Monosteps on extremely flat $YBa_2Cu_3O_{7-x}$ surfaces grown by liquid-phase epitaxy

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We report the growth of extremely flat $YBa_2Cu_3O_{7-x}$ (YBCO) films onto $NdGaO_3$ substrates by liquid-phase epitaxy (LPE). Macroscopic growth spirals with large interstep distances (several μm) and with hollow cores are observed by optical (Nomarski) microscopy and by atomic force microscopy, in contrast to the microscopic spiral islands formed in epitaxy from the vapor phase. Typical step heights of LPE-grown YBCO vary between monosteps (1.2 nm) and 7.2 nm. Extremely flat epitaxial YBCO surfaces with continuous step flow have been achieved. They are of interest for fundamental physical studies (gap, photoemission) and for a reliable high-temperature superconductivity tunnel-device technology.

With the discovery of high-temperature superconductivity (HTSC) above 77 K, its application for electronic devices was suggested. The applicability of HTSC in such devices based on grain-boundary or step-edge junctions has been demonstrated by several groups, and promising device characteristics have been measured. However, the very short coherence lengths and the inherent materials problems of the complex cuprates[1] did not yet allow to develop a reliable planar technology for tunnel devices and SQUIDs.[2] So far, the tunnel structures were fabricated from the vapor phase, either by physical vapor deposition (PVD) like sputtering or pulsed laser deposition, or by chemical vapor deposition (CVD). Typical surfaces of HTSC layers grown from the vapor phase show two-dimensional (2D) nucleation and localized step flow, or spiral-island formation[3,4] as reviewed recently.[5] Surface nucleation can be suppressed by large misorientation angles of the substrates thereby providing kinks and steps. However, step densities are very high with interstep distances between 10 and 30 nm which in the future might be increased to 100 nm. This surface roughness of PVD- and CVD-grown layers is limiting the development of HTSC tunnel-device technology at high reliability and yield. These surface-nucleation and growth phenomena are due to the deviation from equilibrium, i.e., the high supersaturation in epitaxial deposition from the vapor phase.[5] Furthermore, the thermodynamic stability boundaries of $YBa_2Cu_3O_{7-x}$ (YBCO) limit the growth temperatures [depending on the (low) oxygen partial pressures]. Surface diffusion will thus confine interstep distances to about 100 nm, which may be compared with the inherent limitation in molecular beam epitaxy (MBE) of GaAs at 160 to 200 nm.[6]

A different approach is liquid-phase epitaxy (LPE) where growth can occur very near to equilibrium and where surface diffusion allows interstep distances of at least several μm, the limit being set by practical growth times.[5] Epitaxial growth can occur at very low supersaturation which is insufficient for 2D nucleation and which may be $>10^3\times$ smaller than in PVD or CVD, if the misfit with the substrate is accordingly small. This low driving force in LPE allows the Frank–Van der Merwe growth mechanism, i.e., layer-by-layer growth over macroscopic dimensions, if the transition to the equilibrium surface (facet) has been achieved.[7] In this case screw dislocations or other defects act as sources of steps. The Burgers vector of the defect determines the step height which may be an integer of the size of the growth unit. Another cause of multiple step heights is step bunching, the coalescence of smaller steps at relatively high supersaturation and/or substrate misorientation angles (typically, $0.2° \leq \alpha \leq 4°$). In this work the fabrication of macroscopic quasi atomically flat HTSC surfaces is reported for the first time. By liquid-phase epitaxy (LPE) YBCO layers can be prepared on well-matched and well-oriented substrates.[8] The surface morphology is characterized by differential interference contrast microscopy (Nomarski) and by atomic force microscopy (AFM). Macroscopic growth spirals of diameters up to 0.5 mm and with heights of the growth steps between 12 Å (monosteps) and about 80 Å have been measured. Surfaces with large separation (>10 μm) between monosteps may be used as base structures (HTSC substrates) for planar HTSC tunnel device technology. Such flat surfaces will also allow reliable gap and photoemission measurements.

The chemical and structural complexity of YBCO is coupled with a limited stability field with respect to temperature and oxygen partial pressure. For these reasons, the task to establish the technological prerequisites for LPE is quite demanding.[8] Phase diagrams (primary crystallization fields) and the solubility curves have been determined, along with the development of corrosion-resistant crucibles and of substrates with very low misfit. A systematic approach allowed to develop the growth process with optimized temperature gradients and supersaturations. The specific YBCO surface discussed below was grown in a three-zone LPE apparatus with Eurotherm programmer 900 EPC and with a nine-element PtRh6/PtRh30 thermopile as high-sensitivity temperature sensor.[9] The constituents BaO_2, CuO, and Y_2O_3 for a charge of 131.05 g corresponding to 5 wt % YBCO in a

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TABLE I. Characteristic features of LPE-grown (100) and (001) regions.

YBCO	(100)	(001)
Cracks	Parallel cracks vertical [001] Nearly equidistant (30–80 μm)	Irregular Large crack-free regions (100–200 μm)
Twins	Unidirectional domains parallel [001]	Crossed pattern of {110} twins

flux solvent of $BaCuO_2$-CuO at 31 mol % BaO are molten in a conical yttria crucible[10] of 49 cm^3 by heating to 1010 °C during 9 h. After soaking for 7 h the temperature is increased to 1040 °C and reduced to 1000 °C within 90 min. A few particles on the melt surface are removed by a Pt basket and by an alumina rod. After finding saturation by means of test substrates, four 4–6-μm-thick YBCO layers are grown between 997 and 995 °C at growth times between 16′ and 19′. Then a $NdGaO_3$ (110) substrate[11] of ~1 cm^2 is vertically dipped into the solution at 995 °C and rotated at 16 rpm. After slow cooling in 9 h 50 min to 993.6 °C the substrate with layer is slowly lifted out of the melt (23 min) and then removed from the furnace (15 min). The partially oxidized LPE layer contains numerous macroscopic growth spirals that can be seen with a Nomarski microscope of Zeiss. The AFM investigations are performed at ambient temperature and pressure using a beam-deflection-type force microscope (Nanoscope II of Digital Instruments). Microfabricated cantilevers with integrated Si_3N_4 tips (force constant 0.12 N/m) have been employed, and the images were recorded in constant-force mode.

The LPE-grown and partially oxidized YBCO surface contains *a*- and *c*-oriented regions which can be clearly distinguished[12] by the crack and twin patterns according to Table I. Both regions show growth hillocks of, typically, 150-μm diameter (50–500) in Nomarski photographs, thus indicating layer-by-layer growth over macroscopic distances. Several growth spirals on a (001) surface are presented in Fig. 1. The detailed structure of a growth hillock becomes visible by atomic force microscopy at high magnification. A double spiral with two hollow cores, and the correspondingly asymmetric growth hillock with 6- to 7.2-nm step height is given in Fig. 2(a). The higher magnification in Fig. 2(b) reveals the origin of 6 monosteps from the big hollow core, and 5 monosteps coming from the left hollow core. Another multistep screw is shown in Fig. 3. The macrosteps are composed of 4 to 5 monosteps, and during the turns of the spiral monosteps separate towards the periphery. A line section through the hollow core gives the diameter of 600 nm and a depth of at least 125 nm. A screw with double steps is shown in Fig. 4, where in the right lower corner the double steps split into single steps. The interstep distances y_0 and the step heights of several screw hillocks presented in Fig. 5 reveal a proportional relationship. The interstep distances near the centers of the screws are larger than at the periphery (No. 023 and No. 045), a phenomenon also observed in LPE-

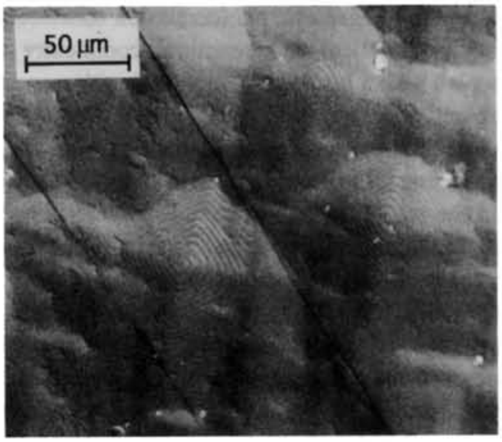

FIG. 1. Nomarski microphotograph of macroscopic growth spirals on YBCO (001).

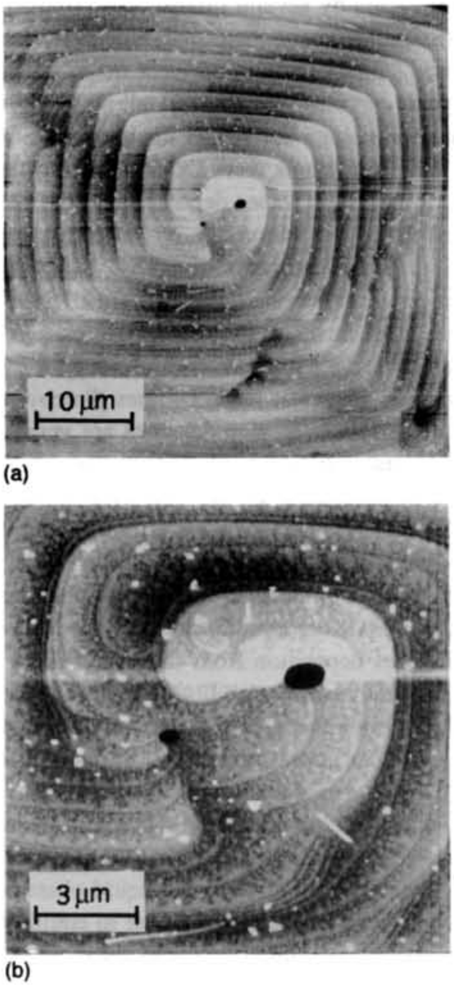

FIG. 2. (a) AFM image of a double spiral with two cores. (b) A magnified view shows the origin of 6 monosteps in the big hollow core, and of 5 monosteps from the left hollow core.

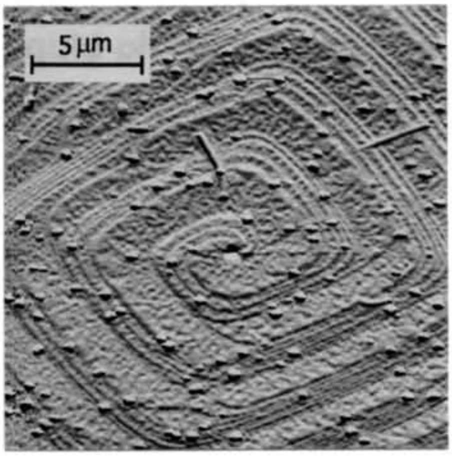

FIG. 3. Presents a single-core spiral with multiple steps which are composed of 4 to 5 monosteps, with individual monosteps occasionally separating towards the periphery.

grown garnet films.[13] However, for deriving the actual supersaturation the precise thermodynamic data are lacking. An estimate indicates an undercooling of <3 °C. The concentration of growth hillocks varies locally between $5\times10^2/\mathrm{cm}^2$ and $10^4/\mathrm{cm}^2$. This should be compared with typical $3\times10^9/\mathrm{cm}^2$ in PVD-grown YBCO layers.[3,4,14] The origin of screw islands in sputtered films is explained by coalescence of slightly misoriented 2D nuclei in the initial phase of film growth.[5] The large Burgers vectors and multistep spirals in our layer may be caused by an initial growth instability before during LPE growth the layer perfection is improved. Further studies have to clarify this when finally monostep spirals with large interstep distances are to be grown. Experiences with LPE-grown GaAs[15] have shown that this is possible. Such structurally perfect and flat HTSC surfaces may become useful as base structures (quasi as substrates) for a reliable tunnel-device technology. Fully oxidized LPE-grown layers have a normal high T_c (90 K), whereas the critical current densities are expected to be as low as in single crystals[16] (j_c at 77 K $\approx 5\times10^2$ to 10^4 A/cm^2).

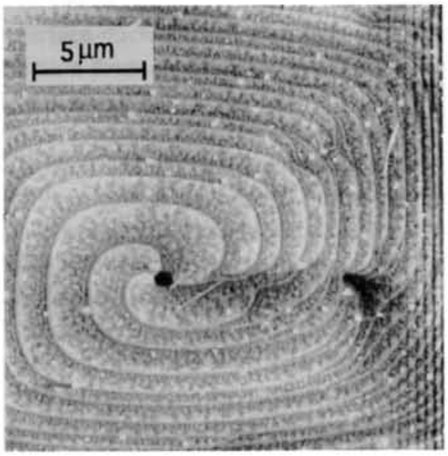

FIG. 4. A single-core spiral with a distant disturbance consists of double steps which split in the lower right corner into monosteps.

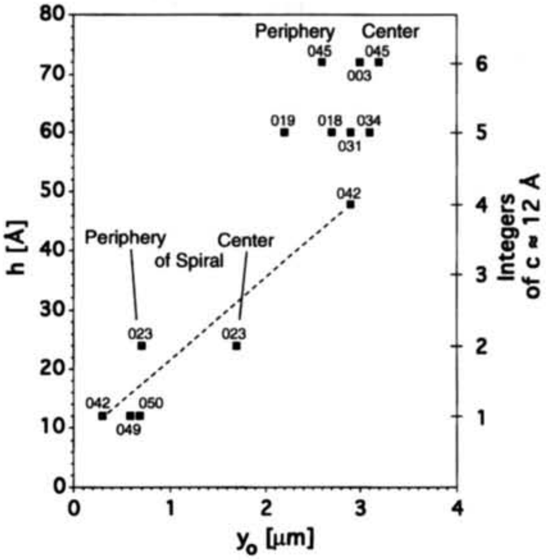

FIG. 5. Measured step heights and interstep distances of growth spirals from a single LPE-grown YBCO (001) surface. Note the differences between center and periphery of the spirals (023 and 045), and the differences between single and fourfold steps of the same spiral (042). Spiral No. 018 is shown in Fig. 2, 041 in Fig. 3, and 023 in Fig. 4.

Despite these promising results there still remain serious problems to be solved like the wetting problem (adhering solidified residual flux on the surfaces); the cracking and twinning problem (caused by misfit, thermal expansion differences and by the tetragonal-orthorhombic phase transition); and the oxidation problem due to the high structural perfection of LPE-grown layers.

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