Superconductivity of One-Unit-Cell Thick $YBa_2Cu_3O_7$ Thin Film

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We have found for the first time that superconductivity can occur in a one-unit-cell-thick layer of $YBa_2Cu_3O_7$ (YBCO). The layer is grown, while monitoring with RHEED oscillations, on a nonsuperconducting $PrBa_2Cu_3O_7$ (PrBCO) buffer layer and covered by a PrBCO layer by reactive evaporation. A reduction of the onset temperature is found to be mainly due to a decrease of the hole carriers but not due to the absence of interlayer couplings. The covering PrBCO layer has been found to provide the YBCO layer with carrier holes sufficient to induce superconductivity.

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The layered structures of high-temperature superconductors (HTSC) based on the CuO_2 planes give the properties of the materials a high degree of anisotropy. Anisotropic and extremely short superconducting coherence lengths are especially important in considering the superconducting nature of HTSC [1]. The zero-temperature coherence length $\xi(0)$ of $YBa_2Cu_3O_7$ (YBCO) is 2–3 Å in the c direction and ~ 15 Å in the a-b direction. It is interesting to notice that $\xi_c(0)$ is much shorter than one unit-cell length along the c direction (~ 12 Å). It might suggest that the high-temperature superconductivity can occur in an isolated one-unit-cell layer.

In the study of thin films of HTSC, much interest has been directed toward the following problems. (1) What is the minimum unit needed for the occurrence of superconductivity in HTSC? (2) How essential is the inter-CuO_2-layer coupling in determining T_c?

Recently, superlattices comprising ultrathin layers of YBCO and nonsuperconducting $PrBa_2Cu_3O_7$ (PrBCO) have been intensively studied in order to give answers to these problems [2–4].

Li *et al.* [3] and Lowndes *et al.* [4] have reported that the zero-resistance transition temperature T_{c0} of one-unit-cell-thick YBCO layers in their superlattices decreased rapidly with increasing PrBCO thickness but did not go down to zero. They concluded that superconductivity can occur in one-unit-cell thick YBCO layers but that a coupling between the layers is needed to achieve a T_c of 90 K.

Strongly anisotropic superconductivity has been studied using transition-metal dichalcogenides MX_2 (M=Ta,Nb, X=S,Se) intercalated with organic molecules [5]. It has been theoretically suggested that a weak but finite interlayer Josephson coupling suppresses the phase fluctuation of the order parameter $\psi=|\psi|e^{i\theta}$ to give rise to a finite T_c. A similar situation seems to be seen in bulk samples of YBCO, Bi 2:2:1:2, Tl 2:2:1:2, and also in YBCO/PrBCO superlattices.

The use of artificial superlattices is, indeed, very effective to address the interlayer-coupling effect. However, the solution of the first problem asking about the minimum unit needed for the occurrence of superconductivity cannot conclusively be derived because the interlayer-coupling effect cannot be eliminated completely in superlattices. Furthermore, interconnection of YBCO layers might be induced during deposition as structural imperfections.

One important reason why superlattices are utilized is that the determination of the layer thickness by x-ray diffraction is feasible. However, recently, we have observed strong intensity oscillations in reflection high-energy electron diffraction (RHEED) caused by a two-dimensional unit-cell by unit-cell growth during the epitaxial growth of YBCO(001) on $SrTiO_3$(100) and found that the oscillation period precisely corresponds to the one-unit-cell height in the c direction [6]. The observation of the RHEED oscillations makes it possible to control the thickness of the film on the unit-cell scale. In this Letter we report the superconductivity in a single few-unit-cells-thick layer of YBCO, focusing especially on a one-unit-cell-thick layer.

There are many problems in the growth of a YBCO film as thin as one unit cell. The structure of the film at an initial stage of the epitaxial growth strongly depends on the substrate crystal [7]. The lattice matching between YBCO and the substrate crystal is of essential importance. Ultrathin films grown directly on $SrTiO_3$ and MgO have distorted lattices, imperfections, and discontinuity. Therefore, we have used a PrBCO buffer layer as a substrate. PrBCO has favorable properties for being the buffer layer for the formation of a one-unit-cell-thick YBCO layer. PrBCO of the same 1:2:3 structure with lattice constants very close to those of YBCO (lattice mismatch $\leq 1.5\%$) is a semiconductor even in its fully oxidized state and has a high resistivity at low temperatures. Second, flatness of the substrate surface on the atomic scale is a basis for the growth of a continuous one-unit-cell-thick YBCO layer. The use of a PrBCO buffer layer has proved to be very effective for the successful growth of ultrathin YBCO layers.

The films were grown by coevaporation of the metal elements under an oxygen atmosphere, which is called reactive evaporation. Details of the method were described elsewhere [8]. Resistivity was measured by a usual four-probe method. A typical distance between the voltage electrodes was 1 mm.

Figure 1 shows RHEED intensity oscillations during the successive growth of the PrBCO buffer layer, the one-unit-cell-thick YBCO, and the top PrBCO layer. As soon as the growth was initiated the intensity I decreased rapidly, and then increased to have a maximum peak. One period (peak to peak) precisely corresponds to the growth of a one-unit-cell-thick layer. The growth of each one-unit-cell layer can thus be attained by monitoring the RHEED oscillations. Note that the intensity is recovered while the growth is interrupted. An interruption time of $\sim$20 s has been taken after every one-unit-cell layer growth in order to improve the surface smoothness.

Figure 2 shows resistive transition curves for PrBCO(6 unit cells)/YBCO(l unit cells, $l=1,2,3,5,10$)/PrBCO(6 unit cells)/$SrTiO_3$(100) trilayer films and a 1000-Å-thick YBCO film. The most significant result in Fig. 2 is that the superconducting transition occurs even for $l=1$. This result reveals that the interlayer coupling between the CuO_2 bilayers is not the key entity for the occurrence of superconductivity in YBCO.

Before discussing the results in Fig. 2, we consider conditions needed for the occurrence of superconductivity in the one-unit-cell-thick YBCO layer. The one-unit-cell-thick YBCO layer is sandwiched between the PrBCO layers. The underlying PrBCO layer, indeed, plays the role of a buffer layer having a very good lattice matching.

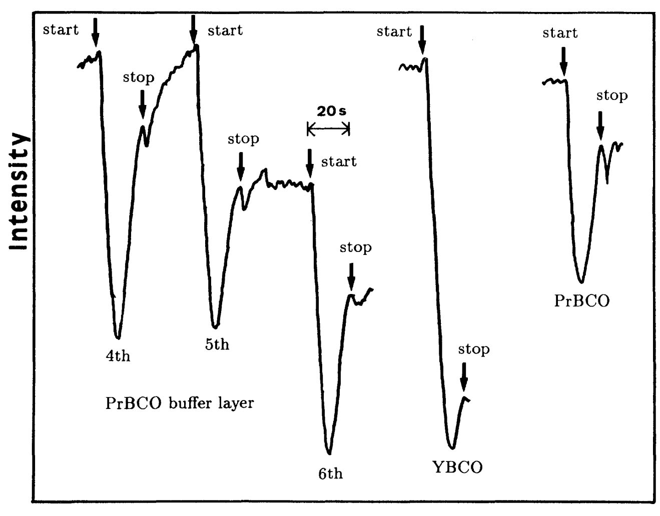

FIG. 1. RHEED intensity oscillations during epitaxial growth of the PrBCO buffer layer (6 unit cells), the YBCO one-unit-cell layer, and the PrBCO overlayer. The RHEED oscillations of the PrBCO buffer layer are shown from the fourth-unit-cell layer.

Then what role does the PrBCO overlayer on the YBCO layer play? Figure 3 shows the resistance versus temperature curves for the one-unit-cell-thick YBCO with various overlayers. When there is no layer on YBCO, the film shows a nonsuperconducting behavior (curve a). When an insulating PrO_x (70 Å) overlayer is grown (curve b), the film is still nonsuperconducting. Furthermore, a La_2CuO_4(001) (70 Å) layer can also be epitaxially grown on the one-unit-cell-thick YBCO layer (curve c), but the film also shows a nonsuperconducting behavior. These results of b and c can rule out the possibility that surface degradation may be the origin for the nonsuperconducting behavior of film a. On the other hand, when a one-unit-cell layer of PrBCO is grown on the YBCO layer, the film turns out to be superconducting (curve d). It is very interesting to note that the superconducting transition for bare two-unit-cell-thick YBCO (curve e) is similar to that of the one-unit-cell-thick YBCO layer with the PrBCO overlayer (curve d). Both T_{c0} and an onset temperature of the resistive transition are increased when a one-unit-cell-thick PrBCO overlayer is grown on the two-unit-cell-thick YBCO layer (curve f).

The two-dimensional growth unit of 1:2:3 compounds is a unit cell which satisfies the chemical composition and electrical neutrality [6], indicating that the unit should always have the same terminating atomic plane. In the present work, we cannot specify the terminating atomic plane, but can give an explanation for the result in Fig. 3 as follows.

It is natural to consider that the superconductivity of one-unit-cell-thick YBCO should occur in the CuO_2 bilayer interposed with an Y layer. Hole doping within the CuO_2 bilayer is of fundamental significance for the occurrence of superconductivity. It is manifested that a shortage of the hole concentration results in the nonsu-

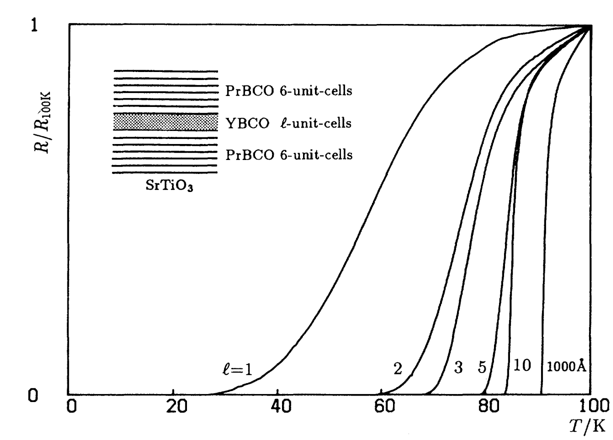

FIG. 2. Normalized resistance $[R(T)/R(100\ K)]$ vs temperature for PrBCO(6 unit cells)/YBCO(l unit cells, $l=1$, 2,3,5,10)/PrBCO(6 unit cells)/$SrTiO_3$ trilayer films and a 1000-Å-thick film.

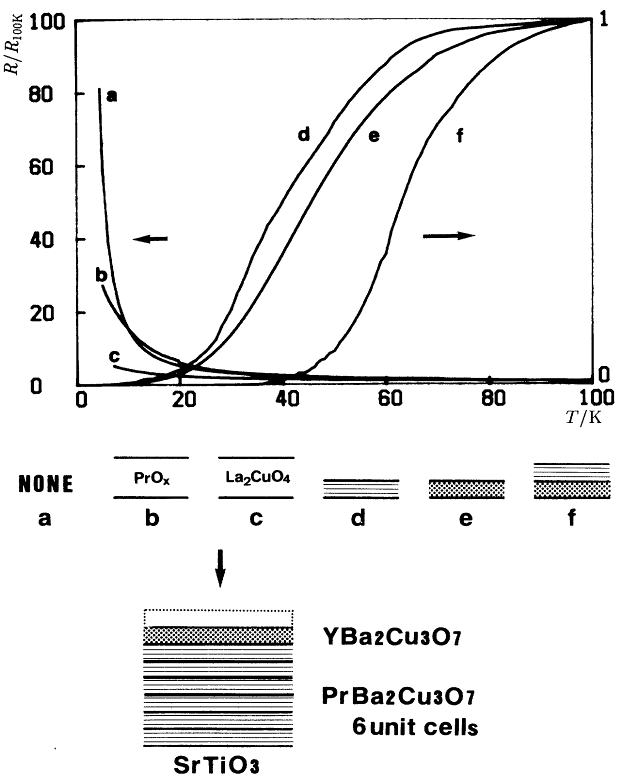

FIG. 3. Normalized resistance $[R(T)/R(100\text{ K})]$ vs temperature for X/YBCO(1 unit cell)/PrBCO(6 unit cells)/$SrTiO_3$: X is, curve a, none; curve b, PrO_x (70 Å); curve c, La_2CuO_4 (70 Å); curve d, PrBCO (1 unit cell); curve e, YBCO (1 unit cell); and curve f, PrBCO(1 unit cell)/YBCO(1 unit cell).

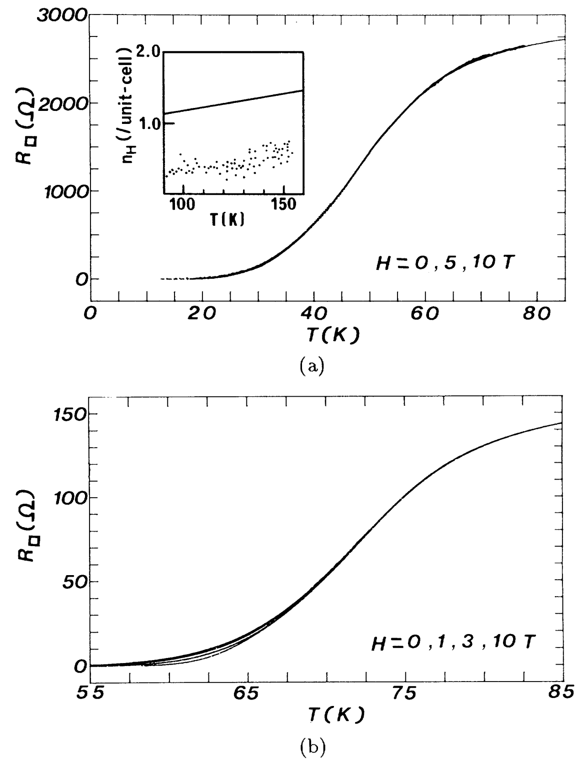

FIG. 4. (a) Resistive transitions for a PrBCO(6 unit cells)/YBCO(1 unit cell)/PrBCO(6 unit cells) film in magnetic fields parallel to the a-b plane. (b) Resistive transitions for a [YBCO(1 unit cell)/PrBCO(1 unit cell)] ×20 superlattice in magnetic fields parallel to the a-b plane. Inset: Hall number per unit-cell volume for the one-unit-cell-thick YBCO. The solid line is that of a bulky film (∼1000 Å).

perconductivity for the films a, b, and c. In order to make the (BaO)-(CuO)-(BaO) block layer capable of hole donation, a one-unit-cell-thick PrBCO overlayer must be formed on YBCO as shown in Fig. 3, curve d. The similarity between the results of Fig. 3, curves d and e suggests that the surface YBCO acts only as a hole dopant for the underlying YBCO layer and does not show superconductivity itself.

The onset temperature of the resistive transition observed for $l=1$ in Fig. 2 is lower than those for $l \geq 2$. The Hall number per unit-cell volume of $l=1$ shown in the inset of Fig. 4(a) is smaller than that of a thick YBCO film (1000 Å). If sufficient hole carriers can be doped into the YBCO layer, the onset temperature is expected to rise to 90 K. The interlayer coupling between CuO_2 bilayers itself may not be needed to achieve an onset temperature of 90 K.

Another remarkable feature in Figs. 2 and 3 is that the resistive transition of the one-unit-cell-thick YBCO is significantly broad. If "amplitude" fluctuation of the order parameter is considered, the temperature range of critical fluctuation is expected to be as small as $|T-T_c|/T_c \leq 10^{-3}$ even in the two-dimensional (2D) ultrathin superconductor [9].

A pure 2D superconductivity would be described by the Kosterlitz-Thouless (KT) theory of the phase transition, considering the "phase" fluctuation of the order parameter and the establishment of a quasi-long-range order of $|\psi|$ at finite temperature T_{KT}. In the superconductor, vortices and antivortices are induced by a thermal fluctuation even in the absence of magnetic field and are bounded in pairs below T_{KT}. Above T_{KT}, depaired vortices and antivortices give rise to a finite dissipation (or resistance) [10]. The KT transition has been studied in single crystals and "thick" films of Bi 2:2:1:2, Tl 2:2:1:2, and YBCO by many authors [11]. They reported that the T_{KT} are located at a few kelvins below the mean-field transition temperatures. However, these bulk systems are different from the one-unit-cell-thick layer because interlayer couplings between the CuO_2 bilayers, such as Josephson coupling and magnetic coupling, are present [12].

If we assume the temperature of zero resistance in one-unit-cell-thick YBCO is identical to T_{KT}, the effective thickness of the superconducting layer is estimated to be about 2 Å [10]. This thickness seems to be rather small. However, any slight local randomness due to, for example, crystalline imperfections which might be introduced during the growth of the extremely thin layer would give rise to a phase-breaking effect in the KT transition and lead to a reduction of T_{KT}. Of course, we should also consider localization effects caused by any local randomness. Further study is needed to elucidate whether the KT transition plays a dominant role in the superconductivity of the one-unit-cell-thick layer.

Figure 4(a) shows resistive transitions in applied magnetic fields parallel to the a-b plane with a precision of 0.1° for the PrBCO(6 unit cells)/YBCO(1 unit cell)/PrBCO(6 unit cells) film. In this measurement, the transport current and the magnetic field are perpendicular to each other. The result reveals that the resistive transition is independent of the fields parallel to the a-b plane when the coupling between CuO_2 bilayers is perfectly absent. For such a film, the magnetic field is assumed to penetrate uniformly without formation of vortices.

Triscone *et al.* [2] have reported that their YBCO(24 Å)/PrBCO(24 Å) superlattice showed a similar field-independent behavior in the parallel-field configuration. However, in their YBCO(12 Å)/PrBCO(12 Å) and YBCO(12 Å)/PrBCO(48 Å) superlattices, a remarkable broadening of the transition was observed. We have fabricated YBCO/PrBCO superlattices the thickness of the constituent layers of which was precisely controlled by monitoring the RHEED oscillations. Figure 4(b) shows resistive transitions of a [YBCO(1 unit cell)/PrBCO(1 unit cell)]×20 superlattice in magnetic fields parallel to the a-b plane. In contrast to Triscone *et al.*, our superlattice film does not show such a remarkable broadening. However, in the tail part of the transition, i.e., $R(T)/R(\text{onset}) \leq 0.3$, a slight broadening can be seen. The slight broadening may be caused by a dissipation relevant to the flux motion, the origin of which comes from the vortices formation in the a-c or b-c plane. In this configuration, the vortex cores would be located in the PrBCO layers and the shielding current along the c direction should be a Josephson current through the one-unit-cell-thick PrBCO layer.

Note that T_{c0} of the superlattice is much higher than that of the single one-unit-cell-thick layer. Considering the result in Fig. 4, we assume that an interlayer Josephson coupling exists between the one-unit-cell-thick YBCO layers in the superlattice and that it suppresses the fluctuation and gives rise to a higher T_{c0}.

We have demonstrated that the high-temperature superconductivity occurs in an isolated one-unit-cell-thick YBCO layer. The reduction of the onset temperature is found to be mainly due to the decrease of the hole carrier density but not due to the absence of the interlayer coupling. The KT transition is assumed to be one possible cause of the observed broad resistive transition. The resistive transition of the one-unit-cell-thick YBCO film is independent of the magnetic field parallel to the CuO_2 planes. The covering PrBCO layer grown on the one-unit-cell-thick YBCO layer has been found to be of significance in providing it with holes and thereby inducing superconductivity.

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