

Atomically layered heteroepitaxial growth of single-crystal films of superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$

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Atomic layering of high-temperature superconducting compounds has been employed to grow films of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ *in situ*, on SrTiO_3 substrates. Atomic monolayers of the constituent atoms were sequentially deposited by shuttering the fluxes from thermal effusion cells, and oxidation of the film was accomplished using a beam of ozone. The films were superconducting as-grown, with complete resistive transitions as high as 86 K. Moreover, reflection high-energy electron diffraction patterns observed during growth, as well as post-growth analysis by x-ray diffraction and high-resolution scanning electron microscopy, indicate the films to be single crystal and heteroepitaxial, with in-plane *a-b* twinning.

Recently, many groups have studied and developed techniques for the growth of thin films of high-temperature superconducting compounds. The efforts generally fall into one of two categories: (a) deposition of the required stoichiometry of metal atoms, followed by a high-temperature *ex situ* anneal where the superconducting phase is formed, or (b) *in situ* growth of the film crystallized during deposition, usually occurring at a substantially lower temperature. For many electronic applications it is likely that such *in situ* growth will be preferred, especially for layered device structures and for compatibility with other materials processes. Previously we have reported the use of atomically layered epitaxy for *in situ* growth of superconducting films, where the layered structure of the film is controlled by the sequence of deposition of the constituent atoms from thermal sources.^{1,2} This is of interest both for phase control in the Bi-Sr-Ca-Cu-O system of compounds³ as well as for the growth of nonequilibrium crystalline structures. Other groups have reported similar experiments,⁴ including approaches based on sputtering⁵ and laser ablation.⁶ In this letter we report progress in the growth of metastable bismuth family compounds using atomically layered epitaxy, in particular, growth of single-crystal films of the 2223 phase that exhibit complete superconducting resistive transitions at temperatures as high as 86 K.

The films described here were fabricated using a technique developed for growing synthetically structured epitaxial superconducting films.¹ The system consists of an ultrahigh vacuum chamber that has a base pressure of 1.0×10^{-8} Torr and contains thermal effusion cells equipped with beam shutters for the controlled, sequential evaporation of individual elements. The sources were temperature controlled, and were allowed to equilibrate at their operating temperatures for several hours before each run. Prior to growth, the beam flux from each metal source was measured individually using an ionization gauge that could be precisely repositioned at the location of the grow-

ing substrate. The sensitivity of the ionization gauge response is different for each element. In order to accurately calibrate this measurement, a series of thin films were grown and analyzed by Rutherford backscattering (RBS). These films were grown on {100} MgO under conditions otherwise identical to those used during the growth of the films discussed below. The calibration films were thin enough to allow the use of the surface layer approximation and integration of the beam current by reference to the substrate signal. This analysis indicated that the ionization gauge sensitivity and RBS measurement accuracy for each atomic species is constant over a period of weeks to within $\pm 3\%$. In some cases, significantly better calibration was observed.

In order to obtain *in situ* growth using this technique, a source of reactive oxygen is necessary. We used a beam of ozone-enriched oxygen from a discharge generator/silica gel cold-trap separator system.⁷ We estimate the ozone fraction of the beam flux to have been greater than 30% based on measurements with a remote quadrupole mass spectrometer. During growth, the ozone/oxygen beam flux, estimated to have been $5\text{--}10 \times 10^{16}$ molecules/cm² s at the substrate position, resulted in a background pressure in the growth chamber of 2×10^{-5} Torr. At such pressures, the mean free path of the metal atoms or molecules is much greater than the source-to-substrate distances. This allows precise control of line-of-sight beams by means of shuttering.

To atomically layer the growing crystal film, the beams for the metal sources were sequentially turned on and off by means of a set of computer-controlled shutters. The shuttering times were chosen to deposit individual monolayers of each element, one at a time, thereby synthetically structuring the film. For example, during the growth of the 2223 phase films the sequence used for each unit cell grown was -Bi-Bi-Sr-Cu-Ca-Cu-Ca-Cu-Sr- where each elemental symbol represents an integrated flux burst of one mono-

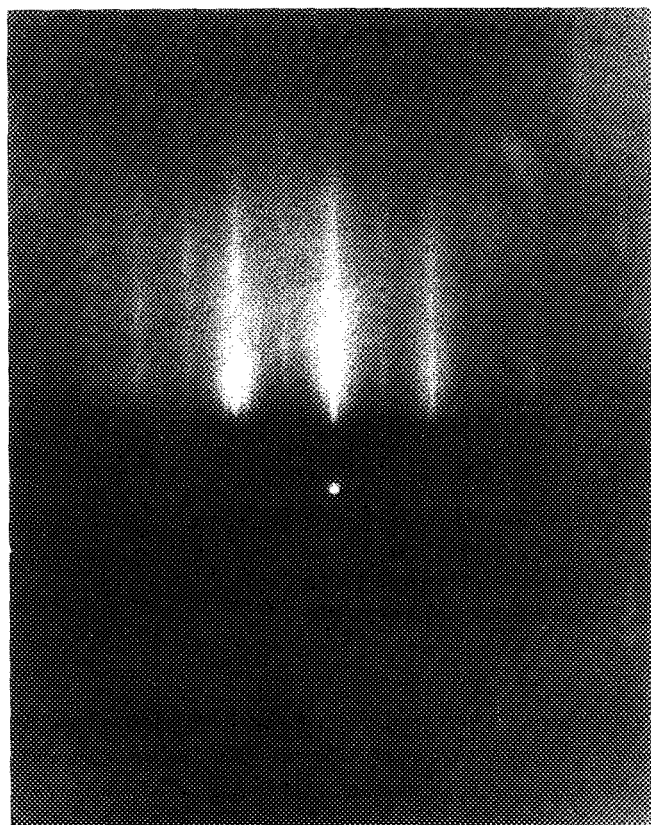


FIG. 1. RHEED pattern observed during growth of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ thin film on SrTiO_3 substrate. The streak spacings indicate that the film $\{100\}$ and $\{010\}$ directions are parallel to the substrate $\langle 110 \rangle$ directions. The incommensurate in-plane modulation of the structure, which has a periodicity of around 25 \AA , is evidenced in the satellite streaks that surround the main streaks, while the in-plane lattice constant of $\sim 5.4 \text{ \AA}$ results in the fainter streaks observed halfway between.

layer or about 6.9×10^{14} atoms per cm^{-2} . Typically, the whole sequence was repeated 15–50 times to grow films 300–1000 \AA thick.

The growths reported here were carried out on $\{100\}$ SrTiO_3 substrates. The substrates were thermally cleaned *in situ* to about 750°C , while being monitored by the reflection high-energy electron diffraction (RHEED) system. Prior to growth streaky RHEED patterns characteristic of a single-crystal surface were observed. Growths were done at substrate temperatures ranging from 650 to 750°C as measured using an optical pyrometer. Typical growth rates used were 500 – 1000 \AA/h .

During growth, the crystal surface was monitored by RHEED. When good calibration was achieved so that one burst corresponded to one monolayer, a diffraction pattern characteristic of a single-crystal surface was observed. An example of such a pattern is shown in Fig. 1; the electron beam was incident along the SrTiO_3 $\langle 110 \rangle$ direction. This RHEED pattern is similar to that observed during the growth of $\text{Bi}_2(\text{SrCa})_3\text{Cu}_2\text{O}_x$ (Ref. 5) and shows several interesting features. The most intense lines are due to a surface periodicity of about 2.7 \AA . The fainter lines halfway in between them indicate the a or b axis lattice constant of about 5.4 \AA . Surrounding the more intense streaks are satellite streaks that are characteristic of an in-plane

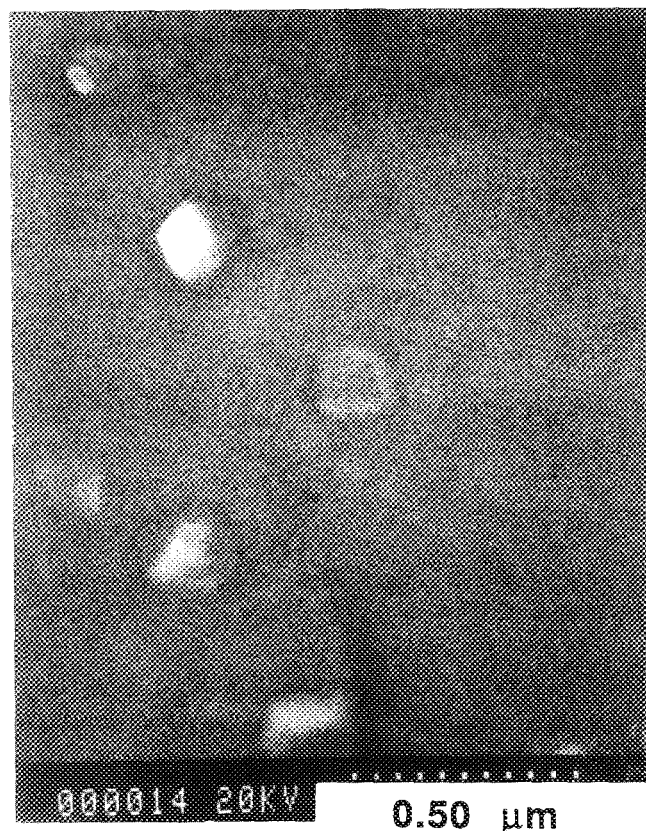


FIG. 2. SEM micrograph of the film surface. Isolated defects are embedded in the smooth field region, with densities ranging from 10^4 to 10^8 cm^{-2} , depending on growth conditions.

structure of about 25 – 30 \AA , presumably due to the incommensurate b -axis structure modulation. As many as six satellite streaks around each main streak have been observed. In addition, the linewidth of the satellite pattern, comparable to the RHEED linewidths of the single-crystal SrTiO_3 substrate itself, indicates an in-plane crystallographic coherence length of at least 200 \AA . During growth the patterns evolved in a complex manner reflecting the nature of the instantaneous surface chemistry occurring. In particular, after growth of the bismuth layers in each unit cell atomically smooth surfaces were observed, as indicated by the RHEED pattern shown here. We have also observed a similar behavior during the growth of 2201, 2212, and 2234 phases.

To further examine the surface morphology, the films were inspected by optical and scanning microscopy (SEM). Figure 2 shows a SEM picture taken under high magnification and is typical of the kind of structure routinely observed. The film shows a connected, featureless, smooth surface in which small isolated defect structures are observable. The defect size is about 1500 \AA or less; their areal density can vary greatly, depending on growth stoichiometry, between 10^4 and 10^8 cm^{-2} . On films with RHEED patterns that showed evidence for a second phase during growth a larger density of defects was seen. Other than the isolated defects, the SEM surface images show no evidence of any grain boundary structure. Based on the RHEED patterns observed during and after growth and

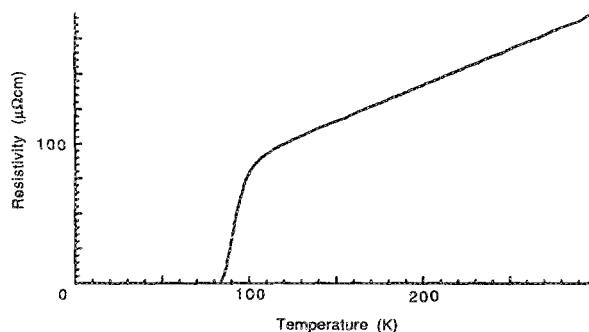


FIG. 3. Resistivity vs temperature for an *in situ* growth $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ film showing a critical temperature of 84 K.

the microscopy images, we believe the connected-field region of the film to be single crystal in nature.

After growth, the films were cooled down inside the chamber; a number of cooling regimes were investigated. The highest resistive transition in a 2223 film, directly from the chamber, was 86 K, full zero. Figure 3 shows a typical resistive transition from a sample from the same growth that exhibits a $T_c(R=0)$ of 84 K. This film was cooled from 725 °C in an oxygen/ozone flow ~20 times that used during growth. This contrasts with the observation on 2212 phase samples,⁵ where higher transition temperatures were achieved by cooling in a less reactive oxygen atmosphere. The transition seen here is broad, starting above 100 K. Other films have shown onsets above 110 K but lower values of $T_c(R=0)$. Just above the superconducting transition, the film had a resistivity of about 100 $\mu\Omega$ cm.

The crystallographic properties of the films were also characterized by x-ray diffraction (XRD) measurements. Figure 4 shows an XRD pattern from a θ -2 θ scan of a superconducting 2223 film; the substrate was tilted 0.5° off alignment to the SrTiO_3 {100} substrate in order to suppress the large substrate reflections. The film can be indexed to a *c*-axis lattice constant of 37.2 Å, in good agreement with the range of measured 2223 values. Other scans sensitive to the in-plane structure show the film to be completely epitaxially aligned to the substrate. There is no evidence of 2223 phase growth in any other orientation. When the *c* axis is aligned normal, the widths of the individual film peaks can be used as a measure of the regularity of the atomic layering throughout the film thickness. The linewidths of the 002 and 0010 peaks indicate coherent Bragg scattering of the incident x rays from the entire film thickness, which demonstrates the ability of atomically layered epitaxy to artificially synthesize the crystallographic structure of the film.

In summary, thin films of the 2223 phase compound from the bismuth family have been grown by atomically layered epitaxy. The films are superconducting as-grown and have shown complete resistive transitions at tempera-

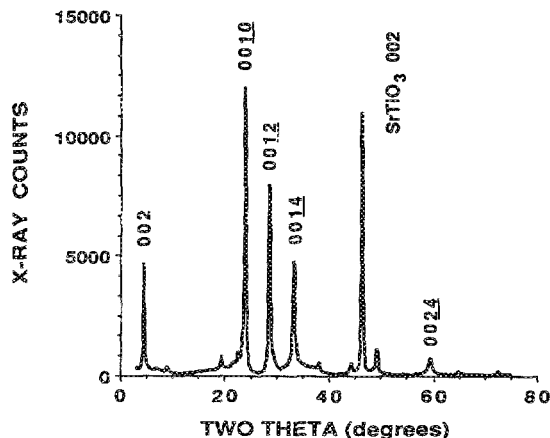


FIG. 4. X-ray diffraction pattern obtained by rocking 0.5° off the SrTiO_3 (100) zone axis to suppress the intense substrate peaks. The linewidths of the 002 and 0010 peaks indicate coherent diffraction from the entire film thickness.

tures as high as 86 K. During growth, the in-plane, incommensurate superstructure along the *b* axis is evident as satellite streaks surrounding the main RHEED streaks. The linewidths of the RHEED streaks indicate in-plane crystallographic coherence of at least 200 Å, while high-resolution SEM images show the film to consist of a featureless field region in which isolated defects are embedded. XRD analysis indicate the films to be aligned to the SrTiO_3 substrate net and *c*-axis oriented, as-layered. This suggests the field region to be heteroepitaxial and single crystal in nature, with in-plane *a*-*b* twinning.

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