Effects of Oxygen Stoichiometry on the Scaling Behaviors of $YBa_2Cu_3O_x$ Grain Boundary Weak-Links

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Abstract

The effects of oxygen stoichiometry on the transport properties of the pulsed laser deposited $YBa_2Cu_3O_x$ bicrystalline grain boundary weak-link junctions were studied. It is found that not only the cross boundary resistive transition foot structure can be manipulated repeatedly with oxygen annealing processes but the junction behaviors are also altered in accordance. In the fully oxygenated state i.e with x = 7.0 in $YBa_2Cu_3O_x$ stoichiometry, the junction critical current exhibits a power of 2 scaling behavior with temperature. In contrast, when annealed in the conditions of oxygen-deficient state (e.g with x = 6.9 in $YBa_2Cu_3O_x$ stoichiometry) the junction critical current switches to a linear temperature dependence behavior. The results are tentatively attributed to the modification of the structure in the boundary area upon oxygen annealing, which, in turn, will affect the effective dimension of the geometrically constrained weak-link bridges. The detailed discussion on the responsible physical mechanisms as well as the implications of the present results on device applications will be given.

1. Introduction

Since the first demonstration of Dimos et al. [1], the YBCO bicrystalline grain boundary weak-link (GBWL) junctions have become one of the most extensively studied fields in high T_c superconductivity researches. From the practical application point of view, such an extensive effort makes the GBWL the most successful structure in superconducting electronic devices realized to-date [2-6]. Even for the step-edge type junction devices developed later with the aid of rapidly maturing deposition techniques [7-9], the basic physics involved were all, at least to some extent, originated from the understanding acquired through the studies on GBWLs. However, despite the successes obtained along this line, there exist many fundamental issues to be clarified. For instance, the low frequency *1/f* noise exhibited in most superconducting quantum interference devices (SQUID) made of GBWLs were tremendous and were believed to be due to either the trapping and detrapping processes of charges situated at the localized states existing in oxygen-depleted regions of about 1 nm thick near the grain boundaries or due to the motion of fluxons trapped in the boundary area. On the other hand, in the step-edge type junctions, the critical current-normal resistance product (I_cR_n product), which determines the detection sensitivity of the devices, were usually too low as compared to the predicted superconducting energy of gaps of the materials [10-13]. As a result, a thorough understanding on the nature the GBWLs and to find a way of manipulating their properties in a fully controllable manner are undoubtedly the most important task to be surmounted if further improvements in devices of this kind are considered.

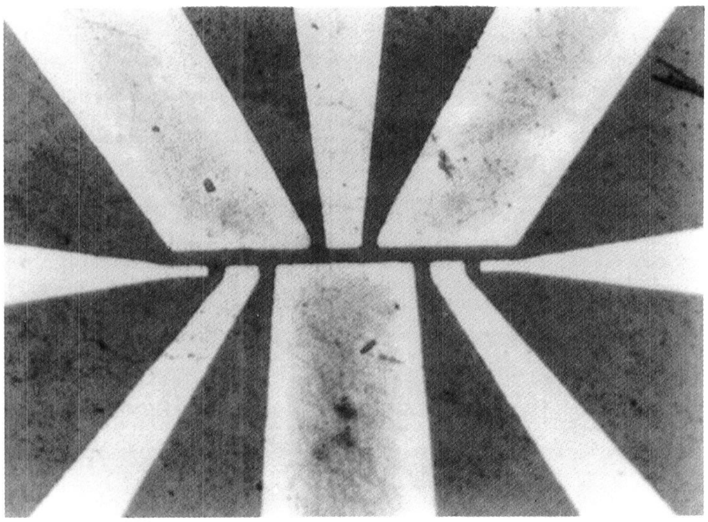
In this paper, we report on the transport properties of YBCO bicrystalline GBWLs deposited *in-situ* onto $SrTiO_3$ bicrystal substrates with various grain misorientations by pulsed laser deposition technique. It was found that by using a novel annealing process to precisely control the stoichiometry of the whole structure, not only the structure of the resistive transition tails (appears when the applied current was across the junction) but the scaling behaviors of the junction critical current as a function of temperature were all able to be altered in a repeatable manner, indicating a fundamental change in the nature of the GBWLs occurred. In the fully oxygenated state *i.e.* with x = 7.0 in $YBa_2Cu_3O_x$ stoichiometry, where the T_c's of the films remote from boundary areas were all above 90 K indicative of high quality films were obtained, the junction critical current exhibits a 3/2 power scaling behavior with temperature. In contrast, when annealed in the conditions of oxygen-deficient state (e.g . with x = 6.9 in $YBa_2Cu_3O_x$ stoichiometry) the junction critical current switches to a linear temperature dependence behavior. The physical mechanisms responsible for the observed switchovers are tentatively attributed to the modification of the effective dimension of the geometrically constrained weak-link bridges during oxygen annealing. More important is that such switchover behaviors were in fully controllable fashion and were dependent only the annealing conditions applied. Since the actual nature of the junction is what determines the all important Josephson effects to be utilized in device manufacturing, the results obtained in the present study are considered significant not only in the understanding of the fundamental physical mechanisms involved but also have important implications from the practical point of views.

2. Experimental

The bicrystalline YBCO films used in this study were deposited *in-situ* onto the $SrTiO_3$ bicrystal substrates with a tilt grain boundary angle of 36.8° by KrF excimer laser. The deposition conditions have been reported in detail previously [14]. Briefly, the substrate temperature was held at 770° C using a CW CO_2 laser as the heating source. The oxygen partial pressure was kept in the range of 0.2-0.3 Torr during deposition with a laser energy density of 2-4 J/cm^2 and a repetition rate of 3-5 Hz. It is noted that it took less than 1 minute to cool the films down to room temperature by the present process. Usually, the films thus obtained are all having rather smooth surface morphology with $T_{co} \sim$ 90 K and nearly perfect c-axis oriented crystalline structure.

In order to define the junction properly, the bicrystalline YBCO films were all patterned into bridge-type configuration, as depicted in Fig. 1, by standard photolithography processes. It is noted that the patterning processes, though involving some acid etching, do not affect the quality of the films noticeably. In Fig. 1, the leads were arranged in way such that both intra-boundary and inter-boundary properties of the same films would be measured and compared. To avoid possible heating effects, which may become crucial in later measurements, gold pads were deposited on each connecting lead and then annealed in oxygen to reduce the contact resistance.

For oxygen stoichiometry control, the thorough equilibrium data of Gallagher et al. [15] were used as a standard reference in setting appropriate annealing conditions. In our practice, samples were sealed in a quartz tube with proper oxygen partial pressures and then the whole assembly was then placed into a tube furnace hold at an appropriate temperature, typically in the range of between 370 ℃ and 470 ℃. Since the whole system was essentially at thermodynamical equilibrium, the oxygen content was thus determined thereby. To make further check the full resistive transition *R(T)* behaviors were compared with those of Ohkubo et al. [16] and Ossandon et al. [17] for samples with different presumed oxygen stoichiometries. It was found that the two independent methods gave rather consistent results, indicating we are indeed obtaining the right oxygen stoichiometry by using the present annealing scheme. All the samples, when



↑

grain boundary

Fig. 1: The optical picture showing the typical geometrical configuration of the grain boundary weak-link junctions formed on YBCO films deposited on bicrystalline $SrTiO_3$ substrates. The arrow shows the location of the grain boundary.

irradiated with microwave with frequency of ~ 12GHz, showed clear current steps at correct voltages in the cross-boundary current-voltage (*I-V*) characteristics, indicating that the GBWLs are indeed Josephson junctions in nature. It is, however, very difficult to distinguish the nature of the junctions directly from the steps appearing in I-V characteristics alone, as the manifestations of Josephson effects are, essentially, indistinguishable for SIS and SNS junctions. Thus, other steps have to be taken to further elucidate the subtle effects of oxygen stoichiometries.

3. Results and Discussion

Figure 2 shows, as an example, the effects of changing oxygen stoichiometry on the *R(T)* transition of one of the GBWLs studied. It is emphasized that the behaviors shown here are completely reversible and fully controllable. That is, depending on the particular annealing condition given, the *R(T)* behaviors shown in Fig. 2 are unique for each condition applied. We have checked this for at least four cycles and found that the uniqueness remains essentially unchanged. As can be seen in Fig. 2, there are several features to be noted. The foot structures shown in Fig. 2 are only observable when the current is applied across the bicrystal grain boundary and does not appear when the current was limited in the intra-boundary regions. Thus it can be considered only arise from the effects of the boundary and not from inhomogenity of the films. Furthermore, the foot structure as well as the whole *R(T)* curve, as depicted clearly by the three conditions given here, change significantly when the oxygen stoichiometry varies, indicative of overall change in oxygen stoichiometry during annealing processes. This

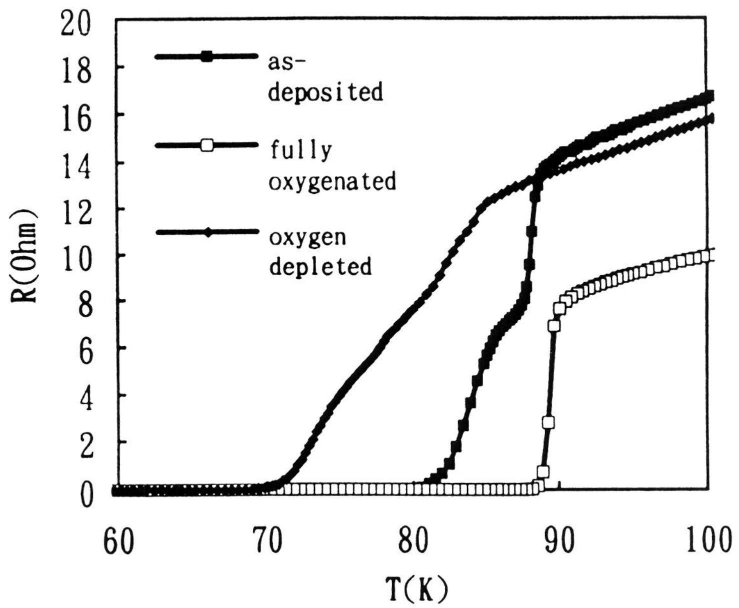


Fig. 2: The typical cross boundary *R(T)* behaviors exhibited by the same GBWL under three different annealing conditions. Three curves depict the as-deposited, fully oxygenated and oxygen-deficient cases, respectively.

is not surprising as has been pointed out earlier [14, 16-17]. The diffusion of oxygen in YBCO films is at least comparable with that in sintered porous bulk samples and it is easy to acquire equilibrium oxygenation states. Consequently, the depression and enhancement in T_c as compared to the as-deposited case are due to overall oxygenation states. The normal state resistance further indicates the effects of annealing in promoting atomic rearrangement and, hence, in eliminating crystalline defects. In our deposition process, the films were all quenched directly from deposition temperatures within a matter of tens of seconds and no intermediate oxygen annealing and slow cooling was involved [14]. Thus, relatively defective structure is expected. This explains why even with higher T_c's as compared to the oxygen deficient case the normal state resistance is higher. The situation, nonetheless, should not affect the general behaviors to be discussed in the following.

Perhaps, the most important feature that is of interest here is the foot structure in $R(T)$ curves. As is clearly demonstrated in Fig. 2, in the fully oxygenated condition, though the foot structure has been suppressed significantly as compared to the other two conditions, it is still existent. As has been mentioned earlier, this is a direct consequence of weak-link behavior. Otherwise, similar effects should also be observable in intra-boundary region. An alternative explanation of such foot structure in $R(T)$ transition was attributed to the fluxon creep effects, first proposed by Tinkham [18]. However, since there were Josephson effects routinely observed in these GBWL's together with the fact that it only appeared when cross boundary properties were measured, the mechanism responsible for the foot structure is believed to be a manifestation of order parameter phase slippage across the boundary instead of being due to flux creep effects. With this in mind, we have proceeded to measure the temperature scaling behavior of the junction critical current to try to delineate the nature of the GBWL's, especially how it would be altered with the change of oxygen stoichiometry.

Figure 3 shows the characteristics of the current-voltage (I-V), which display the overall I-V features can be described by the RSJ model. We have extented our I-V measurements to a linear region and then extrapolate back from the linear region to the zero voltage state to determine I_c. The results thus obtained were then plotted as a function of reduced temperature, define as $t = T/T_c$, and is shown in Fig. 4. For the full oxygenated junction the I_c shows an $I_c \sim (1-t)^{1.98}$ behavior, Fig. 4(a). Such a temperature dependence, is consistent with quadratic dependence (*i.e.* $I_c \sim (1-t)^2$) expected for an SNS proximity effect tunnel junction. Alternatively, one might suggest that it is may comparable to a $(1-t)^{1.5}$ results observed in superconducting whiskers and long bridges, however. Thus, it seems that the present GBWL structures are more likely to be geometrically constrained bridges rather than direct tunnel junctions. In contrast to that described above, for junctions annealed in oxygen-deficient conditions (*e.g.* $x = 6.9$), the $I_c(T)$ exhibits an $I_c \sim (1-t)^{0.93}$ behavior, as shown in Fig. 4(b). Since the nearly linear temperature dependence of junction I_c can be either interpreted as a result of SIS Josephson behavior or direct consequence of a short bridge constriction, the results are to be discussed further.

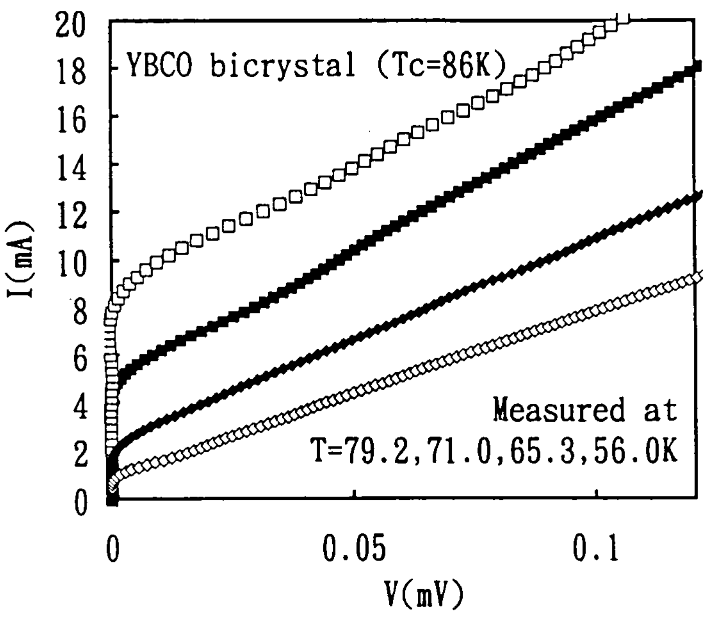


Fig. 3: The characteristics of the *I-V* of a fully oxygenated YBCO GBWL's.

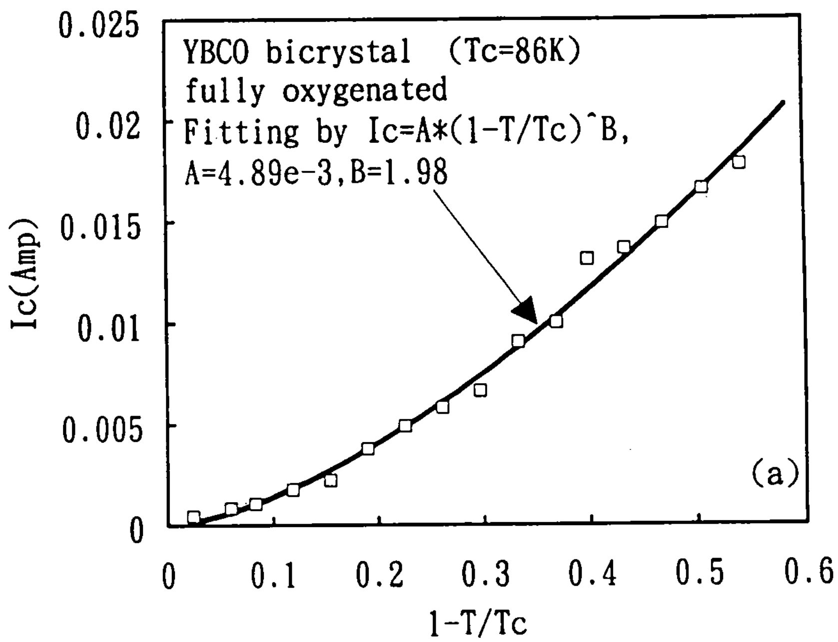
According to Ambegaokar and Baratoff [19], in an SIS Josephson junction, the critical current as a function of temperature is expressed as:

$$I_c(T) = I_o[\Delta(T)/\Delta(0)]\ tanh[\Delta(T)/2k_B T], \qquad (1)$$

with $I_o = \pi\ \Delta(0)/2eR_n$ representing the zero-temperature critical current. Expression (1) can be further reduced to

$$I_c(T) \sim 1/4\ \{I_o[2\Delta(0)/k_B T_c]\}[1-(T/T_c)], \qquad (2)$$

for temperatures very close to T_c and taking the usual BCS expression $\Delta(T) = \Delta(0)$ $[1-(T/T_c)]^{1/2}$ for the superconducting energy gap. Although, it gives the required linear temperature dependence for the observed results, the fact that the observed linear $I_c(T)$ is evidently extended to a region well below where expression (2) is applicable and whether the gap energy is BCS-like or not is still a matter of debate [20, 21], it seems not physically plausible to assume that it is indeed the case. On the other hand, as compared to the results shown in Fig. 4(a), the present case should also be considered as a consequence of geometrical constraint alternation due to oxygen lodgment and dislodgment during annealing. In the fully oxygenated state homogeneous distribution of the much needed oxygen is expected to be fulfilled, thus the whole boundary can be considered as a single weak-link and hence gives rise to a long bridge behavior. On the contrary, in the oxygen deficient condition, localized short bridges are likely to exist due to defective nature of the grain boundaries. By attributing the switching behaviors in $I_c(T)$ scaling of the GBWL's not only the



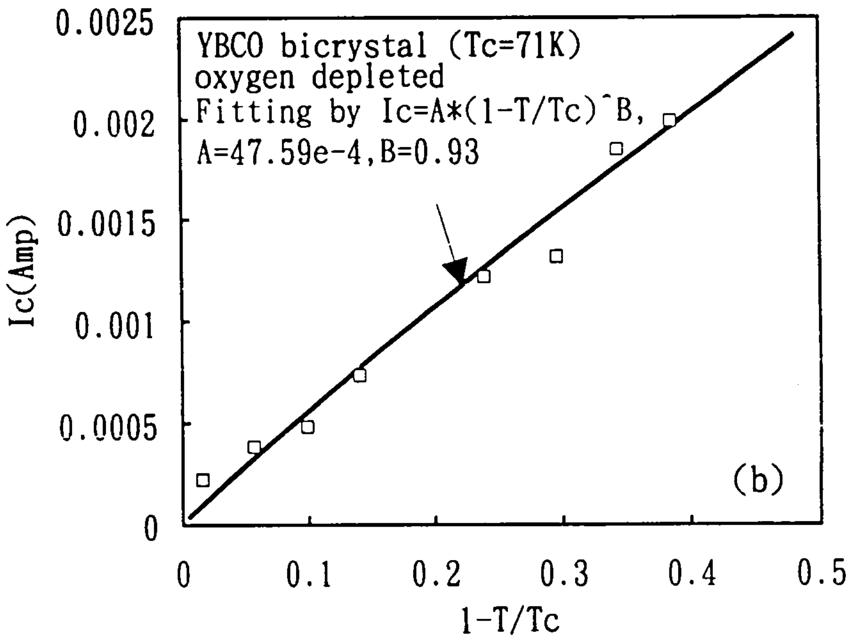


Fig. 4(a): The temperature dependence of the critical current I_c ploted as a function of (1-t) for the fully oxygenated YBCO GBWL's, showing a power of nearly 1.98 behavior for geometrically constrained long bridge characteristics.

Fig. 4(b): Similar plot as in (a) for the oxygen-deficient YBCO GBWL's, demostrating a near linear temperature dependence, a characteristic of geometrically constrained short bridge weak-links.

observed experimental results can be explained in a rather consistent fashion but also on a physically more plausible basis. Certainly the validity of the above assessments has to rely on more detailed microstructural studies of the bicrystalline films to give direct supporting evidences. Nevertheless, the present experiment has, undoubtedly, not only provided a powerful probe to investigate the fundamental electronic properties of these practically important device structure but also has made a further step on the designing of applications.

4. Conclusion

In summary, we have presented a novel technique in controlling the oxygen stoichiometry and investigated its effects on the transport properties of the pulsed laser deposited YBCO bicrystalline GBWL structures. It has been observed that, by precisely manipulating the oxygen stoichiometry the $I_C(T)$ behaviors of the GBWL's exhibit a switchover from the SNS behavior tends to be SIS type, as for fully oxygenated state is de-oxidated to be an oxygen-deficient situation. Alternative may be given as an switchover from a geometrically constrained long bridge weak-link for fully oxygenated state to a short bridges for oxygen-deficient situations. The results are tentatively attributed to the defect structure rearrangements induced by the lodgment and dislodgment of oxygen during the annealing processes.

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