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German Hammerl, Hartmut Bielefeldt, Bärbel Götz, Andreas Schmehl, Christof W. Schneider, Robert R. Schulz, Hans Hilgenkamp, Jochen Mannhart

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# Doping-Induced Enhancement of Grain Boundary Critical Currents

G. Hammerl, H. Bielefeldt, B. Goetz, A. Schmehl, C. W. Schneider, R. R. Schulz, H. Hilgenkamp, and J. Mannhart

**Abstract**—The critical-current density of grain boundaries in high- $T_c$  superconductors was enhanced to values exceeding the previously known limits both at 4.2 K and at 77 K. Noting the importance of space-charge layers and of the  $d_{x^2-y^2}$ -wave pairing symmetry on grain-boundary transport, we have established a model that provides a comprehensive description of the grain boundaries and proposes ways for their improvement, such as overdoping of the grains and of their boundaries. Exploring as example the effects of overdoping of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with Ca, we enhanced significantly the critical current densities and decreased the normal-state resistivities of grain boundaries to unprecedented values.

By introducing doping heterostructures to overdope grain boundaries selectively over a few nanometers by benefiting from grain boundary diffusion, the enhancement of the critical-current density is achieved at all temperatures up to  $T_c$ . At 77 K, critical current densities are obtained which before had been found only at 4.2 K. This concept is proposed as a practical and cost-effective route to enhance the performance of high- $T_c$  coated conductors fabricated by ion beam assisted deposition (IBAD) [1]–[4] or by the rolling assisted biaxially aligned substrate process (RABITS) [5].

**Index Terms**—critical currents, doping, grain boundary, Josephson junctions

## I. INTRODUCTION

THE ENHANCEMENT of grain boundary critical current densities is a challenge which is key for many large scale applications of high- $T_c$  superconductivity. The reasons for this are well known: for coated conductors to be competitive with conventional technologies, their critical current densities have to be increased. In principle, there are two ways to enhance grain boundary critical currents for bulk applications: a) to accurately align the grains in all directions [6] and b) to increase the critical current densities of grain boundaries for a given spread of misorientations. We show,

that the transport properties of grain boundaries with a given misorientation can be optimized and the critical current density be significantly enhanced at all temperatures by doping of the superconductors. In addition it is pointed out that the process developed is a suitable means to tailor the properties of Josephson junctions, which may or may not be based on grain boundaries, as well as of other electronic devices relying on interfaces or surfaces involving high- $T_c$  superconductors.

## II. MECHANISMS OF CHARGE TRANSPORT ACROSS GRAIN BOUNDARIES

As far as applications are concerned, superconductors are usually regarded as canonical metals like for example Nb, Pb or Al, with large carrier densities and very small electric screening lengths as described in the Thomas-Fermi model. Contacts between such metals or grain boundaries within them have an ohmic resistance which is very small [7]. Semiconductors behave differently. Due to their much smaller carrier densities their screening lengths are larger, and consequently space-charge layers, band bending and Schottky contacts are ubiquitous phenomena [8]. Similarly, in most oxides, well known examples being given by doped  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{ZnO}$ , grain boundaries are controlled by charging and band bending [9].

The presence of charges at grain boundaries in high- $T_c$  superconductors has been considered early on [10], and the existence of positive charges at the boundaries was demonstrated by detailed Z-contrast scanning transmission electron microscopy studies of grain boundaries in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  films [11].

Like many other oxides, the high- $T_c$  cuprates are characterized by relatively small carrier densities (a few  $10^{21}/\text{cm}^3$ ). Furthermore, the dielectric constants  $\epsilon$  of the high- $T_c$  cuprates are non-negligible (see e.g. [12]–[14]). Therefore space-charge effects and band bending phenomena have to be considered to be present in the cuprates, which cause drastic differences between the physics of interfaces involving high- $T_c$  superconductors and the interface physics of conventional superconductors.

Based on such considerations we have proposed that, besides strong effects arising from the microstructure of the grain boundaries and from the  $d_{x^2-y^2}$ -wave pairing symmetry of the high- $T_c$  superconductors, the transport across the high- $T_c$  grain boundaries is affected by band bending and by

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J. Mannhart, H. Bielefeldt, B. Goetz, G. Hammerl, A. Schmehl, C. W. Schneider, R. R. Schulz, and H. Hilgenkamp are with the Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany.

H. Hilgenkamp is also with the Low Temperature Division and the MESA+ Institute, University of Twente, P.O. Box 217, 7500 Enschede, The Netherlands.

space-charge layers formed inside the grains close to the grain boundaries, over a distance given by the electrostatic screening length of the grains [15], [16]. In these space-charge layers, which typically are depletion layers, the density of mobile holes is strongly decreased. Consequently, the order parameter is thought to be reduced, too, and, for strong enough depletion, the cuprate is expected to undergo the phase transition into the insulating state and to form a tunneling barrier (see Fig. 1). Due to the faceted microstructure of the grain boundaries and the spatial distribution of the charges present at the boundary, this tunneling barrier will be inhomogeneous. A quantitative treatment of this model has been worked out by the Wisconsin group [18].

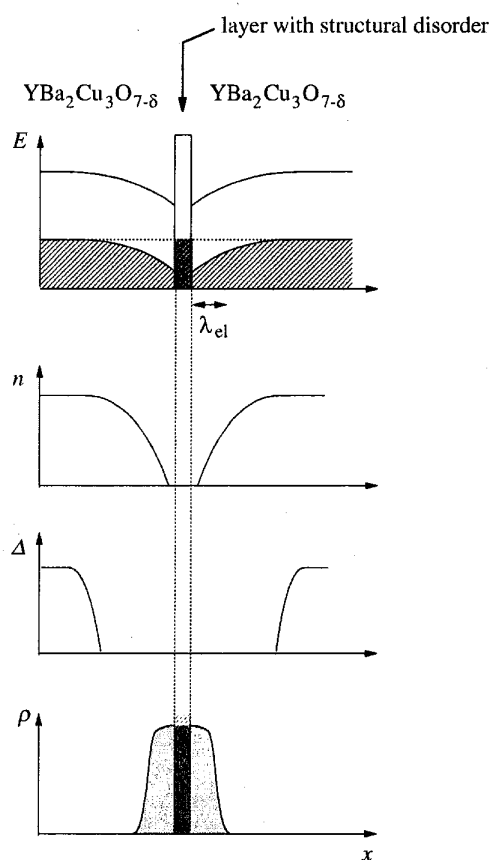


Fig. 1. Possible scenario for bending of the electronic band structure of high- $T_c$  cuprates at a grain boundary. In the example shown, at the grain boundary interface depletion layers are formed, which cause a depression of the order parameter and a transition of the cuprate into the insulating state in the region close to the interface (from [17]).

This understanding suggests doping to be a key to enhance the critical current density and to decrease the normal state resistance of grain boundaries in high- $T_c$  superconductors. First, overdoping of the grains is a means to reduce the electrostatic screening lengths and thereby the width of the

space-charge layers. Second, by substituting excessively charged cations at the boundary by cations with a smaller valency, the built-in potential at the boundary is lowered, which reduces the height and the width of the tunneling barrier. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ , for example, both effects have been predicted to be caused by partial replacement of  $\text{Y}^{3+}$  with  $\text{Ca}^{2+}$  [19]. This substitution is known to overdope the superconductor [20], and the replacement of  $\text{Y}^{3+}$  by  $\text{Ca}^{2+}$  at the boundary is expected to reduce the amount of positive charge present at the boundary layer. Partial replacement of  $\text{Cu}^{2+}$  by  $\text{Co}^{3+}$  is thought to cause the opposite effects and thus to decrease the grain boundary critical current densities [19].

It is noted that doping of grain boundaries has been explored by other groups before [21]–[26], but to our knowledge a systematic  $J_c$ -enhancement has never been reported.

### III. MEASUREMENTS

#### A. Homogeneously Doped Bicrystalline Films

To study the influence of doping  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  with Ca or with Co on grain boundary transport, bicrystalline films of  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  and of  $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7.8}$  were grown by pulsed laser deposition from polycrystalline  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  and  $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7.8}$  targets with  $0 \leq x \leq 0.4$  and  $0 \leq y \leq 0.1$ .  $\text{SrTiO}_3$  bicrystals with [001] tilt grain boundaries were used as substrates. After deposition, the samples were cooled down over an hour in an oxygen atmosphere of 0.4 bar. These are our standard conditions for the oxidation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  films [19], [27]. In several cases, after measuring  $J_c$ , post-anneal experiments were performed. These experiments confirmed that for Ca-doped samples this cooldown-process results in overdoped films [19]. Bridges straddling the grain boundaries in the typically 100–150 nm thick films were patterned by standard photolithography and wet etching to widths of 3–6  $\mu\text{m}$ . Critical current densities  $J_c$  were obtained from the ratios of the critical currents and the cross-sectional areas  $A$  of the bridges, as measured for each of the bridges by atomic force microscopy.

In Fig. 2,  $J_c$  and the normal state resistivity  $R_n A$  at 4.2 K are presented for  $24^\circ$  boundaries as a function of the Ca or Co-concentrations  $x$  and  $y$ . As shown in Fig. 2a, with increasing Ca content,  $J_c$  increases to values as high as  $6.5 \cdot 10^6 \text{ A/cm}^2$  for  $x = 0.3$ . This is an order of magnitude larger than the critical current densities of the equivalent undoped samples. For a Ca concentration of  $x = 0.4$   $J_c$  is reduced again, which is attributed to the fact that this concentration exceeds the solubility limit for Ca in  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ . As expected, the critical current density is reduced by Co-doping.

As shown by Fig. 2b, the  $R_n A$ -values decrease continuously with increasing Ca-content to resistivities as small as  $2.5 \cdot 10^{-10} \Omega\text{cm}^2$ . Due to this decrease also the  $I_c R_n$ -product drops with increasing  $J_c$ , as shown in Fig. 3. This

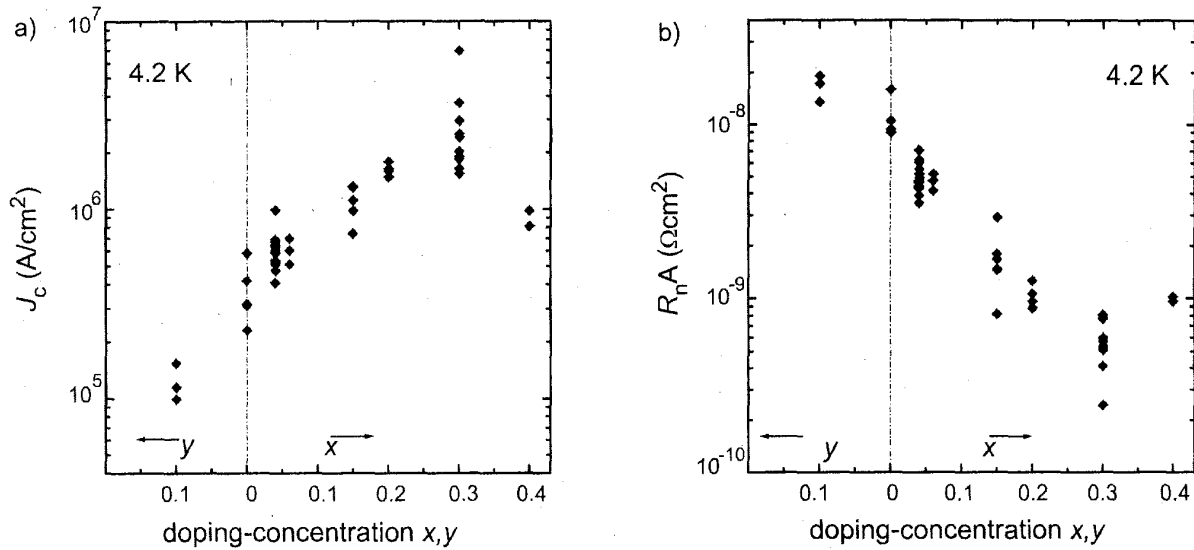


Fig. 2. Dependence of the critical current density  $J_c$  (a) and of the normal state resistance  $R_n A$  (b) of symmetric  $24^\circ$  [001]-tilt grain boundaries in  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  and in  $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7.8}$  films on the Ca and Co-concentrations  $x$  and  $y$  at  $T = 4.2$  K (after Ref. 19).

behavior is not surprising since overdoping reduces the  $I_c R_n$ -product together with the  $T_c$  and increases the  $J_c$  along with the coupling of the grain boundaries.

In Fig. 4, the critical current densities and normal state resistivities of  $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  bicrystalline films are plotted as a function of grain boundary angle. As shown, significant increases of  $J_c$  are also achieved for  $30^\circ$  boundaries. We note that even in applied magnetic fields of up to 3 T large increases of  $J_c$  are now reported for  $5^\circ$  junctions by the group of the University of Wisconsin [30]. For  $45^\circ$  boundaries the enhancements are smaller, which is attributed to the fact that the  $d_{x^2-y^2}$ -wave pairing symmetry has a very strong influence on these junctions. It is remarkable that for all doping concentrations and temperatures the asymmetric  $45^\circ$  grain boundaries showed anomalous dependencies of their critical currents on applied magnetic fields [31], which provides evidence that in the whole parameter range explored the symmetry of  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  is dominated by the  $d_{x^2-y^2}$ -wave component.

With increasing Ca concentration, the  $T_c$  of the samples drops rapidly, as shown in Fig. 5. Due to this  $T_c$  reduction, for a measurement temperature of 77 K, Ca doping of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  grains leads to minor increases of  $J_c$  at best (see Fig. 6).

### B. Doping Multilayers and Superlattices

To achieve large critical current densities across grain boundaries at 77 K it is obviously desirable to obtain good grain boundary coupling and at the same time to preserve a large  $T_c$  of the grains. To achieve this goal, we tried to overdope the superconductors locally at the grain boundaries while keeping the grains optimally doped [27].

To overdope the grain boundaries we devised doping-heterostructures such as  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  bilayers or superlattices, anticipating that during film growth calcium diffuses along the grain boundary into the  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  layers. As the diffusion coefficient along the grain boundary is presumed to exceed considerably the diffusion coefficient in the grains, this process is expected to enhance the calcium-concentration locally at the grain boundaries (see Fig. 7). Therefore the  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  layers are foreseen to have high intergrain  $J_c$ -values at 77 K, combined with good superconducting properties of the grains [27].

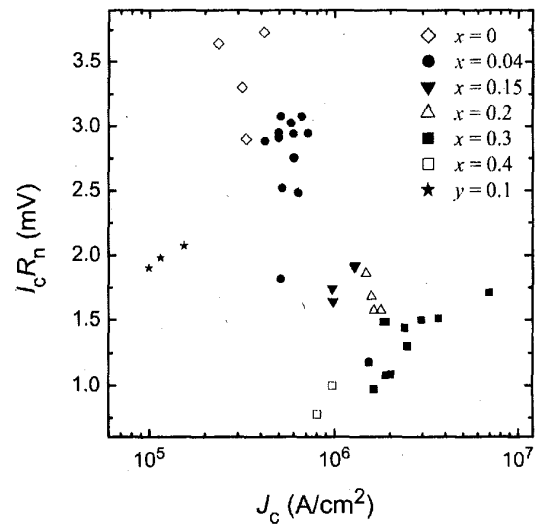


Fig. 3. Dependence of the characteristic voltage  $I_c R_n$  of symmetric  $24^\circ$  [001]-tilt grain boundaries in  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  and in  $\text{YBa}_2\text{Cu}_{3-y}\text{Co}_y\text{O}_{7.8}$  films on the Ca and Co-concentrations  $x$  and  $y$  at  $T = 4.2$  K (from Ref. 28).

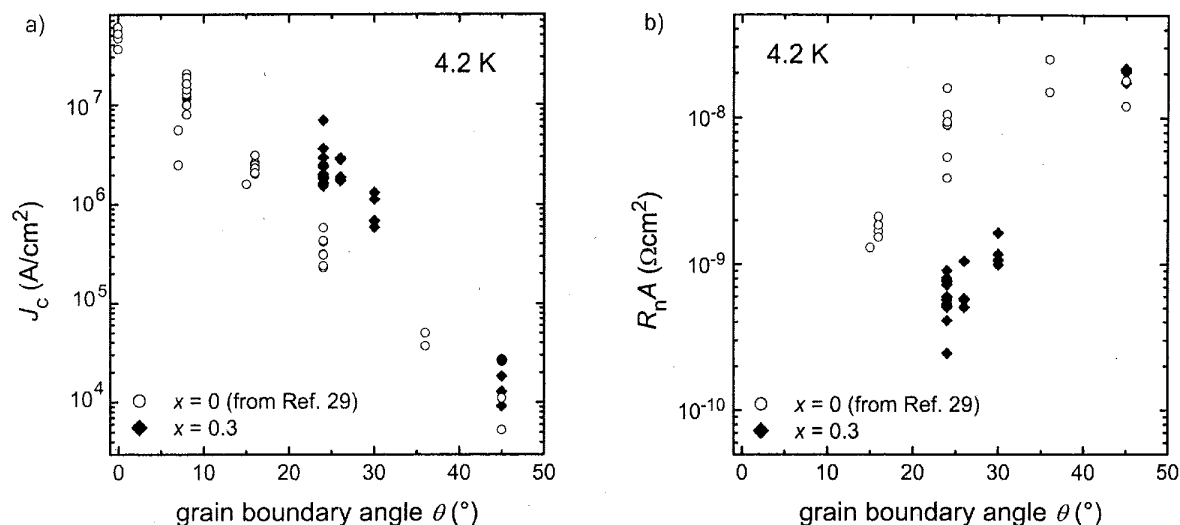


Fig. 4. Dependence of the critical current density  $J_c$  (a) and of the normal state resistance  $R_n A$  (b) of [001]-tilt grain boundaries in  $Y_{1-x}Ca_xBa_2Cu_3O_{7.8}$  films on the grain boundary angle for various doping concentrations at  $T = 4.2$  K.

In the course of these studies, several hundred grain boundary junctions formed by a variety of doping heterostructures, such as bilayers, trilayers, and superlattices were fabricated (see Figs. 8-10), predominantly grown on  $SrTiO_3$  bicrystals containing  $24^\circ$  [001] tilt boundaries. This angle was chosen, as in the past  $24^\circ$  grain boundaries have been widely characterized by many groups. In the following their characteristic behavior will be summarized.

Fig. 11 shows a current-voltage characteristic typical for all doping multilayers investigated. It displays a clear RSJ-type Josephson behavior. This agrees with the magnetic field dependencies of the critical current, which, as shown in Fig. 12, are typical for standard  $24^\circ$  grain boundary Josephson junctions.

Do the doping heterostructures indeed yield large grain boundary critical current densities at 77 K? The answer to this question is provided by Fig. 13, which presents the  $J_c(T)$  dependencies of four samples containing  $24^\circ$  [001] tilt grain boundaries: an undoped  $YBa_2Cu_3O_{7.8}$  film, a homogeneously doped one, and two doping multilayers. The grain boundary of the undoped film plotted has a critical current density of  $5.2 \times 10^5$  A/cm<sup>2</sup> and  $5.5 \times 10^4$  A/cm<sup>2</sup> at 4.2 K and at 77 K, respectively, which agrees with the literature values for very good samples. The critical current density of the homogeneously doped  $Y_{1-x}Ca_xBa_2Cu_3O_{7.8}$  film is huge at 4.2 K, but, as discussed, is vanishing at 77 K. This problem is solved by the doping multilayers. In the plot, the behavior of a typical bilayer is shown, together with the dependence of

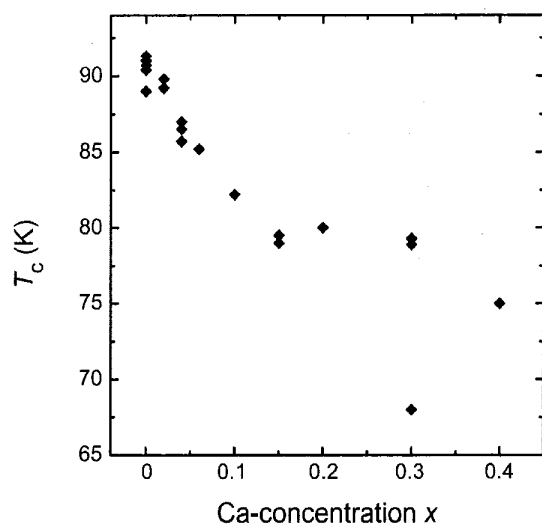


Fig. 5. Dependence of the critical temperature  $T_c$  of symmetric  $24^\circ$  [001]-tilt grain boundaries in  $Y_{1-x}Ca_xBa_2Cu_3O_{7.8}$  films on the doping concentration  $x$  (after Ref. 28).

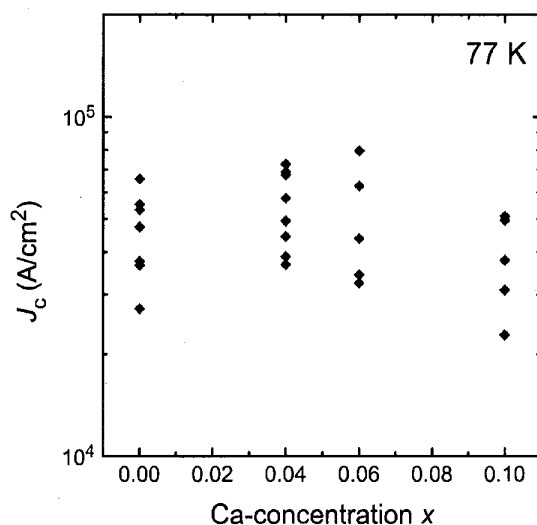


Fig. 6. Dependence of the critical current density  $J_c$  of symmetric  $24^\circ$  [001]-tilt grain boundaries in  $Y_{1-x}Ca_xBa_2Cu_3O_{7.8}$  films on the doping concentration  $x$  at  $T = 77$  K (from Ref. 32).

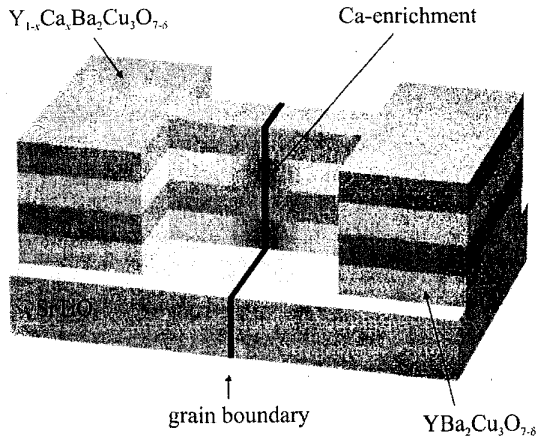


Fig. 7. Illustration of the local doping of grain boundaries intended by the use of grain boundary diffusion in doping heterostructures.

the best sample prepared, which was a  $Y_{1-x}Ca_xBa_2Cu_3O_{7.8}$  /  $YBa_2Cu_3O_{7.8}$  /  $Y_{1-x}Ca_xBa_2Cu_3O_{7.8}$  trilayer. As expected, the multilayers have a high  $T_c$ , for all samples  $T_{c0}$  exceeded 90 K. Consequently the grain boundaries support large critical current densities at high temperatures, which well exceed those of the  $YBa_2Cu_3O_{7.8}$  films in the entire temperature range of  $T < T_c$ . Specifically, the trilayer shown achieved at 77 K a critical current density of  $3.3 \times 10^5$  A/cm<sup>2</sup>, which equals the critical current density usually obtained at liquid nitrogen temperatures for 7° boundaries, or the typical critical current densities of 24° boundaries at 4.2 K (see Fig. 4).

#### IV. OUTLOOK

These results reveal that doping is an effective tool to optimize grain boundary Josephson junctions. The processes employed are cheap and, as much as we know today, readily compatible with the coated conductor technologies. Therefore we propose to apply this advancement to RABITS and IBAD to further improve the performance/cost ratio of the coated conductors.

Also, doping is a powerful technique to modify grain boundary Josephson junctions used in electronic applications. In this work we have focussed on the changes of  $J_c$ ,  $R_n A$  and the  $I_c R_n$ -product, but doping is seen to also affect other junction properties, such as junction capacitance [33], noise, reproducibility or stability. Since band bending is also a concern for other types of high- $T_c$  Josephson junctions, such as ramp-type junctions, or of other interfaces and surfaces involving high- $T_c$  cuprates, we are strongly convinced that doping is a tool to optimize their properties, too (see also [34]).

Comparable to the case of semiconducting electronics, doping introduces several degrees of freedom to modify interfaces in superconductors. For example, instead of calcium other doping elements, or even combinations of various dopants, may be utilized. Furthermore, Y may be

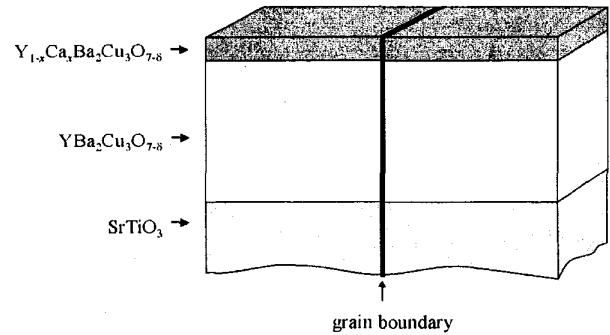


Fig. 8. Sketch of the doping bilayers used in the experiments (after Ref. 27).

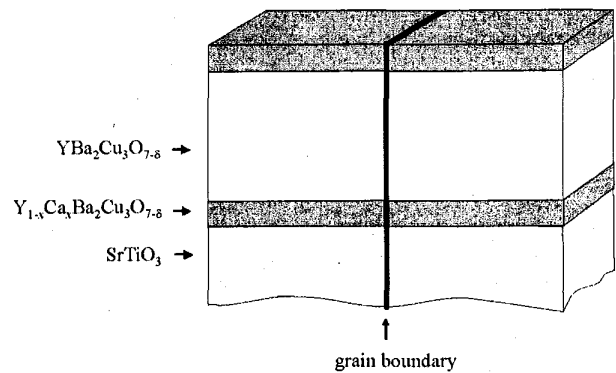


Fig. 9. Sketch of the doping trilayers investigated (after Ref. 27).

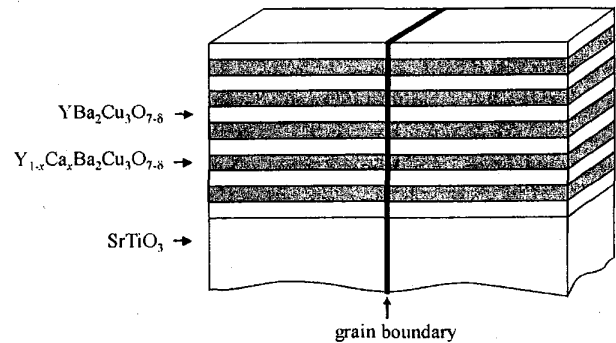


Fig. 10. Sketch of the doping superlattices studied (after Ref. 27).

replaced by a rare earth element which due to slightly different electronic properties, or due to a higher  $T_c$  of the cuprate superconductor, leads to improved grain boundary behavior. For electronic applications, new possibilities for circuit design are provided by the fact that the doping elements or their concentration can be varied across the surface of a chip or between layers in multilayer structures [28].

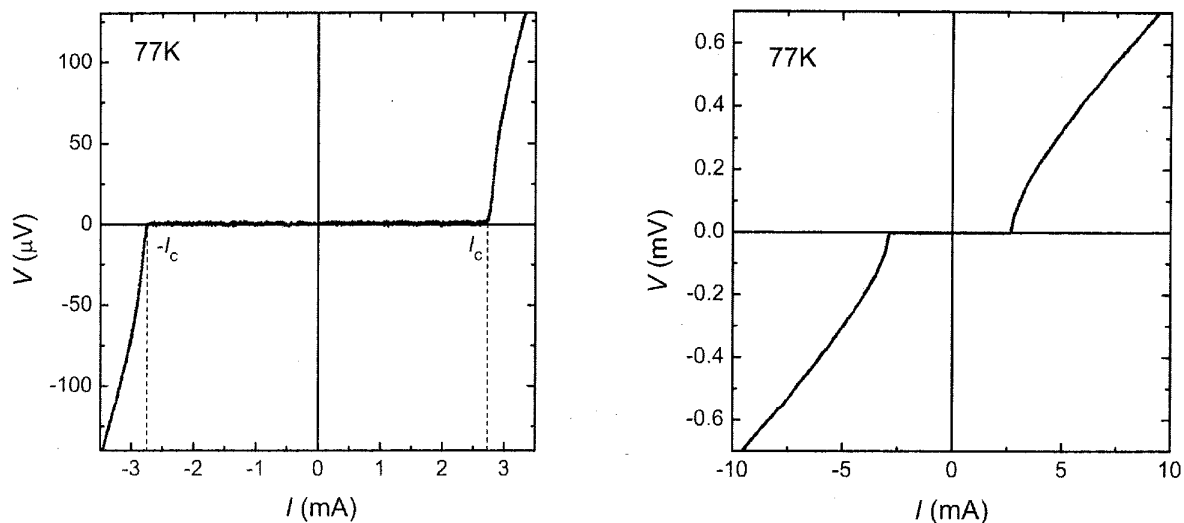


Fig. 11. Typical  $I(V)$ -characteristics of  $24^\circ$  grain boundaries doping multilayers measured at 77 K. The measurements were done with a  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}/\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  bilayer with layer thicknesses of 160 nm and 20 nm, respectively. The width of the superconducting bridge was  $7.7 \mu\text{m}$ .

## V. SUMMARY

Guided by the concept of band bending, we have studied the effects of doping of high- $T_c$  superconductors on the transport properties of grain boundaries and have found it to

be a powerful tool for their optimization. For example, by using  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  based doping multilayers, grain boundary critical current densities have been achieved which at 77 K equal the values usually measured at 4.2 K.

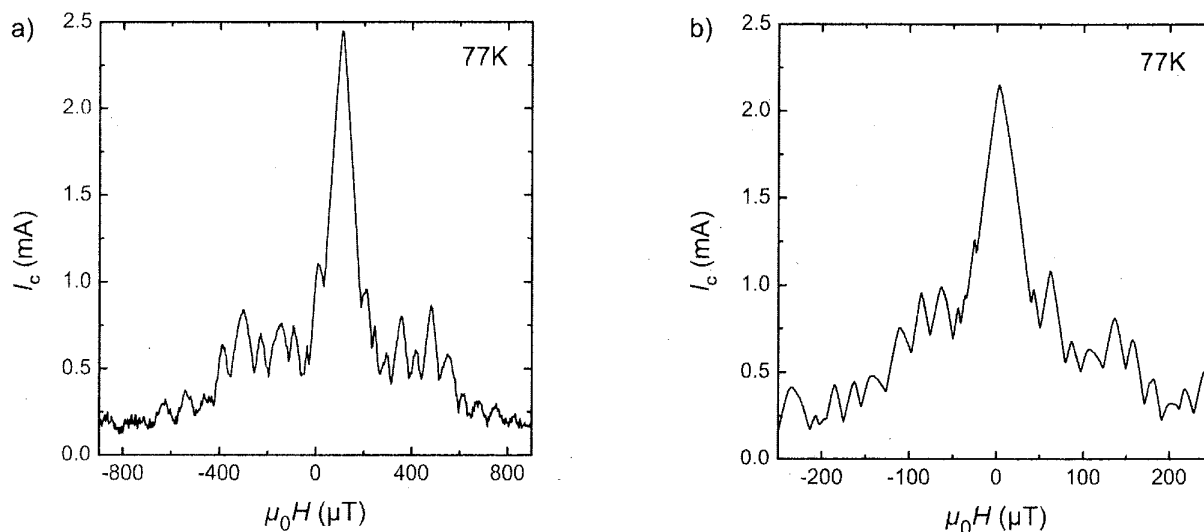


Fig. 12. Magnetic field dependence of the critical currents of  $24^\circ$  grain boundaries in two doping multilayers. a) a multilayer consisting of 6 layers of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  and 5 layers of  $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$ , of about equal layer thicknesses, the total film thickness being  $\sim 290 \text{ nm}$ , the width of the bridge crossing the grain boundary  $\sim 4.7 \mu\text{m}$ ; b) a  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8} / \text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  bilayer. The total film thickness of this sample equals  $\sim 170 \text{ nm}$ , the thickness of the Ca-doped top-layer  $\sim 20 \text{ nm}$ ; and the grain boundary width  $\sim 6.3 \mu\text{m}$ .

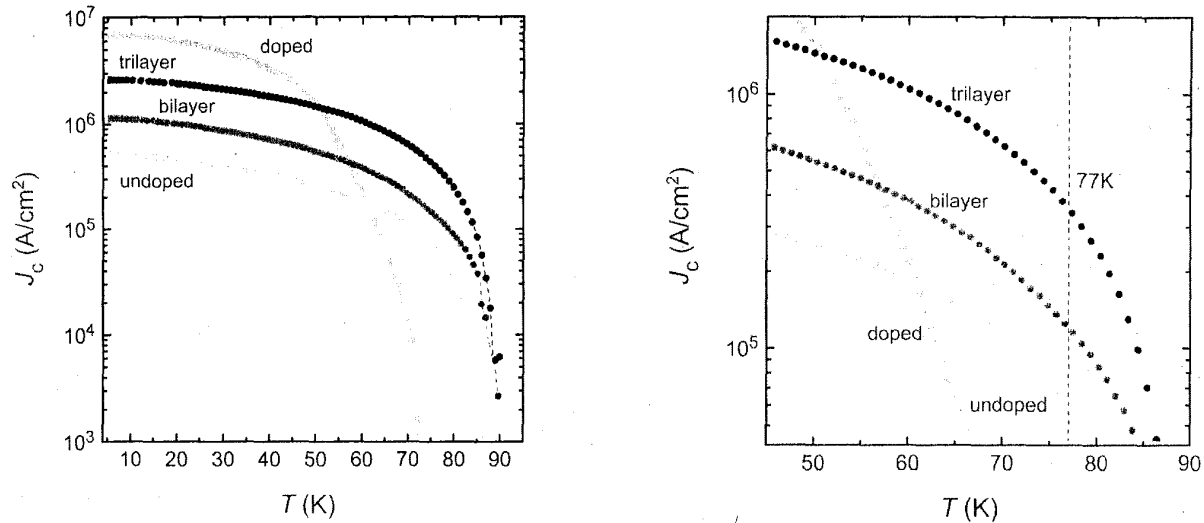


Fig. 13. Dependence of the critical current density of  $24^\circ$  grain boundaries in various films and heterostructures: a  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  film (undoped), a  $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  film (doped), a  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8} / \text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$  bilayer with a  $J_c$  typical for such bilayers, and a  $\text{YBa}_2\text{Cu}_3\text{O}_{7.8} / \text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7.8} / \text{YBa}_2\text{Cu}_3\text{O}_{7.8}$  trilayer with the best  $J_c(77\text{K})$  observed in the study.

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