NanoSIMS analysis of Ca doping at a grain boundary in a superconducting YBCO Ca-123/123 bicrystal

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Abstract. Calcium doping is well known to increase the grain boundary critical current, J_c^{gb}, in polycrystalline $Y_1Ba_2Cu_3O_{7-\delta}$, (YBCO). High resolution Secondary Ion Mass Spectroscopy (nanoSIMS) analysis has been used to map the distribution of Ca^+ ions in three dimensions in an YBCO grain boundary grown on a 24° $SrTiO_3$ bicrystal. High resolution SIMS imaging has produced Ca, Sr, and Ti elemental maps at 20 nm intervals from the YBCO surface. From the variation of Ca concentration with depth a Ca grain boundary diffusion coefficient can be estimated. Moreover, localised 'hot spots' of Ca at the YBCO grain boundary have been observed, perhaps at regions with a high dislocation density. There is also some diffusion of Sr and Ti ions from the substrate along the boundary. This is an important observation because it has been proposed that these ions are electrically active.

1. Introduction

The critical current densities (J_c) of randomly oriented polycrystalline high temperature superconductors containing a large number of grain boundaries are orders of magnitude lower than in epitaxial films of the same phase [1]. Dimos *et al.* [2] investigated the relationship between grain boundary misorientation and J_c values in epitaxial YBCO thin films grown on $SrTiO_3$ [100] tilt boundary bicrystals. The J_c^{gb} values were found to dramatically decrease as the misorientation angle (θ) increased. This experiment has been repeated many times [3][4] confirming the reduction of J_c^{gb} with θ, see for instance Fig. 30 in [5].

YBCO bicrystals can be selectively doped by diffusing Ca^{2+} ions down the grain boundary to substitute on Y^{3+} sites [6], thus doping holes into the intrinsically hole-depleted grain boundary. The measured J_c^{gb} values in zero applied magnetic field increased by up to a factor of 7, even though the grain boundary still showed some weak link behaviour. The selective doping is often achieved by growing multilayers of $YBa_2Cu_3O_{7-\delta}$ and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and allowing the Ca^{2+} ions to diffuse along the grain boundary into the $YBa_2Cu_3O_{7-\delta}$ layer. Song *et al.* have used Z-contrast imaging to show that the Ca^{2+} ions segregate in a non-monatomic fashion to within 1 nm of dislocation cores [6], suggesting that the grain boundary has a width of about 2 nm. Recently, Klie *et al.* have suggested that it is the ionic radii and not the valency of the substitutional atom which is most important in determining the J_c value of a doped grain boundary [7].

There has been one previous study on Ca-diffusion in YBCO [8], which estimated the Ca grain boundary diffusion coefficient by comparing diffusion profiles in both single crystal YBCO films and diffusion through polycrystalline YBCO pellets. In this study a Cameca NanoSIMS 50 has been used to map the Ca^+ concentration at a grain boundary and to estimate a grain boundary diffusion coefficient. Furthermore, the concentration of Sr and Ti ions diffusing from the $SrTiO_3$ substrate has been investigated, since Klie *et al.* [7] suggest that diffusion of even a small concentration of these ions at the YBCO grain boundary could affect the J_c values.

2. Experimental

The YBCO films on both bicrystal and single crystal $SrTiO_3$ substrates were fabricated at the Institute of Physics of the University of Augsburg. 20 nm of Ca-doped YBCO film was deposited by in-situ Pulsed Laser Deposition (PLD) on a 24±1° [001]-tilt $SrTiO_3$ bicrystal using 135 laser pulses at a frequency of 5 Hz, an energy of 450 mJ, and an oxygen pressure of 0.25 mbar. Immediately after the deposition of the Ca-doped layer a 150 nm thick film of pure YBCO was then deposited using 1000 laser shots. The substrate was heated to 750°C for about 15 minutes during this process. The bilayer sample was then annealed at 400°C for 30 minutes in air. A 150 nm thick $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ film, grown on a $SrTiO_3$ single crystal, served as reference for calibration purposes.

3. Results and Discussion

To allow quantification of the calcium concentration in the bicrystal sample, the $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ calibration sample was analysed under the same experimental conditions. A series of $^{40}Ca^+$ maps were acquired with raster sizes between 25 µm x 25 µm and 40 µm x 40 µm. Between each map the NanoSIMS primary beam aperture was opened for 5 minutes to sputter away about 20 nm of material. This process was repeated until the $^{48}Ti^+$ signal increased, indicating that the substrate had been reached. At the surface there is significant contamination from Ca^+ obscuring any grain boundary segregation. Deeper in the material a 'stripe' of higher Ca concentration gradually becomes more noticeable with each subsequent image, or 'slice' (Fig. 1).
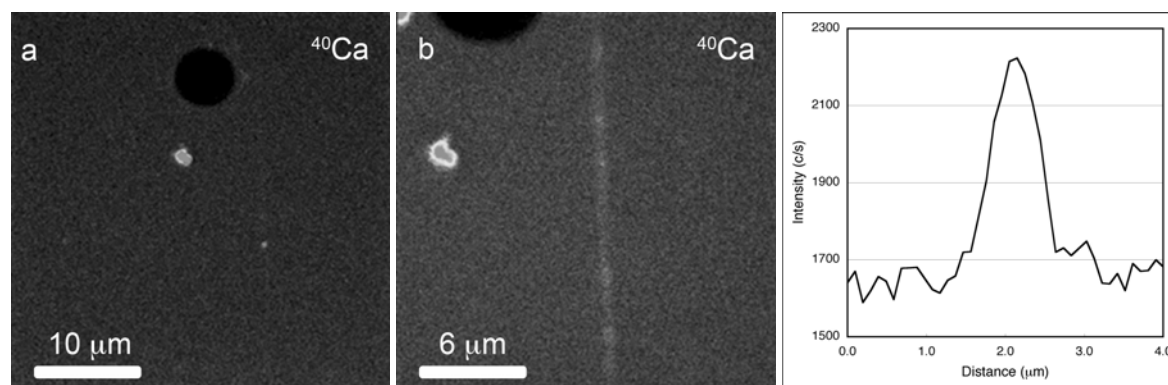

Figure 1: $^{40}Ca^+$ maps of the bilayer acquired at two different depths; (a) 80 nm into the YBCO layer, (b) 130 nm into the YBCO layer, just before the Ca-doped layer is reached. (c) $^{40}Ca^+$ linescan across the grain boundary 130 nm into the YBCO layer.

Linescans clearly show that Ca segregates/diffuses along the grain boundary (Fig. 1(c)), and the $^{40}Ca^+$ maps also suggest that the segregation is not totally uniform, with Ca hotspots occurring perhaps from precipitates nucleating on the grain boundary, or preferential diffusion along grain boundary dislocations. The $^{40}Ca^+$ depth mapping was repeated at 6 separate positions along the grain boundary with extremely similar results.

Linescans like that shown in Fig. 1(c) can be used in conjunction with data from the calibration sample to calculate an approximate Ca concentration along the grain boundary. A typical Ca concentration vs. depth plot is shown in Fig. 2 and suggests that very few Ca ions diffuse all the way along the YBCO grain boundary to the surface. In several scans no excess Ca ions are detected in a 50 nm thick layer below the YBCO surface. This is a direct observation that the Ca-doping of the grain boundary is not uniform within this simple bi-layer sample. Indeed, the highest J_c^{gb} values for Ca-doped YBCO films are achieved with a multilayer structure with many Ca-doped and non-doped YBCO layers [9]. Even with this arrangement, it is not clear that uniform Ca-doping of the grain boundary can be realised unless the YBCO layers are extremely thin, as the Ca ions do not diffuse far

enough. Unfortunately, the 'push-ahead' effect of ions in dynamic SIMS analysis prevents a meaningful study of these multilayer samples.
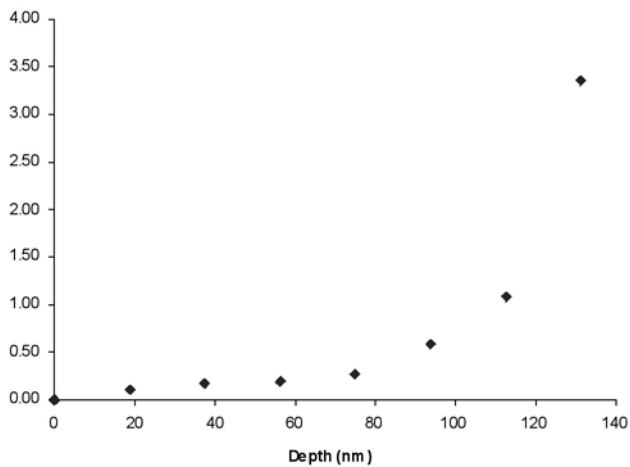

Figure 2: Typical plot of Ca concentration against depth from the YBCO surface. The non-doped YBCO layer is 150 nm thick so the data point at 135 nm corresponds to the last data taken before the Ca-doped YBCO layer was reached.

The Ca grain boundary diffusion coefficient, D_{Ca}^{gb}, has been estimated, using the error function solution from the diffusion equation for an infinite source condition with zero concentration far from the interface. The estimated value for the diffusion coefficient of Ca along an YBCO grain boundary is 1.0×10^{-18} m^2s^{-1} which is significantly lower than the only other D_{Ca}^{gb} value reported in the literature: $3\text{-}4 \times 10^{-15}$ m^2s^{-1} [8]. However, those samples were heat treated at 870°C compared to 750°C for our samples, which can account for the higher D_{Ca}^{gb}.

In addition to Ca segregation from the Ca-doped YBCO layer, both Sr and Ti were found to diffuse along the YBCO grain boundary as shown in Fig. 3. The Sr diffuses further along the grain boundary compared to the Ti. There is evidence of enhanced Sr concentrations only 40 nm from the surface. In contrast, the Ti ions are first detected about 100 nm from the surface. Due to the absence of a calibration sample for Sr and Ti-doped YBCO, the concentrations of both Sr and Ti are impossible to estimate reliably.
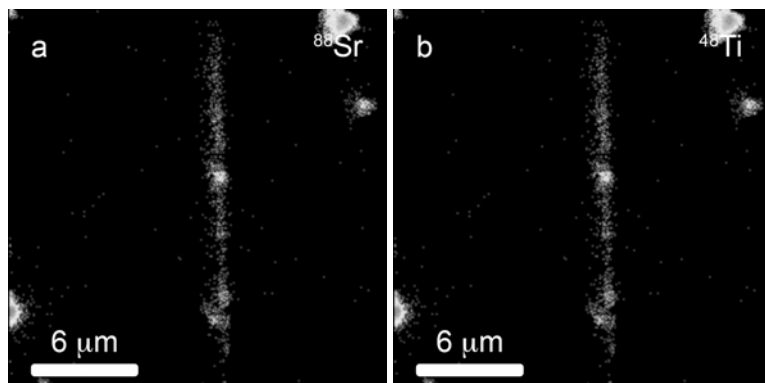

Figure 3: (a) $^{88}Sr^+$ and (b) $^{48}Ti^+$ maps showing segregation from the substrate along the YBCO grain boundary. Both maps were taken at 130 nm below the YBCO surface.

It is interesting to speculate whether these ions could be electrically active at the YBCO grain boundary. There has been no previously reported analysis of Sr or Ti segregation to YBCO grain boundaries; TEM studies have only shown Ca^{2+} ions segregating at similar boundaries [6-7]. This is probably because the concentrations of Ti^{4+} and Sr^{2+} ions are much lower than the Ca^{2+} ion concentration, and therefore not detectable with TEM analysis. As previously mentioned, Klie *et al.* have suggested that it is the ionic radii and not the valency of the substitutional atom which is most important in determining the J_c of a doped grain boundary [7]. The reasoning for this is that the highly strained grain boundary regions contain excess O vacancies, which reduces the local hole concentration. The Ca^{2+} dopant is normally expected to substitute for Y^{3+} [6] but in regions under significant compression or tension can also replace Ba^{2+} and Cu^{2+}, relieving strain and suppressing the O vacancy formation, hence decreasing the hole deficiency at the grain boundary and increasing J_c^{gb}. Ti^{4+} ions (Pauling ionic radius = 68 pm) are much smaller than Y^{3+} ions (93 pm) whereas Sr^{2+} ions are much larger (113 pm). Ca^{2+} ions are similar in size to Y^{3+}, with a Pauling ionic radius of 99 nm, and all the above ions are much smaller than Ba^{2+} (135 nm). Depending on their precise substitutional location in the YBCO grain boundary Sr^{2+} and Ti^{4+} ions would either add to (hence reduce J_c^{gb}) or reduce (hence increase J_c^{gb}) local strain. The extremely large difference in size (especially the small Ti^{4+} ion) could mean that a relatively low concentration of Ti^{4+} or Sr^{2+} ions could make a large difference to the local strain, suppressing the formation of O vacancies very strongly and hence increasing J_c^{gb}. In order to make any further progress with this idea the location of the Ti^{4+} and Sr^{2+} ions would have to be known in order to calculate their contribution to the local stain field.

From these NanoSIMS observations, it is suggested that Ti and Sr ions diffuse along the grain boundary in all YBCO bicrystal samples grown under similar conditions on $SrTiO_3$ substrates, irrespective of any Ca-doping. This kind of sample is very common as reported in the large body of published work on grain boundary properties in YBCO [9]. Therefore, if Ti^{4+} and/or Sr^{2+} ions change the level of hole depletion as suggested by Klie *et al.* [7], this will influence the measured J_c^{gb} values in most YBCO bicrystals. Therefore, whether Ti or Sr ions are electrically active at these grain boundaries remains an important fundamental question.

4. Conclusions

Quantitative NanoSIMS mapping of Ca concentration in YBCO bicrystals has been used to analyse the 3 dimensional profile of Ca at the grain boundaries. These results suggest that the grain boundary diffusion coefficient for Ca in YBCO bicrystals is about 3 orders of magnitude lower than that calculated previously for YBCO pellets, but this may be explained by different diffusion temperatures. It has been shown that Ca does not necessarily distribute uniformly in depth or laterally at the YBCO grain boundary. Furthermore, diffusion of Sr and Ti ions has been observed for the first time, which may affect the electrical properties of all YBCO bicrystals grown on $SrTiO_3$.

Acknowledgements

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