Superconducting properties of a 27-Å phase of Ba-Y-Cu-O

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High-purity (97%) samples of a 27-Å phase of Y-Ba-Cu-O have been prepared in superconducting thin films on (100) $SrTiO_3$. The possibility that the observed superconductivity might arise from a residual 3% $Ba_2YCu_3O_7$ impurity in this sample is ruled out using transmission electron microscopy which shows that it is present only as isolated particles. This allows for unambiguous determination that the 27-Å phase is superconducting with an onset T_c of 82 K and $T_c(R=0)$ of 79 K.

Structural modifications of the orthorhombic $Ba_2YCu_3O_7$ superconducting phase with an increased c axis have been observed as defects in bulk samples.[1-4] One such phase has been recently obtained as a major impurity in thin films[5-7] and ascribed to a variation in the stacking sequence of the normal orthorhombic $Ba_2YCu_3O_7$ phase where the c axis is elongated to 27.2 Å by the addition of copper-oxygen layers such that the stoichiometry becomes $Y_2Ba_4Cu_8O_{20-\delta}$.[4-5,7] The electrical characteristics of the films suggest that this second "27-Å" phase may also be a high-T_c superconductor.[6,7] However, the presence of significant fractions of the superconducting $Ba_2YCu_3O_7$ phase in the films makes it impossible to distinguish with certainty whether the superconductivity comes from the 27-Å phase or from the residual orthorhombic $Ba_2YCu_3O_7$ that is also present in these samples. The possibility exists that the orthorhombic $Ba_2YCu_3O_7$ is present as an interconnected network in the form of coatings on grains of the 27-Å phase, or contiguous sheets along the film surface, interior, or substrate interface. Such a network would be sufficient to establish a percolating superconducting path in this small fraction of $Ba_2YCu_3O_7$ which could then account for the observed superconductivity. Recently, a magnetization measurement has been performed on a film containing 80%–92% of the 27-Å phase with a 8%–20% $Ba_2YCu_3O_7$ impurity.[7,8] Based on this measurement, it would appear that such a network of $Ba_2YCu_3O_7$ would have to have a critical current density (J_c) close to the lower limit of the depairing critical current density which has been determined for this high T_c superconductor.[9] Past experience with thin films of conventional superconductors has shown that J_c's approaching depairing limits can be observed.[10] Given the general practical and theoretical interest in understanding related high-T_c compounds, it is important to rule out this possibility and unambiguously establish the superconducting properties of the 27-Å phase.

Herein, we describe a film we have recently prepared which consists almost entirely of this 27-Å phase. The structure of this film is examined using transmission electron microscopy (TEM). The film matrix is found to consist of individual domains with *Ammm* symmetry, rotated by 90° around the c axis and a lattice image spacing of 27.2 Å. Residual orthorhombic $Ba_2YCu_3O_7$ is found only in the form of isolated particles. The high purity of the 27-Å phase in these films allows for positive characterization of it as a superconductor with an onset T_c of ~82 K and T_c ($R=0$) of ~79 K.

The pulsed excimer laser vaporization methods and subsequent annealing conditions used to prepare these films are described elsewhere.[11] Material is ablated from a composite target of BaF_2-Y_2O_3-CuO and deposited onto $SrTiO_3$ ⟨100⟩ substrates at ~25° C and $\sim 10^{-5}$ Torr. Highest concentrations of the 27-Å phase are obtained on thinner films (≤ 0.2 μm) which have been annealed such that the temperature of the furnace is ramped between the various temperatures used in the annealing procedure. ($T_0=25$°C, ramp to 850 °C over $\frac{1}{2}$ h in flowing O_2, anneal at 850 °C for 1 h in flowing O_2 and H_2O, ramp to 440 °C over 2 h in flowing O_2, furnace turned off; film removed at $T_f=25$ °C.) The occurrence of this phase can be largely suppressed by increasing film thickness and/or rapidly changing the temperature in the annealing process, e.g., by moving the film to another temperature zone in the furnace.

TEM samples are prepared by mechanical polishing and ion milling at liquid-nitrogen temperatures to reduce ion milling damage.[12] TEM micrographs and electron diffraction patterns are obtained using a Philips 420T electron microscope operated at 120 kV. X-ray analysis is performed on a four-circle diffractometer with a rotating anode generator and Cu $K\alpha$ x rays. The longitudinal resolution is about 0.04 $Å^{-1}$ and the dynamic range of the intensity spans at least four orders of magnitude. Electrical transport properties are determined using a low-frequency ac four-point probe in a van der Pauw configuration with fluxless indium soldered contacts. J_c's are determined by scribing a 100 μm constriction in the film with a carbide tool and determining the current required to create a 1 μV potential across the constriction. Rutherford backscattering spectroscopy is used to determine the stoichiometry of the deposited films.

One of the films consists almost entirely of the 27-Å phase (Fig. 1). The lattice parameters of this phase are determined by x-ray diffraction analysis to be $3.86(1)\times3.86(1)\times27.24(6)$, confirming the previous report by Marshall *et al.*[5] The weak $Ba_2YCu_3O_7$ peaks present in the x-ray data shown in Fig. 1 indicate that this film is not single phase. The film is found to consist of 97% of the 27-Å phase relative to 3% of the orthorhombic $Ba_2YCu_3O_7$ phase based on the intensity ratio between the (0,0,12) peak and the (0,0,5′) $Ba_2YCu_3O_7$ peak (visible as a shoulder), and the relative structure factors for these respective reflections.[13]

The microstructure of the film containing 97% of the 27-Å phase was examined using TEM. The film structure, as shown in Fig. 2, is markedly uniform with a sharply delineated interface at the $SrTiO_3$ substrate. The dark lines running parallel to the substrate, have a spacing of ~13 Å, half of the 27-Å cell. This is consistent with the x-ray diffraction data which indicate that the 27-Å phase is oriented with its *c* axis perpendicular to the substrate. The relatively few defects which occur in the film are primarily planar-type defects which run along the *a*/*b* axis of the film. Microdiffraction patterns of the planar defect regions are identical to those obtained in defect-free regions and correspond to the 27-Å phase (see below).

Distinct antiphase domain boundaries that are seen in orthorhombic $Ba_2YCu_3O_7$ are not observed in the lattice images of the 97% 27-Å film.[12] The presence of different domains is evident in this film, however, in the electron microdiffraction patterns. Figures 3(a) and 3(b) show the electron diffraction patterns obtained from two adjacent regions. In Fig. 3(a), the selection rule is $h+l=2n$ observed, whereas in Fig. 3(b) reflections obey $k+l=2n$ observed. (The assignment of *h* and *k* above is arbitrary; the lattice is pseudotetragonal and they cannot be distinguished.) This is a direct observation of individual *A*-centered domains of the 27-Å unit cell which are rotated in the *a*-*b* plane by 90°. The lack of sharp boundaries in

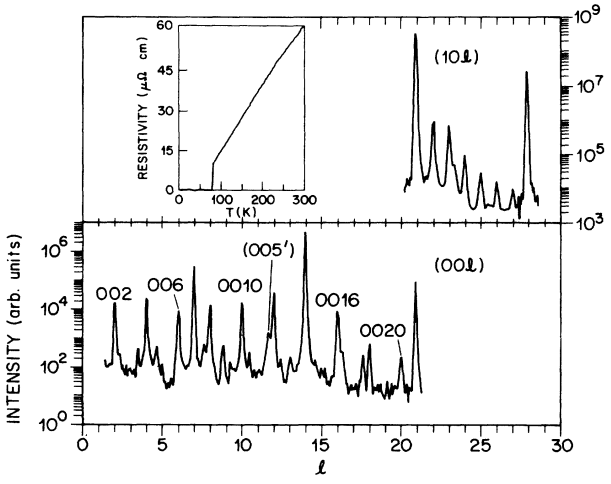

FIG. 1. X-ray diffraction along [00*l*] and [10*l*] and $\rho(T)$ curve (inset) of a 0.3 μm film on $SrTiO_3$ ⟨100⟩. The film contains 97% of the 27-Å phase (marked as 00*l* or 10*l*) and 3% of the $Ba_2YCu_3O_7$ phase (marked as 00*l*′).

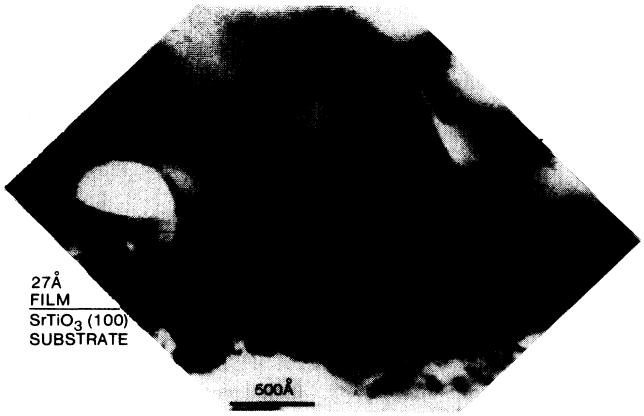

FIG. 2. Dark field TEM of the film containing 97% of the 27-Å phase showing the uniformity of the lattice and characteristic planar defects.

the lattice image between these domains arises because the unit cell is pseudotetragonal in the *a*-*b* plane. The occurrence of these individual domains may result from the intergrowth of adjacent areas on the substrate rather than from twinning in the crystallographic sense. Using the diffraction pattern to identify separate domains indicates that a given domain is at least 2–3 μm across and persists through the entire thickness of the film (0.3 μm).

The x-ray diffraction analysis of this film indicates the presence of orthorhombic $Ba_2YCu_3O_7$. Using TEM, it is possible to scan various regions of the film and study the distribution of this minority phase. Examination of the film matrix, domains, defects, substrate interface, and film surface reveals that orthorhombic $Ba_2YCu_3O_7$ is absent in these regions. Numerous particles are also seen as in-

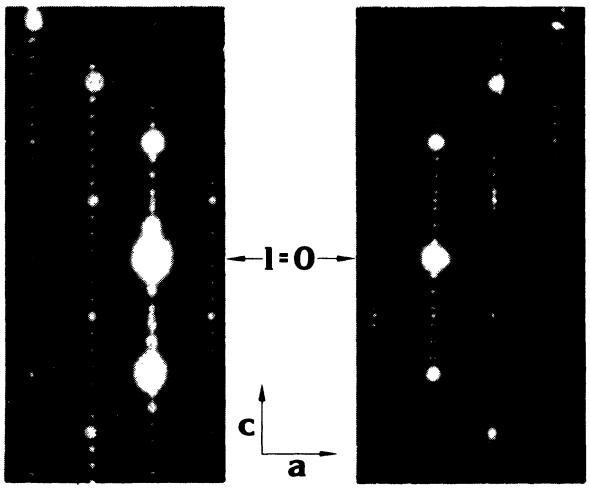

FIG. 3. Selected area diffraction patterns of two adjacent regions of the 27-Å phase. (a) $l=2n+1$ for odd *h*; (b) $l=2n$ for all *h*. The observed reflections indicate *A* centering of the unit cell. These diffraction patterns were obtained in areas which slightly overlap the $SrTiO_3$ substrate so as to have the $SrTiO_3$ diffraction pattern as a reference, e.g., $SrTiO_3$ (001) are marked with an *S*.

clusions throughout the film matrix. A close scrutiny of the lattice images and microdiffraction patterns of these particles indicates that most of them contain amorphous material or a mixture of indeterminate phases. A few of the randomly dispersed particles, however, are found to contain orthorhombic $Ba_2YCu_3O_7$. An example of such a particle can be seen in Fig. 4 with the characteristic lamellar twin structure of the orthorhombic $Ba_2YCu_3O_7$ superconductor.[12] These $Ba_2YCu_3O_7$ particles are not interconnecting and are typically found at least 0.2 μm apart.

The observed microstructure of the film containing 97% of the 27-Å phase indicates the $Ba_2YCu_3O_7$ impurity is segregated as noninterconnecting grains. Therefore, the observed electrical properties are unambiguously attributable to the 27-Å phase which makes up the film matrix. This allows for a definitive determination of the onset temperature of the 27-Å phase as $\sim$82 K and its zero resistivity as 79 K. The measured J_c (67 K) of the 97% film is 1×10^5 A/cm^{-2}. These electrical characteristics are in close agreement with those reported by Char *et al.* for a film containing 80% and 20% of the 27-Å and orthorhombic $Ba_2YCu_3O_7$ phases, respectively.[7]

As previously noted, films containing high concentrations of the 27-Å phase have about a factor of 10 smaller resistivity than is observed in $Ba_2YCu_3O_7$ at a given temperature and intercept zero resistivity at a positive temperature.[5-7] The films which have the highest concentrations of the 27-Å phase show low resistivities at 100 K of $\sim$20 $\mu\Omega$ cm. The 97% 27-Å phase film also exhibits an unusual characteristic in that the slope of the temperature dependent resistivity (Fig. 1) between 80 and 230 K extrapolates to zero at about 40 K. At about 230 K, a break occurs and the slope from 230 to 300 K can be extrapolated through zero resistivity. The onset temperature and $T_c(R=0)$ depend on the interconnection within the two phases. We have prepared other film samples with differing amounts of the 27-Å and $Ba_2YCu_3O_7$ phases. When the concentrations of the two phases are nearly even, the electrical characteristics become mixed as well. For example, onset temperatures of 92 K are observed with T_c $(R=0)=78$ K in some of our samples; other samples have T_c $(R=0)=90$ K, and one film containing about 64% of the 27-Å phase shows a break in the resistivity curve which corresponds to two distinct onset transitions at 90 and 80 K. Furthermore, as the concentration of $Ba_2YCu_3O_7$ increases relative to the 27-Å phase in these other films, the extrapolated intercept of the slope of the resistivity versus temperature from $\sim T_c$ (onset) to $\sim$230 K converges to $\sim$0, the break at 230 K no longer appears, and the overall resistivity rises.

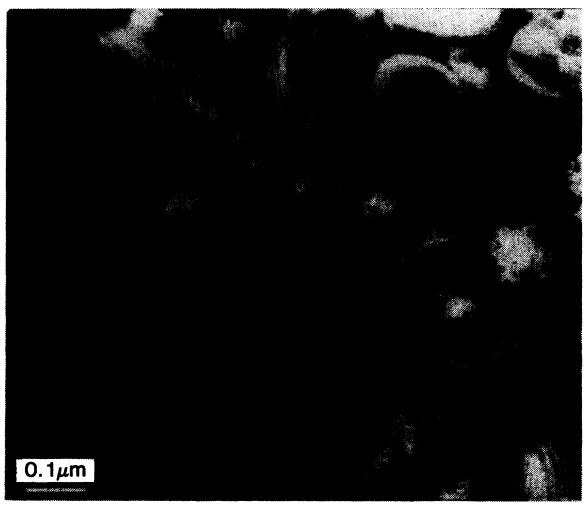

FIG. 4. Planar view TEM of the film showing the randomly dispersed particles (P). The lamellar twin structure characteristic of the orthorhombic $Ba_2YCu_3O_7$ phase can be clearly seen in the central particle.

The properties of two films containing 64% and 86% of the 27-Å phase were remeasured after subjecting them to additional annealing cycles at 850 °C in dry O_2. A comparison of the x-ray diffraction intensities before and after reannealing indicate that the absolute amount of the 27-Å phase remains unchanged although the absolute amount of the orthorhombic impurity increases by factors of 2–4. This indicates that the 27-Å phase is relatively stable and does not revert to the orthorhombic $Ba_2YCu_3O_7$ superconducting phase or any other structure at higher temperatures. The additional intensity that appears for the orthorhombic phase may arise because more of this phase is formed from residual amorphous material upon reheating and/or because the random grains of this phase become more well oriented with respect to the substrate during reannealing. In the case of the 64% film the reannealed film no longer exhibited any onset T_c near 90 K and had only an onset temperature typical of the 27-Å phase at 80 K.

The exact stoichiometry *of the 27-Å phase* has not yet been determined by a chemical analysis in any of our films or those reported elsewhere.[5-7] EDAX of the 97% film matrix does qualitatively indicate that the composition of these films is enriched in copper relative to orthorhombic $Ba_2YCu_3O_7$. The wide range of Y:Ba:Cu ratios which have been reported in films with substantial fractions of this phase makes it impossible to use the deposited composition to pinpoint the actual metals stoichiometry of the 27-Å phase. Although it has been reported that the as-deposited films must be enriched in Cu and slightly Y rich in composition to achieve high concentrations of the 27-Å phase,[7] we do not find that this is necessary. For example, the overall metals composition of the 97% pure film is determined to be $Ba_{1.8}Y_{1.0}Cu_{3.0}$ and another film with $\sim$87% of the 27-Å phase has a metals composition of $Ba_{2.2}Y_{1.2}Cu_{3.0}$. Just as for the $Ba_2YCu_3O_7$ phase, the formation of the 27-Å phase appears to be much more sensitive to the annealing conditions rather than the precise composition of the deposited material. Excess metal is simply sloughed from the film in the form of other phases, which accounts for the appearance of the inclusion particles seen in Fig. 4. It has also been suggested that the inclusion of some halide, e.g., F or Cl, stabilizes this phase.[6] The use of a halide barium source or introduction of a halide carrier appears to enhance the formation of this phase; however, its exact role in this process is not certain.[6,7]

Zandbergen, Gronsky, Wang, and Thomas have given a model for the 27-Å defects in bulk $Ba_2YCu_3O_7$ which consists of two $Ba_2YCu_3O_7$ unit cells with intercalated CuO double layers.[4] Marshall *et al.* have connected the 27-Å phase in thin films with this defect structure, and proposed a revised Zandbergen structure model such that the shift between the unit cells has the observed *A* centering.[5,7] The Marshall model leaves open the question of oxygen vacancies in the additional copper-oxygen layers.[7] Both proposed models have the observed 27-Å spacing with a metal-cation stoichiometry for Ba:Y:Cu:2:1:4. We have recently performed a full x-ray structural analysis of the 27-Å phase which determines the oxygen positions as well as those in the metal framework.[13] The metal cation arrangement of the Marshall model is found to be correct. Moreover, we establish that the oxygen ordering in the inserted copper-oxygen layers produces doubled Cu-O chains, giving an overall ideal stoichiometry of Ba_2Y-Cu_4O_8 for the unit cell.

In summary, films containing 97% of a 27-Å phase of Ba-Y-Cu-O have been prepared on (100) $SrTiO_3$. The symmetry assignment of *Ammm* is substantiated by observation in the TEM microdiffraction patterns of individual *A*-centered domains rotated by 90° in the basal plane. The residual 3% orthorhombic $Ba_2YCu_3O_7$ phase in this film is found to be distributed in the form of noninterconnecting particles. This allows for unambiguous determination of the superconducting properties of this alternative structure which is found to have T_c ($R=0$) of 79 K and an onset T_c of 82 K. This confirms that the 27-Å phase is the majority superconducting carrier in previously reported films which contained significant fractions of the known orthorhombic $Ba_2YCu_3O_7$ superconductor.

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[8]The film is described as having 92% of the 27-Å phase relative to 8% of $Ba_2YCu_3O_7$ (Ref. 7). Examination of the supporting x-ray data indicates that this film contains only 80% of the 27-Å phase and 20% of $Ba_2YCu_3O_7$. The intensities of the (100) and (005) reflections show that the $Ba_2YCu_3O_7$ impurity occurs with about equal amounts of the *a* and *c* axes oriented perpendicular to the substrate.
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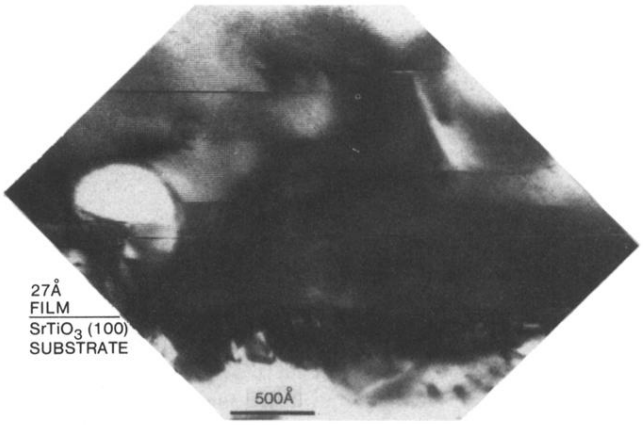

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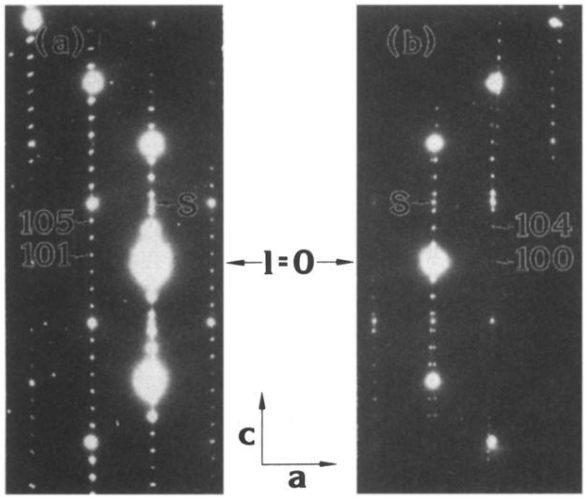

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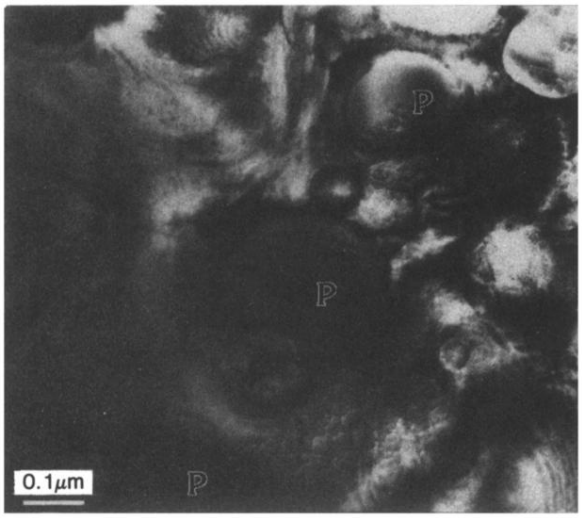

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