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Interfaces in high-T_c superconductors: fundamental insights and possible applications ☆

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1. Introduction

The enhancement of grain boundary critical current densities is a challenge and the 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 [1] and (b) to increase the critical current 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.

2. Mechanisms of charge transport

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 [2]. 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 [3]. 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 [4].

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The presence of charges at grain boundaries in high-T_c superconductors has been considered early on [5], 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 [6].

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. [7,8]). 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 space-charge layers formed inside the grains close to the grain boundaries, over a distance given by the electrostatic screening length of the grains [9–11]. 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. 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 given by the Wisconsin group [12], and an illustration of the band bending phenomena is shown in Fig. 1 (from [11]).

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+} [13]. This substitution is known to overdope the superconductor [14], 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 [13].

To verify the ideas doping could have on the electronic the transport properties of grain boundaries, bicrystalline

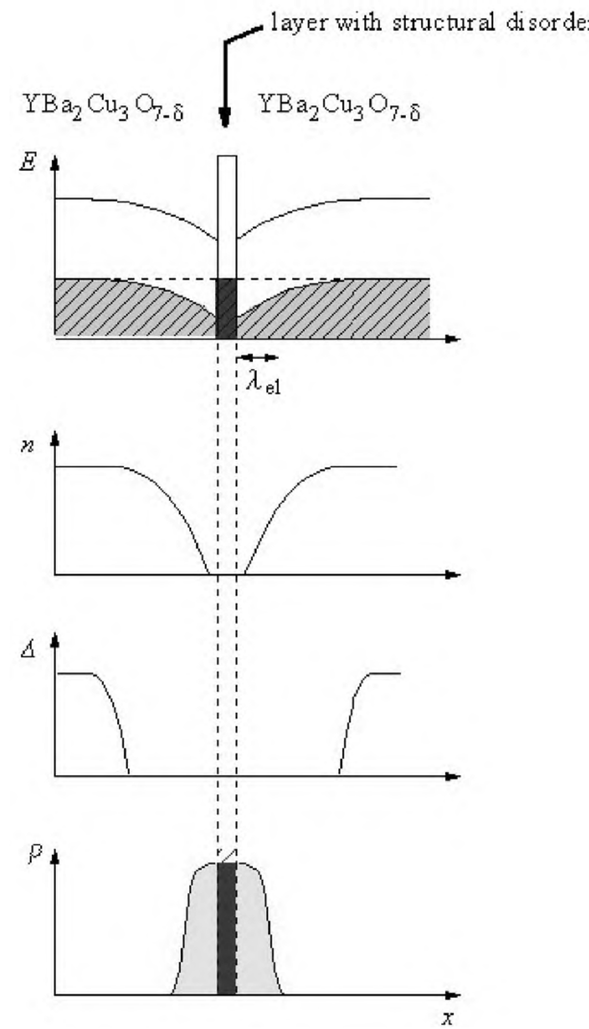

Fig. 1. Possible scenario for bending of the electronic band structure of high-T_c cuprates at a grain boundary. In the example shown, at the grain boundary interface depletion layers are formed, which cause a depression of the order parameter and a transition of the cuprate into the insulating state in the region close to the interface (from [11]).

thin films have been prepared using $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ ($x = 0.02$–0.4) and $YBa_2(Cu_{3-x}Co_x)O_{7-\delta}$ targets as well as undoped $YBa_2Cu_3O_{7-\delta}$ as reference.

3. Sample preparation

Using standard deposition parameters [13], samples were grown within 10 min at a heater temperature of 760°C by pulsed laser deposition (PLD) on $SrTiO_3$ bicrystals containing symmetric $24 \pm 1°$ [0 0 1] tilt grain boundaries. After deposition, the vacuum system was flooded with 0.4 bar of molecular oxygen, and the samples were cooled during 1 h to 400°C. Having held the samples for about 20 min at this temperature for oxygenation, they were cooled quickly to room temperature. By wet etching, superconducting bridges with widths

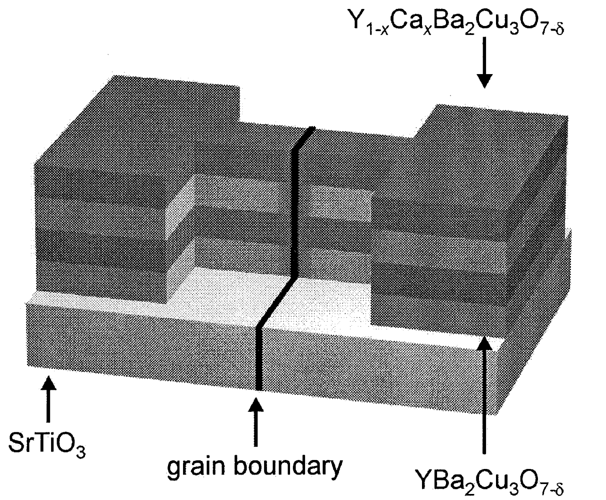

Fig. 2. Illustration of the local doping of grain boundaries intended by the use of grain boundary diffusion in doping heterostructures.

ranging between 5 and 8 μm and lengths of 20 μm were patterned across the grain boundaries and inside the grains. 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.

4. Experimental results

For 24° [0 0 1]-tilt grain boundaries it was found that with increasing Ca content, J_c increases to values as high as 6.6×10^6 A/cm^2 for $x = 0.3$, and the normal-state resistivity decreases to values as small as 2.5×10^{-10} Ω cm^2. As shown by Ransley et al. [15], this doping also causes an enhancement of the grain boundary capacitance, as expected from the band bending model. Ca-induced enhancements of J_c were also found for 5° boundaries by Daniels et al. [16], and for 4° and 8° boundaries by Guth et al. [17]. The enhancements observed in these studies reach about a factor of two, reflecting the larger current densities of grain boundaries with smaller misorientation angles.

As the doping of $YBa_2Cu_3O_{7-\delta}$ with Ca reduces the T_c of the superconductor, it is obviously desirable to selectively overdope the grain boundaries while keeping the grains optimally doped. To achieve this goal, we tried to overdope the superconductors specifically at the grain boundaries [18].

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. 2). 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 [18].

Indeed, measurements, performed at 24° [0 0 1]-tilt grain boundaries in $YBa_2Cu_3O_{7-\delta}$ bicrystalline films

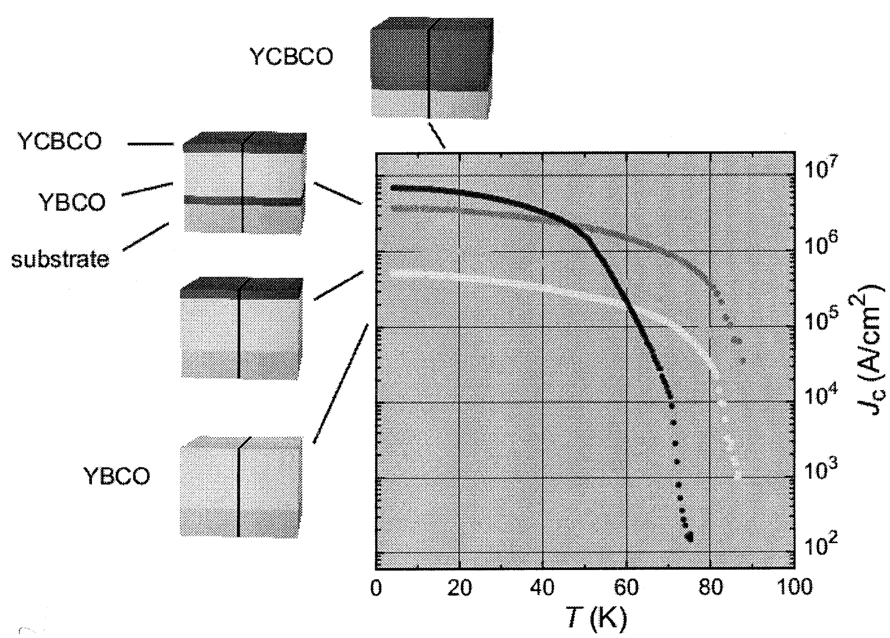

Fig. 3. Temperature dependence of the critical current density of 24° grain boundaries in various films and heterostructures: a $YBa_2Cu_3O_{7-\delta}$ film (YBCO), a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ film (YCBCO), a $YBa_2Cu_3O_{7-\delta}/Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ bilayer with a J_c typical for such bilayers, and a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}/YBa_2Cu_3O_{7-\delta}/Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ trilayer with the best J_c (77 K) observed in this study (after [18]).

with various layer configurations, showed strong enhancements of J_c at all temperatures up to T_c. This is shown in Fig. 3. These enhancements were also observed in large magnetic fields. Although the doped 24° grain boundaries still act as Josephson junctions, for doping trilayers critical current densities of 1.1×10^4 A/cm^2 were measured at 77 K in fields of 1 T applied in the grain boundary plane, as compared to J_c-values of 2.5×10^3 A/cm^2 for undoped sister samples.

Comparable to the case of semiconducting electronics, doping introduces a spectrum of possibilities to modify interfaces in superconductors. Doping heterostructures were reported, e.g., to reduce the surface resistance R_s of $YBa_2Cu_3O_{7-\delta}$-samples [19]. Further, doping effects may be optimized by altering the doping materials. Instead of calcium, other doping elements, or even combinations of various dopants, may be utilized. Also, Y may be replaced by a rare earth element, which due to 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 doping elements or their concentration can be varied across the surface of the chip or between layers in multilayer structures [20].

The use of doping multilayers is seen as a promising approach to further optimize the coated conductor technologies. The application of multilayers may allow to relax the requirements on the grain alignment processes and may also enhance the critical current densities. As state-of-the-art coated conductors have already excellent J_c-values, well exceeding 10^6 A/cm^2 at 77 K in self-field, expectable J_c enhancements are obviously considerably smaller than the ones shown by 24° grain boundaries.

To investigate the possibility to combine doping multilayers with coated conductors, first doping multilayers on RABiTS samples have been grown as sketched in Fig. 4.

The substrates and the buffer layers were fabricated at the Oak Ridge National Laboratory and the doping multilayers were grown at the University of Augsburg. The processes were found to be compatible with each other, yielding at 77 K self-field critical current densities of 2×10^5–2×10^6 A/cm^2 for current flow across grain boundaries, and up to 7×10^6 A/cm^2 for intragranular transport. In all these cases, the $YBa_2Cu_3O_{7-\delta}$ films were 120–150 nm thick.

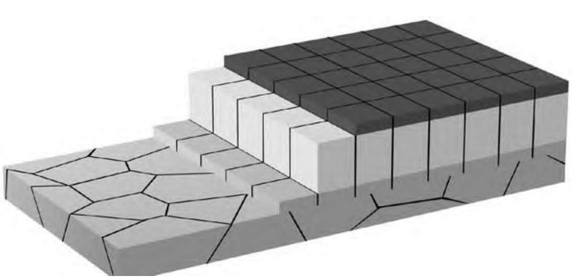

Fig. 4. Drawing of the multilayer arrangement under study to enhance the critical current density of RABiTS samples. On top of a standard RABiTS configuration, a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ film is deposited to enhance the grain boundary J_c in the underlying $YBa_2Cu_3O_{7-\delta}$ film.

5. Summary

In 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 in bicrystalline samples and have found it to be a powerful approach for their optimization. First studies on doping multilayers grown on RABiTS samples suggest doping to be a promising tool to optimize coated conductors.

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