Growth of untwinned $Bi_2Sr_2Ca_2Cu_3O_x$ thin films by atomically layered epitaxy

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We report the growth of untwinned epitaxial thin films of Bi-Sr-Ca-Cu-O by atomically layered heteroepitaxy on $SrTiO_3$ substrates. These films are *c*-axis oriented as-layered and do not exhibit 90° in-plane defects, i.e., *a-b* "twinning." By misorienting the surface normal from {100} by approximately 4° towards ⟨111⟩, the cubic symmetry of the {100} surface is adequately broken to completely align the *b* axis of the superconducting film with respect to the substrate. Reflection high-energy electron diffraction patterns observed during growth and post-growth x-ray diffraction analysis indicate that the incommensurate structural modulation occurs along the same direction as the step edges.

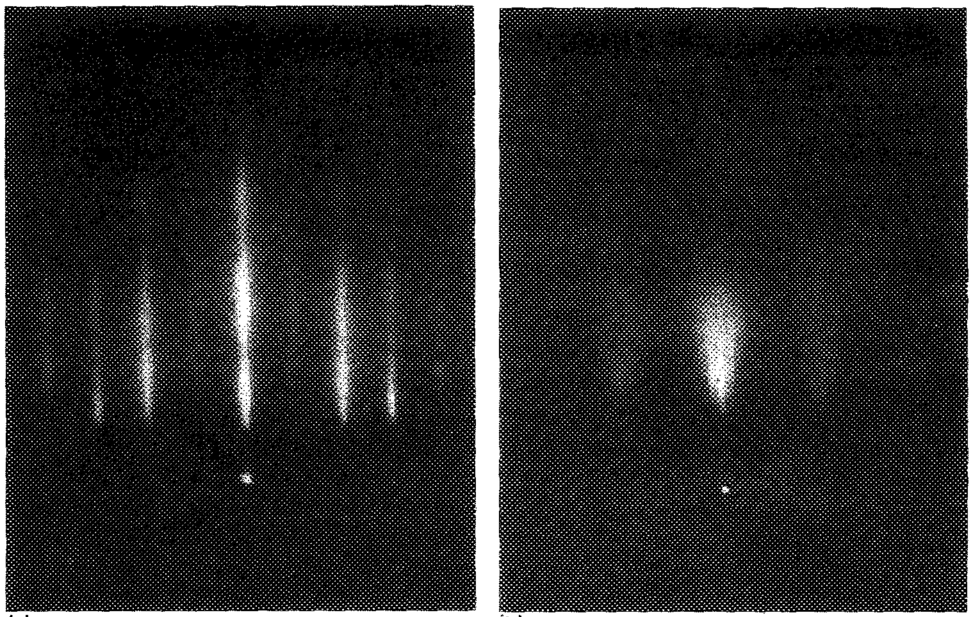
Recently, we reported on the *in situ* heteroepitaxial growth of superconducting thin films of Bi-Sr-Ca-Cu-O by atomically layered epitaxy.[1] Those films had transition temperatures as high as 86 K, as-grown, and were *c*-axis oriented as-layered with in-plane 90° misorientation defects[2] (*a-b* "twinning"). Typically, the films consisted of a single-crystal field region with isolated second-phase defects. In Bi-Sr-Ca-Cu-O compounds the *a* and *b* lattice constants are only slightly different, resulting in a small distortion of the orthorhombic subcell, $a = 5.414$ Å and $b = 5.418$ Å for the 2212 phase.[3] More important, however, is the well known incommensurate modulation, with a period of approximately 26 Å, along the *b* axis of the structure. This has been seen in diffraction experiments,[3] in cross-sectional transmission electron microscopy (TEM) images,[4,5] and by scanning tunneling microscopy.[6] It has been shown to modulate the position and occupancy of the atoms in the unit cell.[7] Thus, the *b*-axis lattice parameter is more properly regarded as a spatial average over many periods of the incommensurate structure and apparently remains close to the *a*-axis value only because the structural modulation is incommensurate. All Bi-Sr-Ca-Cu-O thin films reported to date have been *a-b* "twinned." Here, we report for the first time a technique for growing "untwinned" epitaxial thin films of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ using atomically layered epitaxy on vicinal $SrTiO_3$ {100} substrates, with the step edges aligned along a substrate ⟨110⟩ direction. The substrate tilt serves to adequately break the symmetry of the surface, thereby leading to growth with apparently complete in-plane orientation. Reports have also recently been made of growth of orthorhombic Y-Ba-Cu-O films with reduced twinning.[8] In that system there is no incommensurate structural modulation, but the degree of orthorhombic distortion of the in-plane lattice constants is much higher, $a = 3.82$ Å and $b = 3.89$ Å.[9]

The films reported here were grown in a system, specifically designed for atomically layered growth, that is described elsewhere.[10] In this process, atomic layering of specific structures is accomplished by sequentially opening and closing shutters that control the fluxes from thermal effusion cells that contain the constituent metal atoms. When the system is calibrated properly, the sequential bursts of atoms incident on the surface contain the right number to fill in each succeeding layer of the crystal structure being grown. Resulting films are completely *c*-axis oriented as-layered. In this way a wide variety of synthetic crystal structures related to the parent superconducting compounds can be grown. During growth, the substrates are held at elevated temperatures, typically around 650 °C, to provide adequate surface mobility for the deposited atoms. Additionally, reactive oxygen is supplied from a beam of enriched ozone in oxygen in adequate quantities to oxidize the incident metal atoms and form the superconducting crystal. More details of the growth process can be found in Refs. 1 and 10.

$SrTiO_3$ substrates oriented off {100} by approximately 4° toward {111} were obtained. This results in a vicinal surface with layer steps going down the surface ⟨110⟩ direction and, thus, breaks the fourfold symmetry of the otherwise cubic surface net. The substrate orientation was measured by the Laue method. If it is assumed that the terrace edges are regularly distributed and the steps have unit cell height, the resulting monolayer steps would be about 40 Å apart.

Epitaxial films of the one-layer (2201), the two-layer (2212), and the three-layer (2223) phase were grown. A variety of layer stoichiometries in the vicinity of the nominal values were investigated. Best growth, as evidenced by the absence of isolated second-phase defects, occurred with stoichiometries that were up to 10% reduced from the nominal one, e.g., 2223, in the concentration of the alkaline earth elements, Ca and Sr, according to our calibration.

During growth, the crystal structure was monitored by reflection high-energy electron diffraction (RHEED). After an initial transient thickness of typically less than 15 Å, a RHEED pattern characteristic of single-crystal growth was observed. The pattern seen with the electron beam incident along the step edge direction, which we define to be the [110] $SrTiO_3$ azimuth, is shown in Fig. 1(a). This film was of the three-layer phase. Here the streak spacing indicates a lattice constant of approximately 5.4 Å. There



(a) (b)

FIG. 1. RHEED patterns observed during growth of $Bi_2Sr_2Ca_2Cu_3O_x$ thin films on a vicinal $SrTiO_3$ substrate. The RHEED beam is incident along the (a) [110] azimuth and (b) [110] azimuth of the substrate. The substrate directions are defined such that the surface steps due to the small misorientation are in the [110] direction.

is no evidence of the in-plane incommensurate structural modulation. However, the RHEED pattern observed with the electron beam incident along the azimuth normal to the step edge direction, i.e., rotated by 90° to obtain the $SrTiO_3$ [$1\bar{1}0$] azimuth, appears quite different. This is shown in Fig. 1(b). Here the most prominent feature is the presence of closely spaced satellite streaks surrounding the principal streaks that are due to a 2.7 Å surface periodicity. The spacings between the satellite streaks indicate a periodicity of around 26 Å and, we suggest, are caused by the in-plane incommensurate structural modulation. Furthermore, the center streaks of the low-order diffraction maxima in Fig. 1(b) indicate the same underlying lattice constant as the corresponding, second-order streaks in Fig. 1(a). Identical results have been seen during the growth, on such misoriented substrates, of both the one- and two-layer phases as well. Diffraction patterns similar to a superposition of Figs. 1(a) and 1(b) have been seen during other growths on nominally {100} oriented $SrTiO_3$ substrates. In these cases the same diffraction pattern is observed along both the $SrTiO_3$ substrate [110] and [$1\bar{1}0$] azimuths, indicating the growth of films with 90° in-plane misorientation defects, *a-b* "twins." We attribute the in-plane orientation of the entire film seen here to the broken symmetry introduced by the vicinal surface.

In order to confirm the observations made during growth with RHEED, the film was further analyzed by x-ray diffraction (XRD). Just as the incommensurate superstructure causes satellite streaks to occur in RHEED, it also produces satellite reflections in XRD. In particular the 02<u>12</u> reflection of the 2223 phase has such satellite peaks. Using a four-circle diffractometer the film was oriented to observe diffraction from a satellite peak of the 02<u>12</u> reflection. The sample was mounted on the goniometer in such a way that a rotation of the diffractometer phi axis would rotate the crystal around the [001] zone axis of the film. If the 2223 film contained the 90° in-plane misorientation defects present in previous films and in bulk crystals, a fourfold pattern would be observed when phi is scanned from 0° to 360°, since the satellite reflection would be seen along both the $SrTiO_3$ substrate [110] and [$1\bar{1}0$] directions. The phi axis scan XRD pattern obtained is shown in Fig. 2. Here, phi equals zero was chosen to coincide with the $SrTiO_3$ substrate [100] direction. The two peaks at phi equal to 45° and 225° are due to the incommensurate structure along the film *b* axis. The absence of peaks at 135° and 315° indicates the 2223 film to be an "untwinned" epitaxial film, containing no 90° in-plane misorientation defects.

In conclusion, we have shown that "untwinned" epitaxial films of Bi-Sr-Ca-Cu-O compounds can be heteroepitaxially grown on slightly misoriented {100} $SrTiO_3$ by atomically layered epitaxy. Specifically, a tilt of the substrate ⟨001⟩ axis toward a ⟨111⟩ direction results in adequate symmetry breaking of the otherwise cubic surface net to cause complete alignment of the *b* axis of the superconductor with the step-edge direction on the substrate surface. Such untwinned epitaxial films may find applica-

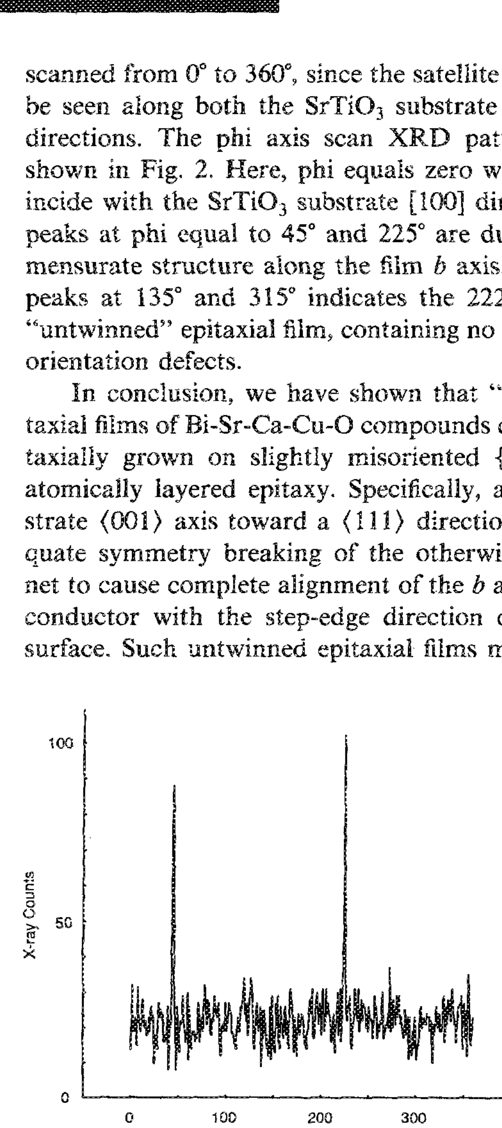


FIG. 2. X-ray diffraction pattern (phi scan) of a satellite peak near the film 0212 reflection showing the in-plane orientation of the incommensurate superstructure in the film. Here phi = 0 is set along the $SrTiO_3$ [100] direction. The two peaks, 180° apart, indicate that the *b* axis of the film occurs only along the $SrTiO_3$ substrate [110] direction.

tion in fundamental studies as well as in superconductive devices.

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