Doping-Induced Enhancement of Grain Boundary Critical Currents

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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 $YBa_2Cu_3O_{7-\delta}$ 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 $SrTiO_3$, $BaTiO_3$, and 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 $YBa_2Cu_3O_{7-\delta}$ films [11].

Like many other oxides, the high-T_c cuprates are characterized by relatively small carrier densities (a few $10^{21}/cm^3$). Furthermore, the dielectric constants ε_r 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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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].

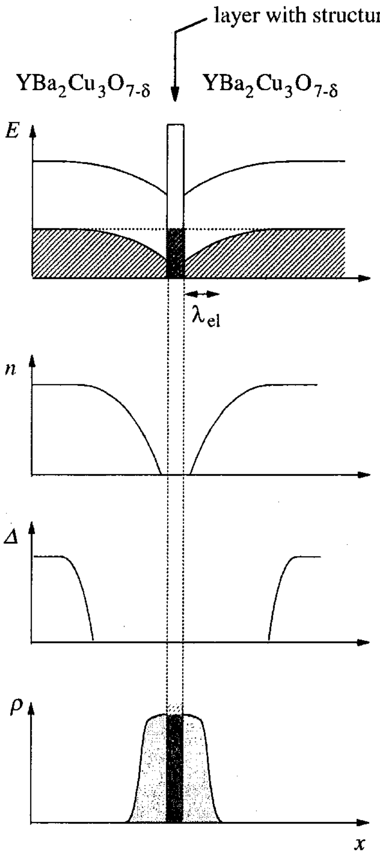

Fig. 1. Possible scenario for bending of the electronic band structure of high-T_c cuprates at a grain boundary. In the example shown, at the grain boundary interface depletion layers are formed, which cause a depression of the order parameter and a transition of the cuprate into the insulating state 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 $YBa_2Cu_3O_{7-\delta}$, for example, both effects have been predicted to be caused by partial replacement of Y^{3+} with Ca^{2+} [19]. This substitution is known to overdope the superconductor [20], and the replacement of Y^{3+} by Ca^{2+} at the boundary is expected to reduce the amount of positive charge present at the boundary layer. Partial replacement of Cu^{2+} by 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 $YBa_2Cu_3O_{7-\delta}$ with Ca or with Co on grain boundary transport, bicrystalline films of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and of $YBa_2Cu_{3-y}Co_yO_{7-\delta}$ were grown by pulsed laser deposition from polycrystalline $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_{3-y}Co_yO_{7-\delta}$ targets with $0 \leq x \leq 0.4$ and $0 \leq y \leq 0.1$. $SrTiO_3$ 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 $YBa_2Cu_3O_{7-\delta}$ 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 µm. 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_nA at 4.2 K are presented for 24° 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 $6.5*10^6$ 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 $YBa_2Cu_3O_{7-\delta}$. As expected, the critical current density is reduced by Co-doping.

As shown by Fig. 2b, the R_nA-values decrease continuously with increasing Ca-content to resistivities as small as $2.5*10^{-10}$ Ωcm^2. Due to this decrease also the I_cR_n-product drops with increasing J_c, as shown in Fig. 3. This

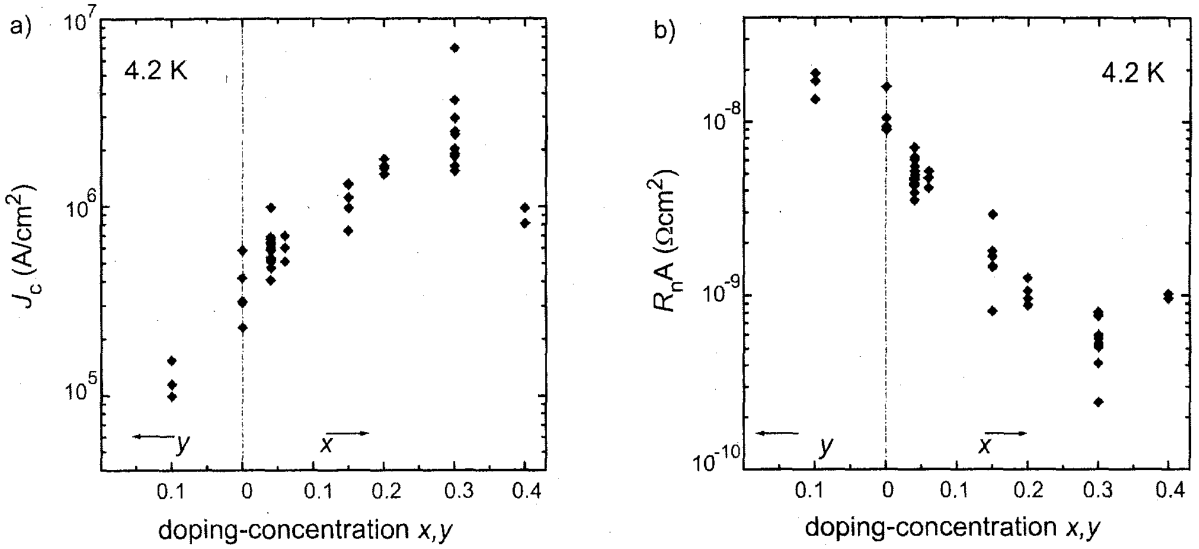

Fig. 2. Dependence of the critical current density J_c (a) and of the normal state resistance R_nA (b) of symmetric 24° [001]-tilt grain boundaries in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and in $YBa_2Cu_{3-y}Co_yO_{7-\delta}$ films on the Ca and Co-concentrations x and y at $T = 4.2$ K (after Ref. 19).

behavior is not surprising since overdoping reduces the I_cR_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 $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ bicrystalline films are plotted as a function of grain boundary angle. As shown, significant increases of J_c are also achieved for 30° boundaries. We note that even in applied magnetic fields of up to 3 T large increases of J_c are now reported for 5° junctions by the group of the University of Wisconsin [30]. For 45° 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° 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 $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ 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 $YBa_2Cu_3O_{7-\delta}$ 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 $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ bilayers or superlattices, anticipating that during film growth calcium diffuses along the grain boundary into the $YBa_2Cu_3O_{7-\delta}$ 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 $YBa_2Cu_3O_{7-\delta}$ layers are foreseen to have high intergrain J_c-values at 77 K, combined with good superconducting properties of the grains [27].

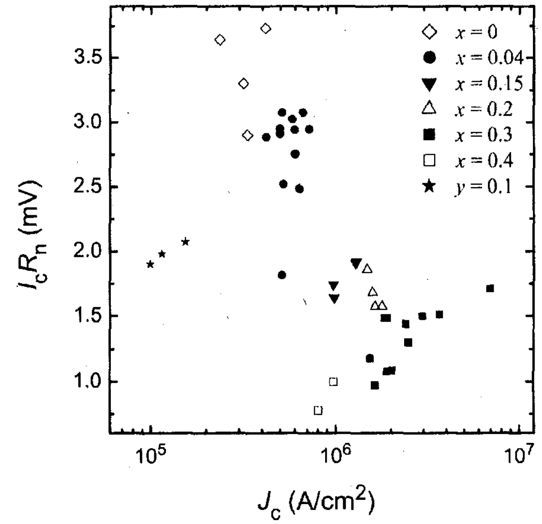

Fig. 3. Dependence of the characteristic voltage I_cR_n of symmetric 24° [001]-tilt grain boundaries in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and in $YBa_2Cu_{3-y}Co_yO_{7-\delta}$ films on the Ca and Co-concentrations x and y at $T = 4.2$ K (from Ref. 28).

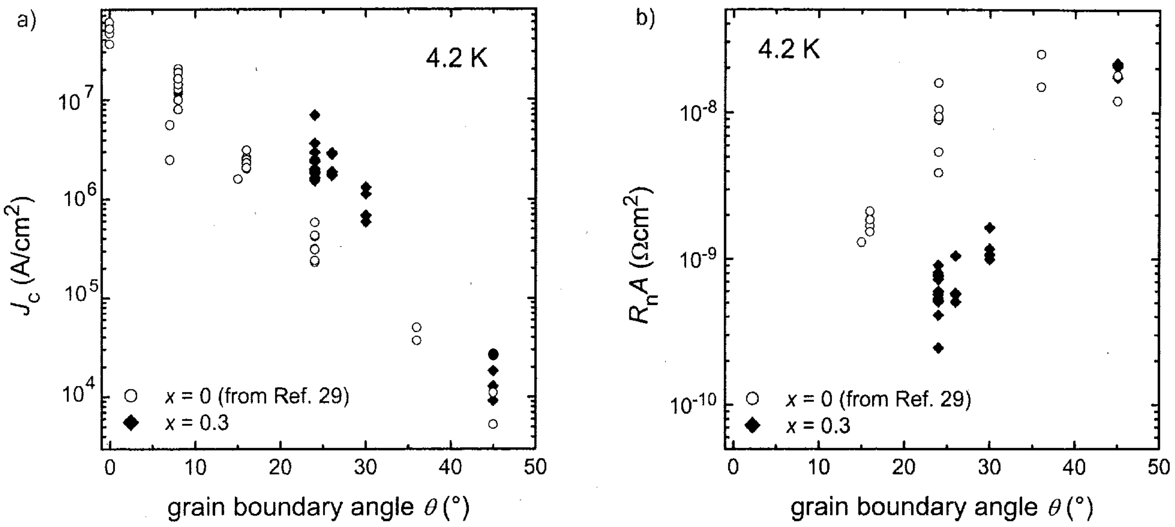

Fig. 4. Dependence of the critical current density J_c (a) and of the normal state resistance R_nA (b) of [001]-tilt grain boundaries in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films on the grain boundary angle for various doping concentrations at $T = 4.2$ K.

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° [001] tilt boundaries. This angle was chosen, as in the past 24° 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° 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° [001] tilt grain boundaries: an undoped $YBa_2Cu_3O_{7-\delta}$ film, a homogeneously doped one, and two doping multilayers. The grain boundary of the undoped film plotted has a critical current density of $5.2*10^5$ A/cm^2 and $5.5*10^4$ A/cm^2 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 $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ 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

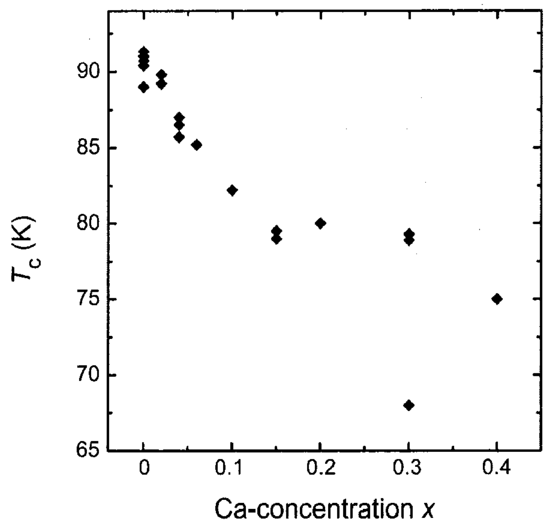

Fig. 5. Dependence of the critical temperature T_c of symmetric 24° [001]-tilt grain boundaries in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films on the doping concentration x (after Ref. 28).

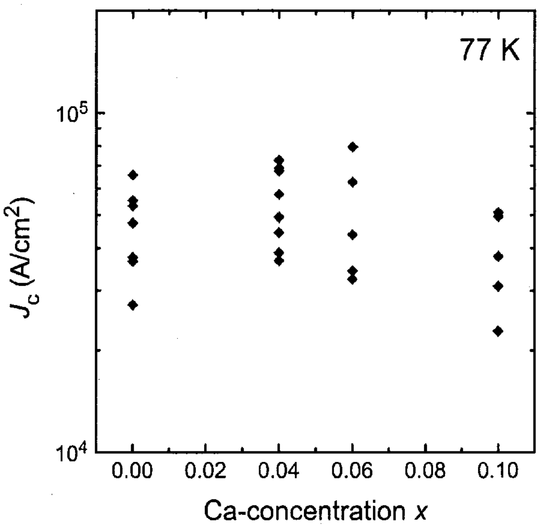

Fig. 6. Dependence of the critical current density J_c of symmetric 24° [001]-tilt grain boundaries in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films on the doping concentration x at $T = 77$ K (from Ref. 32).

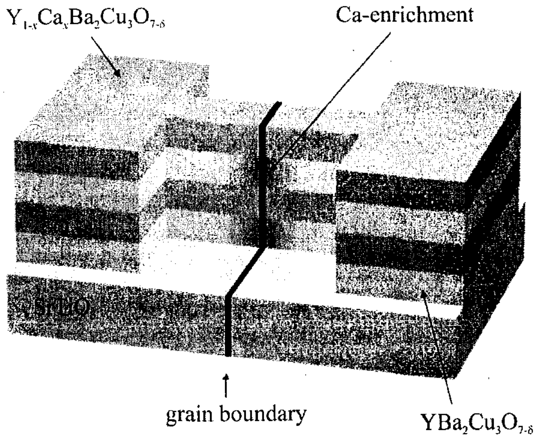

Fig. 7. Illustration of the local doping of grain boundaries intended by the use of grain boundary diffusion in doping heterostructures.

the best sample prepared, which was a $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ / $YBa_2Cu_3O_{7-\delta}$ / $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ 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 $YBa_2Cu_3O_{7-\delta}$ films in the entire temperature range of $T < T_c$. Specifically, the trilayer shown achieved at 77 K a critical current density of $3.3*10^5$ A/cm^2, 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_nA and the I_cR_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 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].

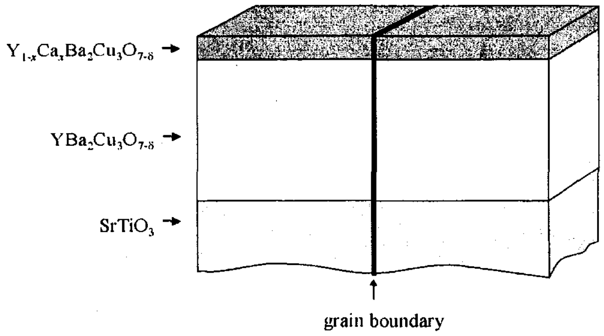

Fig. 8. Sketch of the doping bilayers used in the experiments (after Ref. 27).

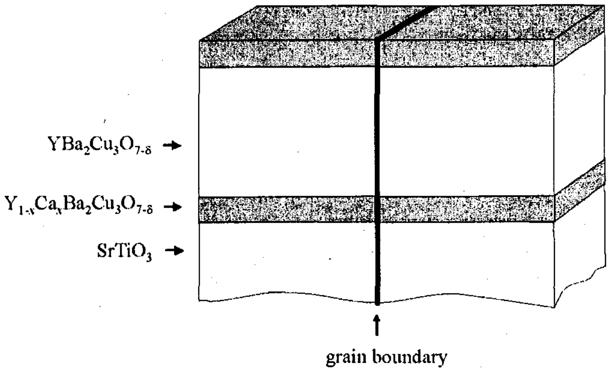

Fig. 9. Sketch of the doping trilayers investigated (after Ref. 27).

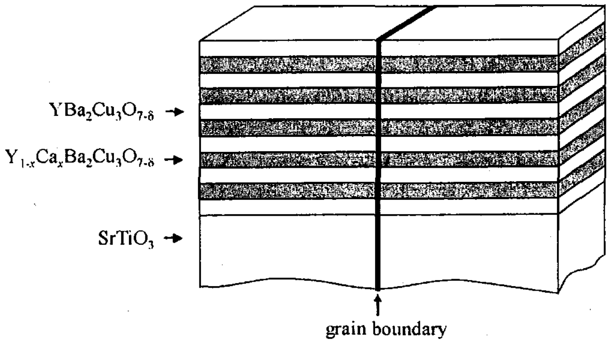

Fig. 10. Sketch of the doping superlattices studied (after Ref. 27).

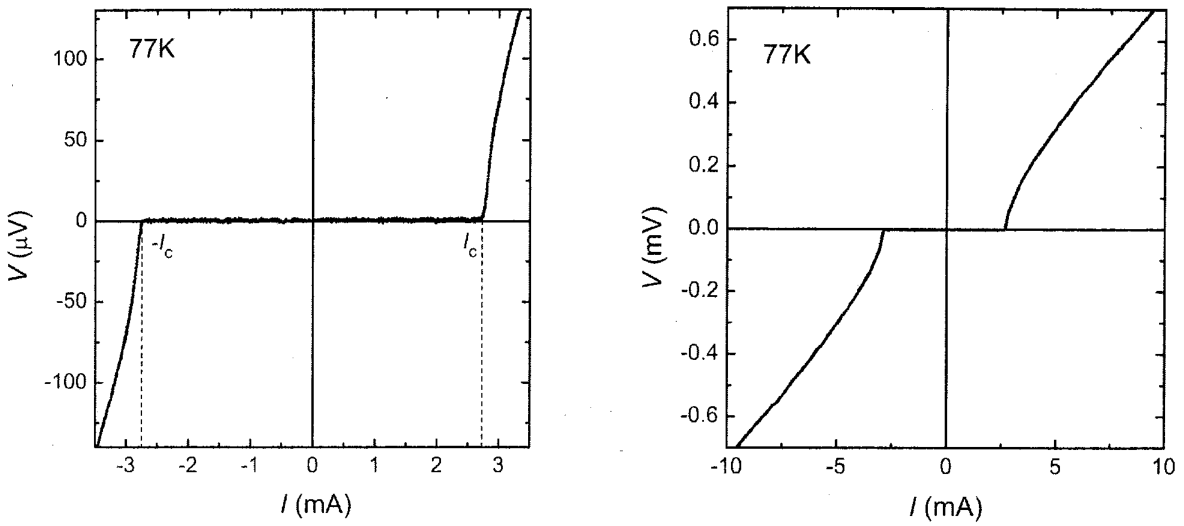

Fig. 11. Typical $I(V)$-characteristics of 24° grain boundaries doping multilayers measured at 77 K. The measurements were done with a $YBa_2Cu_3O_{7-\delta}$/ $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ bilayer with layer thicknesses of 160 nm and 20 nm, respectively. The width of the superconducting bridge was 7.7 μm.

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 $YBa_2Cu_3O_{7-\delta}$ based doping multilayers, grain boundary critical current densities have been achieved which at 77 K equal the values usually measured at 4.2 K.

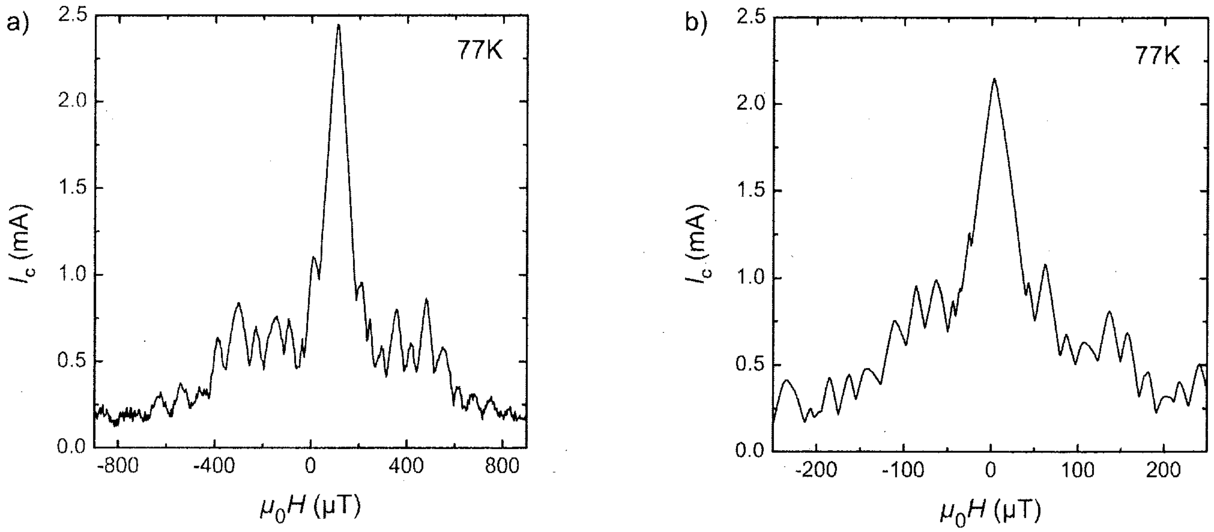

Fig. 12. Magnetic field dependence of the critical currents of 24° grain boundaries in two doping multilayers. a) a multilayer consisting of 6 layers of $YBa_2Cu_3O_{7-\delta}$ and 5 layers of $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$, of about equal layer thicknesses, the total film thickness being ~ 290 nm, the width of the bridge crossing the grain boundary ~ 4.7 μm; b) a $YBa_2Cu_3O_{7-\delta}$ / $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$, bilayer. The total film thickness of this sample equals ~ 170 nm, the thickness of the Ca-doped top-layer ~ 20 nm; and the grain boundary width ~ 6.3 μm.

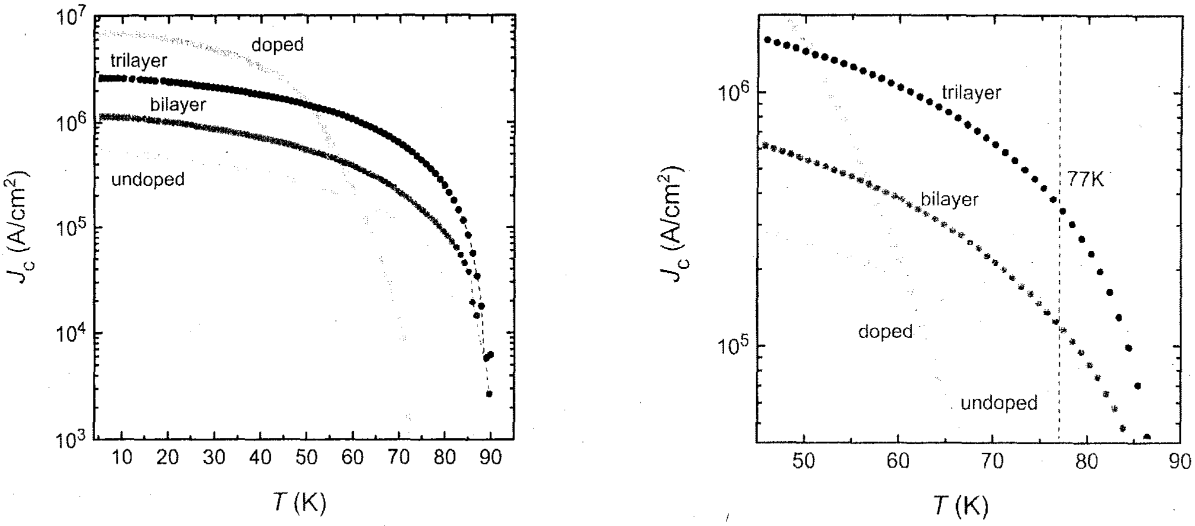

Fig. 13. Dependence of the critical current density of 24° grain boundaries in various films and heterostructures: a $YBa_2Cu_3O_{7-\delta}$ film (undoped), a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ film (doped), a $YBa_2Cu_3O_{7-\delta}$ / $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ bilayer with a J_c typical for such bilayers, and a $YBa_2Cu_3O_{7-\delta}$ / $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ / $YBa_2Cu_3O_{7-\delta}$ trilayer with the best J_c(77K) observed in the study.

REFERENCES

[1] Y. Iijima, N. Tanabe, O. Kohno, and Y. Ikeno, "In-plane aligned $YBa_2Cu_3O_{7-x}$ thin films deposited on polycrystalline metallic substrates," *Appl. Phys. Lett.*, vol. 60, pp. 769-771, 1992.

[2] R.P. Reade, P. Berdahl, R.E. Russo, and S.M. Garrison "Laser deposition of biaxially textured yttria-stabilized zirconia buffer layers on polycrystalline metallic alloys for high critical current Y-Ba-Cu-O thin films," *Appl. Phys. Lett.*, vol. 61, pp. 2231-2233, 1992.

[3] X.D. Wu, S.R. Foltyn, P.N. Arendt, W.R. Blumenthal, I. H. Campbell, J.D. Cotton, J.Y. Coulter, W.L. Hults, M.P. Maley, H.F. Safar and J.L. Smith, "Properties of $YBa_2Cu_3O_{7-\delta}$ thick films on flexible buffered metallic substrates," *Appl. Phys. Lett.*, vol. 67, pp. 2397-2399, 1995.

[4] J. Dzick, J. Wiesmann, J. Hoffmann, K. Heinemann, F. Garcia-Moreno, A. Isaev, and H.C. Freyhardt, "YSZ buffer layers on large technical substrates," *IEEE Trans. Appl. Supercond.*, vol. 9, pp. 2248-2251, 1999.

[5] D.P. Norton, A. Goyal, J.D. Budai, D.K. Christen, D.M. Kroeger, E.D. Specht, Q. He, B. Saffian, M. Paranthaman, C.E. Klabunde, D.F. Lee, B.C. Sales, and F.A. List, "Epitaxial $YBa_2Cu_3O_7$ on biaxially textured nickel [001]: an approach to superconducting tapes with high critical current density," *Science*, vol. 274, pp. 755-757, 1996.

[6] D. Dimos, P. Chaudhari, and J. Mannhart, "Superconducting transport properties of grain boundaries in $YBa_2Cu_3O_7$ bicrystals," *Phys. Rev. B*, vol. 41, pp. 4038-4049, 1990.

[7] I. Nakamichi, "The electrical resistivity due to grain boundary and the boundary structure," *J. Sci. Hiroshima Univ.*, Ser. A, vol. 54, pp. 49-84, 1990.

[8] W.E. Taylor, N.H. Odell, and H.Y. Fan, "Grain boundary barriers in germanium," *Phys. Rev.*, vol. 88, pp. 867-875, 1952.

[9] See, e.g., Electroceramics VI, Reports of the Electroceramics VI'98, Montreux, Switzerland, 24-27 August 1998, in "*Journal of the European Ceramic Society*," Elsevier Science Ltd., vol. 19, 1999, N. Setter, E. Colla, and D. Damjanovic (editors).

[10] P. Chaudhari, D. Dimos, and J. Mannhart, "Critical currents in single-crystal and bicrystal films," *in Earlier and Recent Aspects of Superconductivity*, ed.: J.G. Bednorz and K.A. Müller, Springer, 1990, pp. 201-207.

[11] N.D. Browning, J.P. Buban, P.D. Nellist, D.P. Norton, M.F. Chrisholm, and S.J. Pennycook. "The atomic origin of reduced critical currents at [001] tilt grain boundaries in $YBa_2Cu_3O_{7-\delta}$ thin films," *Physica C*, vol. 294, pp. 183-193, 1998.

[12] Z. Trybula, J. Stankowski, and J. Baszynski, "Dielectric study of $YBa_2Cu_3O_{7-\delta}$ ceramic in a microwave field," *Physica C*, vol. 156, pp. 485-488, 1988.

[13] S.V. Varyukhin and O. Parfenov, "Changes in the static dielectric constant of $YBa_2Cu_3O_y$ and $PrBa_2Cu_3O_y$ toward the insulator-metal transition," *JETP Lett.*, vol. 58, pp. 101-105, 1993.

[14] D. Reagor, E. Ahrens, S.-W. Cheong, A. Migliori, and Z. Fisk, "Large dielectric constants and massive carriers in La_2CuO_4," *Phys. Rev. Lett.*, vol. 62, pp. 2048-2051, 1989.

[15] J. Mannhart and H. Hilgenkamp, "Wave function symmetry and its influence on superconducting devices," Inst. Phys. Conf. Ser., no. 158, pp. 1-6, 1997.

[16] J. Mannhart and H. Hilgenkamp, "Possible influence of band bending on the normal state properties of grain boundaries in high-T_c superconductors," *Materials Science and Engineering B*, vol. 56, pp. 77-85, 1998.

[17] J. Mannhart, H. Bielefeldt, B. Goetz, H. Hilgenkamp, A. Schmehl, C.W. Schneider, and R.R. Schulz, "Grain boundaries in high-T_c superconductors: insights and improvements," *Phil. Mag.*, vol. B 80, pp. 827-834, 2000.

[18] A. Gurevich and E.A Pashitskii, "Current transport through low-angle grain boundaries in high-temperature superconductors," *Phys. Rev. B*, vol. 57, pp.13878-13893, 1998.

[19] A. Schmehl, B. Goetz, R.R. Schulz, C.W. Schneider, H. Bielefeldt, H. Hilgenkamp, and J. Mannhart, "Doping-induced enhancement of the critical currents of grain boundaries in $YBa_2Cu_3O_{7-\delta}$," *Europhys. Lett.*, vol. 47, pp. 110-115, Apr. 1999.

[20] J.T. Kucera and J.C. Bravman, "Transport characterization of calcium-doped $YBa_2Cu_3O_{7-\delta}$ thin films," *Phys. Rev. B*, vol. 51, pp. 8582-8590, 1995.

[21] P. Chaudhari, D. Dimos, J. Mannhart, and C.C. Tsuei, unpublished (1988).

[22] M. Kawasaki, P. Chaudhari, and A. Gupta, "1/f noise in $YBa_2Cu_3O_{7-\delta}$ superconducting bicrystal grain-boundary junctions," *Phys. Rev. Lett.*, vol. 68, pp. 1065-1068, 1992.

[23] Z.G. Ivanov, E.A. Stepantsov, A.Yu. Tzalenchuk, and T. Claeson, "Properties of locally doped bi-crystal grain boundary junctions," *Physica B*, vol. 194-196, pp. 2187-2188, 1994.

[24] Z.W. Dong, V.C. Matijasevic, P. Hadley, S.M. Shao, and J.E. Mooij, "Electric field effect in bicrystal junctions," *IEEE Trans. Appl. Supercond.*, vol. 5, pp. 2879-2882, 1995.

[25] B. Mayer, J. Mannhart, and H. Hilgenkamp, "Electric field controllable Josephson junctions of high quality in high-T_c superconductors," *Appl. Phys. Lett.*, vol. 68, pp. 3031-3033, 1996.

[26] G.Y. Sung, J.D. Suh, and S.-G. Lee, "Properties of doped-YBCO bi-crystal grain boundary junctions for Josephson field effect transistor," *Physica C*, vol. 282-287, pp. 2475-2476, 1997.

[27] G. Hammerl, A. Schmehl, R.R. Schulz, B. Goetz, H. Bielefeldt, C.W. Schneider, H. Hilgenkamp, and J. Mannhart, "Enhanced supercurrent density in polycrystalline $YBa_2Cu_3O_{7-\delta}$ at 77 K from calcium doping of grain boundaries," *Nature*, vol. 407, pp. 162-164, 2000.

[28] C.W. Schneider, R.R. Schulz, B. Goetz, A. Schmehl, H. Bielefeldt, H. Hilgenkamp, and J. Mannhart, "Tailoring of high-T_c Josephson junctions by doping their electrodes," *Appl. Phys. Lett.*, vol. 75, pp. 850-852, 1999.

[29] H. Hilgenkamp and J. Mannhart, "Superconducting and normal-state properties of $YBa_2Cu_3O_{7-\delta}$–bicrystal grain boundary junctions in thin films," *Appl. Phys. Lett.*, vol. 73, pp. 265-267, 1998.

[30] G.A. Daniels, A. Gurevich, and D. Larbalestier, "Improved strong magnetic field performance of low angle grain boundaries of calcium and oxygen overdoped $YBa_2Cu_3O_x$," *Appl. Phys. Lett.*, vol. 77, pp. 3251-3253, 2000.

[31] H. Hilgenkamp, J. Mannhart, and B. Mayer, "Implications of d_{x2-y2} symmetry and faceting for the transport properties of grain boundaries in high-T_c superconductors," *Phys. Rev. B*, vol. 53, pp. 14586-14593, 1996.

[32] J. Mannhart, H. Bielefeldt, B. Goetz, H. Hilgenkamp, A. Schmehl, C.W. Schneider, and R.R. Schulz, "Doping Induced Enhancement of the Critical Currents of Grain Boundaries in High-T_c Superconductors," *Proceedings of the M^2S 2000, Houston (USA)*, to be published in *Physica C*.

[33] J.H.T. Ransley *et al.*, to be published.

[34] A.H. Sonnenberg, I. Oomen, H. Hilgenkamp, G.J. Gerritsma, and H. Rogalla, "Sigma-Delta Converter in HTS Ramp Edge Technology," submitted to *IEEE Trans. Appl. Supercond., Proceedings of the ASC 2000, Virginia Beach.*