

## Monocrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films on vicinal $\text{SrTiO}_3$ (001) substrates

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The correlation between the vicinal properties of  $\text{SrTiO}_3$  (001) substrates and the twinning in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  thin films grown by pulsed-laser deposition is studied using x-ray diffraction with reciprocal space mapping. The vicinal properties, i.e., angle and in-plane orientation, play a significant role in the anisotropic strain starting at the interface between substrate surface and film, and affect the twin behavior of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . On substrates having an [110] in-plane orientation of the step edges, a completely preferred twin pair is observed if the vicinal angle is increased to  $0.60^\circ$ . Whereas on substrates having their step edges oriented along one of the crystallographic axis, the films exhibit a detwinning as the vicinal angle increases. For  $\alpha = 1.10^\circ$  a maximum detwinned, i.e., monocrystalline film is obtained. At this angle, the diffusion length of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  during the growth matches the terrace length of  $\text{SrTiO}_3$ . Up to this specific angle, the films are grown perpendicular to the optical instead of the crystallographic surface. © 2003 American Institute of Physics. [DOI: 10.1063/1.1633010]

The high- $T_c$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) has a large potential in technological applications. The applicability in epitaxial heterostructures is determined by their structural properties, i.e., defect structure, crystalline structure, and surface morphology, which are a direct result of the thin film growth, influenced by the deposition conditions and substrate properties. Understanding of the nucleation and growth mechanisms is, therefore, required to control the structural properties of YBCO films.

Highly textured YBCO thin films deposited by pulsed-laser deposition (PLD) on  $\text{SrTiO}_3$  (STO) substrates are obtained at typical growth temperatures of  $780^\circ\text{C}$ . Because of this high temperature, the YBCO grows in the oxygen depleted, tetragonal phase. The lattice misfit between STO and YBCO leads to epitaxial strain in the first unit cell layers. Introduction of dislocations causes relaxation of the strain in the remainder of the film during subsequent growth. During the cool down of YBCO after deposition, oxygen diffuses into the film accompanied by the well-known tetragonal to orthorhombic phase transition.<sup>1</sup> The strained interface layer between substrate and relaxed bulk, however, remains in a tetragonal phase. The orthorhombic unit cells align the diagonal of its basal plane with the diagonal of this underlying tetragonal interface layer. Twin orientations, named  $S_1^+$  and  $S_2^-$ , align along the [110] diagonal forming the  $[S_1^+, S_2^-]$  twin pair, whereas orientations  $S_1^-$  and  $S_2^+$  form the  $[S_1^-, S_2^+]$  twin pair along the  $[\bar{1}10]$  direction. The orientation angle<sup>2</sup> between  $S_1^+$  and  $S_1^-$  or  $S_2^+$  and  $S_2^-$  is  $2\delta = 0.95^\circ$ , respectively, for lattice parameters  $a = 3.823$  and  $b = 3.887$  Å of the YBCO unit cell.

The vicinal angle of the substrate induces an additional anisotropic strain to the first monolayers originating from the step edges.<sup>3</sup> Parallel to a step edge the substrate surface can

be seen as defect free, whereas perpendicular to it, the steps cause a periodic disturbance. This anisotropy leads to the formation of antiphase boundaries (APBs) in the film along the step edges.<sup>4,5</sup> As a result of the substrate anisotropy, the first monolayers of the YBCO film can be deformed more easily perpendicular than along the step edges. The vicinal conditions of the STO substrate and the twin behavior of the YBCO film are directly related. This relation has been studied extensively and a preferred alignment and detwinning up to 70% has been reported.<sup>6-8</sup>

In an earlier study we observed two distinct atomic stacking sequences<sup>9</sup> of YBCO at the substrate interface on single  $\text{TiO}_2$  terminated STO substrates. This is accompanied by the formation of APBs on the atomically smooth substrate terraces. The distance between these APBs is typically the diffusion length ( $L_D$ ), being 20 nm for PLD grown YBCO.<sup>10</sup> In this study we therefore investigate the twin behavior of YBCO on substrates having terrace lengths comparable to this diffusion length. It is expected that with these substrates the growth behavior, i.e., growth mode, is strongly affected by the step edge density as well as the stacking sequence at the substrate-film interface.

The vicinal angle and its orientation of a series of single  $\text{TiO}_2$  terminated STO substrates<sup>11</sup> were determined using x-ray diffraction (XRD). By means of laser beam alignment, the vicinal angle  $\alpha$  and its in-plane orientation  $\beta$ , see Fig. 1, could be measured with high accuracy ( $0.02^\circ$  and  $1^\circ$ , respectively). Two sets of substrates were selected, one with the in-plane vicinal orientations towards [100] and the other towards [110], henceforward denoted as  $\beta_{[100]}$  and  $\beta_{[110]}$ . The angles  $\alpha$  ranged from  $0.25^\circ$  to  $0.60^\circ$  and  $0.25^\circ$  to  $5.18^\circ$  for  $\beta_{[110]}$  and  $\beta_{[100]}$ , respectively.

YBCO films, with thickness of 100 nm, were grown by PLD.<sup>12</sup> XRD<sup>13</sup> reciprocal space mapping (RSM) was used for analyzing the twin behavior of the YBCO films. The

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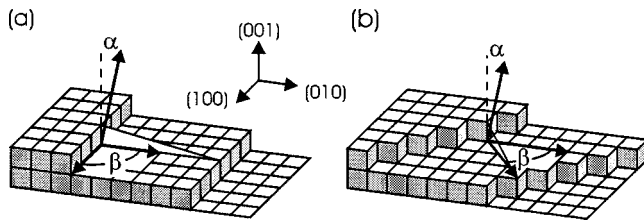


FIG. 1. Schematic representation of the vicinal substrate surface. The step edges are oriented along the [100] crystallographic axis in (a) and along the [110] axis in (b): denoted as  $\beta_{[100]}$  and  $\beta_{[110]}$ , respectively.

scans were performed around the [304] and [034] reflections of YBCO over 0.12 reciprocal space units (stepsize 0.01) in  $h$  and  $k$ . Intensity plots were produced with contour lines drawn for every 10% of the maximum minus background intensity.

The results of the RSMs for YBCO films on  $\beta_{[110]}$  substrates are shown in Fig. 2 with the vicinal angle of  $\alpha = 0.25^\circ$  (a),  $\alpha = 0.39^\circ$  (b), and  $\alpha = 0.60^\circ$  (c). As the vicinal angle increases, the intensity of the  $[S_1^+, S_2^-]$  twin state on the  $\beta_{[110]}$  substrates drops rapidly. For an angle of  $0.60^\circ$  it has decreased to less than 10% of the maximum intensity. The intensity ratio of 7% between the  $[S_1^+, S_2^-]$  and  $[S_1^-, S_2^+]$  twin pairs signifies that one twin pair is preferred. Since the anisotropic strain is perpendicular to the step edges, the terraces and the unit cells at the interface are deformed in this direction. On  $\beta_{[110]}$  substrates this results in a compression of the diagonal in the [110] direction. The diagonal match between film and substrate is not optimal, the STO diagonal is about 1% larger, so the compression leads to a better fit.<sup>3,8</sup> As the vicinal angle increases, the step edge density becomes larger, and more domains have the tendency to align along the compressed diagonal. For  $\alpha = 0.60^\circ$ , the film is almost completely (>93%) grown along the preferred diagonal. This preference does not occur for films grown on the  $\beta_{[100]}$  substrates (Fig. 3). On  $\beta_{[100]}$  substrates all four twin orientations are visible for vicinal angles up to  $0.80^\circ$ . However, for higher angles [Figs. 3(b)–3(f)] the two  $S_2$  reflections are clearly shifted towards each other in reciprocal space, and have higher intensities than the  $S_1$  reflections. A so-called detwinning, earlier reported by Brötz *et al.*,<sup>7</sup> occurs in the YBCO layer. The strain towards [100] results in a deformation in the horizontal planes of the interface layers leading to a more rectangular shape compared to the square lattice of the STO substrate. Due to this effect YBCO tends to align its longer  $b$  axis along the step edges.

As the vicinal angle becomes larger, also the anisotropic strain at the interface increases. A higher step edge density contributes to the amount of YBCO domains that align their  $b$  axis parallel to the terraces. At  $\alpha = 1.10^\circ$  the separate twin orientations have disappeared, see Fig. 3(c). As mentioned

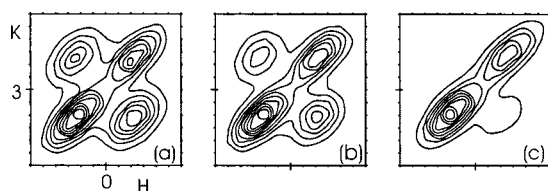


FIG. 2. The [304] RSMs of 100 nm YBCO films on  $\beta_{[110]}$  STO substrates with vicinal angle  $\alpha = 0.25^\circ$  (a),  $\alpha = 0.39^\circ$  (b), and  $\alpha = 0.60^\circ$  (c).

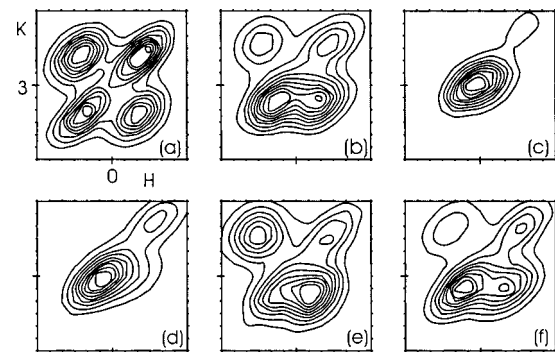


FIG. 3. RSMs of the [304] reflections of 100 nm YBCO on  $\beta_{[100]}$  STO substrates with increasing vicinal angle,  $\alpha = 0.52^\circ$  (a),  $\alpha = 0.80^\circ$  (b),  $\alpha = 1.10^\circ$  (c),  $\alpha = 1.86^\circ$  (d),  $\alpha = 4.92^\circ$  (e), and  $\alpha = 5.18^\circ$  (f).

before, using substrates with vicinal angles of about  $10^\circ$ , Brötz *et al.*<sup>8</sup> achieved an untwinning, defined as  $[S_1^+ + S_1^-]/[S_2^+ + S_2^-]$ , up to 70%, the highest ratio reported so far. The untwinning in Fig. 3(c) exceeds 95% and this YBCO film can be considered as monocrystalline. As the vicinal angle increases further, the separate twin states start to emerge again [Figs. 3(d)–3(f)].

Besides this untwinning, a remarkable phenomenon of film tilt has been observed. Maurice *et al.*<sup>14,15</sup> also reported about this preference of YBCO (001) planes to be parallel to the optical surface rather than to the STO (001) planes in PLD grown films on  $\sim 0.5^\circ$  vicinal substrates. Our results prove that the YBCO  $c$  axis is perpendicular to the optical surface of the STO substrate even up to the specific angle of  $\alpha = 1.10^\circ$ . In our study the film tilt is related to the vicinal conditions of the substrates used. Figure 4 shows the inclination of the YBCO  $c$  axis with respect to the crystallographic surface normal of STO, plotted versus the vicinal angle of the substrate. The data show that on substrates with  $\alpha \leq 1.1^\circ$  all films are tilted towards the optical surface normal. With increasing vicinal angle ( $\alpha > 1.1^\circ$ ) the  $c$  axis of the film becomes perpendicular to the (001) planes of the STO substrate.

A vicinal angle  $\alpha$  of  $1.10^\circ$  corresponds to a terrace length ( $L_T$ ) of 20 nm, which is comparable to the diffusion length ( $L_D$ ) of PLD grown YBCO. At these conditions, we observed an almost completely untwinned YBCO film, with the  $b$  axis oriented along the step edges. Since  $L_T \sim L_D$ , APBs will mainly be formed at the substrate steps as shown in Fig. 5(a). However, the two distinct stacking sequences during the nucleation of Y123 will cause annihilation of a

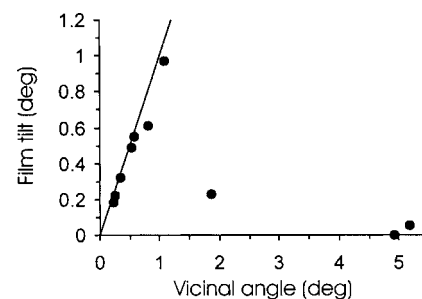


FIG. 4. Inclination of the YBCO  $c$  axis vs the vicinal angle of the STO substrate. The solid line represents the  $c$  axis of YBCO perpendicular to the optical surface.

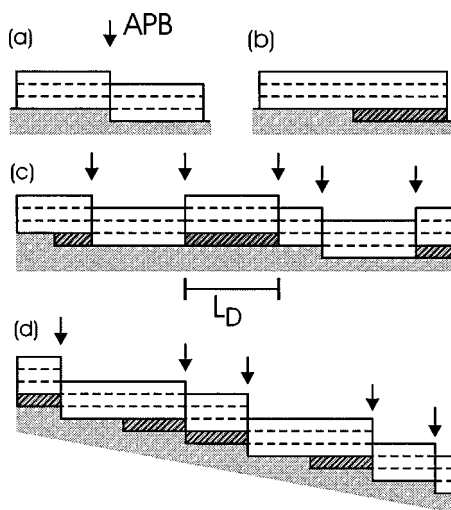


FIG. 5. Schematic view of an APB (a), and APB-annihilation at a substrate step (b). Formation of APBs on the atomically smooth terraces when  $L_T > L_D$  (c). APBs formed only at step edges when  $L_T < L_D$  (d).

fraction ( $\sim 25\%$ ) of these APBs as illustrated in Fig. 5(b). In this special condition, the number of APBs is decreased to a minimum. For  $\alpha < 1.1^\circ$  ( $L_D < L_T$ ), the density of APBs is dominated by the formation on the atomically smooth terraces [Fig. 5(c)] and exceeds the substrate step edge density. For  $\alpha > 1.1^\circ$  ( $L_D > L_T$ ), the APBs will mainly be formed at the substrate steps [Fig. 5(d)], and the high number of steps also leads to a high density of APBs.

The inclination of the YBCO  $c$  axis only occurs on substrates with  $L_T > L_D$ , suggesting a relation with the APB density. Sputtered YBCO thin films produced in our lab did not exhibit the  $c$ -axis inclination even on STO substrates with a vicinal angle down to  $0.3^\circ$ . Given that the diffusion length during sputtering is larger, this is consistent with our assumption that YBCO films are not tilted if  $L_T < L_D$ .

On our single terminated substrates with  $\alpha = 1.1^\circ$  an increase of the untwining is observed up to almost 100%, in contrast to the 70% in earlier studies. Clearly there is a relation between the accommodation of anisotropic strain and the twinning and tilting of the YBCO film. This behavior is determined by the vicinal conditions of the STO substrate and diffusion length of YBCO, resulting in defects on terraces and step edges during the initial growth in PLD. However, the exact cause in this initial process is still not completely understood, and requires further research like experiments on films with Y122 as a starting layer, eliminating the different stacking sequence.<sup>16</sup>

The vicinal angle and orientation of a well-treated  $\text{TiO}_2$  terminated STO substrate influences the crystalline properties of the YBCO film. An inclination of the YBCO  $c$  axis and accompanying film tilt is observed on substrates with vicinal angles up to  $1.1^\circ$ . This phenomenon is only observed in the regime where the YBCO diffusion length during PLD growth is smaller than the substrate terrace length. Here a high number of APBs are formed compared to the number of step edges at the film-substrate interface. Furthermore, the anisotropic strain originating from the stepped substrate surface plays a significant role in the twinning behavior of YBCO. A vicinal orientation towards  $[110]$  gives rise to a preference to one of the two twin orientations. For vicinal angles of the substrate of  $\alpha > 0.6^\circ$ , one twin state is completely suppressed. Substrates, having their step edges along  $[100]$ , exhibit a detwinning for larger vicinal angles. The maximum effect was obtained on a substrate having a vicinal angle of  $\alpha = 1.10^\circ$ . The film contains a minimum of APBs, and large domains for the accommodation of the anisotropic strain, resulting in an untwining of  $>95\%$ . With all the  $a$  and  $b$  axis of the YBCO crystallites oriented in the  $[100]$  and  $[010]$  direction, respectively, this film can be considered as monocrystalline.

<sup>1</sup>V. K. Wadhawan, Phys. Rev. B **38**, 8936 (1988).

<sup>2</sup>D. Schweitzer, T. Bollmeier, B. Stritzker, and B. Rauschenbach, Thin Solid Films **280**, 147 (1996).

<sup>3</sup>J. Zegenhagen, T. Haage, and Q. D. Jiang, Appl. Phys. A: Mater. Sci. Process. **67**, 711 (1998).

<sup>4</sup>J. G. Wen, C. Traeholt, and H. W. Zandbergen, Physica C **205**, 354 (1993).

<sup>5</sup>T. Haage, J. Zegenhagen, H.-U. Habermeier, and M. Cardona, Phys. Rev. Lett. **80**, 4225 (1998).

<sup>6</sup>J. D. Budai, M. F. Chisholm, R. Feenstra, D. H. Lowndes, D. P. Norton, L. A. Boatner, and D. K. Christen, Appl. Phys. Lett. **58**, 2174 (1991).

<sup>7</sup>J. Brötz and H. Fuess, Physica C **339**, 75 (2000).

<sup>8</sup>J. Brötz, H. Fuess, T. Haage, and J. Zegenhagen, Phys. Rev. B **57**, 3679 (1998).

<sup>9</sup>S. Bals, G. Rijnders, D. H. A. Blank, and G. van Tendeloo, Physica C **355**, 225 (2001).

<sup>10</sup>T. Haage, H.-U. Habermeier, and J. Zegenhagen, Surf. Sci. **370**, L158 (1997).

<sup>11</sup>G. Koster, B. L. Kropman, G. Rijnders, D. H. A. Blank, and H. Rogalla, Appl. Phys. Lett. **73**, 2920 (1998).

<sup>12</sup>Deposition conditions are:  $780^\circ\text{C}$ , 0.25 mbar  $\text{O}_2$ , 4 Hz KrF ( $\lambda = 248$  nm) excimer laser with spot energy density  $1.3$  J/cm<sup>2</sup>. Postdeposition treatment: 15 min at  $600^\circ\text{C}$  and 15 min at  $450^\circ\text{C}$  in 500 mBar  $\text{O}_2$ .

<sup>13</sup>Samples were measured on a single crystal diffractometer (CAD4, Enraf Nonius Delft) using Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å).

<sup>14</sup>J.-L. Maurice, O. Durand, M. Drouet, and J.-P. Contour, Thin Solid Films **319**, 211 (1998).

<sup>15</sup>J.-L. Maurice, O. Durand, K. Bouzouane, and J.-P. Contour, Physica C **351**, 5 (2001).

<sup>16</sup>G. Rijnders (unpublished).