INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 12551–12562 PII: S0953-8984(02)39689-9

Misfit dislocations and phase transformations in high-T_c superconducting films

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Received 18 July 2002
Published 15 November 2002
Online at stacks.iop.org/JPhysCM/14/12551

Abstract

A theoretical model is suggested that describes the effects of misfit stresses on defect structures, phase content and critical transition temperature T_c in high-T_c superconducting films. The focus is placed on the exemplary case of YBaCuO films deposited onto $LaSrAlO_4$ substrates. It is theoretically revealed here that misfit stresses are capable of inducing phase transformations controlled by the generation of misfit dislocations in growing cuprate films. These transformations, in the framework of the suggested model, account for experimental data on the influence of the film thickness on phase content and critical temperature T_c of superconducting cuprate films, reported in the literature. The potential role of stress-assisted phase transformations in suppression of critical current density across grain boundaries in high-T_c superconductors is briefly discussed.

1. Introduction

The high-transition-temperature (T_c) superconducting properties of cuprates are highly sensitive to mechanical stresses. Experiments [1, 2] have shown a substantial increase of T_c under external-load-induced hydrostatic pressure, from several degrees for $Bi_2Sr_2CaCu_2O_x$ to about 20 K for $HgBa_2Ca_2Cu_3O_{8+z}$ superconductors. The experimentally observed drastic reduction of the critical current density J_c across grain boundaries (see, e.g., [3–6]) and structural transformations of grain boundaries [7, 8] can be effectively treated as occurring due to stress fields induced by grain boundary dislocations [9–14]. Stresses created by grain boundary and lattice dislocations are also capable of causing enhancement of high-T_c superconductivity in the vicinities of dislocations [15].

In cuprate films, misfit stresses commonly occur (due to mismatch between crystal lattice parameters of films and substrates) and affect their high-T_c superconducting properties. So, recently, the doubling of the critical temperature T_c in LaSrCuO superconducting thin films due to compressive misfit stresses has been reported [16]. Also, following experimental data [17, 18] and results of theoretical analysis [19, 20], misfit stresses are capable of strongly affecting the grain boundary structure and transport properties of polycrystalline high-T_c cuprate films.

Misfit stresses in conventional solid films effectively relax via formation of arrays of the so-called misfit dislocations that create compensating stress fields; see, e.g., [21–31]. These misfit dislocations are formed when the film thickness reaches its critical value [21, 22]. In these circumstances, the film thickness plays the role of macroscopic parameter regulating the stress distribution in solid films and, therefore, their stress-sensitive structural and behavioural features. This leads us to think that the high-T_c superconducting properties of thin-film cuprates are influenced by the film thickness. The aforesaid is confirmed, in particular, by the experimental data [32] indicating that the crystalline structure and the high-T_c superconducting properties of $YBa_2Cu_3O_{7-\delta}$ (YBCO) films on $LaSrAlO_4(001)$ (LSAO) substrates are highly sensitive to the film thickness. So, Raman spectroscopy of YBCO films with different thicknesses (10, 20, 30, 50, 100 and 200 unit cells (uc for short)) gives evidence for growth of the volume fraction of oxygen-deficient crystalline phases in films with decreasing film thickness h [32]. It has been detected by a strong dependence of crystal lattice parameter on the film thickness h. This dependence directly correlates with that of critical temperature T_c of YBCO superconducting films on h. More precisely, a dramatic decrease of critical temperature T_c has been experimentally detected at $h \leqslant 70$ uc; it has been attributed to a structural transformation from the ortho-I phase characterized by $T_c \approx 90$ K to the ortho-II phase characterized by $T_c \approx 60$ K with decreasing film thickness h [32].

Zhang *et al* [32] have suggested that the formation of oxygen-deficient phases in YBCO films is caused by misfit stresses generated at the film/substrate interface owing to geometric mismatch between crystal lattice parameters of the film and the substrate. In doing so, since the lattice parameter of LSAO is considerably smaller than that of the ortho-I phase ($YBa_2Cu_3O_7$), high compressive misfit stresses occur in the ortho-I phase films. Their relaxation can be effectively realized via the formation of the ortho-II ($YBa_2Cu_3O_{6.5}$) and tetragonal ($YBa_2Cu_3O_6$) phases having smaller lattice parameters as compared to the ortho-I phase [32]. However, this qualitative explanation does not account for experimentally observed dependences of the structural characteristics and high-T_c superconducting properties of YBCO films on the film thickness h. The main aim of this paper is to suggest a theoretical model which quantitatively describes the structural and behavioural features of high-T_c cuprate films, depending on the film thickness, with particular emphasis on the exemplary case of YBCO films on LSAO substrates. In doing so, the suggested model is based on the idea that the experimentally detected [32] effects of the film thickness on both the structure and behaviour of high-T_c superconducting films are related to the formation of misfit dislocations and misfit-stress-assisted phase transformations in these films. In the following, we will theoretically examine in detail

(i) the conditions at which the formation of misfit dislocations is energetically favourable in the tetragonal, ortho-I and ortho-II phases of YBCO films deposited onto LSAO substrate and

(ii) the effects of misfit dislocations on both the structure and critical temperature T_c of such films, depending on the film thickness.

2. Coherently strained state of YBCO films

First, let us consider the coherently strained state which is realized in a film, if its crystalline lattice is uniformly strained due to ideal coherent matching with the crystalline lattice of

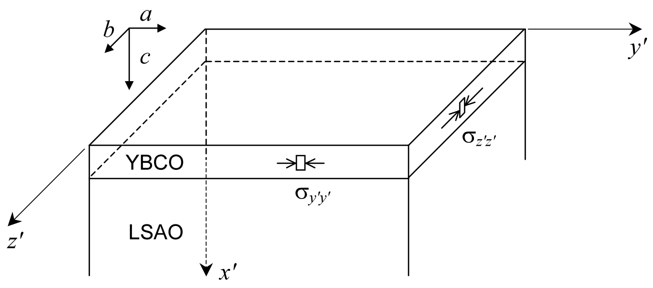

Figure 1. Coherent stress state in a thin YBCO film on an LSAO substrate.

the substrate. In other words, the coherently strained state is realized when any plastic deformation processes causing relaxation of misfit stresses in the film do not occur. In our further calculation of characteristics of the coherently strained state, we will use structural and geometric parameters of YBCO films, presented in paper [32] and book [33].

Let us consider a model heteroepitaxial system consisting of a semi-infinite single-crystalline substrate and a thin single-crystalline film with thickness h. The film and the substrate are assumed to be isotropic solids having the same value of the shear modulus G and the same value of the Poisson ratio ν. Real high-T_c superconducting films are anisotropic. However, the effects of anisotropy commonly do not strongly affect the parameters (e.g., critical thickness h_c for the misfit dislocation generation), while their consideration needs a cumbersome and space-consuming mathematical analysis. In these circumstances, for the aims of this paper focused on the role of misfit dislocations in structural transformations and associated high-T_c properties in cuprate films, we restrict our consideration to a model dealing with elastically isotropic solids, whose accuracy is sufficient to account for the corresponding experimental data [32].

Let us choose a rectangular coordinate system (x', y', z') with the origin being located at an arbitrary point at the film free surface. Let the axis x' be normal to the free surface and oriented along the crystallographic c axis of the YBCO film towards the film/substrate interface (figure 1). The axes y' and z' are oriented respectively along the crystallographic a and b axes of the YBCO film which are parallel to the film free surface and the film/substrate interface plane (figure 1).

The film/substrate interface is characterized by the following dilatation misfit parameters:

$$f_a = \frac{a_f - a_s}{a_f}, \qquad f_b = \frac{b_f - b_s}{b_f} \tag{1}$$

where a_f and b_f (a_s and b_s, respectively) are the crystal lattice parameters of the superconducting film (substrate, respectively). Owing to the geometric mismatch at the interface, the thin film is elastically uniformly distorted. In the coordinate system $x'y'z'$ (figure 1), it is characterized by the elastic strain tensor which, in the framework of the linear elasticity theory [22] conventionally used in analysis of strained thin films, has the following non-zero components:

$$\varepsilon_{x'x'} = \frac{\nu}{1-\nu}(f_a + f_b), \qquad \varepsilon_{y'y'} = -f_a, \qquad \varepsilon_{z'z'} = -f_b. \tag{2}$$

All non-diagonal components of the strain tensor are equal to 0.

In the situation under discussion, the misfit stress tensor has only two non-zero components:

$$\sigma_{y'y'} = -\frac{2G}{1-\nu}(f_a + \nu f_b), \qquad \sigma_{z'z'} = -\frac{2G}{1-\nu}(f_b + \nu f_a). \tag{3}$$

From (1)–(3) we find the misfit strain energy density w^f (per unit volume) of the coherently strained film to be as follows:

$$w^f = \frac{1}{2}(\sigma_{y'y'}\varepsilon_{y'y'} + \sigma_{z'z'}\varepsilon_{z'z'}) = \frac{G}{1-\nu}(f_a^2 + f_b^2 + 2\nu f_a f_b). \tag{4}$$

Let us estimate values of the proper misfit strains f_a and f_b and values of the corresponding energy densities w^f, for all the three phases of YBCO films deposited onto LSAO substrates. The crystal lattice parameters are as follows: $a_s = b_s = 3.754$ Å, $c_s = 12.636$ Å, for the LSAO substrate [34, 35]; $a_t = b_t = 3.858$ Å, $c_t = 11.839$ Å, for the tetragonal phase of YBCO [32, 33]; $a_1 = 3.828$, $b_1 = 3.888$ and $c_1 = 11.65$ Å, for the ortho-I phase of YBCO [32, 33]; $a_2 = 3.843$ Å, $b_2 = 3.879$ and $c_2 = 11.70$ Å, for the ortho-II phase [32, 33]. With these data, we have the following values of f_a and f_b: $f_a = f_b \approx 2.6957 \times 10^{-2}$ in the case of the tetragonal phase; $f_a \approx 1.9331 \times 10^{-2}$ and $f_b \approx 3.4465 \times 10^{-2}$ in the case of the ortho-I phase; $f_a \approx 2.3159 \times 10^{-2}$ and $f_b \approx 3.2125 \times 10^{-2}$ in the case of the ortho-II phase. With the shear modulus G and the Poisson ratio ν assumed to be identical for all the phases under consideration, for $\nu = 0.3$, we find the following estimated values of their elastic energy densities given by formula (4): $w_t^f/G \approx 2.699 \times 10^{-3}$, for the tetragonal phase; $w_1^f/G \approx 2.802 \times 10^{-3}$, for the ortho-I phase, and $w_2^f/G \approx 2.878 \times 10^{-3}$, for the ortho-II phase.

The above estimates allow us to make the following conclusions.

(i) Values of the misfit strain energy densities w_t^f, w_1^f and w_2^f which characterize the tetragonal, ortho-I and ortho-II phases, respectively, are rather close; the differences between these values do not exceed 3%.
(ii) With the film growth assumed to be regulated by the only elastic energy minimum, we find that the tetragonal phase is most energetically favourable. Therefore, the tetragonal phase is expected to be formed at the initial stage of the film growth, where the coherent state of the film is realized.

However, with the chemical terms taken into account in the characteristic thermodynamic potential of the growing film, we should bear in mind the fact that the tetragonal phase is unstable relative to its transformation into the ortho-II phase at some temperature T_2 depending on the oxygen pressure in the atmosphere [33]. (For instance, $T_2 = 440$ and 700 °C at oxygen pressure 10^{-4} and 1 atm, respectively.) As a corollary, the namely ortho-II phase is expected to be formed at the initial stage of the film growth occurring at low temperatures. Since $w_2^f > w_1^f$, the ortho-II phase transforms into the ortho-I phase, when the film thickness exceeds some critical value at which the strain energy contribution (which runs parallel to the film thickness [19, 20]) to the thermodynamic potential of the film becomes dominant.

The above suggested model of the coherent state of the growing YBCO film at large values (2–3%) of the misfit parameter f is valid in the case of only low film thickness ($h < h_c$) being of the order of a few interatomic distances. For $h \geqslant h_c$, the semi-coherent state commonly comes into play, where misfit dislocations are formed at the film/substrate boundary. These dislocations induce stress fields that compensate for, in part, misfit stresses and, therefore, strongly affect strains and the phase content in growing YBCO films. We will theoretically examine in detail the semi-coherent state of strained films in the next section.

3. Strains and phases in semi-coherent state of YBCO films

The semi-coherent state of strained YBCO films is characterized by superposition of strain fields induced by the interphase (film/substrate) boundary and misfit dislocations; see, e.g., [19, 20]. The dislocation-induced strain fields strongly depend on the type of misfit dislocation and their distribution along the interphase boundary. In their turn, both the type and distribution are caused by the crystallography of the film/substrate system and mechanisms for the generation of misfit dislocations. In our model, we will consider edge misfit dislocations at the YBCO/LSAO boundary which form a regular orthogonal net and are characterized by the Burgers vectors of the $a\,[110]$ type. Such misfit dislocation configurations are conventional for the YBCO crystallography [36]. In these circumstances, the axes of the misfit dislocation network are rotated by 45° (exactly in the case of the tetragonal phase and tentatively in the case of the ortho-I and II phases) relative to the y' and z' coordinate axes shown in figure 1. Therefore, for convenience of our analysis, here and in the following we will use the coordinate system (x, y, z), where the x and x' axes are the same, while the y and z axes are rotated by 45° relative to the axes y' and z', respectively. The lines and Burgers vectors of misfit dislocations are directed along the corresponding axes y and z.

The misfit strain tensor written in the coordinate system (x, y, z) has the following non-zero components:

$$\varepsilon_{xx} = \frac{2\nu}{1-\nu} f, \qquad \varepsilon_{yy} = -f, \qquad \varepsilon_{zz} = -f, \qquad \gamma_{yz} = f_b - f_a. \tag{5}$$

Here $f = (f_a + f_b)/2$ is the mean misfit strain. It is worth noting that the normal strains $\varepsilon_{y'y'}$ and $\varepsilon_{z'z'}$ written in the y' and z' coordinates, in general, have different values ($f_a \neq f_b$), whereas the normal strains ε_{yy} and ε_{zz} written in the coordinate system (x, y, z) are identical and equal to $-f$, where f plays the role of the mean proper misfit strain. As a corollary, the densities of corresponding misfit dislocations that form orthogonal rows at the film/substrate boundary are equal. Also, it should be noted that the non-diagonal component γ_{yz} of the strain tensor written in the coordinate system (x, y, z), generally speaking, is non-zero.

The misfit stress tensor in the coordinate system (x, y, z) has the following three non-zero components:

$$\sigma_{yy} = \sigma_{zz} = -2G\frac{1+\nu}{1-\nu} f, \qquad \sigma_{yz} = G(f_b - f_a). \tag{6}$$

The misfit strain energy density w^f is, of course, invariant relative to the coordinate system transformation discussed.

When the YBCO film thickness h reaches some critical value h_c, misfit strain relaxation occurs via the formation of orthogonal rows of misfit dislocations (figure 2). That is, the initial coherent state of the film transforms into the so-called semi-coherent state characterized by the residual uniform misfit strain $\varepsilon = -(f - \varepsilon_d)$. Here $\varepsilon_d = b/l$ denotes a portion of the initial misfit strain, accommodated due to the misfit dislocation formation, b the dislocation Burgers vector modulus and l the interspacing between the neighbouring parallel misfit dislocations. Thus, the residual strain ε strongly depends on l and its magnitude decreases with decreasing l.

The strain energy density (per unit area of the film/substrate boundary) of the film in the semi-coherent state, following the approach [37, 38], consists of the four terms

$$W = W^f + W^d_{el} + W^d_n + W^{fd}_{int}. \tag{7}$$

Here $W^f = w^f h$; W^d_{el} denotes the energy of misfit dislocations, taking into account their interaction with the film free surface and the dislocation–dislocation interaction; $W^d_n = Db(f + \varepsilon)$ is the dislocation core energy; and $W^{fd}_{int} = -8\pi D(1+\nu) f (f + \varepsilon) h$ is the energy that characterizes the interaction between misfit dislocations and misfit stress field. $D = G/[2\pi(1-\nu)]$.

The energy of misfit dislocations can be written as the sum

$$W^d_{el} = W_s + W_{int} \tag{8}$$

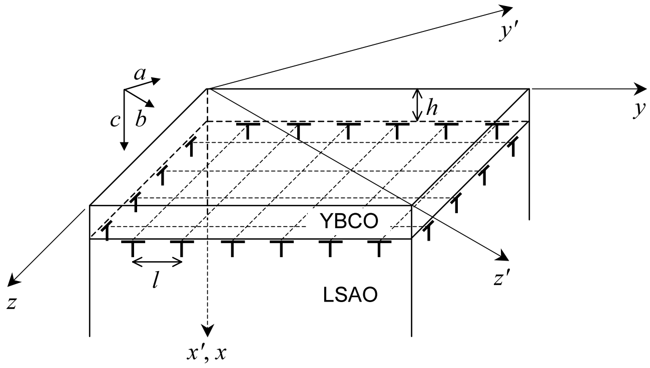

Figure 2. Semi-coherent stress state in a thin YBCO film on an LSAO substrate with an orthogonal network of misfit dislocations at the interface.

where W_s denotes the proper dislocation energy, and W_{int} the interaction energy. The proper energy of a misfit dislocation row is effectively calculated as the work spent to transfer dislocations from the free surface of the growing film to their final positions in their proper stress field [37]. In a similar way, the energy W_{int} that characterizes the elastic interaction between dislocation rows is effectively calculated as the work spent on the generation of the first dislocation row in the stress field of the second row. As a result, the sum energy W_{el}^d reads [38]

$$\frac{W_{el}^d}{\pi Db(f+\varepsilon)^2} = [2(1+2\nu)t-1]p_1 - p_2 - 4\pi t[p_3 + (f+\varepsilon)(t-1)q_1] - \frac{1+2\nu}{2\pi(f+\varepsilon)}\ln\frac{q_1}{q_2}, \tag{9}$$

where $t = h/b$, $p_i = (C_i+1)/S_i$, $q_i = 1/(C_i-1)$, $i = 1, 2, 3$, $C_1 = \cosh[2\pi(f+\varepsilon)(2t-1)]$, $C_2 = \cosh[2\pi(f+\varepsilon)]$, $C_3 = \cosh[2\pi(f+\varepsilon)t]$, $S_1 = \sinh[2\pi(f+\varepsilon)(2t-1)]$, $S_2 = \sinh[2\pi(f+\varepsilon)]$, $S_3 = \sinh[2\pi(f+\varepsilon)t]$.

Thus, we have all the terms of the total energy W given by formula (7). The minimum of W with variation of ε (or, as is equivalent, with variation of l), following the approach [37, 38], corresponds to the equilibrium density of misfit dislocations or, in other words, to the equilibrium semi-coherent state of the YBCO film. With the above formulae, we have numerically calculated the characteristic dependences of the residual misfit strain $\bar{\varepsilon}$ on the film thickness h, for the three phases of YBCO. With these dependences substituted into formula (7), we have calculated the dependences of the equilibrium energy $\bar{W} = W(\varepsilon = \bar{\varepsilon})$ on the film thickness.

The numerically calculated dependences $\bar{W}(h)$ are shown in figure 3. For low values of the film thickness h ($h < 3b$), the coherently strained state of the film is realized (for details, see section 2) which is characterized by linear dependence of $\bar{W}$ on h (figure 3(a)). The film thickness $h_c = 3b$ is critical for the generation of misfit dislocations at the film/substrate boundary in the cases of all the three phases of YBCO film growing on LSAO substrate. At $h = h_c$, the generation of misfit dislocations becomes energetically favourable, giving rise to deviations of $\bar{W}(h)$ from the linear dependence.

The critical thickness h_c may be determined within this approach from the equation

$$\left.\frac{\partial W}{\partial \varepsilon}\right|_{\bar{\varepsilon}=-f} = 0 \tag{10}$$

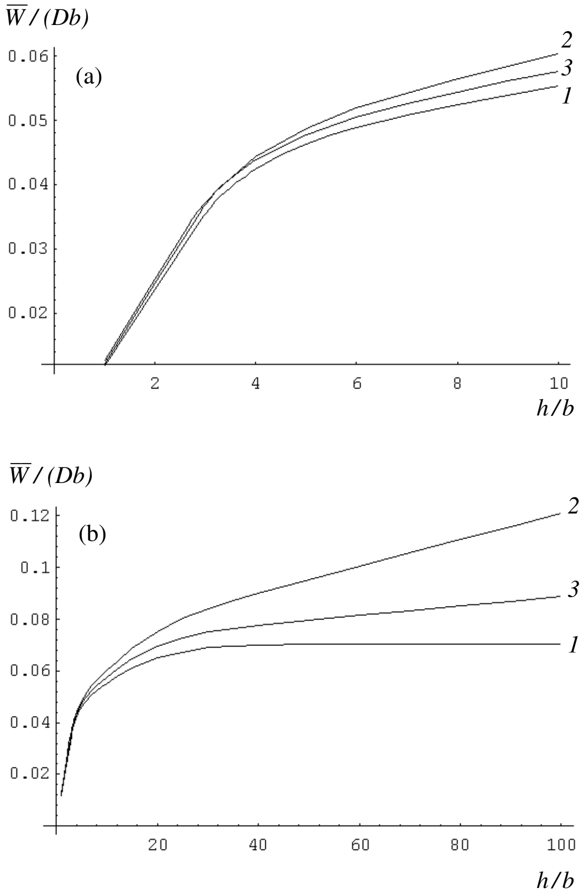

Figure 3. Equilibrium total energy density $\bar{W}$ against the thickness h of the tetragonal (1), orthorhombic-I (2) and orthorhombic-II (3) YBCO films on LSAO substrates: (a) small-thickness case; (b) large-thickness case.

which results in [37]

$$\ln(2t_c - 1) = \frac{2t_c(t_c - 1)}{(2t_c - 1)^2} + 8\pi(1 + \nu) f (t_c - 1) - 1, \tag{11}$$

where $t_c = h_c/b$. Equation (11) may be solved numerically for any heterosystem characterized by its proper parameters f and ν.

Notice that the semi-coherent state of the ortho-II phase (see curve 3) is more energetically favourable than that of the ortho-I phase, in contrast to the situation with the coherent state where the ortho-I phase (see curve 2) is more favourable as compared to the ortho-II phase. This phenomenon occurs owing to the fact that the misfit dislocations effectively accommodate the diagonal components, ε_{yy} and ε_{zz}, of the misfit strain tensor ($\varepsilon_{yy} = \varepsilon_{zz} = f$), but do not affect the shear component γ_{yz} ($= f_b - f_a$). Actually, the orthogonal network of misfit dislocations shown in figure 2 does not create the shear strain and stress yz-components which are capable of compensating for, in part, the corresponding misfit strains and stresses. In this situation, owing to the uncompensated yz-components of misfit strains and stresses, there is a (second) term linear in h in the following expression for the elastic energy of the coherently strained film:

$$W^f = 2G\frac{1+\nu}{1-\nu} f^2 h + \frac{G}{2}(f_b - f_a)^2 h. \tag{12}$$

As a corollary, the phase with the largest term linear in h is energetically unfavourable. According to our estimates (see section 2), $f_b - f_a = 0$, for the tetragonal phase; $f_b - f_a = 1.513 \times 10^{-2}$ and 0.897×10^{-2}, for the ortho-I and ortho-II phases, respectively. In these circumstances, in films with large values of thickness ($h > 50b$), where misfit dislocations almost completely compensate the diagonal components of both the misfit strain tensor and misfit stress tensor, the elastic energy density is tentatively constant in the case of the tetragonal phase (curve 1 in figure 3(b)), and runs parallel with the film thickness h in the case of the ortho-I and II phases. The slope of the dependence of the elastic energy density on h for the ortho-I phase (curve 2 in figure 3(b)) is higher than that for the ortho-II phase (curve 3 in figure 3(b)).

Thus, as with coherent growth of a YBCO film on LSAO substrate (see section 2), the tetragonal phase of YBCO is most energetically favourable in the semi-coherent state of the YBCO film. Generally speaking, if the semi-coherent state of the orthogonal phases on LSAO substrate is realized, one should take into account that shear misfit strains and stresses can relax via the formation of misfit dislocations of the screw type. More precisely, an effective relaxation mechanism is the formation of a network of screw dislocations, which is similar to that shown in figure 2, but is characterized by a comparatively low dislocation density (reaching its limiting value $1/l' = (f_b - f_a)/(2b)$ in the case of orthogonal rows of periodically spaced (with the same period) screw dislocations). Let us estimate a critical film thickness which specifies the energetically favourable generation of misfit dislocations of the screw type in the orthorhombic phases of YBCO films deposited onto LSAO substrates.

The generation of the first screw dislocation leads to a change of the elastic energy of the film by a value of

$$\Delta W = W^d_{scr} + W^n_{scr} + W^{f-d}_{int}. \tag{13}$$

Here $W^d_{scr} = Gb^2/(4\pi)\ \ln(h/b)$ is the elastic energy of the screw dislocation (per unit of its line) distant by h from the film free surface [39], $W^n_{scr} \approx Gb^2/(4\pi)$ is the energy of the dislocation core [39] and $W^{f-d}_{int} = -Gb(f_b - f_a)h$ is the energy that characterizes the interaction between the screw dislocation and misfit stress field or, in other terms, the work spent to transfer the dislocation from the free surface to its final position in the misfit stress field. The generation of the screw dislocation is energetically favourable, if $\Delta W < 0$. The condition that $\Delta W = 0$ allows one to calculate the critical film thickness h'_c at which the screw dislocation generation becomes favourable in a growing film. With values 1.513×10^{-2} and 0.897×10^{-2} of $(f_b - f_a)$, for respectively the ortho-I and II phases, substituted into the condition $\Delta W = 0$, we find the following characteristic values of the critical thickness: $h'_c \approx 20.4\, b$ (ortho-I) and $h'_c \approx 42\, b$ (ortho-II). These values exceed by an order of magnitude the critical thickness $h_c \approx 3\, b$ that specifies the formation of a misfit dislocation of the edge type. As a consequence, in our analysis of energetic characteristics of the tetragonal, ortho-I and II phases on LSAO substrate, we can neglect relaxation of the shear components of misfit strains and stresses.

To summarize, in the situation with the semi-coherent state of films, growth of the tetragonal phase on LSAO substrate is energetically favourable over that of the ortho-II phase, which, in its turn, is preferable to growth of the ortho-I phase. In these circumstances, the following scenario of the growth of YBCO films on LSAO substrates is realized. At the initial stage, the tetragonal phase (or mixed, tetragonal and ortho-II, phase having crystallography close to that of the pure tetragonal phase) grows. When the film thickness reaches its critical value $h_c \approx 3\,b$ (or more; see the discussion in section 4), misfit dislocations are generated and form orthogonal rows (figure 2). As h grows, so does the density of misfit dislocations creating the stress fields that effectively compensate for misfit stresses. After the formation of the misfit dislocation network has completed, misfit strains in the film layer next to the free surface have been almost completely relaxed. As a result, the crystal lattice parameter of the film layer in question is almost the same as in the film material in its ideal (unstrained) state. The phase content in this film layer is similar to that in unstrained material. In doing so, the volume fraction of the tetragonal phase being metastable at low and intermediate temperatures decreases on raising the film thickness (and, therefore, the fraction of unstrained film layer), because the tetragonal phase transforms into the ortho-II phase in the unstrained material. A sharp plane interphase boundary between the tetragonal and ortho-II phases is hardly formed. However, even so, the boundary creates very low misfit strains, in the order of $f_a' = (a_2 - a_t)/a_2 \approx -3.851 \times 10^{-3}$ and $f_b' = (b_2 - a_t)/b_2 \approx 5.363 \times 10^{-3}$, in which case the misfit strain energy density $w^f/G \approx 4.457 \times 10^{-5}$. This value of w^f/G is lower by two orders of magnitude than the characteristic values of the misfit strain energy associated with interphase boundaries between the YBCO phases and LSAO substrate (see section 2). When the sharp interphase boundary between the tetragonal and ortho-II phases is absent, the film consists of grains with different phase contents. In this situation, an effective mechanism for misfit (between the tetragonal and ortho-II phases) strain relaxation is the formation of thin twin lamellae [40]. Notice that, in contrast to the situation with the ortho-II phase, growth of the ortho-I phase on the plane free surface of the tetragonal phase leads to the larger misfit characterized by $f_a'' = (a_1 - a_t)/a_1 \approx -7.785 \times 10^{-3}$ and $f_b'' = (b_1 - a_t)/b_1 \approx 7.767 \times 10^{-3}$ and comparatively large values of the misfit strain energy density $w^f/G \approx 12.094 \times 10^{-5}$. This value exceeds by a factor of three the misfit strain energy density characterizing the interphase boundary between the tetragonal and ortho-II phases. In these circumstances, one expects that the ortho-I phase associated with an ordered arrangement of oxygen in the basic plane of YBCO is capable of growing only onto a plane free surface of the ortho-II phase at large values of the film thickness, that is, in the situation where misfit strain relaxation effectively occurs via the misfit dislocation formation. In doing so, the growth of the ortho-I phase onto the ortho-II phase results in lower misfit strains being in the order of $f_a''' = (a_1 - a_2)/a_1 \approx -3.9185 \times 10^{-3}$ and $f_b''' = (b_1 - a_2)/b_1 \approx 2.4177 \times 10^{-3}$, and the characteristic misfit strain energy density $w^f/G \approx 2.2165 \times 10^{-5}$ has the minimum value among those considered here.

Now let us roughly estimate the characteristic values of the film thickness, which correspond to transitions from respectively the tetragonal phase to ortho-II phase and from the ortho-II phase to ortho-I phase. As evident from figure 3(b), the main part of the plastic relaxation of the initial misfit occurs when the film thickness increases up to $h_t \approx 30\,b$. With the dislocation Burgers vector modulus assumed to be $b = a_t\sqrt{2} \approx 5.456$ Å, we have $h_t \approx 13$ uc, where 1 uc $= c_t \approx 11.839$ Å. Let us suppose that the ortho-II phase starts growing at $h = h_t$ and estimate the critical film thickness h_c' at which the relaxation via the formation of misfit dislocations occurs. With formula (13), we find $h_c' \approx 41\,b$. Since the relaxation processes mostly occur when the film thickness increases up to $30\,b$, we have the following rough estimate: $h_2 \approx h_c' + 30\,b \approx 71\,b$. In terms of uc, for $b = a_2\sqrt{2} \approx 5.435$ Å we get $h_2 \approx 32$ uc. Thus, following our theoretical analysis, YBCO film deposited onto LSAO substrate has mostly tetragonal structure in the layer next to the film/substrate boundary, characterized by thickness $\approx$13 uc. The film layer characterized by the film thickness ranging from $h \approx 13$ to 45 uc has mostly ortho-II structure. The film layer characterized by $h > 45$ uc has mostly ortho-I structure. These conclusions derived from our theoretical model are in a good agreement with experimental data [32] discussed in section 1.

4. Discussion and concluding remarks

In this paper a theoretical model has been suggested describing the role of misfit stresses in phase transformations occurring in high-T_c superconducting films with the focus placed on the exemplary case of YBCO films growing on LSAO substrates. In the framework of the model suggested, the three phases—ortho-I, ortho-II and tetragonal phases—of YBCO, characterized by different values of crystal lattice parameter, are stressed in different ways due to the mismatch at the interphase boundary between YBCO film and LSAO substrate. This selects one of these phases as the energetically favourable phase corresponding to the minimum of the misfit strain energy of the YBCO/LSAO composite system. Thus, the misfit stresses crucially affect the phase content of YBCO films which, in its turn, causes the high-T_c superconducting properties of these films.

Formation of misfit dislocations in a growing cuprate film at some critical value of the film thickness gives rise to a partial relaxation of misfit stresses and, therefore, is capable of inducing phase transformations in the film. This phenomenon leads to a dependence of the film phase content on the film thickness. As a corollary, the high-T_c superconducting properties of cuprate films, which are highly sensitive to the phase content, change with rising film thickness. According to results of theoretical analysis given in this paper, in the exemplary case of YBCO films deposited onto LSAO substrates, the following scenario is realized. At the initial stage, misfit dislocations are absent, and the tetragonal phase (or mixed, tetragonal and ortho-II, phase) grows. Then, misfit dislocations are formed, and the volume fraction of the tetragonal phase decreases with rising film thickness, because of its transformation into the ortho-II phase. The ortho-I phase is capable of growing onto a plane free surface of the ortho-II phase at large values of the film thickness, with misfit dislocations causing effective relaxation of misfit stresses in the film layer next to the film free surface. This scenario corresponds to experimental data [32].

In comparison between theoretical results obtained here and experimental data, one should take into consideration some restrictions of our theoretical model. So, the model does not take into account the nucleation energy of MDs and the friction stress against their glide. At the same time, the frictional stress in cuprates is commonly high, in which case, in particular, the value of the critical film thickness h_c estimated in this paper is lower than values detected in experiments. Also, our theoretical model is based on the assumption that the film growth occurs in a layer by layer mode at equilibrium conditions. Its quantitative results are not exact in out-of-equilibrium situations one often encounters when growing films from the vapour phase. However, after some relaxation time interval, films reach their equilibrium states. That is, after a relaxation time interval, the dislocation structure and phase content in films fabricated at non-equilibrium conditions and characterized by high values of the energetic barriers for the nucleation of MDs and their glide are expected to become close to those in the equilibrium situation examined in this paper. In this context, we think that our theoretical results are relevant in a description of high-T_c superconducting films fabricated at diverse conditions.

Also, here we have focused our analysis on the film phase content along the only direction perpendicular to the interphase (film/substrate) boundary. In doing so, each of the three superconducting phases ($YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_3O_6$) is characterized by its specific oxygen content determining the crystal lattice parameter of the phase and, as a corollary, its elastic energy in the presence of misfit stresses. The approach discussed does not take into account spatial inhomogeneities of MD stresses and the corresponding spatial variations of the oxygen content along the interphase boundary. At the same time, a description of such inhomogeneities is interesting in the context of the technologically interesting possibility of fabricating nano-wires with enhanced superconducting properties in the vicinities of MDs.

Actually, similar to conventional dislocations [15], MDs create stress fields which are capable of causing spatial variations of the oxygen content in nano-scaled regions along MD line cores, which result in enhancement of high-T_c superconductivity in these regions. A detailed analysis of such stress-distinguished nano-wires with enhanced superconducting properties in cuprate films with MDs requires an essential modification of the approach considered in this paper and represents the subject of further theoretical investigations of the authors.

In this paper we have focused our analysis on YBCO films deposited onto LSAO substrates. However, results of our consideration can be easily generalized to the situations with cuprate films and substrates with various crystallographic and material characteristics. These results are worth taking into account in technological applications of high-T_c superconducting films, in particular in design and fabrication of high-T_c superconducting films with critical temperature T_c regulated by substrate material and film thickness.

In addition, the effects of stresses on the phase content and high-T_c superconducting properties of cuprates, theoretically described here, are interesting in identifying the underlying fundamental mechanism(s) responsible for dramatic suppression of the critical current density across grain boundaries in high-T_c cuprates. Actually, grain boundaries are sources of spatially inhomogeneous stress fields capable of inducing phase transformations in stressed regions near grain boundaries. The different phases are chemically distinguished by oxygen concentration which is experimentally measured with large error [41] (due to the low atomic weight of oxygen) in local regions. In this situation, stress-induced deviations from bulk phase in vicinities of grain boundaries may be not detectable in experiments. At the same time, different cuprate phases which are weakly different in oxygen content have essentially different high-T_c superconducting properties. As a corollary, stress-assisted phase transformations in vicinities of grain boundaries result in weakly detectable deviations from the bulk phase, which are capable of giving rise to a dramatic suppression of high-T_c superconductivity near grain boundaries. In doing so, grain boundaries play the role of weak links in polycrystalline high-T_c cuprates. A detailed cumbersome analysis of the effect discussed is beyond the scope of this paper, the results of which can be used as input in such analysis in the future.

Acknowledgments

This work was supported, in part, by the Office of US Naval Research (grant N00014-99-1-0896), the Integration Program (grant B0026) and the Russian Foundation of Basic Research (grant 01-02-16853).

References

[1] Chu C W, Gao L, Chen F, Huang Z J, Meng R L and Xue Y 1993 *Nature* **365** 323
[2] Nunez-Regueiro M, Tholence J-L, Antipov E V, Capponi J-J and Marezio M 1993 *Science* **262** 97
[3] Dimos D, Chaudhari P, Mannhart J and LeGoues F K 1988 *Phys. Rev. Lett.* **61** 219
[4] Dimos D, Chaudhari P and Mannhart J 1990 *Phys. Rev.* B **41** 4038
[5] Ivanov Z G, Nilsson P-Å, Winkler D, Alarco J A, Claeson T, Stepantsov E A and Tzalenchuk A Ya 1991 *Appl. Phys. Lett.* **59** 3030
[6] Heinig N F, Redwing R D, Tsu I F, Gurevich A, Nordman J E, Babcock S E and Larbalestier D C 1996 *Appl. Phys. Lett.* **69** 577
[7] Chisholm M F and Smith D A 1989 *Phil. Mag.* A **59** 181
[8] Tsu I-F, Wang J-L, Kaiser D L and Babcock S E 1998 *Physica* C **306** 163
[9] Chisholm M F and Pennycook S J 1991 *Nature* **351** 47
[10] Agassi D, Pande C S and Masumura R A 1995 *Phys. Rev.* B **52** 16237
[11] Gutkin M Yu and Ovid'ko I A 2001 *Phys. Rev.* B **63** 064515
[12] Alarco J A and Olsson E 1995 *Phys. Rev.* B **52** 13625

[13] Gurevich A and Pashitskii E A 1998 *Phys. Rev.* B **57** 13878
[14] Ovid'ko I A 2001 *Mater. Sci. Eng.* A **313** 207
[15] Gurevich A and Pashitskii E A 1997 *Phys. Rev.* B **56** 6213
[16] Locquet J-P, Perret J, Fompeyrine J, Mächler X, Seo J W and van Tendeloo G 1998 *Nature* **394** 453
[17] Amer M S, Maguire J, Biggers R, Busbee J and Le Clair S R 2001 *J. Appl. Phys.* **89** 8030
[18] Amer M S, Maguire J, Biggers R and Le Clair S R 2002 *Phil. Mag. Lett.* **82** 241
[19] Ovid'ko I A 2001 *J. Phys.: Condens. Matter* **13** L97
[20] Bobylev S V, Ovid'ko I A and Sheinerman A G 2001 *Phys. Rev.* B **64** 224507
[21] van der Merwe J H 1991 *Crit. Rev. Solid State Mater. Sci.* **17** 187
[22] Jain S C, Harker A H and Cowley R A 1997 *Phil. Mag.* A **75** 1461
[23] Fitzgerald E A 1991 *Mater. Sci. Rep.* **7** 87
[24] Jain S C, Gosling T J, Willis J R, Totterdell D H J and Bullough R 1992 *Phil. Mag.* A **65** 1151
[25] Gosling T J, Bullough R, Jain S C and Willis J R 1993 *J. Appl. Phys.* **73** 8267
[26] Gosling T J, Jain S C, Willis J R, Atkinson A and Bullough R 1992 *Phil. Mag.* A **66** 119
[27] Gosling T J and Willis J R 1994 *Phil. Mag.* A **69** 65
[28] Ovid'ko I A 2000 *Nanostructured Films and Coatings (NATO ASI Series)* ed G-M Chow, I A Ovid'ko and T Tsakalakos (Dordrecht: Kluwer) pp 231–46
[29] Ovid'ko I A 1999 *J. Phys.: Condens. Matter* **11** 6521
[30] Gutkin M Yu, Ovid'ko I A and Sheinerman A G 2000 *J. Phys.: Condens. Matter* **12** 5391
[31] Ovid'ko I A and Sheinerman A G 2001 *J. Phys.: Condens. Matter* **13** 7937
[32] Zhang P, Haage T, Habermeier H-U, Kazimirov A, Ruf T and Cardona M 1997 *J. Alloys Compounds* **251** 70
[33] Plakida N M 1995 *High-Temperature Superconductors* (Berlin: Springer)
[34] Byszewski P, Domagala J, Flink-Flinowski J and Pajaczkowska A 1992 *Mater. Res. Bull.* **27** 483
[35] Jezierski A 1998 *Phys. Status Solidi* b **207** 183
[36] Narayan J, Sharan S, Singh R K and Jagannadham K 1989 *Mater. Sci. Eng.* B **2** 333
[37] Vladimirov V I, Gutkin M Yu and Romanov A E 1988 *Poverkhnost* **6** 46 (in Russian)
[38] Gutkin M Yu, Mikaelyan K N and Ovid'ko I A 1998 *Phys. Solid State* **40** 1864
[39] Dundurs J 1969 *Mathematical Theory of Dislocations* ed T Mura (New York: ASME) p 70
[40] Zhu Y 1996 *Mater. Sci. Forum.* **207–209** 381
[41] Babcock S E and Vagras J L 1995 *Annu. Rev. Mater. Sci.* **25** 193