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Modification of transport properties in low-angle grain boundaries via calcium doping of $YBa_2Cu_3O_\delta$ thin films

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The limiting factor for current transport in high-T_c superconductors including grain boundaries is the intergranular critical current density. There have been various attempts to enhance the transport properties of multicrystalline high-T_c superconductors and to understand the mechanisms leading to a reduction of the critical currents over grain boundaries (GB's). We have extensively studied the effects of Ca doping on textured thin films, establishing only a rather small overdoping of the bulk samples. Nevertheless, doping the $YBa_2Cu_3O_\delta$ films with 20% Ca, symmetrical [001] tilt GB's with misorientation angle $\theta=4°$ and 8° showed strong benefits to Ca additions. We found an increase in the critical current density $[J_{gb}(\theta)]$ up to 40% and 100% for the 4° and 8° GB's, respectively. Considering a model of Gurevich and Pashitskii for current transport in low-angle GB's, the improvements can be attached to a reduction of the strain fields ε and the localized charges Q, leading to a reduced built-in potential $|V_{bi}|$ in the dislocation cores.

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Introduction. Understanding the mechanisms of current transport over gain boundaries (GB's) is of great importance for the development of recipes to increase intergranular critical current densities $[J_{gb}(\theta)]$ in high-T_c cuprates, since for the application of multigrain superconductors, like coated conductors, it is indispensable to improve the original GB properties. A widely discussed model to describe the exponential decrease of the intergranular critical currents

$$J_{gb}(\theta)=J_0\exp(\theta/\theta_c) \quad (1)$$

is the so-called model of band bending.[1] The main aspect of this model is a local carrier depleted zone at the GB. Nevertheless, the intrinsic properties leading to the depletion area are still not clearly understood. In the first place, strain field mechanisms and local rearrangements of the bond valence sum in the dislocation cores have to be mentioned as reasons for the reduced carrier density.

As has been shown by Schmehl *et al.*[2–4] for large-angle GB's it is possible to increase $J_{gb}(\theta)$ altering the GB properties by cation doping. They were able to increase $J_{gb}(\theta)$ of 24° [001] tilt GB's at 4.2 K by as much as eight times through the substitution of 30% Y^{3+} by Ca^{2+}. The problem with large-angle GB's is that they have to be modeled as Josephson junctions, which means that an insulating barrier has to be taken into account.

Contrarily, low-angle GB's can be described as arrays of well separated edge dislocations[5–8] with undisturbed superconducting paths in between. A further difference to large angle GB's is that at tilting angles smaller than 5°–7° the decaying length of the strain fields λ_{st} becomes larger than the Debye screening length λ_D. Therefore, in this regime the strain induced modifications of the boundary clearly outweigh the electrical ones. As follows, for a model description at tilting angles smaller than 5°–7° electrical charging effects can be neglected. On the other hand, at tilting angles larger than 5°–7° electrical screening of localized charges Q in the dislocation cores has to be regarded as well. It has to be pointed out that charging effects are present for smaller angles as well, but in accordance to Ref. 9 their influence is very small. This opens up the possibility to distinguish between strain field mechanisms and electrical screening by variation of the tilting angle θ.

Our investigation on symmetrical 4° [001] tilt GB's (in this regime the strain field mechanism clearly outweighs the modification through electrical screening) showed that due to the substitution with Ca^{2+} a reduction of the strain fields ε leads to an improved current transport over the GB. A further increase of $J_{gb}(\theta)$ for the symmetric 8° [001] tilt GB's points to a combination of strain field and localized charge effects. For investigations on 5° [001] tilt boundaries see Ref. 10.

Experimental results. We investigated pairs of Ca-doped and undoped films deposited on 4° and 8° [001] $SrTiO_3$ bicrystals by means of magneto-optics (MO) and transport measurements (TM's) at 4.2 K and 35 K, respectively. All films were ablated with a KrF excimer laser from Lambda Physics offering a wavelength of 248 nm and a pulselength of 30 ns. The repetition rate was 5 Hz. The energy density and the size of the focus on the target surface were calibrated to the needs of the used deposition chamber (1 $J\,cm^{-2}$ and 1×6 mm^2). The oxygen pressure during the ablation process was 0.6 mbar. Figure 1 shows an exemplary magneto-optical picture. The magnetic field distribution can be seen as a black and white contrast and the current distribution as contour lines, calculated from inversion of Biot Savart's law.[11] For the transport measurements 100 μm bridges were patterned by laser ablation. Both methods, MO and TM, showed an improved current transport for the Ca-doped GB's. The improvement could be seen in the increase of the intergranular critical current density as well as in a reduced grain boundary resistance.

First of all, as shown in Tables I and II in detail, we found an increase of $J_{gb}(\theta)$ at 4.2 K and 35 K of up to 100% and 40% for the 8° and 4° GB's, respectively. Since the doped and undoped 4° tilt GB's had large differences in their bulk properties, for these films it was necessary to compare criti-

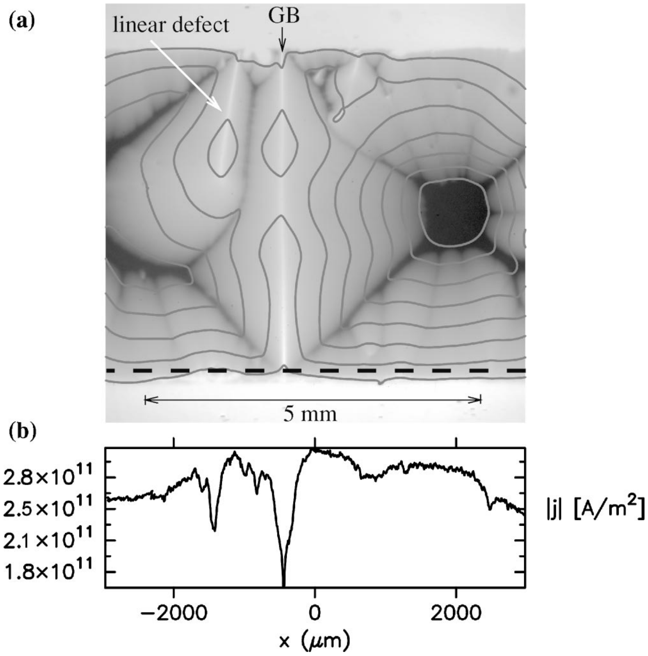

FIG. 1. (a) Magneto-optical picture at 4.2 K from a Ca-doped 8° [001] tilt GB with the current distribution visible as contour lines. The applied field was $B_{exp}=121.6$ mT (zero field cooled). The defect near the upper-left half of the boundary results from a scratch on the substrate surface. (b) Current profile taken at the dashed line in (a).

cal currents $J_{gb}(\theta)$ normalized to their bulk values J_c. This fact should not be interpreted as a systematic problem in the ablation process, since these two films are just a very small number of exceptions if one compares all approximately 50 films that were produced during this study (including Ca-doped films on $SrTiO_3$ single crystals). Furthermore, the quality of the films with j_c's for undoped $YBa_2Cu_3O_\delta$ films of about 3×10^7 A cm^{-2} and the measured angular dependency as can be extracted from Tables I and II is competitive with results of other groups (see Ref. 12).

Second, for the 8° GB we compared the normalized GB resistance $\Delta(T)$ as well. In this context the GB resistance extrapolated to 0 K is defined as

$$\Delta_0=\frac{\rho_0^{GB}-\rho_0^{bulk}}{\rho_0^{bulk}}. \quad (2)$$

TABLE I. Critical current densities at 4.2 K for doped and undoped films calculated from *magneto-optical* measurements ($B_{exp}\approx100$ mT). The range for each value describes the J_{gb} and J_c distribution over the whole GB and grain, respectively.

Film-GB angle	J_{gb}^{GB} (10^6 A cm^{-2})	J_c (10^6 A cm^{-2})	J_{gb}^{GB}/J_c
Undoped 8° [001]	7–11	30–38	0.26
Doped 8° [001]	11–21	30–35	0.49
Undoped 4° [001]	10–15	25–33	0.43
Doped 4° [001]	6–9	10–16	0.58

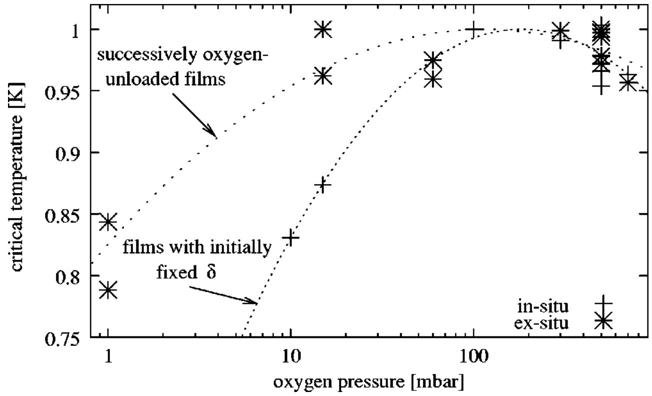

FIG. 2. Oxygen pressure dependency of the critical temperature as a measure of the doping state for the films. × displays the data from the annealing experiments and + the data from the films with an initially fixed oxygen content.

Here we found a reduction of Δ_0 from values of about 9 for the undoped samples down to 1.7 for the doped ones. This is a decrease of the GB resistance of more than a factor of 5. Since ρ_0^{GB} mainly describes the resistance caused by defects, the observed reduction of Δ_0 points to a reduction of the strain fields ε and the built-in potential $|V_{bi}|$.

In order to get a profound insight into the mechanisms that lead to this observed increase of $J_{gb}(\theta)$, we made additional experiments with Ca-doped films on $SrTiO_3$ single crystalline substrates. In a first series we compared $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_\delta$ films that were all oxygenated at different pressures ranging from 10 to 1000 mbar. In order to validate these experiments and to rule out any differences in the superconducting parameters due to changes in the ablation process we additionally made postannealing experiments with some of these films. The postannealing was done at 400 °C and the films were kept at this temperature for 1 h. In between the postannealing steps critical temperatures and currents were measured at bridges of 100 μm width using standard four-point technique. Figure 2 displays the T_c dependence from the oxygen pressure for both sets of films. Analyzing the data with respect to the relation

$$\frac{T_c}{T_c^{max}}=1-82.6(p-0.167)^2 \quad (3)$$

between T_c normalized to its maximum value T_c^{max} and the carrier concentration p as described in Ref. 13, one would expect a maximum in T_c at lower pressures for films overdoped with charge carriers. As can be seen in Fig. 2 an extrapolation of the T_c data yields a hole overdoping of about 15–20 % which is much less than expected for fully oxygenated $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_\delta$. Furthermore, the higher scatter in the data (see 500 mbar) compared to our Ca-free films leads to the conclusion that there is a tendency of charge carrier compensation by local disorder of the calcium or oxygen.[14,15]

Discussion. An overdoping of the grains of about 20% has only small impact on the Debye screening length

TABLE II. Critical current densities at 35 K in self-field and T_c values for doped and undoped films. The data were taken from *pulsed transport* measurements over 100 μm wide bridges with a voltage criterion of 100 μV.

Film-GB angle	J_{gb} (10^6 A cm^{-2})	J_c (10^6 A cm^{-2})	J_{gb}/J_c	T_c (K)
Undoped 8° [001]	5.18	14.3	0.36	90.4
Doped 8° [001]	8.64	12.5–14[a]	0.62–0.69	79.8
Doped 8° [001]	5.91	12.5–14[a]	0.42–0.47	79.0
Doped 8° [001]	5.05	12.5–14[a]	0.36–0.40	78.0

[a]Local variation of J_c as can be seen in the magneto-optical data.

$$\lambda_D \approx \sqrt{\frac{1}{n_0}}. \tag{4}$$

As a result, it is not possible to explain the observed increasement of $J_{gb}(\theta)$ simply in the framework of the band bending model. Therefore we think that it is indispensable to take local GB attributes into account that are sensitive to Ca doping (such as strain fields and localized charges).

For undoped GB's Gurevich and Pashitskii[9] have already calculated the angular dependency of $J_{gb}(\theta)$ for low-angle GB's with respect to the tilting angle. Within this model isolating regions of radius r_i caused by the GB dislocations and for tilting angles larger than 5°–7° also charge effects have to be introduced for an accurate description of the current transport over low-angle GB's.

As can be looked up in Ref. 9, $J_{gb}(\theta)$ can be described by the equations

$$J_{gb}(\theta,r_i,Q)=\frac{J_m}{\nu}\left[\frac{1-9\alpha^2+(1+3\alpha^2)^{3/2}}{(1+\alpha)(1-\alpha^2)}\right]^{1/2}, \tag{5}$$

$$J_m=\frac{J_0 b\sqrt{\tau}}{2\sqrt{2}\beta\xi_0\sin(\theta_c/2)}, \tag{6}$$

$$\alpha=\frac{\beta\nu^2(2-\nu)}{2\tau(1-\nu)^2+\beta\nu^2(2-\nu)}, \tag{7}$$

$$\nu=\frac{\sin(\theta/2)}{\sin(\theta_c/2)}, \tag{8}$$

$$\beta=\frac{e^2 n_0\zeta\ln(b/r_i\theta)}{8\pi\epsilon_0\kappa_\infty\mu_c\lambda_\infty}\left[\frac{b\lambda_D(1-2\sigma)}{\xi_0(1-\sigma)}\right]^2. \tag{9}$$

Here the parameter β mainly determines how fast $J_{gb}(\theta)$ decreases with θ. The values for all constants that appear in these formulas were taken from Ref. 9 and have the following meaning: ξ_0 is the coherence length, b the Burgers vector and $\tau=(T_c-T)/T_c$ a normalized temperature, μ_c the critical shift of the chemical potential which causes the superconductor-insulator transition. Furthermore, λ_∞ is the coupling constant away from the GB, ζ the Grüneisen parameter, κ_∞ the dielectric constant, σ the Poisson ratio, and λ_D the Debye screening length.

For the following considerations we replace the factor en_0 by

$$en_0=\frac{en_0A}{A}=\frac{Q}{A}, \tag{10}$$

$$[Q]=\mathrm{Cm}^{-1} \tag{11}$$

and introduce a localized linear charge density Q at the dislocation core. For an undoped sample with a carrier density of $n_0=5\times10^{27}$ m^{-3} and a radius $r_i=b=4$ Å of the isolating regions, we find

$$Q_0=4.027\times10^{-10}\ \mathrm{Cm}^{-1}. \tag{12}$$

Additionally, to get a more accurate result for the r_i dependence of $J_{gb}(\theta)$, we replaced the approximated factor b^2 in Eq. (9) with the exact factor $b\cdot r_i$. With these changes Eq. (9) becomes

$$\beta(r_i,Q)=\frac{Q\zeta e\ln(b/r_i\theta)}{8\pi^2\epsilon_0\mu_c\lambda_\infty b^2\kappa_\infty}\left[\frac{\sqrt{br_i}\lambda_D(1-2\sigma)}{\xi_0(1-\sigma)}\right]^2. \tag{13}$$

As described in Eq. (4), a possible variation of the Debye screening length due to an overdoping of the grains of about 20% is rather small. Additionally, it has only small impact on $J_{gb}(\theta)$, so that we regard λ_D as a constant ($\lambda_D=8$ Å) for the following considerations.

With all constants [$\xi_0=13$ Å, $\mu_c\lambda_\infty=9$ meV, $\zeta=2$, $\kappa_\infty=20$, $\sigma=0.25$, $\lambda_D=8$ Å, $b=4$ Å, $\theta_c=30°$, $\tau=(T_c-T)/T_c=0.95$] taken from Ref. 9 for pure $YBa_2Cu_3O_\delta$ and $J_{gb}(\theta)$ as described above it is now possible to study the dependence of the critical current $J_{gb}(\theta)$ for a fixed angle $\theta=4°$ and 8° as a function of r_i and Q.

As outlined before, for the 4° GB's, the decaying length of the strain fields λ_{st} is much larger than the Debye screening length λ_D. Therefore, an electrically neutral boundary can be assumed. With this assumption and the r_i dependence of β,

$$\beta\propto r_i\ln r_i, \tag{14}$$

we were able to attach the $J_{gb}(\theta)$ increase of 40% for the 4° GB to a reduction of r_i by 35% to $r_i=0.65\cdot b$. Neglecting charge effects for the 8° GB as well, a r_i reduction by 50% is necessary to explain the improved critical currents for these samples. Since for 8° tilt boundaries λ_{sp} and λ_D are of the same order, it is more appropriate to assume a combined strain field and charge screening mechanism in the angular region of $8°-12°$. Therefore, we transferred the result for the r_i reduction of 35% from the 4° tilt GB to the 8° tilt GB and subsequently calculated the linear charge density to $Q = 0.81 \cdot Q_0$.

A similar calculation could be done adopting a more simple model by Chisholm and Pennycook[16] that assumes a linear r_i dependence of $J_{gb}(\theta, r_i)$ for small angles. In the mainframe of these assumptions the $J_{gb}(\theta)$ increase of 40% for the 4° GB yields a reduction of r_i by 40% which is in accordance to the nonlinear model of Gurevich. For the 8° GB one would come to a r_i reduction of 70% which stands in contrast to the 50% calculated above. Nevertheless, we think that a linear model is only applicable for very small angles and therefore is not able to describe the 8° GB correctly any more.

As it is not possible to eliminate any of the two effects, it is rather difficult to separate the strain field and charge effects. Nevertheless, with some more $J_{gb}(\theta)$ data, including other tilting angles, it should be possible to obtain a more distinct picture of the differences in these two active mechanisms.

Summary. In summary, by Ca doping it is possible to obtain record values of the critical current density for low-angle GB's in $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_\delta$ thin films. In comparison to undoped films, it was possible to increase J_{gb} for 8° [001] tilt GB by as much as 100%. Simultaneously, the normalized GB resistance Δ_0 for the doped films reduced by a factor larger than 5. The comparison with the model showed that for the 4° GB a reduction of the radius r_i of the strain fields ε by 35% could be attached to the measured J_{gb} increase of 40%. Considering the screening lengths λ_{st} and λ_D leads to the conclusion that for the 8° GB's combined strain field and charge screening effects are responsible for the J_{gb} enhancement.

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