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X-ray study of in-plane epitaxy of $YBa_2Cu_3O_x$ thin films

J. D. Budai, R. Feenstra, and L. A. Boatner
Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6024
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Detailed x-ray scattering measurements in three dimensions are reported for thin $YBa_2Cu_3O_x$ films on (001) $SrTiO_3$ and $KTaO_3$ substrates. The films, produced by coevaporation followed by a postdeposition anneal, consist of domains epitaxially oriented with either the *a* axis or the *c* axis aligned with the substrate normal. The in-plane epitaxy of grains with the *c* axis parallel to the normal shows an alignment of the ⟨110⟩ directions of the film and the substrate, rather than of the ⟨100⟩ directions as is generally presumed. We associate this alignment with a strain relaxation during the high-temperature tetragonal-to-orthorhombic phase transition.

Numerous investigations of superconducting thin films have been generated by both the fundamental scientific interest in and the possible technical applications of high-T_c materials.[1] For the cuprate oxides, the superconducting properties are found to be highly anisotropic, thus making the epitaxial relationship between film and substrate particularly important. The x-ray characterization of epitaxial oxide films grown on $SrTiO_3$ and other substrates has, in most studies, been limited to reciprocal space scans along the substrate normal, yielding lattice parameter information on atomic planes parallel to the substrate surface. $YBa_2Cu_3O_x$ (Y 1:2:3) films grown on $SrTiO_3$ (001) substrates are generally found to consist of grains oriented with either the *a* axis ($a_\perp$ grains) or *c* axis ($c_\perp$ grains) aligned with the surface normal. Relatively little attention has been given to the in-plane epitaxy, although it is generally believed from x-ray-diffraction studies[2-6] that the in-plane thin-film and substrate ⟨100⟩ directions are aligned.

This paper reports an x-ray-diffraction study of thin Y 1:2:3 superconducting films grown by coevaporation on (001) $SrTiO_3$ and $KTaO_3$ substrates in which measurements were made "away from" as well as "along" the surface normal in order to determine the alignment and lattice parameters for the thin films in three dimensions. As a new result, we find that it is the ⟨110⟩ in-plane directions of the $c_\perp$ Y 1:2:3 phase and the substrate that align, rather than the ⟨100⟩ directions. This conclusion and other results described here are general to the extent that they apply to Y 1:2:3 films on both $SrTiO_3$ and $KTaO_3$ substrates.

Details of the preparation and superconducting properties of the thin-film samples have been presented elsewhere.[7] Briefly, the films were deposited in a vacuum chamber by coevaporation of Y, BaF_2, and Cu onto single-crystal $SrTiO_3$ and $KTaO_3$ (001) substrates. Film thickness (typically 3500 Å) and composition ratios were determined using Rutherford backscattering spectroscopy. The deposition occurred at a substrate temperature of 450 °C and was followed by an *ex situ* anneal at 850 °C in wet oxygen. The x-ray-scattering measurements were obtained using a rotating anode Cu $K\alpha$ x-ray source, a vertically focusing LiF monochromator, a Huber four-circle diffractometer, and a flat Ge analyzer crystal. The samples were mounted with the (00*l*) axis of the substrate parallel to the ϕ axis of the diffractometer.

Figure 1 shows a schematic diagram of the Bragg peaks expected in the reciprocal-lattice plane which contains the (0*kl*) reflections from the substrate (large filled circles). The Y 1:2:3 reflections (smaller symbols) have been included based on the assumption that the orthogonal axes of the film are parallel to the ⟨100⟩ axes of the substrate (as we will show below, this is not exactly true) with the expected lattice parameter progression $a < b < c <$ substrate a_0. This diagram proved to be a useful guide for independently investigating reflections from different grain orientations. The validity of the assumptions used in constructing Fig. 1 was tested by scanning through various locations in orthogonal directions in reciprocal space. In particular, by means of θ-2θ scans, intensities were mea-

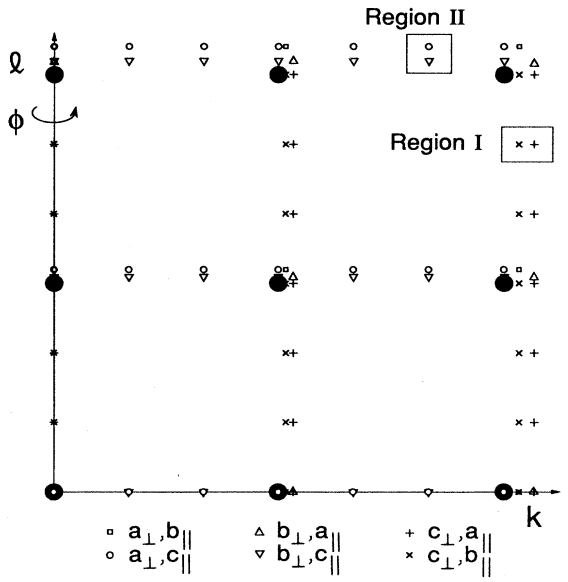

FIG. 1. Schematic drawing of the reciprocal-lattice plane containing the substrate (0,*k*,*l*) reflections (large filled circles). The Y 1:2:3 peaks are located assuming that $a_\perp$, $b_\perp$, and $c_\perp$ grains are all present and have their orthogonal axes aligned with the substrate ⟨*h*00⟩ axes.

sured along a line passing through the origin of Fig. 1 while ϕ scans provided measurements along a circular path around the l axis (i.e., perpendicular to the plane of the diagram).

θ-2θ x-ray intensity scans along the substrate l axis showed Y 1:2:3 $(h00)$ and $(00l)$ peaks associated with the $a_\perp$ and $c_\perp$ orientations, respectively. No evidence for $(0k0)$ peaks or any other Y 1:2:3 peaks was typically observed. The a and c lattice parameters measured along the surface normal for various samples fell within the ranges $a = 3.82 \pm 0.01$ Å and $c = 11.66 \pm 0.03$ Å, consistent with published values for bulk Y 1:2:3 material with nearly complete oxygen concentration.[8]

Figures 2(a) and 2(b) show off-normal θ-2θ scans from a typical mixed $a_\perp$ and $c_\perp$ film on $KTaO_3$ through the peaks enclosed in the rectangles in Fig. 1 labeled Region I and Region II, respectively. The observation of separate peaks in Fig. 2(a) reveals that grains in the $c_\perp$ orientation are indeed orthorhombic $(a \neq b)$, and the relative peak widths indicate a larger degree of disorder along the $[205]c_\perp$ direction than along the $[025]c_\perp$ direction. Both peaks appear in a single θ-2θ scan due to the vertical beam divergence associated with the focusing monochromator. As typified in Fig. 2(b), the $(025)b_\perp$ peak was extremely weak or absent in all films examined indicating that very little, if any, $b_\perp$ material was present. Note that since this off-axis scan probes intensities far from any strong substrate diffraction peaks, it provides a more sensitive test for the presence of $b_\perp$ grains than a scan along the surface normal where the near coincidence of Y 1:2:3 and substrate $(0k0)$ reflections can obscure a weak Y 1:2:3 peak.

Lattice parameters measured on the sample used in Fig. 2 are given in Table I and show that the overall agreement between our thin-film values and those measured for bulk Y 1:2:3 is good, particularly for the $a_\perp$ domains. Upon closer examination, however, we note small but systematic differences between the values measured for the two different domain orientations occurring within the same sample. For the $c_\perp$ domains, a slightly smaller c value is observed, accompanied by somewhat larger values for a and b. These differences do not correlate with expected lattice changes due to differences in oxygen stoichiometry, as incomplete oxygenation should increase both a and c simultaneously.[8] In addition, these systematic differences were observed in films produced on both $SrTiO_3$ and $KTaO_3$ crystals and thus, did not depend on substrate properties.

Instead, it appears that small deformations in the $c_\perp$ grains result from a lattice mismatch between the Y 1:2:3 films and the underlying substrates. From TEM cross sections and x-ray measurements of films before and after amorphizing the surface region by oxygen implantation,[9]

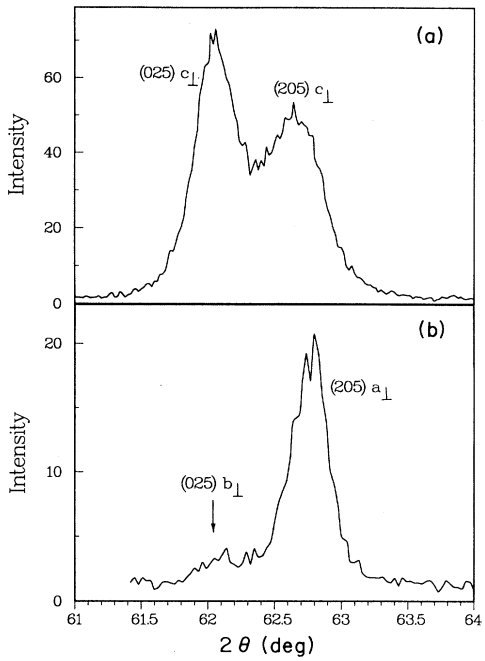

FIG. 2. θ-2θ scans for Y 1:2:3 on $KTaO_3$: (a) through $(205)c_\perp$ and $(025)c_\perp$ peaks contained in Region I in Fig. 1; (b) through $(205)a_\perp$ and $(025)b_\perp$ peaks contained in Region II.

we have found that the portion of the film which lies nearest the film-substrate interface consists primarily of $c_\perp$ domains. Thus, we note that the observed lattice parameter trends are consistent with strains induced by interactions with the slightly larger lattice parameters of the cubic substrates $SrTiO_3$ (3.905 Å) and $KTaO_3$ (3.99 Å). The lattice parameter systematics exhibited by our results are similar to those reported by Edwards *et al.*[6] for Y 1:2:3 films on $SrTiO_3$ produced using a different technique which also included high-temperature annealing, but did not include the use of BaF_2.

Turning to the question of the in-plane epitaxy, Fig. 3(a) shows a schematic diagram of the reflections from $c_\perp$ grains expected in a plane perpendicular to the l axis. This plane passes through an $(00l \neq 3n)$ reflection and, like Fig. 1, was constructed under the assumption that the a and b axes of the Y 1:2:3 grains are exactly aligned with the in-plane $\langle h00 \rangle$ axes of the substrate. Using the measured $c_\perp$ orthorhombic lattice parameters, the angle between the $[h00]$ and the $[hh0]$ is expected to be 44.6°. Thus, in this construction, the $\langle hh0 \rangle$ directions of the film and the substrate are not exactly parallel. Instead, this misalignment should be manifested in a splitting of the

TABLE I. X-ray lattice parameter measurements from a typical Y 1:2:3 thin film.

	a	b	c
$a_\perp$	3.820 ±0.002 Å	3.885 ±0.007 Å	11.69 ±0.01 Å
$c_\perp$	3.838 ±0.004 Å	3.894 ±0.003 Å	11.656 ± 0.005 Å

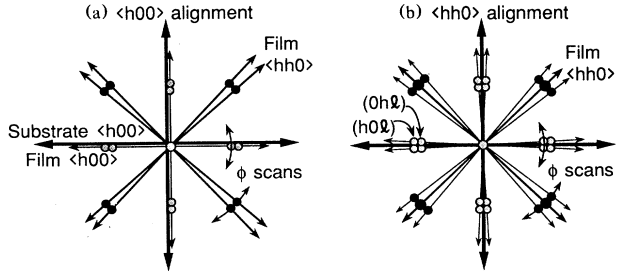

FIG. 3. Schematic drawing showing two possible epitaxial orientations of the Y 1:2:3 axes for $c_\perp$ grains (fine lines) and the substrate $\langle h00\rangle$ axes (heavy lines) in a reciprocal-lattice plane perpendicular to the l axis. (a) Thin film a and b axes aligned with the cubic $\langle h00\rangle$ substrate axes. (b) Thin film and substrate $\langle hh0\rangle$ axes aligned.

(hhl) reflections in ϕ scans (corresponding to the arcs as shown). Assuming equal proportions of Y 1:2:3 grains with a and b axes parallel to each of the two in-plane principal substrate axes, for $c_\perp$ domains the situation depicted in Fig. 3(a) will produce a single peak in ϕ scans through $(h0l)$ or $(0kl)$ reflections and a double peak (split by 0.8°) in ϕ scans through (hhl) reflections.

Experimental ϕ scans through the $(025)c_\perp$ and $(225)c_\perp$ reflections are presented in Figs. 4(a) and 4(b), respectively. Here, the in-plane $[h00]$ direction of substrate corresponds to $\phi=0°$. Surprisingly, the predictions described in the preceding paragraph are not qualitatively consistent with the experimental observations, particularly for the $(225)c_\perp$ line shape. An alternative proposition for the in-plane epitaxy is presented in Fig. 3(b). In this diagram, either the Y 1:2:3 $[hh0]$ or $[h\bar{h}0]$ direction is assumed to be parallel to an in-plane substrate $\langle hh0\rangle$ axis. Using the fourfold symmetry of the substrate and the orthorhombic lattice parameters, this second case should produce a double peak (split by 0.8°) in ϕ scans through $(h0l)$ or $(0kl)$ reflections and a triple peak (with the intensity of the central peak approximately twice that of the side peaks) in ϕ scans through (hhl) reflections. In Fig. 4, the solid curves represent fits of Pearson VII functions[10] to the data using two peaks in Fig. 4(a) and three peaks in Fig. 4(b). Excellent agreement is obtained with the predictions of the epitaxy model proposed in Fig. 3(b). Thus, we conclude that it is the $\langle hh0\rangle$ rather than the $\langle h00\rangle$ axes which are consequential in the in-plane epitaxial alignment of the $c_\perp$ grains.

Note that the experimental observation of the characteristic ϕ-scan line shapes requires samples with a small mosaic spread (typically less than 1°), and that the magnitude of the splitting depends on the actual values of the in-plane orthorhombic lattice parameters. Similar scans through peaks associated with the $a_\perp$ orientation indicate alignment such that the in-plane b and c axes lie close to the cubic substrate axes. However, in the samples investigated, the peak splitting in the ϕ scans for $a_\perp$ grains was not sufficiently large to distinguish between the two different alignment possibilities analogous to those presented in Fig. 3.

In an effort to understand the observed in-plane epitaxy, we note that after crystallization at 850 °C, the film is in the high-temperature tetragonal $(a=b)$ phase. In this phase, the angle between $\langle h00\rangle$ and $\langle hh0\rangle$ is exactly 45° and the in-plane alignments shown in Figs. 3(a) and 3(b) are equivalent. We speculate that the $c_\perp$ Y 1:2:3 films reduce the long-range strains associated with the transition into the orthorhombic phase during cooling by a-b twinning while retaining the epitaxial relationship with the (110) substrate planes. This twinning process is commonly observed during the cooling of Y 1:2:3 single crystals[11,12] even without additional substrate-induced strains. This speculation is consistent with the high density of conventional (110) a-b twins within the $c_\perp$ grains which have been observed in TEM studies of Y 1:2:3 thin films on $SrTiO_3$ (001) substrates.[13] In contrast, as has been pointed out by others,[6] the absence of $b_\perp$ grains implies that the $a_\perp$ grains do not contain the conventional (110) twins. This difference in twinning behavior between domains with different orientations as well as the lattice parameter differences described earlier in this paper indicate that the substrate plays a significant role in determining the thin-film microstructure.

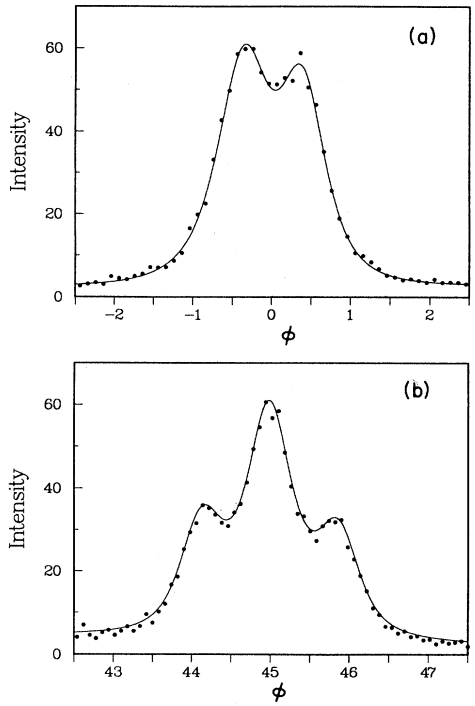

FIG. 4. ϕ scans for Y 1:2:3 on $KTaO_3$: (a) through $(205)c_\perp$ peak. [Note that this scan is orthogonal to the scan shown in Fig. 2(a).] (b) through $(225)c_\perp$ reflection.

In conclusion, we have obtained detailed three-dimensional x-ray measurements from thin Y 1:2:3 films grown on (001) $SrTiO_3$ and $KTaO_3$ substrates. We have investigated the structure and epitaxy of grains with distinct orientations by scanning through the expected positions for selected $a_\perp$, $b_\perp$, and $c_\perp$ reflections. We find that the films contain almost no $b_\perp$ grains, and attribute small but systematic lattice parameter differences between grains with $a_\perp$ and $c_\perp$ orientations to substrate-induced

strain. Of particular significance is our conclusion that the distinctive in-plane diffraction line shapes establish that the $\langle hh0 \rangle$ directions of the $c_\perp$ domains are aligned with the $\langle hh0 \rangle$ axes of the substrate. We speculate that this type of epitaxy results from strains associated with lattice distortions occurring during the tetragonal-to-orthorhombic transition. However, the extent to which the in-plane alignment depends on the specifics of the fabrication process remains to be established. In particular, we anticipate that twin formation during *in situ* growth of orthorhombic Y 1:2:3 films at temperatures below the tetragonal-to-orthorhombic transition[14,15] could be different than formation during high-temperature processing.

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[1]See, for example, *Proceedings of the Conference on the Science and Technology of Thin Film Superconductors, Colorado Springs, Colorado, 1988,* edited by R. McConnell and S. Wolf (Plenum, New York, 1989); *High Temperature Superconductors, 1988,* edited by M. B. Brodsky, R. Dynes, K. Kitazawa, and H. L. Tuller, Materials Research Society Symposia Proceedings, Vol. 99 (Materials Research Society, Pittsburgh, PA, 1988).

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