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Angaben zur Veröffentlichung / Publication details:

Hammerl, German, Andreas Schmehl, Robert R. Schulz, Bärbel Götz, Hartmut Bielefeldt, Christof W. Schneider, Hans Hilgenkamp, and Jochen Mannhart. 2000. "Enhanced supercurrent density in polycrystalline YBa₂Cu₃O_{7-δ} at 77 K from calcium doping of grain boundaries." Nature 407 (6801): 162-64.
<https://doi.org/10.1038/35025014>.



Enhanced supercurrent density in polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 77 K from calcium doping of grain boundaries

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With the discovery of high-temperature superconductivity¹, it seemed that the vision of superconducting power cables operating at the boiling point of liquid nitrogen (77 K) was close to realization. But it was soon found that the critical current density J_c of the supercurrents that can pass through these polycrystalline materials without destroying superconductivity is remarkably small^{1,2}. In many materials, J_c is suppressed at grain boundaries²⁻⁴, by phenomena such as interface charging and bending of the electronic band structure⁵⁻⁹. Partial replacement ('doping') of the yttrium in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with calcium has been used to increase grain-boundary J_c values substantially, but only at temperatures much lower than 77 K (ref. 9). Here we show that preferentially overdoping the grain boundaries, relative to the grains themselves, yields values of J_c at 77 K that far exceed previously published values. Our results indicate that grain-boundary doping is a viable approach for producing a practical, cost-effective superconducting power cable operating at liquid-nitrogen temperatures.

The realization that the electronic properties of grain boundaries in high- T_c superconductors are controlled to a large extent by interface charging and band bending⁵⁻⁹ provided the clue to the enhancement of grain-boundary critical current densities by overdoping⁹ (that is, doping the grain boundaries beyond the composition that is optimal for superconductivity in the bulk). Overdoping reduces the built-in potential of the interfaces and increases the carrier density of the superconductors, so that the boundaries' tunnelling barriers are reduced in height and width. By partially replacing Y^{3+} by Ca^{2+} , Schmehl *et al.*⁹ experimentally investigated the effects of doping bicrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films on the intergrain J_c . They found that calcium doping leads to strongly enhanced J_c values at low temperatures. At 77 K, however, the critical current densities were only insignificantly increased, because overdoping not only enhances the grain boundary coupling but also reduces the transition temperature T_c of the superconductors. This T_c reduction counteracts the positive effects the doping exerts on the

grain boundary coupling. To achieve enhanced coupling across the boundaries in combination with a large intragrain T_c value, we sought a way to overdope the superconductors locally at the grain boundaries, while keeping the grains optimally doped. By exploiting grain boundary diffusion, local doping of the boundaries has been tried before, using silver (Chaudhari, P. *et al.*, unpublished work), iron¹⁰ and platinum¹⁰ in experiments which were not designed to reduce charging or band bending. No J_c enhancements were observed in these studies.

To overdope the grain boundaries, we devised doping heterostructures, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ superlattices (Fig. 1a), anticipating that during film growth calcium would diffuse along the grain boundary into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ layers. As the diffusion coefficients in the grains are presumed to be small compared to coefficients for grain boundary diffusion, this process should enhance the Ca concentration at the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries specifically. Therefore these layers were foreseen to have high intergrain J_c values at 77 K, combined with good superconducting intragrain properties. Thus, one material of the heterostructure, in this work $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, was employed to optimize the properties of the bulk, whereas the other compound, $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ was used to improve the characteristics of the grain boundary.

To gain a detailed understanding of the possibilities and limitations

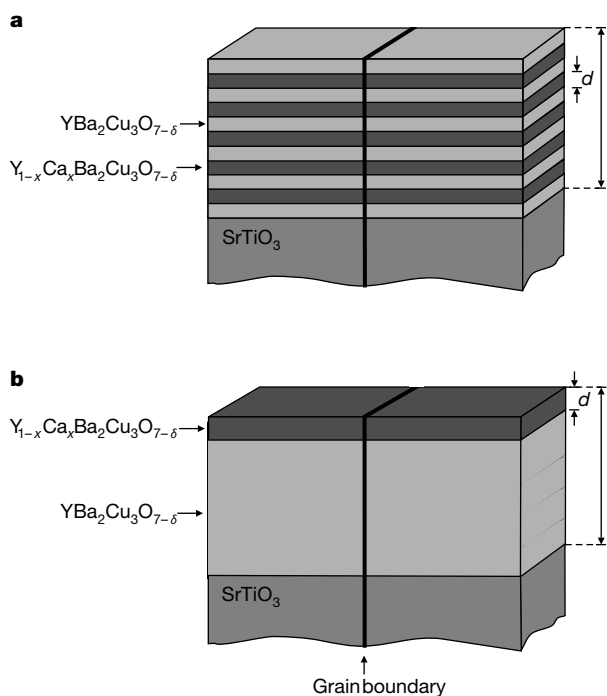


Figure 1 Illustration of the doping superlattices and bilayers investigated. Using standard deposition parameters⁹, the heterostructures and Ca-free control samples were grown within 10 minutes at a heater temperature of 760 °C by pulsed laser deposition on SrTiO_3 bicrystals containing symmetric $24 \pm 1^\circ$ [001] tilt grain boundaries. After deposition, the vacuum system was flooded with 0.4 bar of molecular oxygen, and the samples were cooled during 1 hour to 400 °C. The samples were held for about 20 minutes at this temperature for oxygenation and were then cooled quickly to room temperature (see Fig. 2). To investigate the potential of post-annealing steps to enhance grain boundary diffusion, several of the samples were post-annealed in 0.4 bar of O_2 at about 420 °C for half an hour. These additional anneals changed the sample properties only marginally. By wet etching, superconducting bridges with widths of 5–8 μm and lengths of 20 μm were patterned across the grain boundaries and inside the grains. Measurements at 77 K were done in a liquid nitrogen cryostat. The critical current densities were obtained from the ratios of the critical currents and the cross-sectional areas of the multilayer bridges, all of which were measured by scanning force microscopy. The entire film thickness, not just the thickness of the undoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ layers, was used in calculating J_c .

of doping heterostructures, several multilayer configurations and undoped control samples were investigated, fabricated on symmetric 24° [001] tilt SrTiO₃ bicrystals. In total, about 200 intergrain bridges on 40 substrates were analysed, as well as numerous bridges inside the grains. Details about the investigated configurations and the sample fabrication are given in Figs 1 and 2. To rule out inadvertent Ca doping of the YBa₂Cu₃O_{7- δ} layers, a specially designed deposition system was used for the fabrication of the bilayer samples. This system was composed of two identical deposition chambers, one of which was dedicated to the growth of the Ca-free layers only. To keep this chamber completely free from calcium, separate heaters were used for the two chambers. Therefore, after the first layer was deposited, the samples were cooled to room temperature at 0.4 bar of O₂, the vacuum was broken and the samples mounted onto another heater. To allow *in situ* growth and to limit the number of sample transfers, the trilayers and the superlattices were completely grown in the vacuum-chamber used for the deposition of the Ca-doped samples. In this case, a small amount of residual calcium present in the chamber was expected to be incorporated into the growing films and diffuses partially to the grain boundaries.

As anticipated, all grains except the homogeneously doped ones had critical temperatures above 90 K and critical current densities of approximately 6×10^6 A cm⁻² at 77 K. All grain boundaries showed Josephson-junction type $I(V)$ characteristics with a distinct voltage step at J_c . Therefore, the intergrain critical currents could be unambiguously determined from the current–voltage characteristics, using a voltage criterion of 1 μ V. The characteristic behaviour of the grain boundaries is presented in Fig. 3. This figure displays the $J_c(T)$ -dependencies of four samples: a YBa₂Cu₃O_{7- δ} film, a homogeneously doped Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} film, a bilayer consisting of a 130-nm YBa₂Cu₃O_{7- δ} layer and a 20-nm-thick Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} layer on top as illustrated in Fig. 1b, and a 20-nm Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} /130-nm YBa₂Cu₃O_{7- δ} /20-nm Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} trilayer which had the highest J_c value of all the samples. As expected, the homogeneously doped Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} sample shows a very large critical current density of approximately 7×10^6 A cm⁻² at 4.2 K, but, as the Ca doping depresses its T_c , the sample is not superconducting at all at 77 K. At this temperature, however, the critical current densities of the 24° grain boundaries in the average doping bilayer and in the trilayer have already reached 1.2×10^5 A cm⁻² and 3.3×10^5 A cm⁻², greatly exceeding the J_c value of the undoped sample of 5.5×10^4 A cm⁻². As the T_c of the individual layers doped with 30% Ca cannot exceed 77 K significantly, the supercurrent is presumably flowing completely in the YBa₂Cu₃O_{7- δ} layer, which therefore in the trilayer sample has a net

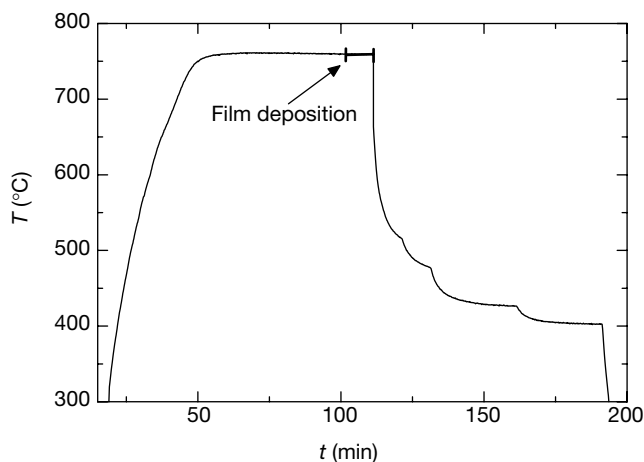


Figure 2 Measured temperature sequence of the substrate heater block used for the growth of the doping trilayers and superlattices.

critical current density of approximately 4.3×10^5 A cm⁻² (77 K). These current densities equal those usually reported for 24° grain boundaries in YBa₂Cu₃O_{7- δ} films at 4.2 K (ref. 7) and are an order of magnitude larger than other 77 K data^{3,4}. Clearly, by combining the Ca-doped and the Ca-free films, both characterized by a small J_c value at 77 K, a multilayer system with an unprecedentedly high J_c has been obtained. The enhancement of the grain boundary J_c in comparison with the homogeneously doped samples occurs above a crossover temperature T^* , which is dependent on the sample design. For the bilayer and trilayer samples shown in Fig. 3, the crossover temperatures are 57 K and 52 K, respectively. We note that for any temperature a doping heterostructure exists which yields J_c values surpassing those of pure YBa₂Cu₃O_{7- δ} .

To investigate the influence of the multilayer configuration on the J_c enhancement, several variations of the heterostructures were explored. First, bilayers with a total thickness t of 150–160 nm were fabricated and their J_c values measured as a function of the thickness d of the Ca-doped top layer. Figure 4 shows the critical current densities of the 85 superconducting bridges, with the error bars displaying the σ -spread of all samples fabricated. The values of d are given with an accuracy of 10%. The critical current density displays a maximum as a function of the top layer thickness and is enhanced by a factor of two for $d \approx 20$ nm. The J_c enhancement is smaller for thicker top layers, presumably because of the excessive doping. In addition to the overdoped samples, the J_c values of YBa₂Cu₃O_{7- δ} /YBa₂Cu_{2.9}Co_{0.1}O_{7- δ} bilayers were also plotted in Fig. 4. Substitution of Cu by Co causes underdoping, and, as we expected, we measured a reduction of the critical current density.

Bilayers for which both t and d were scaled up by a factor of two display almost the same J_c increases achieved by standard bilayers. Likewise, after performing a post-anneal step, the bilayer J_c increased by only 3% at best. If the bilayer sequence was reversed, so that the undoped film was grown on top of the Ca-doped one, much smaller J_c enhancements were observed. Large critical current densities, however, have been obtained in superlattices. Superlattices, consisting of five and a half pairs of bilayers as sketched in

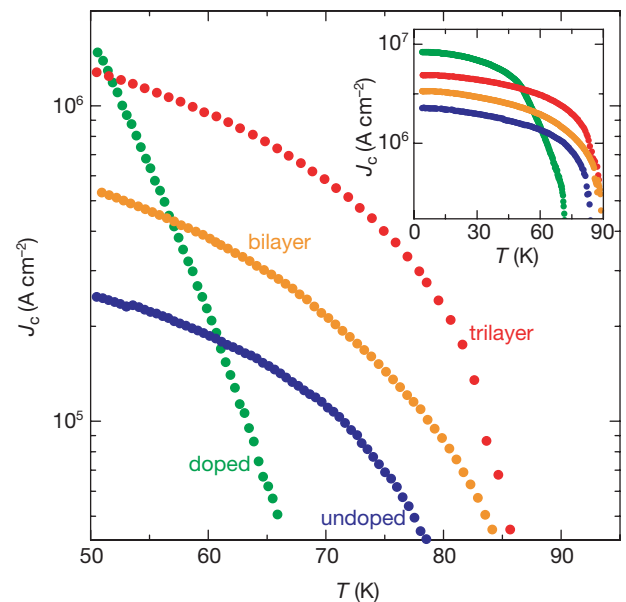


Figure 3 Temperature dependence of the critical current densities J_c of grain boundaries with various doping configurations, indicating the strong enhancement of J_c in doping heterostructures. Displayed are the $J_c(T)$ dependencies of symmetric 24° [001] tilt grain boundaries in various bicrystalline samples: a YBa₂Cu₃O_{7- δ} film (undoped), a Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} film (doped), a YBa₂Cu₃O_{7- δ} /Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} bilayer with a J_c value typical of such bilayers, and a Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} /YBa₂Cu₃O_{7- δ} /Y_{0.7}Ca_{0.3}Ba₂Cu₃O_{7- δ} trilayer with an excellent critical current density.

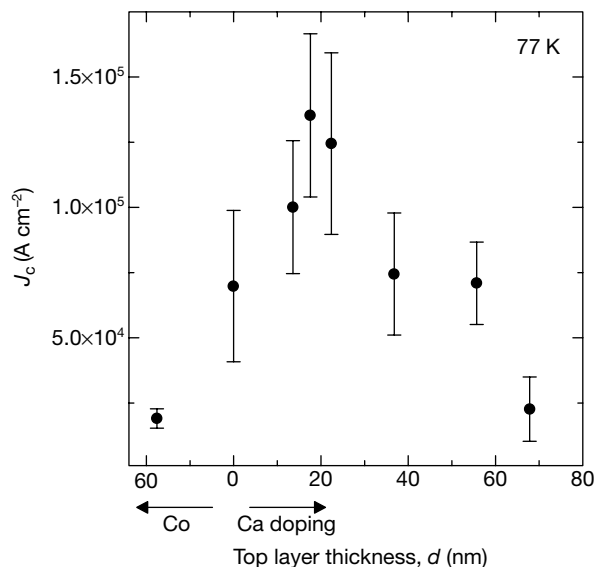


Figure 4 Dependence of the grain boundary critical current density J_c on the thickness of the doped top layer in doping bilayers. The figure shows the critical current density of 24° symmetric [001] tilt grain boundaries in doping bilayers about 160 nm thick at 77 K, plotted as a function of the thickness d of the doping top layer. On the right side of the figure, the data from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ bilayers are plotted. On the left side the data from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{YBa}_2\text{Cu}_{2.9}\text{Co}_{0.1}\text{O}_{7-\delta}$ bilayers are shown. For the Co-doped samples the scale of the x -axis is compressed by a factor of three.

Fig. 1a, achieve critical current densities of $1.6 \times 10^5 \text{ A cm}^{-2}$ at 77 K for $x = 0.1$, $d = 25 \text{ nm}$, and a periodicity of 50 nm.

For several samples, the dependence of the critical current on the applied magnetic field H , oriented parallel to the c -direction of the films, was measured. The maximum fields applied were $250 \mu\text{T}$. All samples showed the $I_c(H)$ dependencies expected for 24° grain-boundary Josephson junctions.

For the large-scale fabrication of coated-conductor-based superconducting cables, techniques such as ion beam assisted deposition (IBAD)^{11–13} or the rolling assisted biaxially aligned substrate process (RABITS)¹⁴ are being developed in order to enhance J_c by providing an optimal alignment of the grains^{2,3}. It is extremely desirable to lessen the required accuracy of the grain alignment. The use of doping heterostructures, which can easily be incorporated into these processes, may achieve this goal, as it presents a way of extending the established grain-boundary-angle-dependent limits on the critical current densities at 77 K (refs 2, 3). We anticipate that this will indeed be the case, considering that interface-charging and band-bending play an important role for small-angle grain boundaries as well^{8,9}.

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Acknowledgements

We are grateful for valuable discussions with D. G. Schlom. This work was supported by the Bundesministerium für Bildung und Forschung, H.H. thanks the Royal Dutch Academy of Sciences for its support.

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