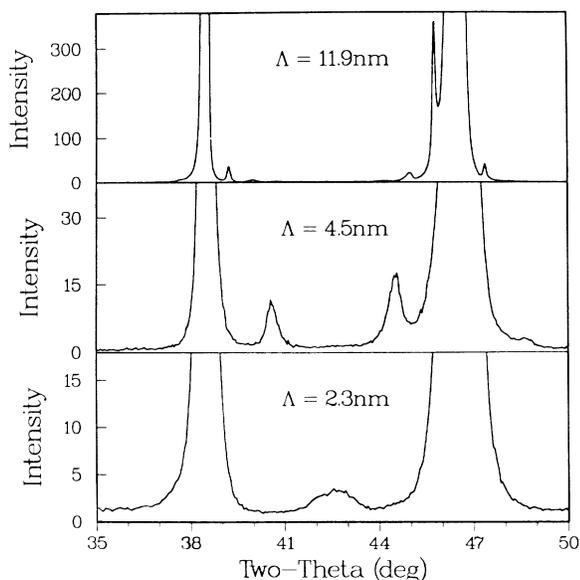
FIG. 1. θ-2θ x-ray-diffraction scans along the (00l) axis from nominally $M=1$ YBCO/PrBCO superlattices with modu-lation wavelengths of $\Lambda=2.3$ nm (30 periods), $\Lambda=4.5$ nm (30 periods), and $\Lambda=11.9$ nm (20 periods). Note the higher-harmonic sidebands for the $\Lambda=11.9$ nm structure.

has its c axis aligned with the (00l) of the SrTiO₃ sub-strate. Rocking curves (θ scans) through the (00l) peaks showed that the mosaic spread of the atomic planes lying parallel to the substrate surface is excellent, typically less than 0.4° full width at half maximum (FWHM). In addition, the position and width of (hkl) Bragg peaks with $h,k\neq0$ were measured and revealed that the in-plane epitaxy such that the $\langle110\rangle$ directions of the film and the substrate are aligned (in-plane mosaic spread $\leq0.5°$), as has been observed previously for pure YBCO films on perovskite substrates.[12]

The "signature" of a periodic superlattice is that each (00l) peak in Fig. 1 is modulated by diffraction side-bands (satellite peaks). The modulation wavelength (the sum of consecutive layer thicknesses) can be calculated from the satellite positions using the equation[13] $\Lambda=\lambda/2(\sin\theta_i-\sin\theta_{i-1})$, where here $\lambda=0.15406$ nm is the Cu $K\alpha_1$ x-ray wavelength and θ_i and θ_{i-1} are the Bragg an-gles for consecutive diffraction maxima. The most signi-ficant feature in Fig. 1 is the presence of observable sa-tellite intensity and hence direct evidence of a Y/Pr com-position modulation for the $\Lambda=2.3$ nm (1×1) structure. Since this sample was deposited as alternating single unit cells of YBCO and PrBCO, interdiffusion must be limit-ed to much less than a single cell during the *in situ* growth process. Z-contrast TEM[14] images that we have obtained confirm that our $1\times N$ superlattices contain single-cell-thick YBCO layers with sharp interfaces and no evidence of alloying.[15] We also have annealed both $1\times N$ and $2\times N$ superlattices at temperatures up to 800°C with no experimentally significant effect on their superconducting properties;[15] thus, they are highly stable against interdiffusion along the c-axis direction of com-positional modulation.

Information concerning the extent of both structural and compositional order can be obtained from the x-ray peak widths since these widths are inversely related to the average domain size via the Scherrer equation.[16] We find that the widths of the main (00l) peaks increase only slightly with order and yield domain sizes on the or-der of the film thickness. Since these widths are related to the overall crystalline coherence of the M-1:2:3 phase,[8] we conclude that the films are extremely well or-dered structurally. In contrast, we find that the widths of the superlattice reflections increase more rapidly with order and yield coherence lengths several times smaller than the film thickness. Since these widths are related to the coherence of the Y/Pr composition modulation, we conclude that although the superlattices are fairly well ordered, the periodicity of the chemical order is not per-fectly constant throughout the film.

Figure 2 displays the normalized resistances $R(T)/R(100$ K) for our $1\times N$ and $2\times N$ YBCO/PrBCO super-lattices. The peaks in the normalized resistances shown in Fig. 2 result from conduction through a superlattice structure that consists of insulating (PrBCO) and metal-lic (YBCO) layers that are electrically in parallel. The
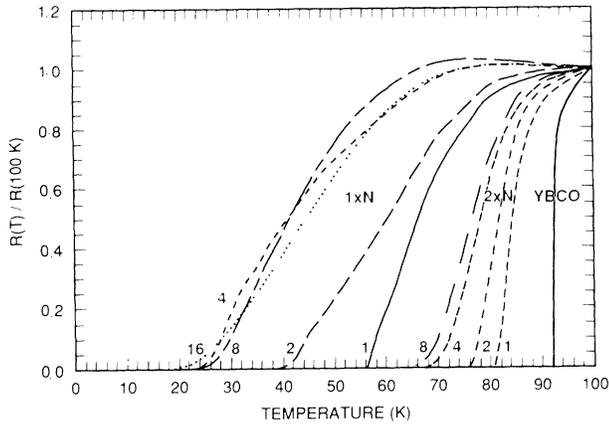
FIG. 2. Normalized resistance $R(T)/R(100 \text{ K})$ vs temperature for nonsymmetric $M(\text{YBCO}) \times N(\text{PrBCO})$ superlattices containing single-cell-thick $(M=1)$ and double-cell-thick $(M=2)$ YBCO layers. The superconducting transition for a pure YBCO film is also shown.

FIG. 3. T_{c0} (K) vs PrBCO layer thickness (in nm) for nonsymmetric YBCO/PrBCO superlattices containing 1- (●), 2- (■), 3- (▲), 4- (□), and 8- (△) cell-thick YBCO layers and for pure YBCO (solid line). Measured values of T_c (10% of normal resistance) for the $1 \times N$ structures from Ref. 6 are also shown.

temperature at which the peak resistance occurs depends upon the relative thicknesses of the PrBCO and YBCO layers; similar peaks occur for the other structures above 100 K. It is important to note that the 1×1, 1×2, and 1×4 superlattices have the same average composition as the 2×2, 2×4, and 2×8 structures, respectively. However, their zero-resistance transition temperatures T_{c0} are very different (Fig. 2). These striking differences in T_{c0}, for structures that have the same average composition, accompanied by the sharp satellite peaks shown in Fig. 1, demonstrate that we are observing the superconducting behavior of periodically layered superconducting structures and not alloys. Furthermore, the very different T_{c0} values for the $1 \times N$ and $2 \times N$ structures illustrate the importance of having YBCO in adjacent unit cells in order to raise T_{c0}. All of the $2 \times N$ structures have higher T_{c0} than all of the $1 \times N$ structures.

Figure 3 demonstrates that increasing the thickness d_{Pr} of the PrBCO layers results in an initial decrease of T_{c0}, *followed by saturation of T_{c0} at a nonzero value* for large PrBCO layer thicknesses, for all of the $1 \times N$, $2 \times N$, and $3 \times N$ superlattices. Our conclusion that T_{c0} is nonzero for superlattices containing isolated single-cell-thick YBCO layers is in contradiction with Triscone *et al.*[6] who found a linear reduction in T_c (10%) out to $d_{Pr} \sim 7.2$ nm (also shown in Fig. 3) and inferred from this that coupling between Cu-O double layers is necessary in order to produce superconductivity. In contrast, our results (carried out to $d_{Pr} \sim 19$ nm) show that the Cu-O bilayers in single-cell-thick YBCO are superconducting with $T_{c0} \sim 19$ K, when embedded in a PrBCO matrix. Figure 3 also shows the end-point $(N=16)$ T_{c0} values for the $4 \times N$ and $8 \times N$ superlattice series.

The T_{c0} values for $M \times N$ superlattices are very different from those for alloys having the same average composition. For large d_{Pr}, T_{c0} saturates for all of the
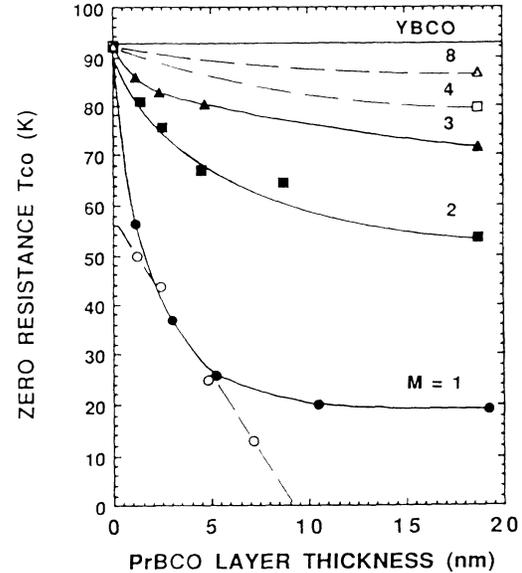
superlattices, while T_{c0} for Pr-rich alloys goes to zero.[4,5] Figure 3 shows that the superlattice T_{c0} depends strongly on the number of adjacent YBCO-containing unit cells in a layer, suggesting either that coupling is required between YBCO cells in order to *increase* their T_{c0}, or that YBCO cells immediately adjacent to PrBCO have their T_{c0} *depressed* by PrBCO. Thus, several different effects may contribute to the dependence of T_{c0} on the PrBCO and YBCO layer thicknesses. Rogers *et al.* recently observed weak dc and ac Josephson effects in YBCO/ PrBCO/YBCO trilayer structures in which the PrBCO layers were 50 nm thick.[17] Earlier, Moreland *et al.* also reported forming a superconducting Josephson point contact between two YBCO films coated with 5 nm of Ag, in the squeezable electron-tunneling geometry.[18] The Ag layer was believed to become superconducting by proximity-effect coupling. For our superlattices, although ξ_c is expected to diverge as $(1 - T/T_c)^{-1/2}$, the very small and T-dependent carrier concentration in PrBCO would make any proximity-effect contribution largest for the thicker (higher T_{c0}) YBCO layers and for the thinnest PrBCO layers. The evidence for Josephson effects, even through 50-nm-thick PrBCO, suggests that Josephson coupling may affect the T_{c0} of our YBCO/ PrBCO superlattices.

However, an alternative interpretation of our data is that a YBCO cell's electronic structure (and intrinsically high T_c) is severely modified if it is located adjacent to PrBCO. We note that for $d_{Pr} \sim 1.2$ nm the 2- or 3-cell-thick YBCO layers have much higher T_{c0} than for 1-

cell-thick YBCO, consistent with the interior cells of a thicker YBCO layer not being affected much by PrBCO. Consequently, T_{c0} for a YBCO layer only 4 cells thick can reach ~ 80 K (Fig. 3). Possible mechanisms by which PrBCO could affect the superconductivity of a neighboring YBCO cell include strain (either average or local), altered oxygen stoichiometry and/or a change of electronic structure (hole carrier density), Cooper pair breaking by PrBCO local moments, or the introduction of superlattice zone boundaries. Zone-boundary effects appear unlikely since the T_{c0} depression does not seem to be associated with any particular modulation wavelength. Pair breaking by local moments has been suggested as the mechanism responsible for the T_c depression and reentrant superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ random alloys.[5] Oxygen depletion certainly could change the hole concentration, but experiments on polycrystalline $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ random alloys indicate that the entire alloy range can be prepared with $\delta = 0.0 \pm 0.04$.[5] Thus, if the superlattice T_{c0} depression results from a local oxygen deficiency, it also must be associated with the epitaxial, layered, and periodic (as opposed to random alloy) nature of these structures. Strain also may be a factor, since the average lattice constant is expected to change from that of YBCO to that of PrBCO with increasing d_{Pr}, and Pr's ionic radius (~ 0.1013 nm) is significantly larger than Y's (~ 0.0905 nm). However, our data suggest that average strain alone is unlikely to provide a complete explanation, since even 3- or 4-cell-thick YBCO layers have high T_{c0} for $N_{Pr} \sim 16$, despite being (80–85)% PrBCO on average.

In summary, the T_{c0} for epitaxial YBCO/PrBCO superlattices initially decreases with increasing d_{Pr}, but T_{c0} then saturates as the separation of the YBCO layers is increased further. The limiting T_{c0} values for 1-, 2-, 3-, 4-, and 8-cell YBCO layers separated by ~ 190 nm in a PrBCO matrix are ~ 19, ~ 54, ~ 71, ~ 80, and ~ 87 K, respectively. Single-cell-thick YBCO layers, in particular, are superconducting in a PrBCO matrix. The available evidence suggests that Josephson coupling of YBCO layers can occur through relatively thick PrBCO layers, but PrBCO also may severely modify the electronic structure of adjacent YBCO unit cells. Additional experiments, and model calculations designed to evaluate the various mechanisms in the superlattice geometry, are needed in order to understand our results.

Note added.— Since this manuscript was submitted, a similar study has been published by Li *et al.*[19]

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