

Strain release and twin structure in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films on (001) SrTiO_3 and NdGaO_3

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Ultrathin films of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grown by pulsed laser deposition on $\text{NdGaO}_3(001)$ and $\text{SrTiO}_3(001)$ were studied by grazing incidence x-ray diffraction. The critical thicknesses t_c was found to be 50 nm on $\text{SrTiO}_3(001)$. On $\text{NdGaO}_3(001)$, the shear distortion introduced by the substrate is released in two stages at 15 nm and 40 nm thickness by the formation of disclinations with orthogonal pseudo-Burgers vectors. The twin structure forms in the films at the first stage of strain relief, and as a consequence the twin boundaries are aligned unidirectionally. Calculated values for the critical thickness are too small for GdBCO/STO suggesting the existence of other mechanisms of strain relief, which is corroborated by our experimental findings.

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The growth, microstructure, morphology, and electronic properties of epitaxial high-temperature superconductors (HTS) are a subject of intense research activities. Given the complex nature of the materials, it is a challenging task to understand growth mode, strain release mechanism, and structural transitions at the pseudomorphic limit. However, because of their dominating influence on the transport properties of the thin films, an understanding is also important in view of device applications. For thick $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films on the (001) surface of the orthorhombic NdGaO_3 (NGO), twin domain boundaries that are usually oriented in two orthogonal directions, were found to be oriented only in one direction.¹ For thicker films preferentially oriented nanocracks along with a strong anisotropy in current transport were observed.^{1,2} The current anisotropy was proposed to be related to the nanocracks *and* the preferential twin boundary orientation. The underlying reason for these structural peculiarities was never conclusively established. We show here that they can be understood by the growth mode and the way in which misfit disclinations are introduced.

Commonly, the critical thickness (t_c) for pseudomorphic growth³⁻⁵ simply scales with the inverse of the lattice mismatch and qualitatively this has been experimentally verified also for orthorhombic $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RBCO, $R = \text{Y}$ or lanthanide except Ce and Tb) grown on the (001) faces of cubic SrTiO_3 (STO). Here, t_c (Refs. 6-9) can be tuned by the choice of R , which determines the lattice mismatch via the different rare earth covalent radii.^{10,11} Thus, we investigate here a system that is better lattice matched than YBCO/NGO, i.e., $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (GdBCO) on NGO (NGO/GdBCO). Since the critical thickness is expected to be larger, the growth transitions can be more carefully studied.

NGO(001) exhibits an orthorhombic crystal structure and its a and b axes match well with the diagonal of the rectangular a - b plane of RBCO. Thus, RBCO adopts the pseudo-square (001) unit cell of NGO as a template. The mismatch is -0.1% and less than 0.6% for the GdBCO a and b axis, respectively. However, in the pseudomorphic regime the epitaxial RBCO is not only dilatationally strained but also sheared, because of the lower crystallographic symmetry of

the substrate, and because the orthorhombic unit cells of RBCO and NGO do not match. The implications of this have not been thoroughly investigated. We find that films grown on NGO exhibit much lower t_c (≈ 15 nm) than films grown on STO (≈ 50 nm), but relax their misfit strain in two stages. Despite comparable lattice mismatch, t_c for GdBCO on STO(001) is found to be much larger, suggesting either a significantly larger threshold energy for dislocation formation or other mechanisms for strain relief.

We deposited a series of *ultrathin* GdBCO films of different thickness *simultaneously* on untwinned NGO and on STO substrates using pulsed laser ablation. Films of 10, 20, 40, 60, 80, and 100 nm thickness, calibrated by x-ray thickness oscillations, were studied. The deposition procedure^{12,13} and the superconducting transition temperatures^{9,13} have been reported previously. Briefly, films were deposited at 760°C under 50-Pa oxygen pressure and annealed 30 min at 450°C in 8×10^4 Pa oxygen before letting them naturally cool down to room temperature. All films are c axis oriented and fully oxygenated.^{9,13} X-ray-diffraction measurements were performed at the BW2 Wiggler beamline at the Hamburg Synchrotron Radiation Laboratory (HASYLAB), complemented by measurements at the ID32 insertion device beamline at the ESRF. Reciprocal space maps (RSM's) were recorded with a point detector under grazing incident geometry, $\alpha = 0.3^\circ$ at 10.0 keV and 0.5° at 8 keV for films on NGO and STO, respectively. The RSM's of 10-nm-, 20-nm-, and 40-nm- (40-nm and 60-nm) thick films grown on NGO (STO), scanned around $(2\ 0\ \frac{1}{3})$ and $(4\ 0\ \frac{1}{3})$, are shown in Fig. 1. Reciprocal lattice units are normalized to the values of the corresponding substrate unit cell, which is a pseudo-tetragonal cell for the NGO (see text below).

Bulk crystals and free-standing thin films on STO(001) exhibit two rotationally equivalent twin couples, i.e., four equivalent twin domains. Correspondingly, the diffraction peaks show fourfold splitting in the fine structure.¹⁴ Thin films beyond the critical thickness on NGO(001) are, however, so-called unidirectionally twinned and the fine structure of the film reflections shows only two peaks.¹

For the 10-nm-thick film on NGO(001) [Fig. 1(a)], the diffraction peaks from the film exhibit only one central com-

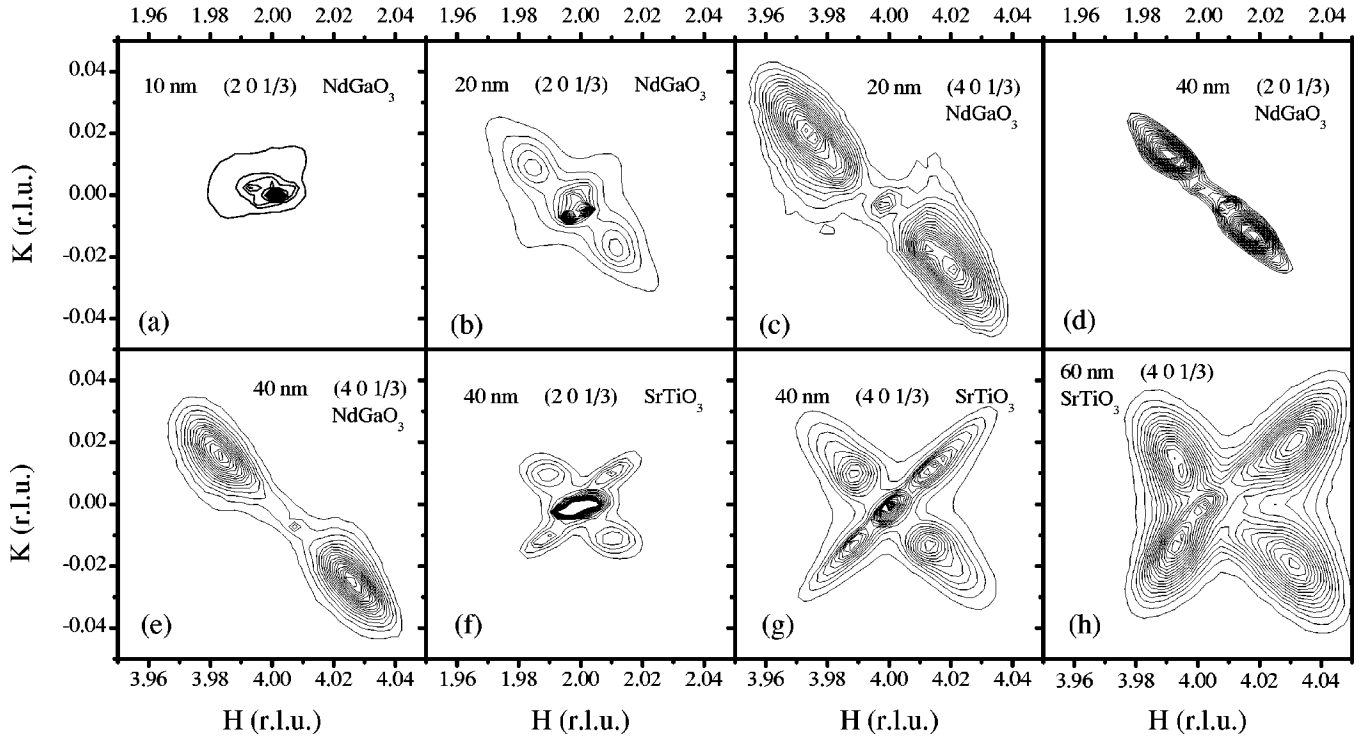


FIG. 1. Reciprocal space maps in the H, K plane at $L = \frac{1}{3}$ for GdBCO films grown on $\text{NdGaO}_3(001)$ and $\text{SrTiO}_3(001)$ given in reciprocal lattice units of the corresponding substrate, which is pseudotetragonal for NdGaO_3 with an angle between a and b of 89.27° . Film thickness and substrate material are indicated in the plots.

ponent, the H and K component of which are located exactly at the reciprocal lattice position of the substrate. This means that the film is pseudomorphic. The RSM of the 20-nm-thick film shows [Figs. 1(b),(c)] that aside from the central peak two side wings emerge, which become stronger for the 40-nm film [Figs. 1(d),(e)]. The side wings are symmetric to the integer H, K position for the 20-nm film, but not for the 40-nm films. As the comparison of Figs. 1(b) with 1(c), and Figs. 1(d) with 1(e) shows, the distance between the wing centers increases proportionally with increasing in-plane Q values. This shows that the GdBCO film is pseudomorphic up to just above 10 nm, then starts to relax below 20 nm along \mathbf{a}_{or} toward its orthorhombic, twinned structure and further relaxes along \mathbf{b}_{or} at a thickness close to 40 nm (see text below). Thus, the strain is released in two stages at $t_{c,1} = 15 \pm 5$ nm and $t_{c,2} \approx 40$ nm. Only two instead of four peaks are found in the RSM of the relaxed film, which confirms that only twin boundaries aligned along the \mathbf{b}_{or} direction are formed.

For the films on the STO substrate, up to a thickness of 40 nm [Figs. 1(f),(g)], four weak satellite peaks are symmetrically distributed around the strong central peak, which is attributed to a pseudomorphic film. Unlike for GdBCO on NGO, these satellite peaks cannot be due to twinning since: (a) they are symmetric to the central peak, which is at the integer H, K values defined by the substrate (note that at $L = \frac{1}{3}$ substrate reflections are not allowed); (b) they remain at constant ΔQ with respect to the center independent of the magnitude of the in-plane Q vector. The weak satellites arise from structural modulations in the GdBCO epilayer, as observed previously for SmBCO films.⁸ They can be regarded as a precursor to twinning and will be discussed in a forthcoming publication. The typical fourfold peak splitting, characteristic of the bidirectional twinning, is observed for 60 nm [cf. Fig. 1(h)]. The strain relaxation at this thickness is not complete as a comparison between peak positions and mismatch values (cf. Table I) shows.

Lattice parameters for GdBCO on $\text{STO}(001)$ and

TABLE I. Lattice constants of GdBCO, SrTiO_3 , and NdGaO_3 for the orthorhombic (or) and pseudotetragonal (pt) notation, respectively, accordingly calculated strain for pseudomorphic GdBCO, and critical thicknesses.

	d (nm)		ϵ (%)		t_c (nm)		
	GdBCO	STO or NGO ^a	pt NGO	GdBCO/STO	GdBCO/NGO	GdBCO/STO	GdBCO/NGO
a	0.3859	0.3905	0.5428	-1.18	-0.10		
b	0.3885	0.3905	0.5498	-0.51	+0.57		
c	1.1759	0.3905	0.7710	(+0.71)	(-0.25)	≈ 50	≈ 15

^aReference 22.

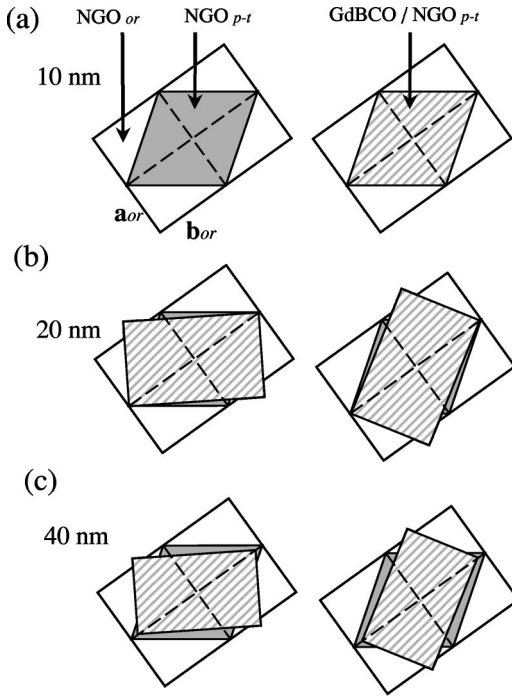


FIG. 2. Schematic representation of the epitaxial relationships between $\text{NdGaO}_3(001)$ and c axis oriented GdBCO and the process of strain relaxation in the a - b plane. (a) Left: orthorhombic and pseudotetragonal unit cells of NGO; right: pseudomorphic GdBCO on NGO(001). (b) The two possible orientations of GdBCO, which are partially relaxed along the \mathbf{a}_{or} direction, remain aligned along the \mathbf{b}_{or} direction. (c) Fully relaxed GdBCO.

NGO(001) are listed in Table I. For NGO, two unit cells are commonly in use: the orthorhombic (or) unit cell or a smaller pseudotetragonal (pt) cell. For the latter one, the surface unit cell is in size half of the rectangular surface unit cell of the NGO(001) face (cf. Fig. 2). The angle between \mathbf{a}_{pt} and \mathbf{b}_{pt} of the pseudotetragonal NGO unit cell is 89.27° .¹⁵ This results in a lattice twist distortion up to 6.37×10^{-3} in a pseudomorphic RBCO films, which adapts to the pseudosquare surface unit cell of NGO(001). For RBCO on STO(001), the square surface unit cell serves as a template for the growth of RBCO, introducing bidirectional, anisotropic strain into the film but without any shear strain component.

As shown in Fig. 2, the two diagonals of the pseudosquare NGO(001) unit cell are not equivalent. The pseudomorphic GdBCO film is strained by $+0.88\%$ and -0.40% along the diagonals of its a - b plane, i.e., along \mathbf{a}_{or} and \mathbf{b}_{or} of NGO, respectively [Figs. 1(a) and 2(a)]. The film relaxes first along the heavily strained \mathbf{a}_{or} direction as schematically shown in Fig. 2(b), but remains pseudomorphic along the less strained diagonal, i.e., the \mathbf{b}_{or} direction. This is obvious from Figs. 1(b),(c), which shows that the two reflections of the twin couple remain exactly centered with respect to the substrate in-plane \mathbf{Q} values. Consequently, the twin domains will be aligned exclusively along the less strained diagonal, i.e., along \mathbf{b}_{or} . At a thickness of about 40 nm, the film relaxes along the \mathbf{b}_{or} direction as well [Fig. 1(d),(e) and 2(c)]; the reflections of the twin couple are no longer centered about the substrate in-plane reciprocal lattice point. However, the

film relaxes only $\approx -0.1\%$, whereas the total mismatch is -0.44% . This may eventually cause the formation of “nano” cracks inside the epilayer^{1,2} once the threshold energy for the fracture formation is reached when the film gets thicker. These cracks form since now only an incoherent twin boundaries between the two orthogonal twin pairs¹⁶ can be created.

For YBCO films, the strain along \mathbf{a}_{or} and \mathbf{b}_{or} of NGO are $+0.31\%$ and -0.96% , respectively. The film relaxes also first along the heavier strained diagonal, but which is now \mathbf{b}_{or} and, contrary to GdBCO, only twin boundaries aligned along \mathbf{a}_{or} are observed.^{1,17}

For RBCO on STO, we can estimate the stress and the strain energy from $\sigma_i = c_{ij}\epsilon_j$ and $e = \frac{1}{2}c_{ij}\epsilon_i\epsilon_j$, where σ_i is the stress tensor, c_{ij} is the elastic constant, ϵ_j is the strain tensor, and e is the strain energy per unit volume. The matrix notation $i, j = 1, 2, 3, 4, 5$, and 6 , corresponds to the tensor notation a, b, c, bc, ca , and ab , respectively. Using the boundary condition $\sigma_c = 0$ and the known elastic constants at room temperature,¹⁸ one gets ϵ_c and furthermore σ_a, σ_b , and e for a pseudomorphic film. The calculated strain energies are thus 67.2 MPa, 23.7 MPa, and 22.9 MPa for pseudomorphic YBCO, SmBCO, and GdBCO on STO, respectively. The criterion for t_c is a minimum of the interfacial energy per unit area ϕ_I (Refs. 3–5)

$$\frac{\partial \phi_I}{\partial \epsilon_k} = \frac{\partial (\phi_E + \phi_D)}{\partial \epsilon_k} = \frac{\partial (et + \phi_D)}{\partial \epsilon_k} = 0, \quad (1)$$

in which ϕ_E is the elastic energy, ϕ_D is the misfit dislocation energy, ϵ_k is the in-plane strain, and t the film thickness. Using the simplified assumption that the misfit strain relaxation in RBCO films happens exclusively via edge dislocation, we can apply the Ball-van der Merwe-Matthews (BMM) model in an anisotropic form

$$\frac{\partial e}{\partial \epsilon_k} t_c = \frac{Gb_k}{2\pi(1-\nu)} \left(1 + \ln \frac{t_c}{b_k} \right), \quad (2)$$

with G the shear modulus, ν Poisson ratio, and b_k the magnitude of the Burgers-vector projection on the interface plane. The tensor notation k only refers to those components parallel to the interface plane. Note, t_c is determined by the relatively larger component of the in-plane differential strain energy $\partial e / \partial \epsilon_k$. Calculated t_c values are thus 8 nm, 17 nm, and 17 nm for YBCO, SmBCO, and GdBCO, respectively, on STO(001). These values have to be compared with the experimentally observed, which are for the above three cases ≈ 10 nm,^{7,6} ≈ 50 nm,⁸ and ≈ 50 nm, respectively.

Because of the complication of the twist distortion, the BMM model is not applicable for RBCO on NGO in the simplified way as applied above for the films on STO, in which only in-plane biaxial strain energy terms are considered. Due to the twist distortion, RBCO films on NGO facilitate strain release by forming disclinations. They possess an energy equivalent to an edge dislocation of Burgers vector $\frac{1}{2}L\vartheta$,¹⁹ where L is half the distance between the thus formed defects and ϑ is the rotation angle of the pseudomorphic RBCO. With $L \approx 10$ nm, i.e., half the distance of the twin

boundaries in GdBCO,²⁰ the pseudo-Burgers vector is 0.0319 nm for GdBCO on NGO and we can estimate $t_c = 10$ nm, which is in reasonable agreement with the experimental finding of ≈ 15 nm.

For GdBCO on STO the theoretically estimated critical thickness is significantly larger than the measured one. However, for the total energy of the epitaxial system, some other mechanisms of strain release have not been considered. The observed precursor state of twinning, in fact a modulation wave, and the surface roughening, i.e., columnar growth,⁹ can both facilitate strain relief and thus could enhance the critical thickness. Even other factors, such as the substrate surface termination and the surface ledges,²¹ may also affect the energy for the formation of defects in the film and therefore the critical thickness. Work, designated to address these questions, is currently in progress.

In conclusion, we studied the initial growth of GdBCO films on STO(001) and NGO(001), i.e., substrates with higher and lower surface plane groups symmetry, respec-

tively. The unidirectional twin structure and critical thickness for films on NGO is dictated by the twist distortion induced by the substrate. Misfit disclinations with two orthogonal pseudo-Burgers vectors are induced in the GdBCO films at two different (critical) thicknesses. The twin domain structure is created at $t_{c,1} \approx 15$ nm, leading to the unidirectionally twinned structure of the films. Twin domain boundaries are aligned along the less strained diagonal of the HTS film, i.e., along \mathbf{b}_{or} for GdBCO and \mathbf{a}_{or} for YBCO on NGO(001). The anisotropic Ball-van der Merwe-Matthews model gives reasonable t_c values for GdBCO on NGO(001), but too small values for GdBCO on STO. This can be explained by other mechanisms of strain relief, such as the observed modulation wave and island growth.

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