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QUARTERLY REPORT
for
DARPA/ONR
HIGH TEMPERATURE SUPERCONDUCTIVITY

PERIOD ENDING: June 30, 1990

I. PROGRAM INFORMATION

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II. PROGRAM SUMMARY

The overall goals of this program are to develop the technology of MBE growth of HTSC material, to optimize the performance of HTSC films with high transition temperatures and critical current densities, and to explore the development of electronic devices based on such material.

III. PROGRAM STATUS

The recently-developed MBE system is functioning well, and superconducting films with T_c's above 77K are now routinely being grown, in-situ, by atomic layer epitaxy on both MgO and $SrTiO_3$. Work is continuing on understanding such issues as required stoichiometric control and methods of improving kinetic control precision, oxidation capacities of reactive oxygen sources, and the effect of crystallographic quality on superconducting properties.

IV ACCOMPLISHMENTS

Work has continued on development a technique for atomically-layered growth of high-T_c films, aimed at developing a capability suitable for fabricating advanced Josephson junction devices. This quarter, we discovered a way to grow "untwinned" $Bi_2Sr_2Ca_{m-1}Cu_mO_x$ single-crystal films, i.e. films with the c-axis pointing in the growth direction and the b-axis macroscopically aligned to a specific substrate direction. Such films may have in-plane anisotropic transport properties, and ultimately may be important in the fabrication of optimal superconductive devices such as step-edge Josephson junctions.

Recently, we reported on the in-situ heteroepitaxial growth of superconducting thin films of Bi-Sr-Ca-Cu-O by atomic-layer epitaxy. Those films had transition temperatures as high as 86K, as-grown, and were *c*-axis oriented as layered with in-plane 90° misorientation defects (*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. 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, in cross-sectional transmission electron microscopy (TEM) images, and by scanning tunneling microscopy. It has been shown to modulate the position and occupancy of the atoms in the unit cell. 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 describe for the first time a technique for growing "untwinned" epitaxial thin films of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ using atomic-layer 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.

$SrTiO_3$ 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 four-fold 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 15Å, 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. 1a. This film was of the three-layer phase. Here the streak spacing indicates a lattice constant of approximately 5.4Å. There 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. 1b. Here the most prominent feature is the presence of closely spaced satellite streaks surrounding the principal streaks that are due to a 2.7Å 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. 1b indicate the same underlying lattice constant as the corresponding, second order, streaks in Fig 1a. 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. 1a and 1b 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 $02\underline{12}$ 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 $02\underline{12}$ 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 four-fold 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.

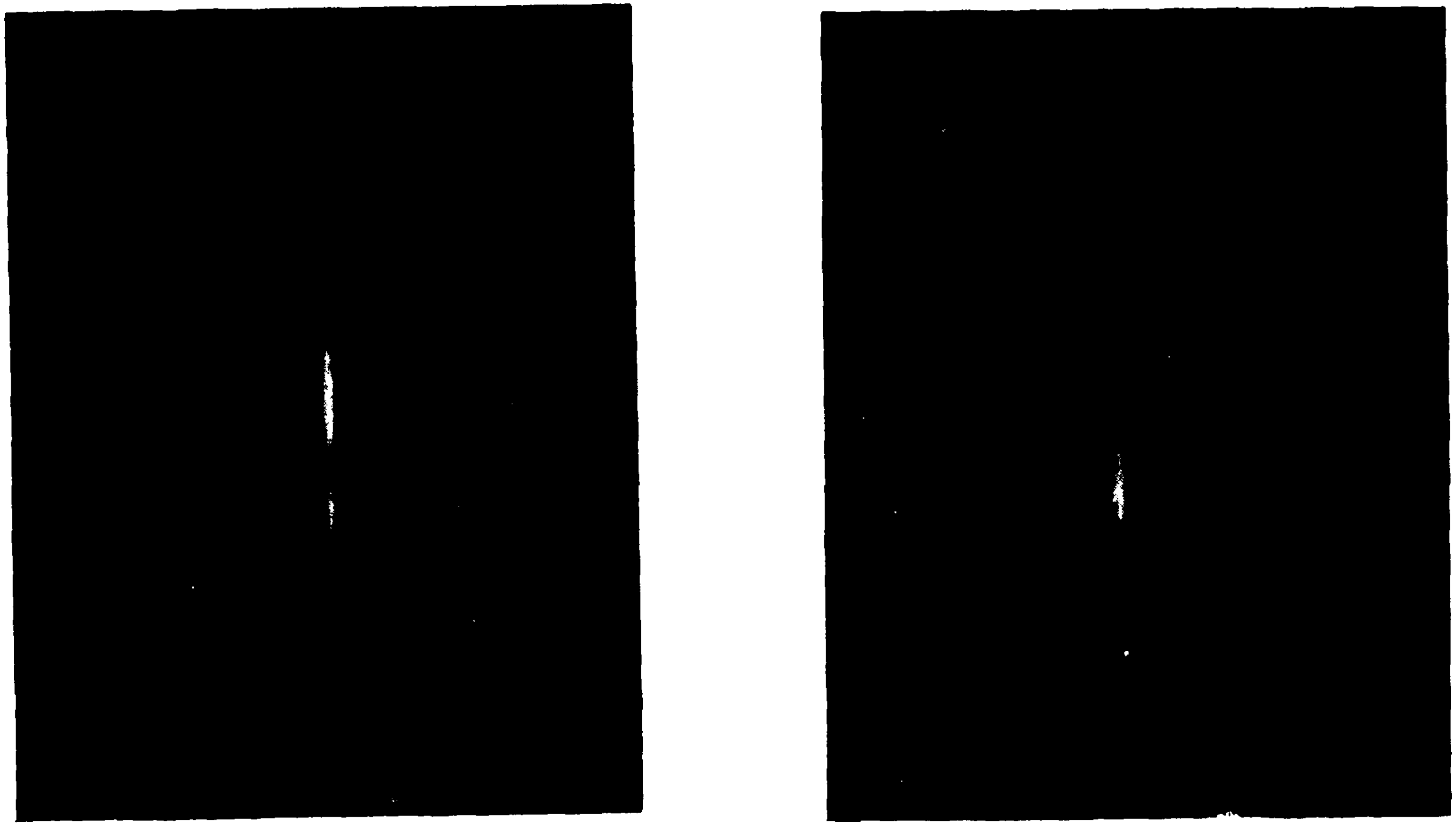
In conclusion, we have shown that "untwinned" epitaxial films of Bi-Sr-Ca-Cu-O compounds can be heteroepitaxially grown on slightly misoriented {100} $SrTiO_3$ by atomically layered epitaxy. Specifically, a tilt of the substrate <001> axis toward a <111> direction results in adequate symmetry breaking 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 application in fundamental studies as well as in superconductive devices.

V PROBLEM AREAS

No specific problem areas exist at the present time. More film growth is required to improve film properties and attempt the fabrication of metastable structures.

VI CORRECTIVE ACTION

None required at present



(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) [$1\bar{1}0$] azimuth of the substrate. The substrate directions are defined such that the surface steps due to the small misorientation are in the [110] direction.

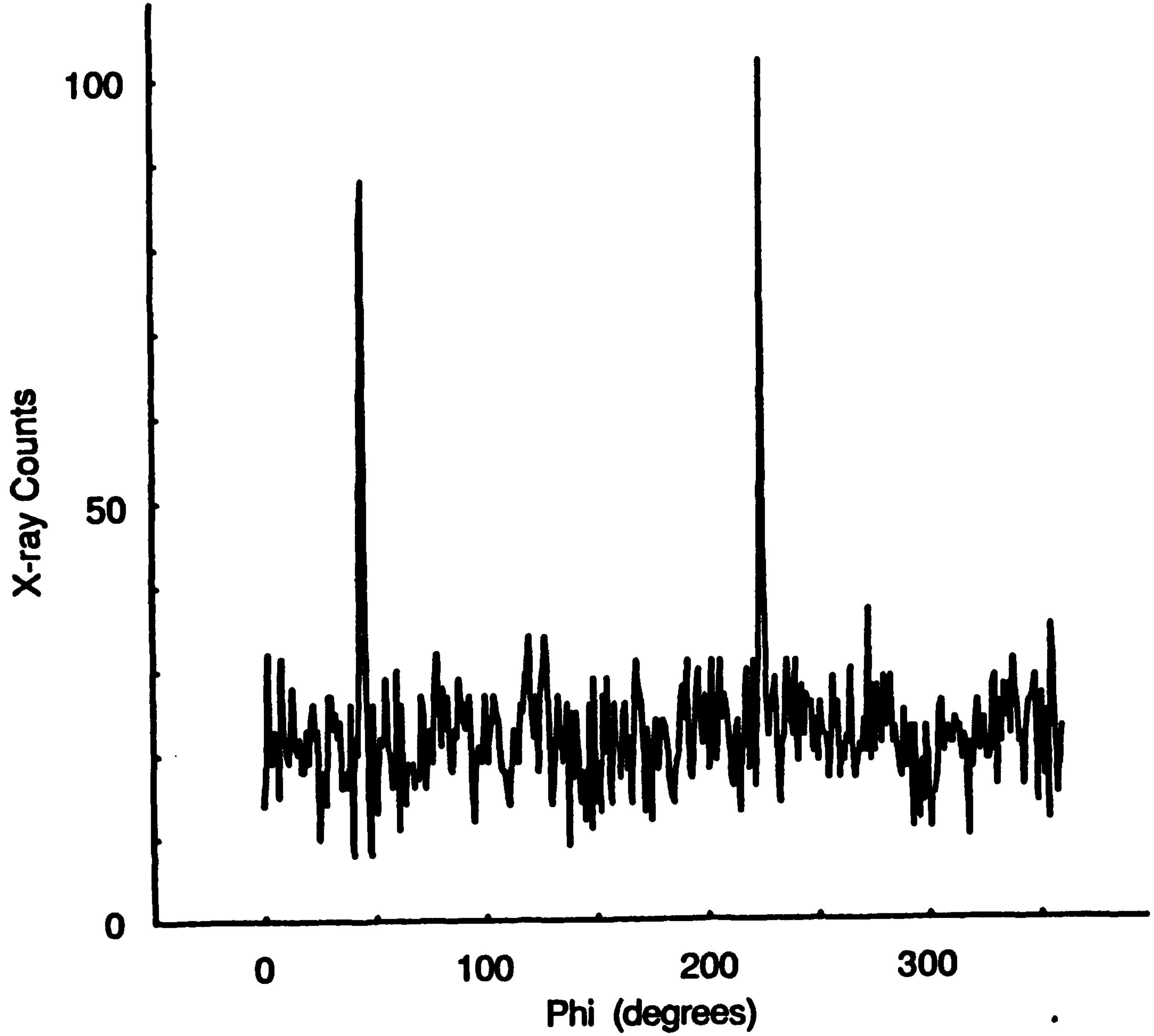


Fig. 2 X-ray diffraction pattern (phi scan) of a satellite peak near the film 02<u>12</u> reflection showing the in-plane orientation of the incommensurate superstructure in the film. Here phi=0 is set along the $SrTiO_3$ [100] direction. The two peaks, 180° apart, indicate that the *b*-axis of the film occurs only along the $SrTiO_3$ substrate [110] direction.