

Thickness dependence of the superconducting transition temperature of YBCO

I.N. Chan, D.C. Vier, O. Nakamura¹, J. Hasen, J. Guimpel², S. Schultz and Ivan K. Schuller
Physics Department-0319, University of California, San Diego, La Jolla, CA 92093-0319, USA

Received 2 February 1993; accepted for publication 16 February 1993
Communicated by L.J. Sham

We have performed detailed structural and superconducting studies of YBCO single layers, YBCO/PrBCO/YBCO tri-layers, and YBCO/PrBCO superlattices. The results for single layers indicate that a nominally one unit cell thick YBCO film sandwiched between PrBCO layers is not superconducting. However, a superlattice with nominally one unit cell thick YBCO layers has a measurable superconducting temperature onset (T_c^0). These apparently contradictory results are reconciled by experiments on YBCO/PrBCO/YBCO tri-layers which, due to coupling across the PrBCO insulating layer, exhibit superconductivity for PrBCO thicknesses below 200 Å. Structural studies show that the length scale of the superconductive coupling is much larger than the length scale of the step disorder and interdiffusion present in the film.

The thickness dependence of the superconducting critical temperature (T_c) for very thin layers has been of theoretical and experimental interest for many years [1–6]. In a variety of conventional superconductors, gradual [4,5] or sudden [6] transitions from the superconducting state to an insulating state have been observed with decreasing thickness. Gradual changes in T_c have also been observed in a variety of conventional superconducting superlattices [7–9]. In high temperature superconductors, Terashima et al. reported that a one unit cell thick single layer of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) is not superconducting when directly prepared on a variety of insulating substrates, although it is superconducting with an onset ~ 70 K when sandwiched between $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (PrBCO) layers on a SrTiO_3 substrate [10]. However, their analysis of X-ray diffraction to calibrate the thickness of their films is flawed and is discussed elsewhere [11]. An alternate way in which related studies have been performed is by preparing superlattices of the superconductor with a non-superconducting separator [12–14].

Ascertaining the integrity of a very thin layer is by no means trivial, even with modern state of the art characterization techniques. Two important issues have to be addressed quantitatively when studies of very thin layers are performed: (1) the absolute thickness must be determined with an accuracy higher than one unit cell and (2) quantitative measurements of interdiffusion and step disorder must be performed. Misleading conclusions may be obtained without a quantitative analysis of these issues. We present a detailed, comparative study of the structural, chemical, and superconducting properties of single layer, tri-layer, and superlattice configurations of YBCO and PrBCO films. Quantitative structural studies, based on refinement of X-ray diffraction spectra of superlattices, allow us to determine thicknesses with high accuracy and set limits on the amount of step disorder and interdiffusion. Our study indicates that a nominally one unit cell thick single layer of YBCO sandwiched in between PrBCO layers is not superconducting. In contrast, we find that a superlattice with nominally one unit cell thick YBCO layers has a measurable superconducting transition temperature onset (T_c^0). Tri-layer YBCO/PrBCO/YBCO configurations with nominally one unit cell thick YBCO layers sandwiched

¹ On leave from: Corporate Research and Development, Tonen Corp., Saitama 354, Japan.

² On leave from: Centro Atómico Bariloche, 8400 Bariloche, Argentina.

between additional PrBCO layers are superconducting for a separating PrBCO layer thickness less than 200 Å.

High temperature superconducting oxide films were prepared either by the standard 0°-off-axis method [15] or using a new sputtering technique (NACHOS). Briefly, in the NACHOS technique the sample is positioned outside the sputtering plasma in a 0°-off-axis configuration and moved periodically to symmetric positions across the target in order to improve thickness uniformity [16]. Structural measurements of 200 Å single layer films grown using this technique show that the film thickness fluctuates by no more than one unit cell.

The samples were grown on (100) single crystal MgO, (100) single crystal ZrO₂, or random cut single crystal yttria stabilized zirconia (YSZ) substrates kept at approximately 750°C. A *c*-oriented crystalline PrBCO buffer layer, with an approximate thickness of 1000 Å was grown before deposition of the single and tri-layer configurations. After deposition, the films were capped by either an amorphous or crystalline 200 Å PrBCO layer. For the superlattices, the first deposited layer was always PrBCO. The sputtering gas was a O₂(10%)/Ar(90%) mixture at a total pressure of 300 mTorr. After deposition the substrates were cooled to room temperature in approximately two hours in either 1 or 100 Torr of pure O₂. The amorphous capping layer was deposited with the substrate held at room temperature. We have examined our films using scanning electron microscopy and have found them to be featureless to 300 000× magnification.

As the film thickness of a superconductor is reduced, superconductivity can disappear either because of phase decoupling between superconducting grains or because of a change in the magnitude of the order parameter. Phase decoupling may occur in oxide superconductors for a variety of reasons, including inhomogeneous oxygen or metal ion stoichiometry distribution, weakening of the Josephson type coupling across grain or twin boundaries, etc. All these mechanisms will lead to loss of superconducting percolation across the whole film. Additionally, for very thin films the substrate surface roughness may result in island formation and loss of percolation. Since we are interested in establishing whether the magnitude of the order parameter is finite for

YBCO films with thicknesses near one unit cell, we have used the magnetic field modulated (MFM) microwave absorption technique [17] to determine the onset of superconductivity. This technique is applicable to determine T_c^0 even in non-percolating samples. The sensitivity of the MFM microwave method is such that we can detect a 0.1% superconducting volume fraction of a one unit cell thick film (this corresponds to detecting a superconducting volume of $\sim 5 \times 10^{-11}$ cm³).

Figure 1 shows a comparison of the temperature dependence of the MFM microwave absorption signal and the resistivity for a single 500 Å YBCO layer sandwiched between PrBCO layers. The T_c^0 determined from resistivity measurements corresponds to the T_c^0 determined from the onset of a sharp change in the MFM microwave signal.

As noted earlier two important structural issues must be addressed for an analysis of superconductivity in very thin films: (1) determination of the absolute thickness and (2) determination of the structural and chemical integrity of the superconducting film. High resolution X-ray diffraction provides a convenient method to address both issues. Figure 2b shows the X-ray diffraction spectra of a *c*-axis oriented [YBCO(1 unit cell)/PrBCO(8 unit cells)] \times 19 superlattice. This spectra compares well with data presented by other groups as far as intensity and line shapes are concerned [12,13]. Mea-

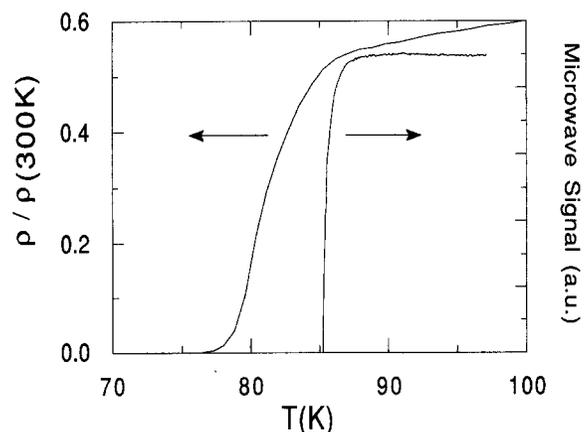


Fig. 1. Resistivity and MFM microwave absorption signal as a function of temperature for a 500 Å single layer of YBCO sandwiched between PrBCO layers.

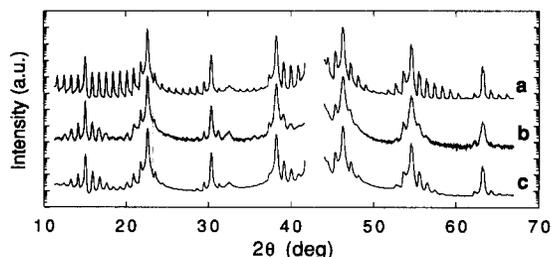


Fig. 2. θ - 2θ X-ray diffraction spectra for a c -oriented [YBCO(1 unit cell)/PrBCO(8 unit cells)] \times 19 superlattice. (a) Simulated spectrum for a perfect superlattice; (b) experimental data; (c) refined spectrum including interface roughness and interdiffusion. The curves have been offset and the (200) MgO peak at 42.8° has been erased for clarity.

surement of the superlattice period as a function of the YBCO to PrBCO deposition time ratio allows calibration of the deposition rate with 5% accuracy. This calibration has been compared with two other independent thickness determination methods: (a) stylus step profilometry for thick films, and (b) observation of finite size XRD peaks [16] in thin single layer films (100–300 Å). The deposition rates obtained by the three methods agree within 10%. Thus we can be confident that the average thickness of the layers is determined in the present experiments to an accuracy better than 10%.

The structural study of the individual layers requires a more sophisticated analysis. In our case, since the YBCO layer is structurally very similar to PrBCO, we must be particularly concerned with step disorder and interdiffusion. In fig. 2a we show the simulated spectrum for an ideal, perfect superlattice. Step disorder and interdiffusion in the layers are important and not negligible, as is clearly demonstrated by the difference in the relative intensity of the diffraction peaks between the perfect superlattice simulation (fig. 2a) and the experimental data (fig. 2b). Using a technique described previously [18] we model the structure including interdiffusion between the Y and Pr sites and step disorder in integer number of unit cells. Figure 2c shows the refined spectrum including quantitative parametrization of the interdiffusion and roughness at the interfaces. The results indicate that: (a) in the YBCO layer there is a $(30 \pm 5)\%$ substitution of Pr in the Y sites due to interdiffusion at the interfaces; (b) the YBCO layer has thickness fluctuations of one unit cell around the

average value of one unit cell; (c) there is only a limited amount of step disorder; (d) the c lattice parameter of the YBCO layer (11.63 Å) is contracted with respect to the bulk value (11.677 Å), indicating an in-plane expansion possibly due to epitaxial strains. Structural refinements of superlattices with thicker YBCO layers indicate that there is a 15% substitution of Pr in the Y sites at the first interfacial unit cell.

Figure 3 shows T_c^0 as a function of YBCO thickness (d_{YBCO}) for single layers sandwiched between PrBCO buffer and capping layers deposited on various substrates. These samples were prepared over a period of one year using a variety of growth methods, capping layers, and substrate combinations. Several of the samples were remeasured after a few weeks with no decrease in the observed T_c^0 . The reproducibility of the superconducting data between different runs, long term stability, and the independence of the capping layer structure (amorphous or crystalline) implies that the results are repeatable and reliable, and are not dependent on uncontrolled, unknown factors. The most striking feature of this data is the sharp increase in T_c^0 with thickness at ~ 15

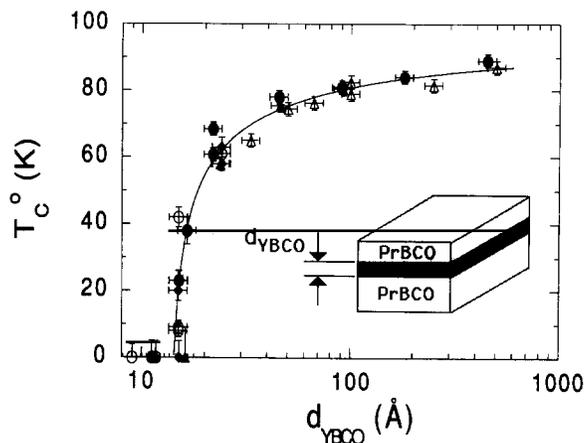


Fig. 3. T_c^0 of single layer YBCO as a function of thickness (d_{YBCO}) sandwiched between a 1000 Å c -oriented PrBCO buffer layer and a 200 Å PrBCO capping layer. (●) NACHOS deposition, YSZ substrate and amorphous capping layer; (▲) 0° -off-axis deposition, YSZ substrate and amorphous capping layer; (◆) NACHOS deposition, YSZ substrate and crystalline capping layer; (○) NACHOS deposition, MgO substrate and crystalline capping layer; (△) 0° -off-axis deposition, ZrO_2 substrate and amorphous capping layer. The solid line is a guide to the eye.

Å (one and a quarter unit cells of YBCO). This effect is probably caused by changes in the order parameter and not by phase decoupling since the observation is based on microwave measurements which do not require long range coupling across the whole sample. Clearly a nominally one unit cell thick layer of YBCO sandwiched between PrBCO layers exhibits no measurable superconductivity down to 5 K. This result might be expected if interdiffusion and lattice expansions are present as shown by the structural refinement. It should be remembered that 30% Pr doping depresses the superconducting transition temperature of bulk YBCO [19] by as much as 30 K, and therefore this amount of interdiffusion cannot be neglected.

In order to investigate the apparent discrepancy between these single layer results and those obtained from YBCO/PrBCO superlattices [12–14], we have performed a series of experiments on YBCO/PrBCO superlattices and YBCO(1 unit cell)/PrBCO(d_{PrBCO})/YBCO(1 unit cell) tri-layers sandwiched between PrBCO buffer and capping layers. These studies were conducted to determine the possible coupling across a separating PrBCO layer. For superlattices, our superconducting transition temperature data is in agreement with measurements reported by other groups [12–14]. For tri-layers the superconducting transition temperature decreases with increasing PrBCO separator thickness (d_{PrBCO}), as shown in fig. 4. The study of tri-layers indicates that the coupling length across PrBCO is of the order of 200 Å, as might be expected for a material which has a conductivity between a good metal and an insulator. The coherence length in conventional metals and semiconductors can be quite long depending on electronic parameters of the material. To the best of our knowledge, no measurements of the Fermi surface of PrBCO have been performed to date. However, based on the fact that the resistivity of PrBCO falls between a good metal and a conventional semiconductor, it is not totally unexpected that the coherence length is also in between these two extremes.

Since the coupling length is determined by the coherence length in PrBCO [20], T_c^0 of a YBCO/PrBCO superlattice may only be representative of the single YBCO layer if the thickness of the PrBCO separator is larger than 200 Å. It should be noted that this distance will be strongly dependent on the elec-

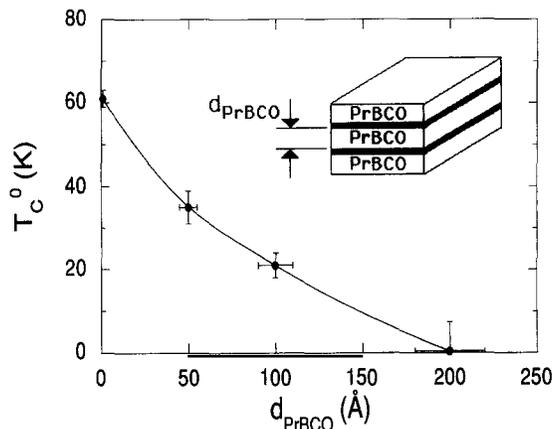


Fig. 4. T_c^0 for a YBCO(1 unit cell)/PrBCO(d_{PrBCO})/YBCO(1 unit cell) tri-layer as a function of PrBCO layer thickness (d_{PrBCO}) sandwiched between a 1000 Å *c*-oriented PrBCO buffer layer and a 200 Å capping layer. The solid line is a guide to the eye.

tronic properties of the separator and therefore a large variability may be expected from group to group.

We have investigated a large number of films of single layer, tri-layer, and superlattice configurations in order to ascertain whether the enhancement of superconductivity for superlattices, as compared to single layers, is a structural or intrinsic effect. As more and more layers are built up there may be cumulative disorder which can produce: (a) increases in roughness, (b) thicker layers than nominal, (c) random changes in the crystal structure, i.e. strains, which may occasionally create a superconducting region. The structural measurements performed to date indicate that this is not the case, i.e. no significant changes in the superlattice structure are observed with increasing number of layers. We are left, therefore, to conclude that for superlattices the enhancement of T_c^0 is an intrinsic effect.

In summary, we have performed a detailed study of the structural, chemical, and superconducting properties of YBCO films, in three configurations: (a) YBCO single layers sandwiched between PrBCO buffer and capping layers, (b) YBCO(1 unit cell)/PrBCO(d_{PrBCO})/YBCO(1 unit cell) tri-layers sandwiched by PrBCO buffer and capping layers and (c) YBCO/PrBCO superlattices. Detailed structural studies indicate the presence of interfacial roughness of the order of one unit cell and non-negligible Pr and Y interdiffusion. The superconducting proper-

ties are found to be independent of the crystalline or amorphous nature of the PrBCO capping layer. The T_c^0 for single layer YBCO films sandwiched between PrBCO layers increases abruptly from zero at $d_{\text{YBCO}} \sim 15 \text{ \AA}$. The coupling length across the PrBCO layer is of the order of 200 \AA in accordance with expectations. For superlattices the observed increase of T_c^0 appears to be intrinsic. The issue of the superconducting properties of a single unit cell thick, uniform, perfectly segregated, smooth YBCO layer is still open.

We would like to thank E. Fullerton for initial structural refinements, and R.C. Dynes and Y. Bruynseraede for useful conversations. We thank Professor K. Kitazawa and Dr. T. Izumi for arranging the Tonen-UCSD collaboration. Work supported by the Office of Naval Research grant no. N00014-88K-0480 (INC, ON, JH, JG, IKS), AFOSR-90-0365 and NSF-DMR-89-15815 (DV, SS). Some international travel provided by NATO. JG acknowledges CONICET, Argentina, for some international travel provided through a fellowship.

References

- [1] S.A. Wolf, J.J. Kennedy and M. Nisenoff, *J. Vac. Sci. Technol.* 13 (1976) 145.
- [2] J.E. Crow and M. Strongin, *Phys. Rev. B* 3 (1971) 2365.
- [3] M. Fukuyama, *Physica B* 126 (1984) 306.
- [4] A.E. White, R.C. Dynes and J.P. Garno, *Phys. Rev. B* 33 (1986) 3549.
- [5] M.M. Jaeger, D.B. Haviland, B.G. Orr and A.M. Goldman, *Phys. Rev. B* 40 (1989) 182.
- [6] D.B. Haviland, Y. Liu and A.M. Goldman, *Phys. Rev. Lett.* 62 (1989) 2180.
- [7] I.K. Schuller, in: *Physics, fabrication and applications of multilayered structures*, eds. P. Dhez and C. Weisbuch (Plenum, New York, 1988) p. 139.
- [8] V. Matijasevic and M.R. Beasley, in: *Metallic superlattices*, eds. T. Shinjo and T. Takada (Elsevier, Amsterdam, 1987) p. 187.
- [9] S.N. Song and J.B. Ketterson, in: *Materials science and technology*, Vol. 3, ed. K.H.J. Buschow, to be published.
- [10] T. Terashima, F. Shimura, Y. Bando, Y. Matsuda, A. Fujiyama and S. Komiyama, *Phys. Rev. Lett.* 67 (1991) 1362.
- [11] J. Hasen, D. Lederman and I.K. Schuller, *Phys. Rev. Lett.*, to be published.
- [12] Ø. Fischer, J.-M. Triscone, L. Antognazza, O. Brunner, A.D. Kent, L. Mieville and M.G. Karkut, *J. Less Common Met.* 164/165 (1990) 257.
- [13] D.H. Lowndes, D.P. Norton and J.D. Budai, *Phys. Rev. Lett.* 65 (1990) 1160.
- [14] Q. Li, X.X. Xi, X.D. Wu, A. Inam, S. Vadlamannati, W.L. McLean, T. Venkatesan, R. Ramesh, D.M. Hwang, J.A. Martinez and L. Nazar, *Phys. Rev. Lett.* 64 (1990) 3086.
- [15] O. Nakamura, I.N. Chan, J. Guimpel and I.K. Schuller, *Appl. Phys. Lett.* 59 (1991) 1245.
- [16] O. Nakamura, E.E. Fullerton, J. Guimpel and I.K. Schuller, *Appl. Phys. Lett.* 60 (1992) 120.
- [17] K. Khachatryan, E.R. Weber, P. Tejedor, A.M. Stacy and A.M. Portis, *Phys. Rev. B* 36 (1987) 8309; A.M. Portis, K.W. Blazey, K.A. Müller and J.G. Bednorz, *Europhys. Lett.* 5 (1988) 467, and references therein.
- [18] E.E. Fullerton, I.K. Schuller, H. Vanderstraeten and Y. Bruynseraede, *Phys. Rev. B* 45 (1992) 9292.
- [19] L. Soderholm, K. Zhang, D.G. Hinks, M.A. Beno, J.D. Jorgensen, C.U. Segre and I.K. Schuller, *Nature* 328 (1987) 604.
- [20] P.G. de Gennes, *Rev. Mod. Phys.* 36 (1964) 225; N. Werthammer, *Phys. Rev.* 132 (1963) 2440.