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Abstract

Artificially-layered structures, consisting of (Sr,Ba,Ca)CuO_2 layers in the tetragonal, "infinite layer" crystal structure, have been grown by pulsed-laser deposition. Superlattice chemical modulation is observed for structures with $SrCuO_2$ and (Sr,Ca)CuO_2 layers as thin as a single unit cell (~3.4 Å). In addition, novel thin-film superconductors were formed by using the constraint of epitaxy to stabilize $SrCuO_2/BaCuO_2$ superlattices in the infinite layer structure. Using this approach, two new structural families, $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ and $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$, have been synthesized which superconduct at temperatures as high as 70 K. These results represent not only the synthesis of new structural families of superconductors, but also demonstrate that pulsed-laser deposition and epitaxial stabilization can be effectively used to engineer artificially-layered thin-film materials.

Advances in the understanding of epitaxial thin-film growth of the cuprates have heightened interest in creating artificially layered superconductors.(1–3) The layered structure of the copper oxide superconductors opens the possibility of forming novel materials by carefully controlling the epitaxial growth of sub-units of the crystal structures. Thin-film growth methods offer unique opportunities for the atomic engineering of new high-temperature superconducting (HTSc) materials through the ability to form artificially layered crystal structures.(4,5) Moreover, the surfaces of single-crystal substrates provide an "atomic template" that can be used to stabilize epitaxial films in metastable crystal structures.

An important development in forming new HTSc compounds by artificially-layered epitaxy has been the epitaxial growth of (Sr,Ca)CuO_2 films in the so-called infinite layer structure.(6–17) This material, which can be considered the parent compound of all of the copper oxide superconductors, has a relatively simple, layered structure consisting of CuO_2 planes separated by planes of alkaline earth elements.(18) Bulk synthesis of (Sr,Ca)CuO_2 with the tetragonal, infinite layer structure generally requires the use of high pressure and high temperature bulk processing techniques.(19–24) However, recent experiments show that this metastable compound can be epitaxially stabilized at less than atmospheric pressure, resulting in the growth of tetragonal (Sr,Ca)CuO_2 single crystal thin films of the infinite layer defect perovskite structure by pulsed-laser deposition (PLD) over a wide range of growth conditions.(6–17)

A necessary milestone in the effort to form new artificially-layered HTSc structures is to control the growth of (Sr,Ca)CuO_2 at the unit-cell level (~3.4 Å). We have shown that unit-cell control of (Sr,Ca)CuO_2 growth is possible with a relatively simple film growth technique over an oxygen pressure regime in which in situ surface analysis techniques, such as reflection high-energy electron diffraction, are not possible useful. We have successfully grown $SrCuO_2$/(Sr,Ca)CuO_2 superlattice structures utilizing a conventional PLD multi-target system operating at an oxygen pressure of 200 mTorr. X-ray diffraction peaks attributed to the superlattice structures are observed, even for $SrCuO_2$/(Sr,Ca)CuO_2 superlattice structures with $SrCuO_2$ and (Sr,Ca)CuO_2 layer thicknesses of a single unit cell (~ 3.4 Å). The x-ray diffraction data also reveal finite-thickness oscillations in the x-ray intensity, which is indicative of films with extremely flat surfaces. The growth of superlattice structures by PLD is made possible, in large part, by this surface flatness.

Using this approach, we have also synthesized two new series of artificially-layered HTSc compounds, grown as $SrCuO_2$/$BaCuO_2$ crystalline superlattice structures. By sequentially depositing from $BaCuO_2$ and $SrCuO_2$ ablation targets in a PLD system, artificially-layered crystalline materials were constructed in which the layering sequence was controlled on nearly the atomic-layer scale. The $SrCuO_2$ and $BaCuO_2$ layers are epitaxially stabilized in the infinite layer structure, and form the building blocks for the compounds. Note that $SrCuO_2$ in the infinite layer structure

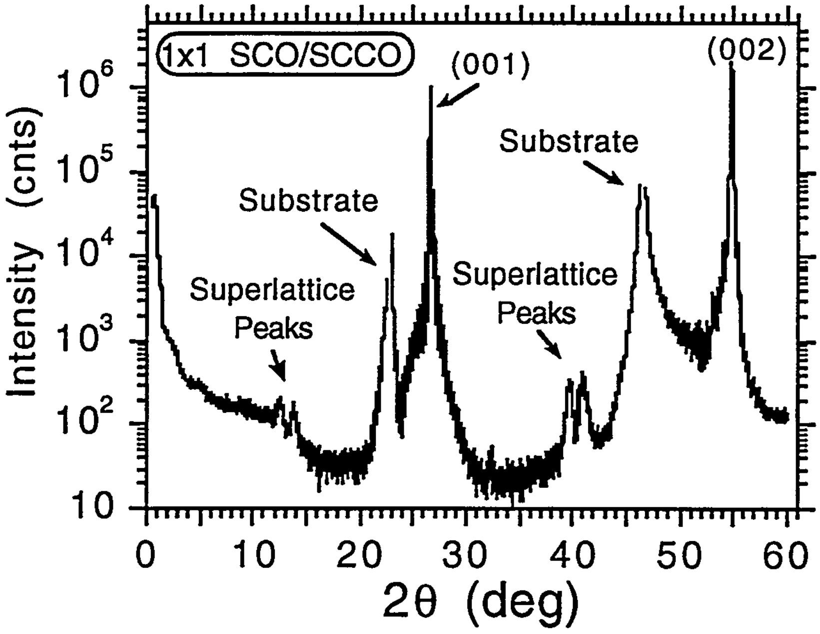

Fig. 1. X-ray diffraction data for a 1 × 1 $SrCuO_2/Sr_{0.2}Ca_{0.8}CuO_2$ (SCO/SCCO) superlattice showing diffraction peaks due to the Sr/Ca chemical modulation of the superlattice thin-film structure. The superlattice peaks are split due to the fact that the chemical periodicity is slightly incommensurate with the infinite layer structural periodicity. From the superlattice peak locations, the superlattice period is 7.0 Å.

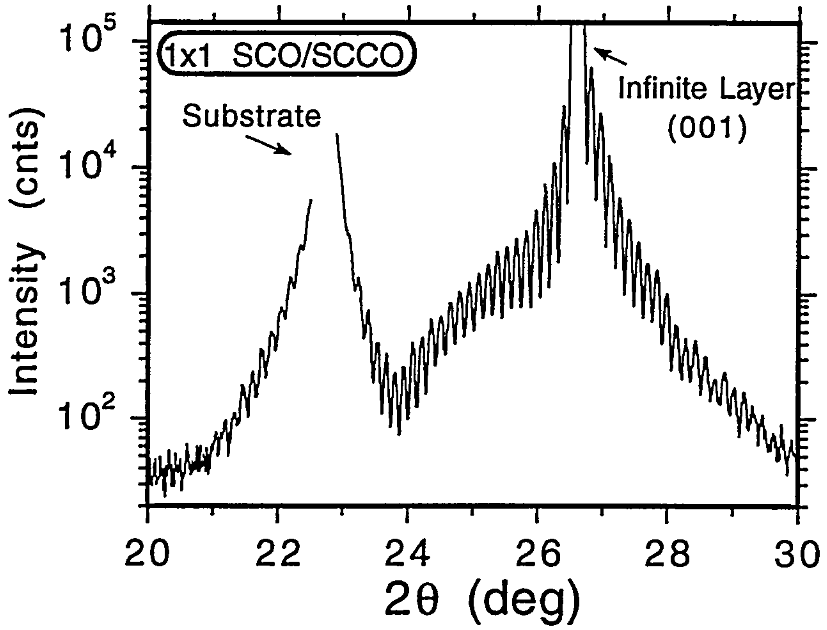

Fig. 2. X-ray diffraction data for a 1 × 1 $SrCuO_2/Sr_{0.2}Ca_{0.8}CuO_2$ (SCO/SCCO) superlattice about the (001) infinite layer peak showing x-ray intensity oscillations due to the finite thickness of the film. The number of resolvable oscillations suggests that the film thickness varies by only 20 Å over a length scale of several thousand angstroms.

is an insulator, while $BaCuO_2$ normally does not form the infinite layer structure, even by high-pressure synthesis techniques. Utilizing this approach, we have synthesized two new HTSc series, $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ and $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$, with T_c(onset) and T_c(resistance, R=0) as high as 70 K and 50 K, respectively. The $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ series, with n = 2, 3, and 4, is structurally analogous to the recently discovered $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ high-pressure HTSc phase (25–27), and is obtained by artificially-layering two-unit cells of $BaCuO_2$ and (n-1) unit cells of $SrCuO_2$ in the infinite layer crystal structure. The $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$ series, formed by layering 4 unit cells of $BaCuO_2$ and (n-1) unit cells of $SrCuO_2$ in the infinite layer structure, exhibits superconductivity for the n=3 member with T_c(onset) = 70 K and T_c(R=0) = 40 K.

The films were prepared on (100) $SrTiO_3$ substrates utilizing conventional multi-target PLD. Polycrystalline, orthorhombic $(Sr,Ca)CuO_2$ and cubic $BaCuO_2$ ablation targets were mounted in a multi-target carousel. The $(Sr,Ca)CuO_2$ target was made by solid state reaction of high-purity $SrCO_3$, $CaCO_3$, and CuO which was pressed and fired at 1025°C. Powder x-ray diffraction confirmed complete decomposition of the carbonates. The $BaCuO_2$ target was prepared using high-purity $BaCuO_2$ powder. (100) $SrTiO_3$ substrates were cleaned with solvents prior to being mounted with silver paint on the substrate heater. The KrF excimer laser ablation beam was focused to a 1 cm horizontal line and vertically scanned over the targets to improve film thickness uniformity. The focused laser energy density was approximately 2 J/cm^2, and the substrates, heated to 500–600°C, were placed 10 cm from the ablation targets. Film growth was carried out in 200 mTorr of oxygen.

The structure and epitaxy of the films were investigated by x-ray scattering measurements obtained using both two-circle and four-circle diffractometers with monochromated $CuK\alpha$ x-ray sources. In addition, more sensitive synchrotron x-ray measurements were obtained for one film using beamline X14 at the National Synchrotron Light Source (NSLS) operating with a Si(111) monochromator and a Ge(111) analyzer set near the $CuK\alpha$ wavelength.

The growth of superlattice structures by PLD requires a well-calibrated and controlled growth rate. Initial estimates of the film thickness per laser shot were obtained by growing single-component $(Ca,Sr)CuO_2$ films and measuring their thickness. However, for superlattice growth, the growth rate and/or sticking coefficient of each component layer can deviate from the values obtained from single-component film growth. For instance, growth of a single unit cell of $SrCuO_2$ on a $Sr_{0.2}Ca_{0.8}CuO_2$ surface involves slightly different surface chemistry than growth on $SrCuO_2$, and can lead to a different growth rate. Thus, the final growth rate calibration was obtained from the superlattice satellite peak locations in the x-ray diffraction data.

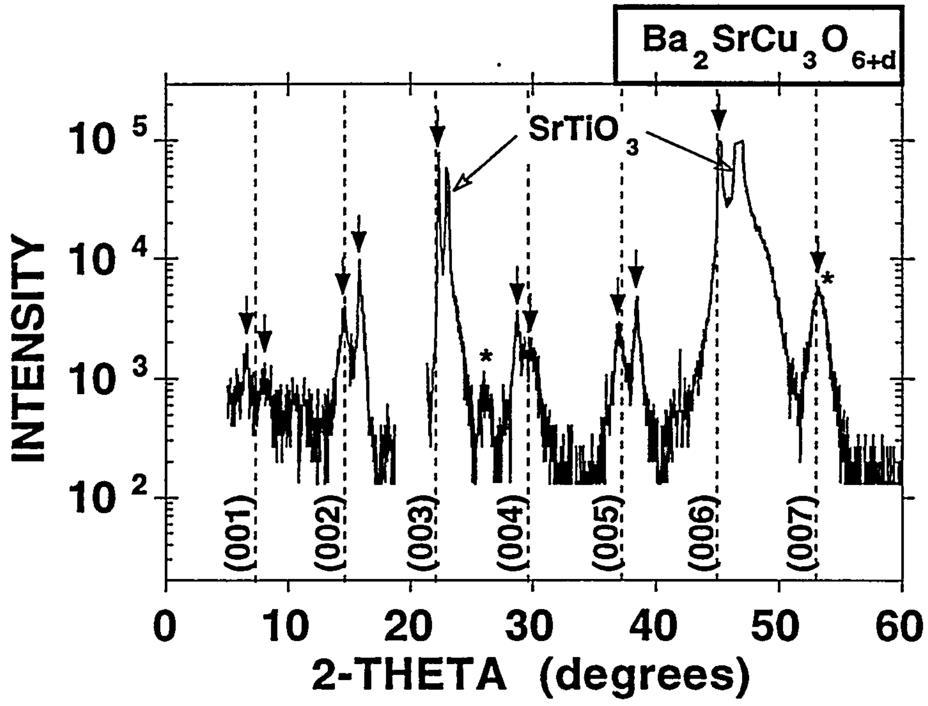

Fig. 3. X-ray diffraction pattern (Cu Kα radiation) for the $n = 2$ member of the $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ series. The dashed lines indicate the nominal locations of the (00ℓ) peaks, while the solid arrows indicate diffraction peaks due to the artificially-layered structures.

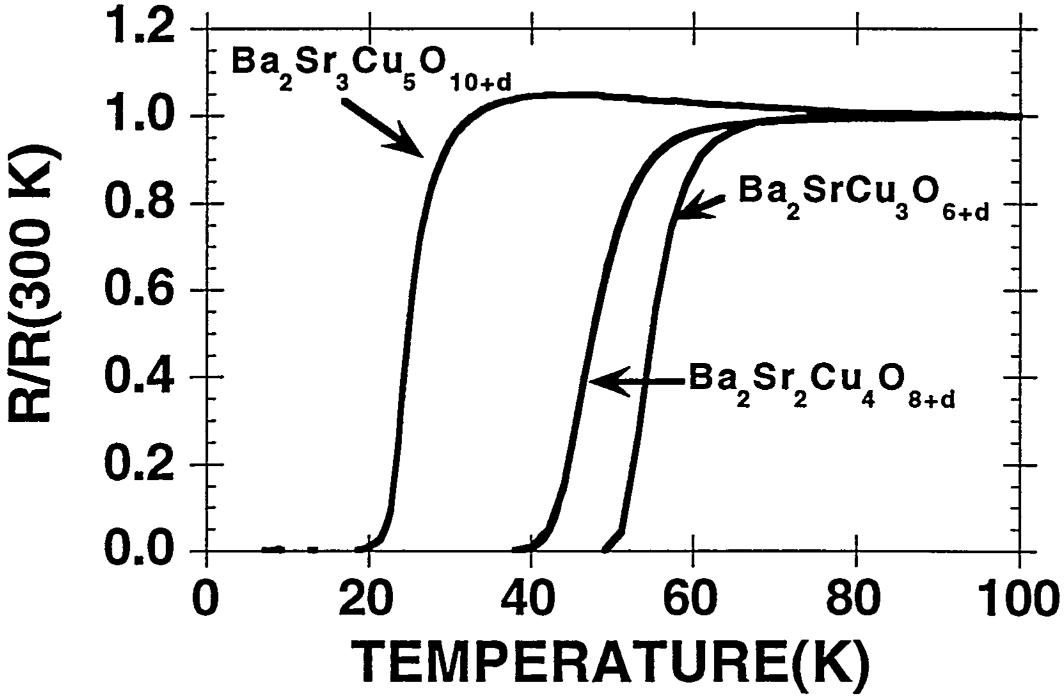

Fig. 4. Normalized resistance plotted as a function of temperature fore $n = 2, 3$, and 4 members of the $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$

For $SrCuO_2/(Ca,Sr)CuO_2$ superlattices with the infinite layer crystal structure, the x-ray diffraction data should show the infinite layer (001) and (002) peaks, along with superlattice satellite peaks due to the additional chemical modulation from the superlattice structure. The nomenclature used to describe the nominal superlattice structures is M × N, where M is the number of unit cells of the first component, and N is the number of unit cells of the second component. Figure 1 shows the x-ray diffraction pattern for a 1 × 1 $SrCuO_2/Sr_{0.2}Ca_{0.8}CuO_2$ superlattice. Even for this structure, with $SrCuO_2$ and $Sr_{0.2}Ca_{0.8}CuO_2$ layers only 1 unit cell thick, x-ray diffraction peaks attributed to the superlattice are observed indicating control of the film growth at the infinite layer unit cell level of ~3.4 Å. The superlattice modulation periodicity for the 1 × 1 structure is 7.0 Å and the average lattice parameter is c~3.35Å. For $SrCuO_2$ and $Sr_{0.2}Ca_{0.8}CuO_2$, the nominal ideal lattice constants are 3.45 and 3.25 Å, respectively.

It is interesting that superlattice structures with component layer thicknesses as small as 3.3 Å can be obtained with a relatively simple thin-film growth system which has no in situ surface analysis capability. This result implies that the growing surface of the infinite layer films must be quite smooth, on a near-atomic scale. A direct measure of this surface smoothness is given in the x-ray diffraction pattern of the 1 × 1 $SrCuO_2/Sr_{0.2}Ca_{0.8}CuO_2$ superlattice. Figure 2 shows an expanded plot about the (001) infinite layer peak, which shows oscillations in the x-ray diffraction intensity due to the finite film thickness. Finite thickness oscillations are observed only if the film surface is flat over a length scale on the order of the coherence length of the x-ray source. For these synchrotron measurements, the coherence length is at least of the order of thousands of angstroms. Over 30 oscillations are present on each side of the (001) peak, giving a fractional variation of film thickness relative to the total film thickness of 1/30, which yields a thickness variation of only 20 Å over thousands of angstroms.(28) This is on the order of the expected substrate surface roughness, and indicates that these infinite layer films are extremely flat under the growth conditions utilized.

In addition to $SrCuO_2/Sr_{0.2}Ca_{0.8}CuO_2$, we have also grown $SrCuO_2/BaCuO_2$ superlattices. These materials, fabricated by alternative ablation of $SrCuO_2$ and $BaCuO_2$ targets, can be nominally described either as $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ and $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$, or as M × N $SrCuO_2/BaCuO_2$ superlattices, with $N = 2$ for $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ and $N = 4$ for $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$. The accurate formation of any artificially-layered phase depends on the precision with which growth of the constituent $BaCuO_2$ and $SrCuO_2$ layers can be controlled. X-ray diffraction patterns give a direct measure of the accuracy of the artificially-layered growth scheme in producing the intended structure. The x-ray diffraction pattern for a $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$ film with $n = 2$ is shown in Fig. 3. The solid arrows indicate diffraction peaks from the artificially-layered compounds, while the asterisks designate peaks from a $SrCuO_2$ buffer layer. The vertical dashed lines show the expected locations of the (00ℓ) peaks for an ideal artificially-layered structure. The diffraction pattern clearly indicates the presence of mulitlayer modulation along the c-axis. While the diffraction peaks are close to the ideal (00ℓ) locations, some of the peak intensities are weaker than that predicted from structure calculations, with slight deviations or splitting of some of the peaks about the expected peak locations. The most consistent interpretation of the diffraction pattern is to view the peaks as originating either from the structural modulation or from the superlattice chemical modulation. The structural modulation arises from the crystallinity of the compound. It represents, for instance, the average cation spacing along the c-axis (the growth direction), with some structure peaks present even with no Ba/Sr chemical modulation. For instance, the (003) and (006) peaks for $Ba_2SrCu_3O_{6+\delta}$ would be present for an infinite layer alloy film with no Ba/Sr ordering along the c-axis. Only as Ba/Sr ordering is realized are other (00ℓ) structure peaks expected. If the Ba/Sr chemical modulation is slightly incommensurate with the structural modulation, superlattice satellite peaks will be present on either side of strong structural peaks at positions which deviate from the ideal (00ℓ) locations. Peaks from the structural and chemical periodicities converge if the deposition process yields exactly integral numbers of $SrCuO_2$ and $BaCuO_2$ infinite layer unit cells per multilayer period. The deviations observed in the peak locations indicate that the chemical modulation is slightly incommensurate with the structural modulation. The fact that the peak intensities are somewhat weaker than expected indicates the presence of some Ba/Sr disorder. Since these thin films were formed as artificially-layered superlattices by sequentially depositing $SrCuO_2$ and $BaCuO_2$ layers, such disorder is expected to arise from substrate surface roughness and slight inaccuracies in the deposition rates. The x-ray diffraction pattern gives c-axis lattice constant of the structural periodicities for the $n = 2$ film of 12.1 while the chemical periodicities for the same structure is 14.0. These values yield $SrCuO_2$ and $BaCuO_2$ sub-unit cell spacings of 3.55Å and 4.28 Å, respectively, which are within 5% of the bulk value for $SrCuO_2$, and the assumed value for $BaCuO_2$ layers in the high-pressure $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ phase (25–27). Four-circle x-ray diffraction data show these structures to be tetragonal with in-plane lattice constants of 3.9 Å, thus matching the lattice constant for the $SrTiO_3$ substrates.

In these artificially-layered structures, the $SrCuO_2$ and $BaCuO_2$ sub-units could have the ideal infinite layer structure consisting of four-fold coordinated CuO_2 planes separated by oxygen-free alkaline earth (Sr or Ba) layers, with no apical oxygen for any of the copper atoms. However, this seems unlikely as all of the hole-doped superconductors have apical oxygen associated with at least some of the copper atoms, and thermoelectric power measurements indicate that these materials are hole conductors (29). The more reasonable possibility is for the Ba planes to contain some oxygen, thus creating apical oxygen and increasing the Cu coordination. It is not clear, however, whether oxygen on the Ba planes resides there at the expense of oxygen on specific Cu planes. Because of this uncertainty, we have designated the materials as $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+n+\delta}$ and $Ba_4Sr_{n-1}Cu_{n+2}O_{2n+6+\delta}$ which makes no inference as to whether inequivalent Cu sites are present, although this may occur.

Figure 4 shows the normalized resistance for the $n = 2$, 3, and 4 members of $Ba_2Sr_{n-1}Cu_{n+1}O_{2n+2+\delta}$. The room-temperature resistivities are 1–5 mΩ-cm. The $n = 2$ member has the highest superconducting transition temperature with T_c(onset) = 70 K and T_c (R=0) = 50 K. The $n = 3$ member has T_c (onset) = 60 K, T_c(R=0) = 40 K, and the $n = 4$ member has T_c (onset) = 40 K and T_c(R=0) = 20 K. The measurement current density used was ~50 A/cm^2. Thus far, only modest attempts have been made to optimize the superconducting properties of these materials. In addition to $Ba_2Sr_{1-n}Cu_{n+1}O_{2n+2+\delta}$, superconductivity is also observed in the series designated as $Ba_4Sr_{n-1}Cu_{n+3}O_{2n+6+\delta}$ with T_c (onset) = 70 K and T_c (R=0) = 40 K. These films are stable over time if stored in a dry atmosphere.

In conclusion, we have grown $SrCuO_2$/(Sr,Ca)CuO_2 superlattice structures in the tetragonal, infinite layer crystal structure using conventional pulsed-laser deposition. X-ray diffraction reveals peaks due to the superlattice chemical modulation, even for structures with $SrCuO_2$ and (Sr,Ca)CuO_2 layers as thin as a single infinite layer unit cell (~3.4 Å). The x-ray diffraction data also show intensity oscillations due to the finite thickness of the film, indicating extremely flat film surfaces with thickness variations of only 20 Å over a length scale of several thousand angstroms. We have also grown $SrCuO_2$/$BaCuO_2$ superlattices which superconduct at temperatures as high as 70 K. The ability to grow infinite layer (Sr,Ca)CuO_2 layers as thin as a single unit cell using conventional pulsed-laser deposition greatly expands the possibility of atomic engineering of new, artificially-layered high-temperature superconducting phases via layer-by-layer growth schemes.

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