Electromagnetic and microstructural properties of pure c-axis twist $Bi_2Sr_2CaCu_2O_{8+\delta}$ bicrystal junctions

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ABSTRACT

Bulk $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) bicrystals containing a single high quality [001] twist grain boundary junction were prepared in order to investigate the orbital symmetry of the superconducting order parameter in highly anisotropic Bi-based high temperature superconductors. The misorientation angles of the bicrystals ranged from 0° to 180°. The microstructure in the vicinity of the junction was characterized using high-resolution, nano-probe analytical microscopy. We found that some high angle twist junctions were able to carry a critical current density similar to their constituent single crystals. These results cannot be interpreted in terms of a pure $d_{x^2-y^2}$-wave order parameter for superconducting Bi2212.

Keywords: Bicrystal, $Bi_2Sr_2CaCu_2O_{8+\delta}$, c-axis twist, Josephson junction, critical current, misorientation angle

1. INTRODUCTION

The orbital symmetry of the superconducting order parameter in the high temperature superconductors has been one of the most debated issues in recent years. Though many experiments[1-3] were interpreted in terms of a pure $d_{x^2-y^2}$-wave order parameter, a convincing proof by direct measurements of ac and dc Josephson effects is still lacking. So far, most of the experiments were performed on $YBa_2Cu_3O_{7-\delta}$ (YBCO), where strong in-plane anisotropy due to the conducting CuO chains may complicate the interpretation. On the other hand, experimental investigations of the order parameter symmetry in Bi-based system by means of phase-sensitive techniques are quite limited and inconclusive. It is well known that Bi-based system, like $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212), is another important group of high temperature superconductors. A nearly tetragonal lattice structure of Bi2212 has much less in-plane anisotropy than that of YBCO, which is a significant advantage for phase-sensitive measurements. One other important difference between Bi2212 and YBCO is the anisotropy along the a- and c-axis. In Bi2212, the coherence length along the c-axis is of the order of 0.1 nm. This is much less than the interlayer spacing between the CuO double layers (1.5 nm). Therefore, Bi2212 can be described as a stack of discrete superconducting layers whose order parameters are coupled by Josephson interaction. This long series of Josephson junctions consists of superconducting CuO double layers separated by the BiO and SrO layers acting as weak links. This layered structure provides great opportunities to make direct observation of intrinsic dc and ac Josephson effects when the current is driven across the layers.[4, 5]

The superconducting order parameter symmetry in Bi2212 can be directly probed by measuring the Josephson tunneling effect across c-axis twist junctions consisting of two identical Bi2212 single crystals. In the case of a pure $d_{x^2-y^2}$-wave order parameter, Josephson critical current across the junction strongly depends on the misorientation (or twist) angle. It is expected that the normalized value of Josephson critical current across the junction decreases monotonically from 1 to almost zero as the twist angle increases from 0° to 45°. This is in a striking contrast to the case of a pure s-wave superconductor, where Josephson critical current across the junction is independent of the twist angle. Klemm, *et. al.*[6] recently made a detailed calculation on the angular dependence of the Josephson critical current in c-axis twist junctions of high temperature superconductor with both s- and d-wave types of order parameter symmetry.

In the present study, we have made direct measurements of Josephson critical current across a series of pure c-axis twist junctions. Each junction is the grain-boundary of a bulk bicrystal, and was prepared in a solid state sintering process from a piece of single crystal. The misorientation angles of the bicrystals ranged from 0° to 180°. We have devoted a significant effort to the structural characterization of the grain-boundary to assess the quality of the junctions. Our detailed structural investigation of five different bicrystals revealed a perfectly defined junction interface on the atomic scale. These extremely

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high quality c-axis twist junctions made it possible for us to observe a pronounced dc Josephson effect. We found that some high angle twist junctions were able to carry a critical current density similar to their constituent single crystals, an observation cannot be interpreted in terms of a pure $d_{x^2-y^2}$-wave order parameter.

2. EXPERIMENTALS

The key to the success in preparing high quality twist grain-boundary junctions is the quality of the starting single crystals. In this work, the c-axis twist bicrystal grain boundaries were prepared from extremely high quality Bi2212 single crystals grown by the traveling solvent floating zone technique.[5] Selected single crystals have a rectangular shape with a length of 4.1 mm along the a-axis, ~ 2-3 mm along the b-axis, and ~ 0.2-0.6 mm along the c-axis. No trace of plane or line structural defects, such as edge dislocation, stacking fault, intergrowth, were found in these single crystals examined in both conventional and high resolution transmission electron microscopy. The single crystals were first cut and cleaved into smaller pieces with a similar size of 0.3-0.6 mm along a- or b-axis and 30-100 μm along the c-axis. The bicrystal samples were made by cleaving each sub-divided single crystal along the a-b plane into two similar pieces. One piece was rotated a desired angle about the c-axis, then placed atop the other. This process was performed in air, and normally took only a few seconds. Special care had been taken during the cleavage to ensure the fresh cleaved surfaces have no steps in the junction area, which were regularly checked in both optical and electron microscopes. A c-axis twist grain boundary was formed by sintering the sample at high temperatures a few degrees below the melting of Bi2212 crystals for 30 hours. We have sintered the bicrystals in air and in controlled oxygen partial pressure environment. The strength of the bonding at the grain boundaries does not seem to be affected. The actual bicrystals studied in this paper were sintered at 865°C for 30 hours in 7.5% O_2 (balance N_2) at ambient pressure. This process produces excellent twist boundaries at near 100% successful rate. The sintering process at the partial O_2 environment results in oxygen over-doped Bi2212 bicrystals with the superconducting transition temperature T_c of the crystals around 80 K. Annealing the bicrystals at 575°C in Ar for 2 hours followed by a fast quench can bring the bicrystals to optimal doping level with T_c around 90 K.

Fig. 1 shows an optical micrograph of a typical 45° c-axis twist bicrystal with the six-probe configuration used for transport measurements. The common c-axis is perpendicular to the flat surface of the bicrystals. The overlapped area between

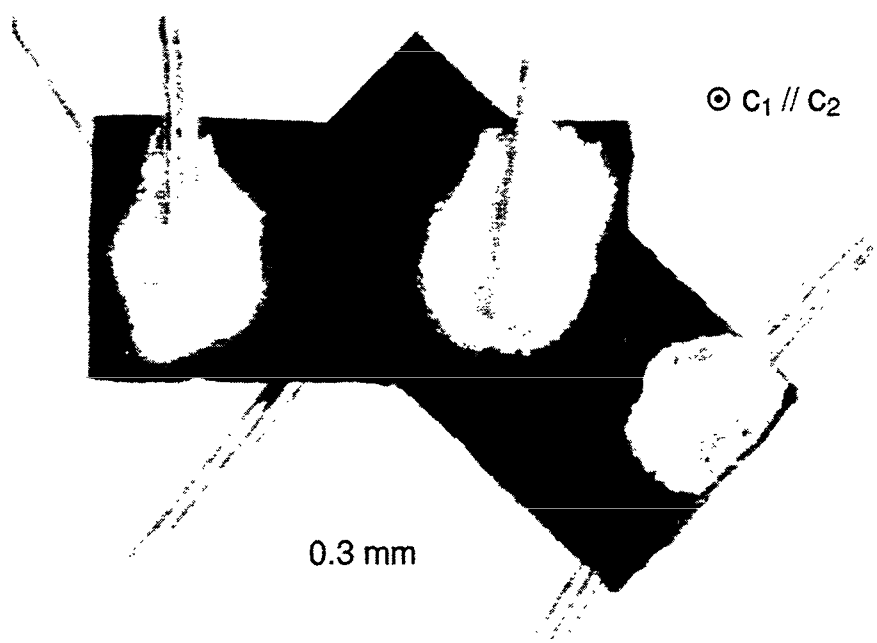

Fig. 1 An optical micrograph of a 45° c-axis twist bicrystal and the six-probe configuration used for measuring dc Josephson effect along the common c-axis

two single crystals is normally taken as the cross-section of the twist junctions. In this case, the junction area is calculated to be around 0.1 mm^2, one half of the cross-section area of the single crystal along the c-axis.

Fig. 2 shows a schematic of the side-view of a bicrystal and electrical leads arrangements. Electrical contacts were made by first sputtering six silver pads (~ 1 μm thick) on both sides of the bicrystal surface with subsequent annealing in pure oxygen at 570°C for about 10 min. 0.002'' gold wires were attached to these silver pads with silver-loaded epoxy, and cured on a hot plate. This method usually resulted in a contact resistance of 1 Ω or less.

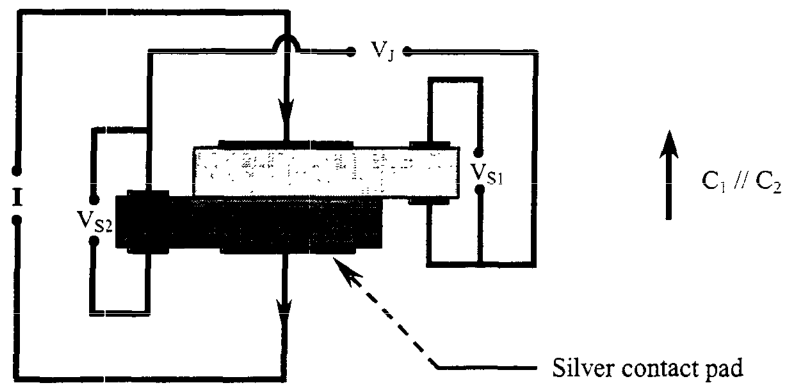

Fig. 2 A schematic of the side-view of a bicrystal and electrical leads arrangements

Current was fed along the common c-axis as shown in Fig. 2. Two pairs of voltage contacts were placed on both sides of each single crystal, while junction voltage was measured by the voltage leads from the *bottom* surface of the *top* single crystal and *top* surface of the *bottom* single crystal. This configuration permitted us to measure the resistance and the voltage-current (*V-I*) characteristics of the grain boundary junction (V_J) and of their constituent single crystals (V_{S1} and V_{S2}) simultaneously for a direct comparison. For *V-I* measurements at low current level, dc-currents were supplied by a bi-polar dc current source (HP 6825 A). dc-voltages were measured over six orders of magnitude with a resolution of 1 nV using a combination of a Keithley 2001 multimeter and a Keithley 1801 nanovolt preamplifier. At high current levels, a programmable bi-directional pulse current source was used to avoid self-heating. A pulse of 50 - 200 ms width was followed by a few second time interval before the next current pulse. Voltages were measured over six order of magnitude with a resolution of 10 nV, and averaged for both current directions several times to eliminate thermal EMF.

The transport measurements were performed in an exchange-gas cryostat equipped with a 9 T superconducting magnet, where temperature can be controlled within an accuracy of 0.01 K between 2 and 350 K. Magnetic fields can be applied either along the common c-axis of the bicrystals, or along the ab-plane of the single crystal.

3. MICROSTRUCTURE OF C-AXIS TWIST GRAIN BOUNDARY JUNCTIONS

The microstructure of these twist grain-boundary junctions was carefully characterized using advanced transmission electron microscopy (TEM), including 0.17 nm high-resolution imaging (HRTEM), electron energy-loss spectroscopy (EELS), and energy dispersive x-ray spectroscopy (EDS) with a 2 nm field-emission probe. Because of the relatively low success rate in cross-sectional TEM sample preparation using a dedicated mechanical polishing technique that provides a large area of view of the sample, five bicrystal junctions was examined. The TEM cross-sections were prepared in such a way that the a-axis of both crystals could be tilted parallel to the incident beam sequentially to reveal a two-dimensional image of the crystal superlattice (0.54×2.7×3.1 mm^3) over a length scale of tens of microns along the junction planes.

Figure 3(a)-3(c) are the HRTEM images from one of these structurally characterized bicrystals. The 37.45° misorientataion angle was measured using Kikuchi patterns. To examine the boundary structure at an atomic level, we first individually titled the a-axis of the top crystal along the incident beam, as shown in Fig 3(a), to examine its two-dimensional image of crystal lattice. Then, we tilted the a-axis of the bottom crystal along the incident beam, as shown in Fig 3(b), to examine its crystal lattice. Afterwards, we tilted both crystals off any major zone axis, as shown in Fig. 3(c), to measure possible lattice expansion along the c-axis and the interplanar distance of BiO double layer. From these structural images of the boundary, we concluded that there is little lattice distortion in its vicinity. The layered crystal structure is well ordered up to the boundary plane on an atomic scale. The superlattice, seen as a body-centered black-cage-like pattern, is essentially undisturbed by the grain boundary.

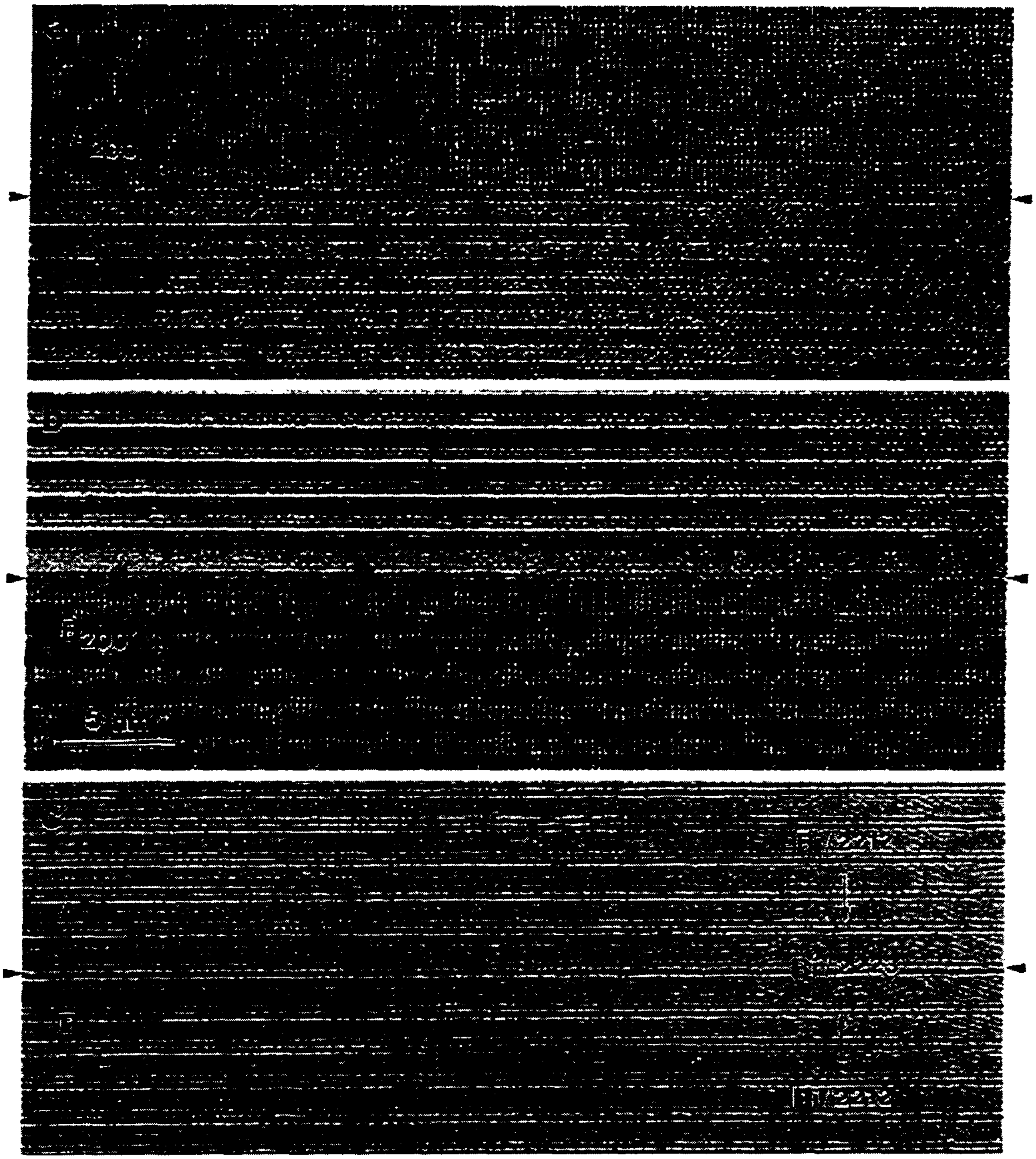

Fig. 3 (a)-(c): High resolution TEM images of the same area from a 37.45° twist grain boundary junction, with the boundary position marked by a pair of arrowheads. (a) The top crystal is viewed along the a-axis. (b) The bottom crystal is viewed along the a-axis. (c) Both crystals are viewed off any low-index zone. Note that the narrowly spaced doubled dark lines in (c) are the lattice image of the double BiO layers.

EDS and EELS with a 2 nm field-emission probe were also performed on these bicrystal boundaries to evaluate the concentration variation of cations and oxygen, respectively, at the boundary regions. The analysis of the oxygen K edge using EELS is particularly useful since it can directly reveal local hole concentration.

Based on our detailed TEM characterizations for five bicrystals with various misorientations, the structural features of the boundaries are summarized as following.[8] (1) All the boundary planes are microscopically flat, suggesting they are pure twist in character. (2) The boundaries are clean and structurally intact without any visible amorphous materials. (3) EDS and EELS measurements show that there is no detectable off-stochiometric composition including oxygen/hole concentration along and across the boundaries. (4) HRTEM image simulation reveals that, without exception, the boundaries are located in the middle of the double BiO layers. (5) There is no detectable boundary expansion. The interplanar distance of the double BiO layer measured with line scan at the boundary is the same as those far from the boundary, within measurement error. (6) Often, there is an intercalation of Ca/CuO_2 bilayer near the boundary, either on one, or both sides, forming a local Bi2223 structure of half unit cell. Further details can be found in Ref. 8-10.

4. SUPERCONDUCTING PR0PERTIES

The c-axis resistivity ρ_c of single crystal in our bicrystal junctions depends on the post-annealing conditions. At room temperature, ρ_c ranged between ~ 2 Ωcm for partial oxygen annealed samples to ~ 15 Ωcm for Ar annealed samples, while critical current density j_c at 5 K ranged from ~ 1200 A/cm^2 to ~ 200 A/cm^2 and T_c ranged from ~ 80 K to ~ 91 K, respectively. All these values are similar to the published data by other groups.[4, 5] The lowest value of ρ_c of the single crystal among all our samples near T_c is ~ 0.6 Ωcm.

A direct measurement of junction resistance in the normal-state is not possible for this specific configuration. Primarily, this is due to the possible diffusion of silver into the crystal at the voltage contact, and the huge resistivity anisotropy of Bi2212, which distorts current distribution from perfectly along the c-axis. Small ab-plane current flow in the normal-state is unavoidable. Nevertheless, we made the following estimate of the lower limit of the junction resistance R_n by using the c-axis resistivity of the single crystals. The parameters used are: the junction cross-section area ~ 0.1 mm^2, the junction width taken to be 1.5 nm (the separation of the double CuO layers), the lowest measured normal-state ρ_c for the single crystal ~ 0.6 Ωcm. Using these values, the lower limit of R_n for the c-axis twist junctions is ~ 0.07 mΩ. At a current of 100 mA (normally used for V-I curves measurement), the voltage drop across the junction, if driven into the resistive state, would be ~ 7 μV, which is at least two orders of magnitude higher than our voltage resolution and noise background. Even if one takes the thickness of the junction insulating layer to be the double BiO layers (0.35 nm), the expected voltage will be of a few μV. This simple estimate shows that the relatively large junction area and very short length of the grain boundary should not affect the accuracy of our critical current measurements.

The measurement of V-I characteristics of the bicrystal junctions has been very carefully performed, particularly for the constituent single crystal part. The value of the c-axis critical current observed in some of these single crystals can reach well over 1.0 Amperes at low temperatures. At this high level of dc current, the junctions easily burn out when the single crystal is driven to the resistive state, with resistance ranging from 0.1 Ω to 2 Ω. Relatively high resistance of our single crystals is due to the thickness of crystals (30 ~ 60 μm along the c-axis) used in the junctions. These single crystals are much thicker than those normally used by other groups, but this is necessary to prevent crystal bending at high sintering temperatures during the formation of the grain-boundary junction. It is precisely this sample heating effect that limited our V-I characteristics measurement on most of the bicrystals, given the present aspect ratio, on the temperature region 10-20 K below T_c at zero field. Further reduction in the cross-section may be necessary to measure the V-I characteristics of all samples at full temperature scale.

A typical set of V-I characteristics of a 45° twist grain-boundary junction and one of its constituent single crystals is shown in Fig. 4a. This particular bicrystal, with dimensions similar to the one shown in Fig. 1, was post-annealed in Ar. The superconducting onset T_c is 90 K, and transition width $\Delta T_c \approx 1.8$ K. The relatively broad transition width is believed to be the result of short-time oxygen annealing for the silver contact pads. This was confirmed by the magnetization measurements of the bicrystals in the same batch using SQUID magnetometer before the contact sputtering. The magnetic measurement showed the same T_c, but $\Delta T_c \approx 0.7$ K. The data shown in Fig. 4 were taken at 80 K and zero field. Increasing the bias current beyond I_c leads to a sharp voltage jump. A protective voltage limit was used in the measurement of V-I characteristics of the single crystals to prevent the junction being destroyed by the Ohmic heating once the single crystal was driven normal. Hence, for this particular bicrystal, the resistive part of V-I curve for the single crystal was not taken at this temperature, and is absent in Fig. 4. At higher temperatures, ~ 86 K where the critical current was much lower, the full V-I characteristics for the single crystal were measured. Hysteresis is generally observed for both the junction and the single crystals at lower temperatures. As temperature increases, the hysteresis decreases, and disappears at temperatures above 83

K for this bicrystal. The *V-I* characteristic of this c-axis twist junction, depicted in Fig. 4(a), is a type of SIS Josephson tunnel junction.

Fig. 4(b) displays a log-log plot of the same data shown in Fig. 4(a), together with the *V-I* characteristic of the same single crystal obtained at superconducting onset temperature 90 K. The voltage jump for the junction is over four orders of magnitude. The normal-state resistance of the single crystals at T_c is 1.2 Ω. The thickness of this single crystal is around 40 μm corresponding to a stack of approximately 26000 intrinsic Josephson junctions. Thus, the normal-state resistance of each individual intrinsic junction inside the single crystal is approximately 50 μΩ. However, the twist junction dynamic resistance estimated from the resistive branch of the *VI*-characteristic is in the order of mΩ-10 mΩ. For the time being, we can not rule out the possibility that a few intrinsic junctions near the grain-boundary within the single crystal was also driven to the resistive state at the same time as the twist junction became resistive.

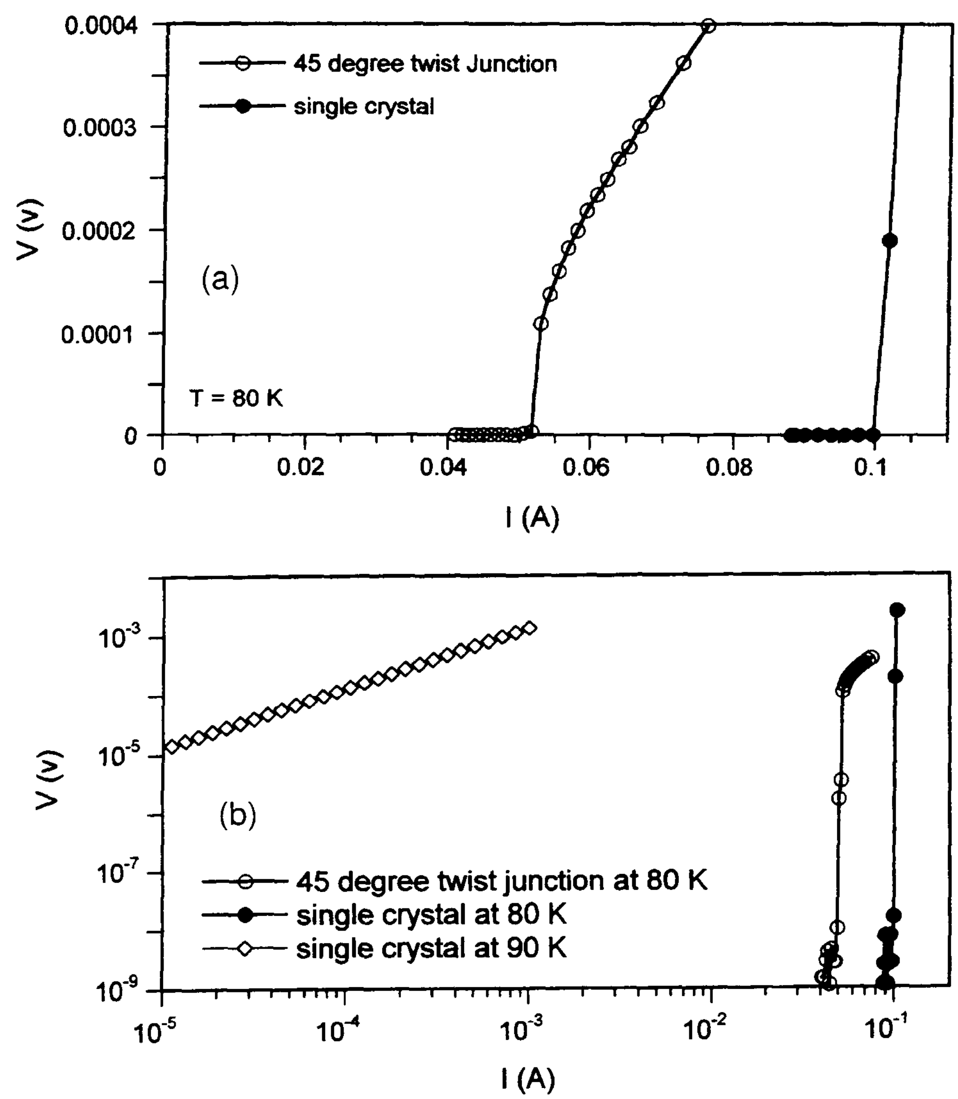

Fig. 4 (a) a set of *V-I* characteristics of a 45° twist grain-boundary junction and one of its constituent single crystals at T = 80 K. (b): The same data plotted in log-scale. Also shown is the *V-I* characteristic of the single crystal obtained at superconducting onset temperature 90 K.

image taken near the twist boundaries shows that the bonding-length of double Bi-O planes at the boundary is the same as those in single crystals. Furthermore, no significant structural disorder along the basal-plane was observed across the interface. This microstructure at the grain boundary junction suggests that the array of Josephson junctions continues uninterrupted from one single crystal across the grain boundary to the next single crystal, with no change of the coupling strength due to the in-plane rotation of the Cu-O double layers.

5. CONCLUSIONS

In summary, Bi2212 bicrystals with high quality c-axis twist grain boundary junctions were successfully prepared. We observed the same critical current density across the 45° twist junction as the intrinsic c-axis critical current density in the constituent single crystals. Furthermore, I_c for both the twist junction and the intrinsic junctions depends linearly on $(1-T/T_c)$ near T_c. These results were found in both optimal and in overdoped bicrystal junctions. This observation cannot be interpreted in terms of a pure $d_{x^2-y^2}$-wave order parameter for Bi2212 superconductors. The sample heating at high current level limited our present studies to relatively high temperature region. By further reduction of the cross-section area of the single crystals, we may eventually be able to directly probe the low temperature pairing state of Bi-system in the future.

6. ACKNOWLEDGEMENTS

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