Y-Ba-Cu-O/Dy-Ba-Cu-O Superlattices: A First Step towards the Artificial Construction of High-T_c Superconductors

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We have for the first time epitaxially grown superlattices of Y-Ba-Cu-O/Dy-Ba-Cu-O by dc magnetron sputtering onto $SrTiO_3$ and MgO substrates. The wavelengths range from 24 (twice the c axis) to 300 Å and x-ray diffractograms show satellite peaks characteristic of multilayers for each wavelength. The 24-Å-wavelength sample consists of, on the average, alternate planes of Y and Dy. The multilayers are superconducting with T_{c0}'s between 85 and 89 K, transition widths of 2 K, and resistivity ratios of about 3.

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The new high-T_c superconductors are naturally layered materials. Superconductivity is related to the presence of CuO planes separated by Y planes in $YBa_2Cu_3O_7$ or by Ca planes in the $Bi_2Sr_2Ca_nCu_{n+1}O_{2n+6}$ and $Tl_2Ba_2Ca_nCu_{n+1}O_{2n+6}$ series. These CuO planes are sandwiched in a stack of layers giving a variety of highly anisotropic structures. In the Bi and Tl series there exist stacking sequences having different numbers of CuO_2 planes in the unit cell. Associated with the 1:2:3 phases is the different ordered structure $Y_2Ba_4Cu_8O_{10}$ which has a c parameter of 27.2 Å.[1] This phase is difficult to obtain in bulk form as are the Bi and Tl phases with large n. A fundamental problem is that different phases having comparable free energies can form, and since the starting material for bulk or single crystals is a random mixture of all the constituents, it becomes increasingly more difficult to stabilize single large-n phases far away from a random distribution. In recent years, advances in thin-film technology has permitted the growth of various metastable phases and multilayers—both superconducting and semiconducting—of very high quality. Thus a major challenge is to grow high-T_c superconductors layer by layer using thin-film techniques. Large-n structures, various substitutions, and new materials would then be feasible.

In this Letter we report a significant step in this direction: the *in situ* epitaxial growth of $YBa_2Cu_3O_7$/$DyBa_2Cu_3O_7$ superlattices having modulation wavelengths Λ, determined by x-ray diffraction, as small as 24 Å. The crystalline coherence of the films in the c direction is very large—on the order of the thickness of the films or about 2000 Å—and the T_c's of these multilayers are similar to those of single films. The $\Lambda = 24$-Å sample is the alternation of unit cells of $YBa_2Cu_3O_7$ and $DyBa_2Cu_3O_7$. Thus we were able to grow a 1:2:3 structure in which, on average, every other Y plane in the c direction is replaced by a Dy plane. This is an important result because it demonstrates that, in spite of the complexity of the structure and the extreme conditions required to form the 1:2:3 phase *in situ*, it is possible to manipulate these materials over a distance comparable to the size of the unit cell, thus opening up the prospect of new experiments designed to elucidate the superconducting and magnetic nature of these compounds.

Before multilayers can be made, the ability to make *in situ* thin films is necessary. To form the 1:2:3 phase *in situ*, the deposition must be carried out on heated substrates in a high O_2 partial pressure. The preparation details for single layers have been reported elsewhere.[2] Briefly, our films have been prepared by single-target dc planar magnetron sputtering. We have exploited the idea of Li *et al.*[3] by sputtering at very high pressures. During deposition the total pressure ($Ar+O_2$) is about 300 mTorr with the partial pressure of O_2 maintained at 20 mTorr. The substrate temperature determined by optical pyrometry is about 700 °C. The substrate is placed at 3 cm directly in front of the target and the deposition rate is ~0.5 Å/s. After deposition the films are cooled in 1 mbar of O_2 to 400–450 °C at which point we increase the pressure to 20 mbar and keep the temperature constant for 15 min to 2 hr before cooling to room temperature. This procedure consistently produces films having zero resistances T_{c0} between 87 and 90 K, residual resistivity ratios (RRR) between 2.5 and 3, and resistivity at 100 K of about 60 $\mu\Omega\,cm^2$. Scanning electron and tunneling microscopy and reflection high-energy electron diffraction analyses show that the surfaces of these films are extremely smooth[2]—a prerequisite for multilayer growth. Films of $DyBa_2Cu_3O_7$ have been prepared using the same deposition procedures mentioned above and we find that the superconducting properties for these films are similar to $YBa_2Cu_3O_7$ films. Finally, we have used substrates of (100) $SrTiO_3$, (110) $SrTiO_3$, and (100) MgO. On these substrates $YBa_2Cu_3O_7$ and $DyBa_2Cu_3O_7$ films grow mixed a axis and c axis, (110) and (001), respectively.

To produce multilayers, two stoichiometric targets of $YBa_2Cu_3O_7$ and $DyBa_2Cu_3O_7$ are mounted on two guns placed 180° apart in our UHV system. A computer-controlled step motor positions the samples in front of

the desired gun for a given time. We follow the same deposition procedure as for the single thin films. Figure 1 shows a schematic illustration of an ideal $DyBa_2Cu_3O_7/YBa_2Cu_3O_7$ superlattice having a wavelength Λ of about 24 Å or twice the unit-cell distance and the c axis parallel to the growth direction. Note that the modulation comes about by the alternation of the Dy and Y atoms in the unit cell. Longer-wavelength samples can be made by increasing the number of consecutive Y and/or Dy planes. We have made superlattices with wavelengths ranging from 24 to 300 Å and having total film thicknesses of about 2000 Å on substrates of (100) $SrTiO_3$, (110) $SrTiO_3$, and (100) MgO.

A major result of this Letter is the characteristic superlattice x-ray signature shown in Fig. 2 in the region of the (001) and (002) reflections for a $\Lambda = 60$-Å $YBa_2Cu_3O_7/DyBa_2Cu_3O_7$ multilayer on MgO. The presence of satellite peaks (indicated by the arrows) on the θ-2θ x-ray diffractogram is characteristic of periodic chemical modulation. For multilayers, the x-ray reflections are related to the artificially imposed modulation Λ. This produces, close to the usual Bragg reflections, satellite peaks whose angular positions are inversely related to the modulation wavelength by[4] $\Lambda = \lambda_x/2(\sin\theta_n - \sin\theta_{n+1})$, where λ_x is the x-ray wavelength [in our case λ_x(Cu $K\alpha$) = 1.542 Å], and θ_n and θ_{n+1} are the angular positions of two consecutive satellites. The two small peaks labeled with stars will be discussed below. Also displayed are the diffractograms of a $DyBa_2Cu_3O_7$ single film and an $YBa_2Cu_3O_7$ single film. There is no (002) reflection for the $DyBa_2Cu_3O_7$ single film [the interrupted (002) $YBa_2Cu_3O_7$ peak in the figure should not be mistaken for a $DyBa_2Cu_3O_7$ peak]. This absence of the (002) reflection has also been noted[5] for $GdBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$ and is due to the electronic structure of these rare-earth materials. We observe the consistent result that the intensity of the multilayer (002) line is between the intensities of the (002) lines of $YBa_2Cu_3O_7$ and $DyBa_2Cu_3O_7$.

The crystalline coherence in the growth direction can be determined from the θ-2θ diffractogram peaks by putting the full width at half maximum (FWHM) of the peaks into the Scherrer formula.[6] What we observe for the $DyBa_2Cu_3O_7/YBa_2Cu_3O_7$ multilayers is that, unlike, say, metallic multilayers such as Nb/Cu[4] or Mo/V,[7] there are two coherence lengths involved. This is be-

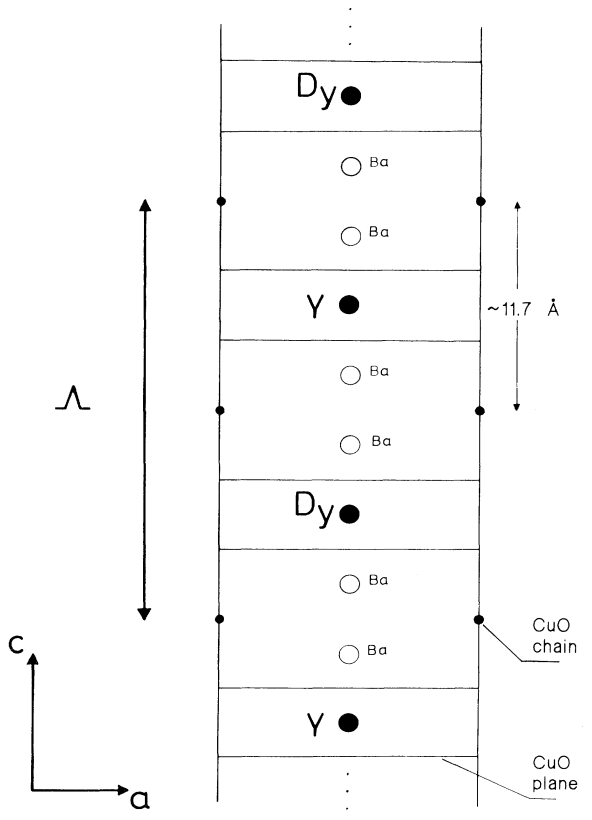

FIG. 1. Schematic representation of an ideal 24-Å-wavelength $YBa_2Cu_3O_7/DyBa_2Cu_3O_7$ multilayer. The sizes of the atoms and interatomic distances are not to scale.

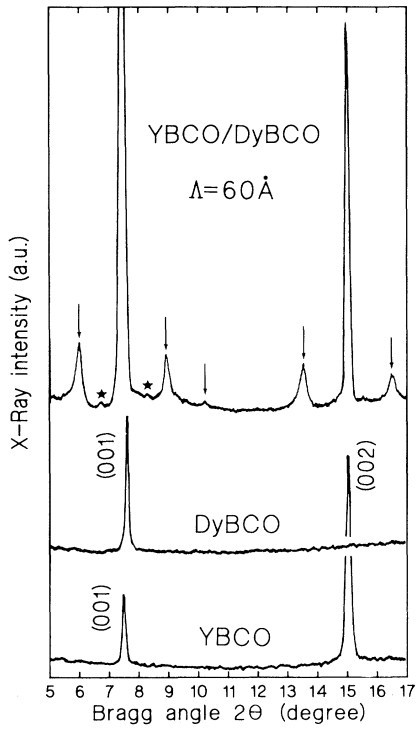

FIG. 2. X-ray diffractograms of an $YBa_2Cu_3O_7/DyBa_2Cu_3O_7$ multilayer with $\Lambda = 60$ Å on MgO (top), a $DyBa_2Cu_3O_7$ single layer on $SrTiO_3$ (100) (middle), and an $YBa_2Cu_3O_7$ single layer on $SrTiO_3$ (100) (bottom). The arrows indicate the multilayer satellite peaks, and the starred peaks an additional modulation. Note that the (002) reflection is absent for the $DyBa_2Cu_3O_7$ single layer.

cause the modulation of the rare-earth planes takes place within the Ba-Cu-O matrix. Thus the FWHM of the (001) and (002) peaks is a measure of the coherence throughout the entire crystal whereas the FWHM of the satellite peaks is a measure of the coherence of the rare-earth planes. The coherence of the chemical modulation determined from the satellite peaks is fairly large—about 360 Å, or about 30 unit cells in length. The FWHM of the (001) and (002) peaks for the $\Lambda=60$-Å superlattice is due solely to that of the instrumental broadening of the diffractometer, which implies the crystalline coherence is on the order of the thickness of the film—about 2000 Å. The reason for this difference is that the 1:2:3 structure does not care whether it is the Dy or the Y which occupies the rare-earth site. This long crystalline coherence also implies that the interfaces are extremely clean and that the time spent to go from one gun to the other one, about 2 s, does not disturb the growth. In fact, it may even aid in the growth process since the coherence of single thin films is not as good as for the superlattices.

The peaks marked with stars are, we believe, due to a third modulation in the multilayer Λ^* (there is the atomic modulation c and the artificial modulation Λ). The nature of this rare-earth substitutional modulation is unusual in the sense that the sites are fixed by the geometry of the 1:2:3 structure. Thus with the growth direction parallel to the c axis the modulation wavelengths are necessarily quantized in units of this axis. Now, if, in the best of all possible worlds, the deposition rates of the two sputter guns are precisely controlled for a certain fixed time t, the multilayer will grow by $\Lambda/2$, and $n/2$ (n even, say) planes will be completely filled with Dy atoms. After an additional time t under the Y gun, the multilayer will again grow by $\Lambda/2$; this process repeats continuously. This is straightforward and an x-ray θ-2θ diffractogram will have only the standard superlattice satellite peaks. However, in reality, the rates are not perfectly controlled and the time t spent under the Dy gun, say, will not fill $n/2$ planes completely. There will be a little more or a little less. When the sample moves to the Y gun, the Y atoms will then complete the plane of Dy atoms, because the integerity of the 1:2:3 structure must be maintained. After time t, there will be a partially filled top plane of Y atoms. Now the Dy atoms will finish the filling of this plane and this process is repeated. There will thus be, in addition to the modulation Λ, a supermodulation Λ^* whose value depends on the deviation of the sputtering rates from the exact values needed to produce a wavelength Λ which is a multiple of $c=11.7$ Å. When the deviation of the rate is small, then Λ^* will be large and the intensity of the Λ modulation peaks will be strong. However, when the deviation of the rates is large, Λ^* will become small and the intensity of the Λ modulation satellite peaks will decrease. The starred peaks in the figure are the result of this supermodulation and here $\Lambda^*=120$ Å or about ten unit cells.

Figure 3 shows the x-ray diffractogram in the region of the (001) and (002) reflections for a multilayer on MgO with $\Lambda=24$ Å: a two-unit-cell sample. The arrows indicate the satellite peaks due to Λ and the dashed lines in the figure are used to highlight the satellites. This 24-Å sample consists of 160 alternating planes of yttrium and dysprosium. Calculation of the x-ray spectrum for a two-cell superlattice in which a plane of $Y_{1-x}Dy_x$ atoms alternates with a plane of Y_xDy_{1-x} atoms shows that the ratio of the integrated intensities of the satellite at 11.5° to the (001) peak at 7.7° varies from 0.15 for $x=0$ (pure Y alternating with pure Dy) to 0.0 for $x=0.5$ (no modulation). The experimental ratio of these peaks is 8% to 9% which implies that $x=0.13$. Thus this 24-Å sample shows that we are at the threshold of controlling and modulating the growth of the 1:2:3 phase in a layer by layer manner. This is very exciting since new substitutions, new stacking sequences, and new materials are now within reach using thin-film technology. The main difficulties which remain are the precise control and adjustments of the deposition rates and times necessary to have modulation wavelengths Λ which are commensurate with the c-axis lattice parameter. Otherwise a higher-order modulation will result at the expense of the intended modulation.

We now briefly discuss some superconducting properties. Figure 4 shows the normalized resistance as a function of temperature $R(T)/R(100\text{ K})$ for the $\Lambda=24$ and 60 Å multilayers. The inset shows the result of an ac susceptibility measurement for the $\Lambda=24$ Å multilayer. These curves are indistinguishable from those of individual $YBa_2Cu_3O_7$ or $DyBa_2Cu_3O_7$ films. The T_{c0}'s are above 85 K, the transition widths are about 2 K, and residual resistivity ratios RRR are about 2.7. Thus, even for the $\Lambda=24$Å sample there is no degradation, due to the multiple interfaces, of either the RRR or the T_c.

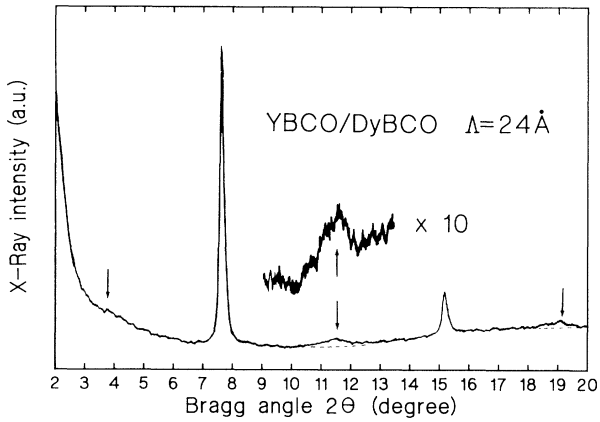

FIG. 3. X-ray diffractogram of a 24-Å-wavelength multilayer prepared on MgO. The arrows indicate the satellites. The dashed lines are to highlight the necessarily small multilayer peaks.

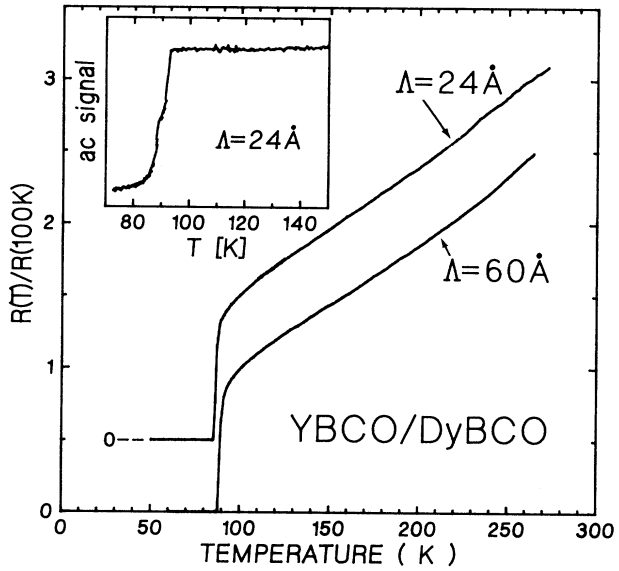

FIG. 4. Resistance as a function of temperature for 24- and 60-Å-wavelength samples, both grown on $SrTiO_3$ (100). The vertical axis is displaced for clarity. Inset: An ac-susceptibility measurement on the 24-Å sample.

Measurements on thin $YBa_2Cu_3O_7$ films show that below about 30 Å thickness the films are no longer superconducting.[8] This suggests that the additional scattering due to the multilayering is very weak because of the unusual nature of the modulation.

In conclusion, we have been able to grow magnetron-sputter c-axis superlattices of $YBa_2Cu_3O_7/DyBa_2Cu_3O_7$, in which planes of Dy replace planes of Y, down to the shortest possible wavelength of $\Lambda = 24$ Å, or twice the c-axis lattice parameter. These superlattices exhibit very large crystalline coherence in the growth direction and a modulation coherence as high as 360 Å. A third modulation appears in some samples due to the deviation of the deposition rates from the ideal values, and to the inherent layered nature of the 1:2:3 structure. The superconducting properties of these superlattices are as good as single layers with T_{c0} between 85 and 88 K.

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