Strong, Asymmetric Flux Pinning by Miscut-Growth-Initiated Columnar Defects in Epitaxial $YBa_2Cu_3O_{7-x}$ Films

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Strong flux pinning and a pronounced asymmetric angular dependence of $J_c(H,\theta)$ have been discovered in $YBa_2Cu_3O_{7-x}$ films grown on miscut, mosaic $LaAlO_3$ substrate surfaces. A new pinning peak, which at low fields is nearly as strong as the "intrinsic pinning," is observed for magnetic field orientations between the c axis and the CuO_2 plane. Cross-section transmission electron microscopy reveals columnar growth defects (2–3 nm diameter) aligned near the c axis, in concentrations $\sim 10^{10}$ cm^{-2}. The results demonstrate that deliberately modified substrate surfaces may introduce technologically useful flux pinning in $YBa_2Cu_3O_{7-x}$ films.

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Epitaxial $YBa_2Cu_3O_{7-x}$ (YBCO) films grown by pulsed laser ablation (PLA) or off-axis magnetron sputtering are known to exhibit strong flux pinning and high J_c [1–3]. Although it has been assumed that the strong pinning is due to growth-related defects [4], and striking correlations have been established between J_c and the density of certain growth features [5], the particular defect specie(s) responsible for the strong pinning in epitaxial YBCO films has not been identified. In contrast, high quality single-crystal YBCO (c-YBCO) exhibits weak flux pinning and quite low J_c, typically a factor of ~ 1000 less than for epitaxial films [6,7]. This difference has motivated systematic studies of the effects of specific defects on flux motion and J_c through their controlled introduction into initially low-J_c single-crystal specimens. In particular, recent studies have shown that irradiation with high-energy heavy ions produces nearly continuous columns of heavily damaged or amorphous material [8–11]. The columns are 5–10 nm in diameter, nearly ideal ($r \sim \xi_{ab}$) to produce strong pinning of line vortices.

While columnar defects in YBCO greatly enhance flux pinning and the irreversibility line for all magnetic field orientations at high temperatures (77 K), the enhancements are greatest when H is aligned with the ion-damage tracks [8]. In contrast, there is little angular selectivity in the increased vortex pinning of single-crystal $Bi_2Sr_2CaCu_2O_8$ (BSCCO) [9–11]. This is ascribed to the very different anisotropies, as typified by the superconductive effective mass ratios, $\gamma = (m_c/m_{ab})^{1/2}$, of YBCO [12] ($\gamma \sim 5.5$) and BSCCO [13] ($\gamma > 60$). The large anisotropy leads to a greatly diminished vortex line tension in BSCCO, and the vortices may behave as segmented stacks of "pancakes," confined to the CuO_2 plane groups and only weakly interacting across the ionic "block layers" [14,15].

In this Letter we report a quite different approach, namely the controlled *use of growth mechanisms themselves* to create extended defects with dimensions appropriate to strongly pin vortex lines in YBCO. A pronounced angular asymmetry and a new peak in $J_c(H,\theta)$ have been observed for epitaxial YBCO films grown on deliberately miscut $LaAlO_3$ substrates that also contain a small mosaic spread of subgrain orientations. The anomalous peak in $J_c(H,\theta)$ occurs for magnetic field orientations between the c axis and the CuO_2 planes, normally a relatively low-J_c region. For miscut $SrTiO_3$ that has no significant subgrain structure, asymmetry is present in $J_c(H,\theta)$ but no large new peak appears. Cross-sectional high-resolution transmission electron microscope (HRTEM) images of the YBCO/(miscut $LaAlO_3$) specimens reveal the source of the anomalous pinning: columnar growth defects with near-ideal diameters of 2–3 nm that are aligned near the c axis and that penetrate clear through the ~ 0.5 to 1.0 μm thick YBCO films. TEM images confirm that some columnar growth defects initiate at terrace steps on the miscut substrate surface. In low fields ($H \leq 1$ T), the magnitude of the anomalous peak in $J_c(H,\theta)$ is comparable to the strong "intrinsic pinning" peak that occurs with H parallel to the CuO_2 planes. The combined J_c anisotropy and TEM measurements suggest that it may be possible to tailor imperfect substrate surfaces or to fabricate crystalline buffer layers that contain imperfectly aligned grains, in order to introduce technologically useful amounts of flux pinning in high-temperature superconducting films and deposits.

YBCO films with thicknesses of 0.5–1.0 μm were grown by pulsed KrF (248 nm) laser ablation on miscut near-(001) $SrTiO_3$ and $LaAlO_3$ substrates using standard procedures for PLA film growth that have been described elsewhere [16]. Recent scanning tunneling microscope (STM) studies in our laboratory [17] and elsewhere [18] have revealed that the prominent screw-mediated growth mechanism of YBCO films [19,20] can be completely

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suppressed by growth on substrates miscut by $\sim 2°$ away from (001). Our STM images show that the usual screw-mediated morphology is replaced by a "tilted platelet" surface microstructure consisting of very regular steps and terraces, even for thick YBCO films [17]. High-resolution x-ray diffraction shows that the miscut-grown YBCO films are entirely c-axis-perpendicular [to the substrate (001) plane] with no detectable a-axis-oriented (or other) material. Indeed, *even in the complete absence of any screw dislocation microstructure* these films exhibit consistently high $J_c(H)$.

As shown in Fig. 1(a), the anisotropy of $J_c(H,\theta)$ is strongly modified in YBCO films grown on miscut $LaAlO_3$. While the highest J_c still occurs for H parallel to the CuO_2 planes, the minimum-J_c points are no longer placed symmetrically between the two J_c peaks, and a large new asymmetrically positioned J_c peak appears. [$\theta = 0°$ is defined during sample mounting by optically positioning the film surface approximately perpendicular to H ($\pm 1°$). Thus, the peaks at $H \parallel a\text{-}b$ are shifted beyond the $\theta = \pm 90°$ positions by approximately the substrate miscut angle.] For all samples, the miscut is such that the largest component of the c-axis projection onto the film surface is orthogonal to the basal plane transport current, as illustrated in the inset.

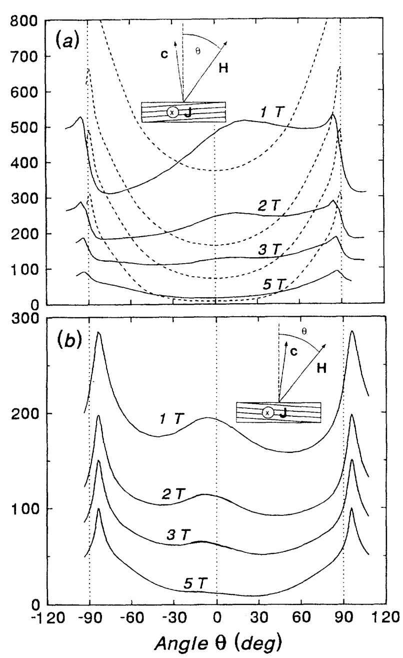

FIG. 1. (a) $J_c(H,\theta)$ at $T = 77$ K and $H = 1$, 2, 3, and 5 T, for epitaxial YBCO films grown (solid curves) on $LaAlO_3$ miscut $\sim 1.6°$ away from (001) and (dashed lines) on accurately cut (001) $SrTiO_3$. The angular shift of the YBCO/$LaAlO_3$ data by the $\sim 1.6°$ miscut angle is apparent, as are the angle-asymmetric enhancements in J_c for field orientations near the c axis. The intrinsic pinning peaks at $H \parallel a\text{-}b$ are reduced due to the miscut, perhaps because of defect-induced misorientations of the lattice planes. (b) $J_c(H,\theta)$ at $T = 77$ K and $H = 1$, 2, 3, and 5 T, for epitaxial YBCO grown on a $SrTiO_3$ substrate miscut 5.7° from ⟨001⟩ toward ⟨0$\bar{1}$0⟩. The current is along ⟨100⟩.

We note that the miscut-grown YBCO film of Fig. 1(a) has quite good superconducting transport, with $J_c(H = 0, T = 77\text{ K}) = 2.02\text{ MA/cm}^2$, despite the substrate miscut. At $H = 1$ T and 77 K its intrinsic pinning peak ($H \parallel a\text{-}b$ plane) was reduced by the miscut to $J_c \sim 0.53\text{ MA/cm}^2$, compared with $\sim 1.06\text{ MA/cm}^2$ for a YBCO film grown under similar conditions on (001) $SrTiO_3$. However, the absolute magnitude of $J_c(H = 1\text{ T}) \sim 0.52\text{ MA/cm}^2$ *at the new peak* ($\theta \sim +20°$) for the film grown on miscut $LaAlO_3$ *is* $\sim$*34% greater than* J_c *at this orientation for the comparison YBCO film on (001)* $SrTiO_3$. Similarly, for $H = 3$ T, near $\theta \sim 15°$, the absolute J_c was enhanced by nearly 50% in the YBCO film grown on miscut $LaAlO_3$. Clearly, the pinning represented by the new peak in J_c is very strong, since it is being compared with the already-strong pinning in laser-ablated YBCO films, and with the intrinsic pinning for H parallel to the CuO_2 planes.

YBCO films grown on miscut $SrTiO_3$ substrates also exhibit asymmetric pinning, as shown in Fig. 1(b). However, for $SrTiO_3$ the magnitude of the miscut effect on J_c is much smaller than for $LaAlO_3$. Consequently, larger miscut angles were required to display the asymmetry, with a concomitant reduction in the absolute J_c. For $SrTiO_3$ no large J_c peak similar to that seen for YBCO on miscut $LaAlO_3$ was observed. However, the shift in the angular orientation of $J_c^{\max}$ by the miscut angle of 5.7° is apparent in Fig. 1(b).

The full (H,θ) dependence of J_c can be displayed compactly be defining the normalized $J_c(H,\theta)$ anisotropy,

$$J_c^{\text{norm}}(H,\theta) = [J_c(H,\theta) - J_c^{\min}(H)]/[J_c^{\max}(H) - J_c^{\min}(H)], \tag{1}$$

in which $J_c^{\min}(H)$ and $J_c^{\max}(H)$ are the minimum and maximum values of $J_c(H,\theta)$ at each field value. From $J_c^{\text{norm}}(H,\theta)$, plotted in Fig. 2, it is apparent that the anomalous peak in $J_c(H,\theta)$ shifts toward the c axis with increasing H. The peak reaches a maximum, relative to the intrinsic pinning, for $H \sim 0.5$ T and then decreases more rapidly than does the intrinsic pinning for $H > 1$ T. This behavior suggests that if the new J_c peak is due to growth-related extended defects, then (i) these defects must be aligned near the c-axis direction, (ii) their density must be sufficient to pin nearly every vortex line in $H \sim 0.5$ T, but (iii) either their density, alignment, or their continuity is insufficient to pin all the vortices in much stronger fields.

To help identify the origin of the differences in vortex pinning in films grown on miscut $LaAlO_3$ and $SrTiO_3$ substrates, the substrates first were examined by four-circle x-ray diffractometry. The $LaAlO_3$ substrates were

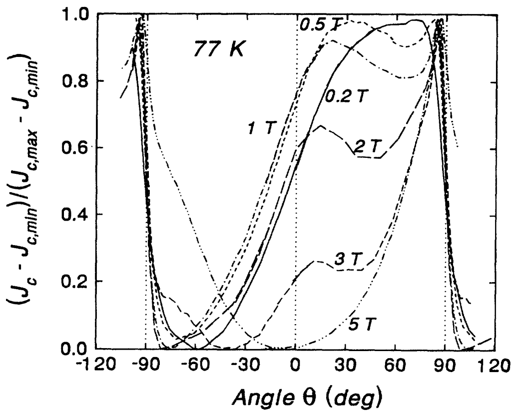

FIG. 2. Normalized $J_c(H,\theta)$ [see Eq. (1)] for the YBCO/(1.6° miscut $LaAlO_3$) specimen of Fig. 1(a), for $H = 0.2$, 0.5, 1, 2, 3, and 5 T.

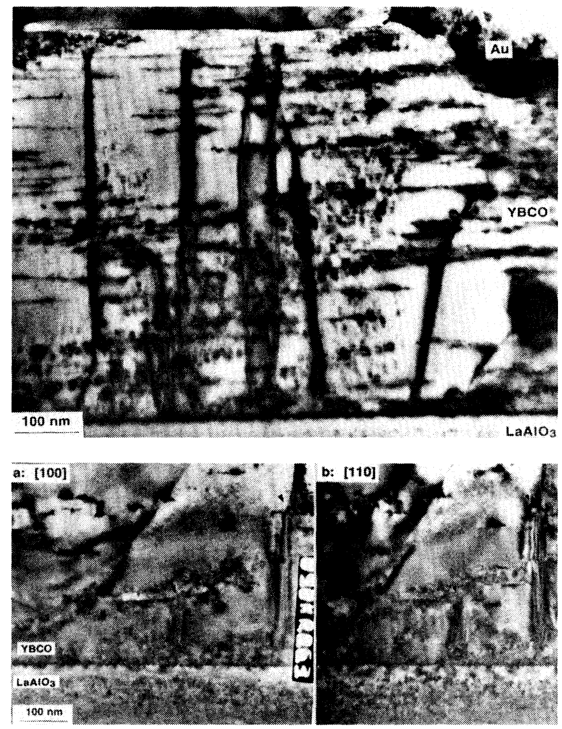

FIG. 3. (Top): Low-magnification cross-section TEM image of YBCO film grown on miscut $LaAlO_3$. (Bottom): Two views of the same columnar defect from orientations 45° apart. Gold was evaporated on the YBCO film as an electrical contact for $J_c(H,\theta)$ measurements.

found to contain a distinct subgrain structure, with a mosaic spread of subgrain orientations as large as 0.5° at some locations, but more typically 0.3°. A YBCO film grown on this substrate exhibited a ~0.6° wide (005) $c_\perp$ diffraction peak, much greater than the 0.1°–0.3° width typical of YBCO films on (001) $SrTiO_3$, or the ~0.03° (instrumental) width for the $SrTiO_3$ substrates themselves.

To obtain direct information about the defect microstructure responsible for the anomalous J_c peak, the YBCO/(miscut $LaAlO_3$) films were examined by HRTEM. A Phillips CM30 TEM/STEM was used at 300 kV with 2.3 Å image resolution. Low-magnification images (Fig. 3, top) show that nearly columnar defects penetrate most of the way through the YBCO/(miscut $LaAlO_3$) films. Figure 3 (bottom) views a growth-induced defect from two orientations 45° apart, and verifies that it is columnar, not planar. The strain-field diameters of the defective columnar regions (obtained directly from high-resolution images) were 2 to 3 nm, which is nearly ideal to provide vortex core pinning in YBCO. The defective columns in Fig. 3 (top) are oriented both perpendicular and askew to the substrate surface; this possibly accounts for the anomalous pinning and high-J_c values observed over a range of H field orientations between the c axis and the CuO_2 planes [21].

Clearly there must be some orientational bias in the defect structure in order to account for the observed asymmetric flux pinning. Indeed, our measurements of five films on both $LaAlO_3$ and $SrTiO_3$ miscut substrates have established a firm connection between the miscut direction and the sense of asymmetry: There is "extra" flux pinning in the quadrant *opposite* the projected c-axis direction. In addition, all these samples exhibited strong flux pinning in field, with irreversibility lines that approach those of heavy ion-irradiated YBCO, which appear to represent an upper limit [22]. Recent theoretical descriptions of vortex depinning from columnar defects [14,15] may provide some insight into qualitatively understanding the observations. Because of the large anisotropy, the line tension for vortex bending is effectively reduced by a factor of γ^{-2} with respect to the isotropic case. This provides a mechanism by which flux lines may wander and accommodate to nearby pinning sites without undue cost in elastic energy. In addition, when the flux density is less than or equal to the columnar defect density, dissipative mechanisms are greatly suppressed (Bose glass and Mott insulator vortex phases) [14,15]. The gradual shift of the new peak in J_c toward the c axis with increasing field is likely due to a combination of (i) a stiffening tilt modulus with increased vortex interactions, (ii) a field-matching selection of appropriately oriented columnar defects, and (iii) a complex interplay between the pinning of vortex segments within the columns and by the point defects between the columns. The relationship between these and other effects has not been worked out, although recently it was proposed that an array of splayed columnar defects could provide more effective pinning than parallel columns [23].

This qualitative picture is quantitatively consistent with a "matching field" concept, which allows us to compare directly the areal density of defect columns with the vortex density at a given field strength. Since $B = n\Phi_0$, where $\Phi_0 = 2.07 \times 10^{-11}$ T cm^2 is the magnetic flux quantum and n is the areal vortex density, then if σ_d is the areal density of defective columns, the matching field is $B_\phi = \sigma_d \Phi_0$. Figure 3 (top) shows ten defect columns (six of which penetrate clear through the YBCO film) in a distance of 900 nm, corresponding to $\sigma_d \sim 1.2 \times 10^{10}/\text{cm}^2$ and to $B_\phi = 0.25$ T. This value is in reasonable agreement with our observation (Fig. 2) of a relative maximum of the anomalous peak in J_c that corresponds to nearly every vortex line being pinned for $H = 0.5$ T, and the fact that the anomalous peak decreases more rapidly than the intrinsic pinning peak for higher fields.

HRTEM images also reveal a slight rotation of crystallite orientation on opposite sides of some defect columns as well as a slight change in tilt of the a-b planes. These observations suggest that the defective columns are associated with subgrain boundaries, and thus establish a connection with the substrate mosaic spread that XRD revealed as the key requirement to produce the anomalous J_c peak in YBCO grown on miscut $LaAlO_3$, but not miscut $SrTiO_3$. Numerous stacking faults also exist in the a-b planes of the YBCO/$LaAlO_3$ films. HRTEM shows these are produced by insertion of extra Cu-O layers in (001) planes; these faults also can act as effective fluxpins [24].

A final point relevant to recent efforts to grow ultrathin YBCO films with good transport properties [25–27] is that our HRTEM images reveal that many of the columnar growth defects originate at substrate steps [28]. These images show quite clearly that the YBCO unit cells grown on the upper and lower terraces (to either side of the substrate step) are shifted vertically by $c/3[001]$. Consequently, the CuO_2 planes are broken, disrupting the superconducting order parameter and locally weakening superconductivity. However, these images also show that many of the $c/3$ stacking faults are cured within $\sim$10 nm from the substrate by insertion of extra Cu-chain planes [28].

In conclusion, defective columns aligned near the c axis are formed in concentrations $\sim 10^{10}/\text{cm}^2$, corresponding to an equivalent pinning field $B_\phi \sim 0.25$ T, in YBCO films grown on deliberately miscut $LaAlO_3$ substrates that contain significant mosaic subgrain structure. The defective columns have diameters of 2–3 nm, near ideal for the core pinning of line vortices, and penetrate clear through 0.5–1.0 μm thick YBCO films. These growth-induced defects produce a pronounced angular asymmetry in $J_c(H,\theta)$, including a new pinning peak that is asymmetrically placed between the c axis and the CuO_2 planes. With increasing field, the anomalous J_c peak shifts toward orientations near the c axis, where pinning normally is weak and J_c is relatively low. These experiments demonstrate that miscut-induced columnar growth defects can produce useful amounts of flux pinning at what are normally low-J_c magnetic field orientations. Moreover, they suggest that *imperfect* substrates could play an important role in practical applications of cuprate superconductors.

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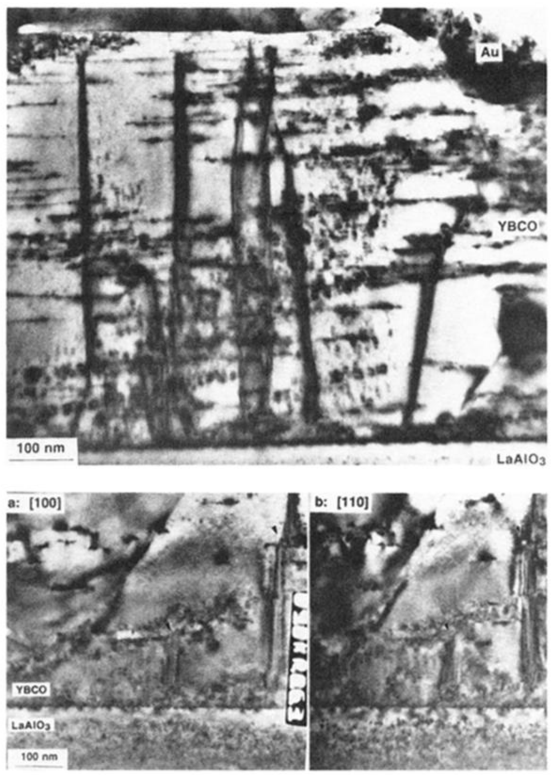

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