LA-UR-00-4571
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Author(s): Andrey **V.** Berenov, Imperial College of Science Technology and Medicine, LONDON
Roger Marriott, Imperial College of Science Technology and Medicine, LONDON
Steven R. Foltyn, MST-STC
Judith L. MacManus-Driscoll, Imperial College of Science Technology and Medicine, LONDON

Submitted to: Proceedings of 2000 Applied Superconductivity Conference

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Form 836 (8/00)

Effect of Ca-doping on grain boundaries and superconducting properties of $YBa_2Cu_3O_{7-\delta}$

Andrey V Berenov, Roger Marriott, Steven R Foltyn, Judith L MacManus-Driscoll

***Abstract*— It is well known that the properties of grain boundaries in $YBa_2Cu_3O_{7-\delta}$ films differ drastically from bulk material. It has been shown both experimentally and theoretically that the grain boundaries in $YBa_2Cu_3O_{7-\delta}$ superconductors are depleted of carriers as compared to the bulk. This depletion leads to weak intergrain links and limits critical currents in superconductor. Recently, the promise for improved grain boundaries has been shown in Ca-doped $YBa_2Cu_3O_{7-\delta}$ thin films and in Ca doped $YBa_2Cu_3O_{7-\delta}$ biaxial grain boundaries. In this study, the effect of Ca-doping of grain boundaries in $YBa_2Cu_3O_{7-\delta}$ films and bulk have been investigated in an attempt to increase hole concentration at the grain boundaries and to improve Jc.**

Ca-gels were applied to sintered $YBa_2Cu_3O_{7-\delta}$ pellets and thin films. High temperature post-anneals were used to diffuse Ca preferentially into the grain boundaries. The distribution of Ca in the samples was studied by secondary ion mass spectrometry (SIMS). The effect of Ca-doping on T_C and J_C was studied by VSM. In epitaxial thin film increased J_C were found at 40K, but not at 77K.

***Index Terms*—Critical currents, Grain boundaries, SIMS.**

I. Introduction

GRAIN boundaries in $YBa_2Cu_3O_{7-\delta}$ plays an important role in modifying superconducting properties. It has been suggested that a charge transport across a grain boundary occurs by the tunneling through an insulating layer of thickness $2I_d+\delta$, where I_d and δ are widths of one charge depletion layer and a grain boundary, respectively [1].
The width of depletion layer, is given as [1]

$$I_d \cong \sqrt{\frac{2\mathring{a}_0\mathring{a}_r V_{bi}}{en}} \qquad (1)$$

where $\varepsilon_0\varepsilon_r$ is dielectric constant of material, V_{bi} is built-in potential of the boundary, e is the carrier charge and n is the carrier concentration. Hence aliovalent doping of the grain boundary with cation like Ca would increase the number of carriers and improve superconducting properties. Recently Schmehl et al. [2] have demonstrated an order of magnitude increase of inter-granular J_C's in artificial 24° [001]-tilt grain boundaries after Ca doping.

In order to preferentially dope grain boundaries, the knowledge of Ca diffusion in the bulk as well as along the grain boundaries is required. Several studies of the cation diffusion in $YBa_2Cu_3O_{7-\delta}$ have been published [3,4]. However no data on Ca diffusion in $YBa_2Cu_3O_{7-\delta}$ was found in the literature.

The aim of our research was to measure Ca diffusion in $YBa_2Cu_3O_{7-\delta}$ and, based on this data, preferentially dope grain boundaries with Ca to enhance inter-granular J_C. Before studying specific grain boundary angles, we have undertaken a preliminary study of epitaxial thin films and bulk material to fin the optimum conditions for grain boundary doping.

II. Experimental

A. Sample Preparation

Thin films of $YBa_2Cu_3O_{7-\delta}$ were grown epitaxially on (100) single crystal $SrTiO_3$ by pulsed laser deposition (PLD). A detailed description of the film deposition conditions is given elsewhere [5]. A deposition, the Films were cut in 5 x 2 mm pieces. In order to study Ca diffusion in polycrystalline ceramics, several pellets were isostatically pressed up to 300 MPa from $YBa_2Cu_3O_{7-\delta}$ powder (SSC Inc.) and sintered in air at 1000°C for 12 hrs. The density of the obtained pellets was greater than 95%.

A dilute (0.05M) solution of $Ca(NO_3)_2$ (99.99+% Aldrich Chemical Co.) was dropped on the surface of the films and pellets on a hot plate. One set of films (YE1 series) was annealed at 870°C in air for different times in order to study the effect of Ca-doping on the superconducting properties, and another set of films (YE2 series) was annealed at different temperatures, in air, in order to determine the activation energy of Ca diffusion in $YBa_2Cu_3O_{7-\delta}$. All the films annealed at 870°C (YE1 series and YE202) were later oxygenated in flowing air at 500°C for 2 days. In order to determine the Ca diffusion coefficient in the bulk ceramic samples, they were annealed at 870°C in air for 2 hrs. Several films and pellets were not doped and used as reference samples. The preparation conditions of all samples are given in Table I.

B. SIMS measurements

The isotope concentration profiles were measured by a secondary ion mass-spectrometer (Atomika 6500) using a 8 kV Xe^+ primary beam at normal incidence. The rastered area

Manuscript received September 17, 2000. This work was supported in part by the EPSRC under Grant No. GR/L 98749.

A.V.Berenov, R. Marriott, J.L. MacManus-Driscoll are with the Department of Materials, Imperial College of Science Technology and Medicine, Prince Consort Road, London, SW7 2BP, UK (telephone: +44 207 -594-6742, e-mail: a.berenov @ic.ac.uk).

S.R. Foltyn is with Superconductivity Technology Center, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

TABLE I
PREPARATION CONDITIONS AND T_C OF THIN FILMS

Sample	Ca-doped	Preparation conditions	T_C, K
YE102	yes	870°C, 30 min	89.5
YE103	yes	870°C, 20 hrs	92.0
YE104	no	870°C, 20 hrs	92.8
YE105	yes	870°C, 6 hrs	91.6
YE202	yes	870°C, 2 hrs	92.6
YE203	no	870°C, 2 hrs	NA
YE204	no	798°C, 6 hrs	NA
YE205	yes	700°C, 24 hrs	NA

was 300 x 300 μm. In order to avoid crater wall effects, only the data from the central part of the crater (150 x 150 μm) was used in the analysis. Intensities of secondary ions ($^{40}Ca^+$, $^{44}Ca^+$, $^{138}Ba^+$, $^{47}Ti^+$, $^{63}Cu^+$) were recorded as a function of time (Fig. 1.). The depth of the crater was measured by a surface profilometer (Maxim GP200, Zygo) using filtered light optical interferometry. The raw data was converted into the Ca diffusion profiles, by calculating the isotopic fraction from the raw intensities and converting the sputter time to depth assuming a constant sputtering rate. The assumption of constant sputtering rate was supported by the fact that a linear relationship was observed between the crater depth and the sputtering time and the bottom of crater was smooth without irregularities.

It was assumed that the amount of Ca on the surface was sufficiently high to consider Ca diffusion from a constant source into a semi-infinite medium. The solution of Fick's second law under these boundary conditions is [3]:

$$C(x,t)/C_0 = \exp\left(-\frac{x^2}{4D_{bulk}t}\right) \qquad (2)$$

where C(x,t) is the concentration of Ca as a function of distance from the surface, x, for an annealing time, t. D_{bulk} is the bulk diffusion coefficient, and C_0 is the concentration at the surface. Since the concentration of Ca is proportional to the intensity of the ^{40}Ca signal, the bulk diffusion coefficient was calculated by fitting (2) to a curve of $I(x)/I_0$ where I(x) and I_0 are intensities of the ^{40}Ca signal at distance x and, on the surface, respectively.

In several diffusional profiles, short-circuiting tails were observed which can be due to pores, cracks, grain boundaries, etc. Although indisputable distinction between these diffusion profiles is rather difficult, those short-circuiting tails were attributed to the fast Ca diffusion along the grain boundaries as no cracks or pores were observed in the bottom of the crater by SEM. The grain boundary diffusion was calculated by the method proposed by Chung and Wuensch method [6]. In their method the diffusional data are replotted as LnC(x) vs. $\eta^{6/5}$ where

$$ç = \frac{x}{\sqrt{D_{bulk}t}} \qquad (3)$$

The product of the grain boundary diffusion coefficient, $D_{g.b.}$, and the thickness of the grain boundary, δ, is given by

$$D_{g.b.}ä = D_{bulk}^{3/2} t^{1/2}\left[10^A\left(-\frac{\partial \ln C}{\partial ç^{6/5}}\right)^B\right] \qquad (4)$$

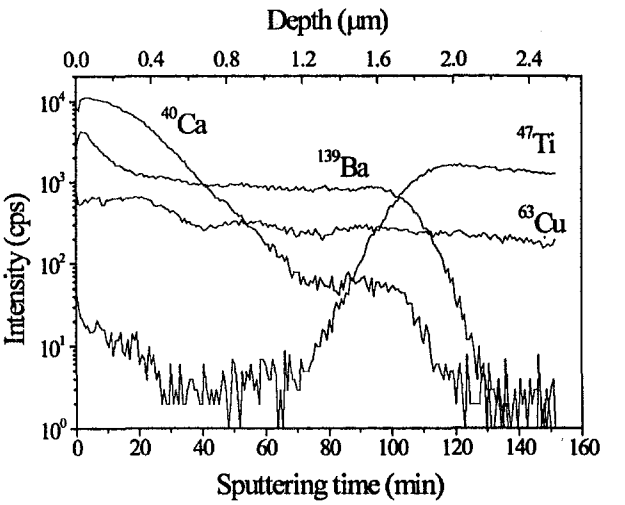

Fig. 1. Intensities of secondary ion signal as a function of sputtering time. The annealing temperature was 870°C, and the annealing duration 30 min (YE102).

where A and B are constants tabulated by Chung and Wuensch [6]. Only the data in the range $6<\eta<10$ were fitted to (4).

C. *Sample characterization.*

XRD scans in Bregg-Brentano geometry were used for phase determination. Φ scans (in plane rotation) were obtained from pole figures for texture analysis.

Magnetisation measurements were performed using a vibrating sample magnetometer (OI-3001, Oxford Instruments). The length scale in the samples was determined by analysing of the m (H) behaviour after reversing field sweeps [7]. Critical current densities were calculated using Bean model [8].

Tc was determined from magnetic permeability measurements using LCR circuits with pancake coils positioned close to the sample. A radio frequency signal (3.5 MHz) was used.

III. RESULTS AND DISCUSSIONS

XRD scans of starting PLD films showed only highly intense 001 peaks with the c-axis oriented perpendicular to the film surface. Pole figures on (111) peak showed a-b alignment of the film. No secondary phases were observed in the starting thin films and polycrystalline pellets.

After Ca annealing some remnant CaO was observed by XRD. Interestingly, Ba-rich phases were observed on the surfaces of both the polycrystalline pellets ($BaCO_3$) and the thin films (BaO). Pole figures of the BaO impurity showed preferential orientation of the (lll) plane parallel to the film surface. The formation of BaO and $BaCO_3$ could be

attributed to the decomposition of the $YBa_2Cu_3O_{7-\delta}$ surface by contact with water vapor and/or CO_2 when annealed in air. However, the fact that no Ba-rich phases were observed in the undoped reference specimens annealed in air and no other decomposition products (CuO, $(CuCO_3)Cu(OH)_2$, etc.)

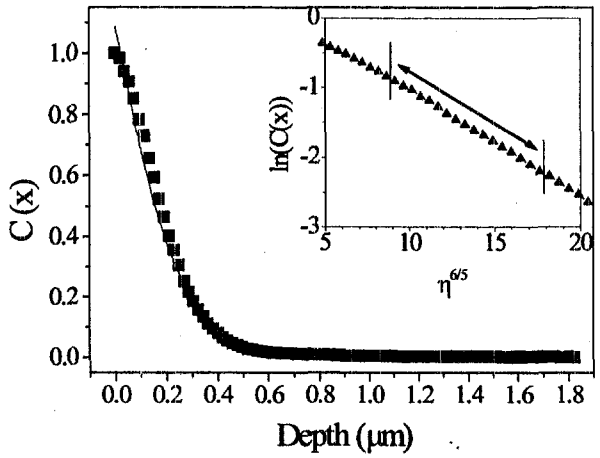

Fig. 3. Ca concetration profile determined by SIMS. The annealing temperature was 870°C, and the annealing duration 30 min (YE102). Solid lines is the fit to (1). Plot of lnC(x) vs. $\eta^{6/5}$ is shown in inset. Arrows indicate the data used for the calculation of grain boundary diffusion according the method of Chung and Wuensch [6].

were detected by XRD, may suggest that the formation of $BaCO_3$ and BaO was caused by the Ca doping. No peaks belonging to Y rich (except $YBa_2Cu_3O_{7-\delta}$) phases were observed by XRD. Therefore it is possible to conclude that some Ca is substitute onto the Ba site in $YBa_2Cu_3O_{7-\delta}$. This observation is supported by the structural study of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ which showed that Ca substituted onto Y site at low Ca concentrations (<11%), whereas at higher concentrations, Ca also substituted onto Ba site [9]. In addition, a computer simulation study of cation doping in $YBa_2Cu_3O_{7-\delta}$ has shown that Ca substitution onto the Ba site is more energetically favorable than the substitution onto the Y site [10].

The intensity of several secondary ion signals as a function of the sputtering time is plotted in Fig. 1. Segregation of Ba on the surface in the form of BaO and/or $BaCO_3$ was observed in several SIMS profiles. This segregation is in contrast with the finding of Rothman et al. [11] where depletion of Ba was observed only very close to the surface of $YBa_2Cu_3O_{7-\delta}$. Cu diffused fast into the $SrTiO_3$ substrate as well as into other substrates [11].

Ca penetration profiles were fitted to (2) and (4), as

TABLE II
BULK AND GRAIN BOUNDARY DIFFUSION COEFFICIENTS OF CA IN $YBA_2CU_3O_{7-\delta}$

Sample	T, °C	D_{bulk}, cm^2s^{-1}	$D_{g.b.}\delta$, cm^3s^{-1}
YE202 (film)	870	6.2×10^{-14}	4.2×10^{-18}
YE204 (film)	798	2.7×10^{-14}	3.1×10^{-18}
YE205 (film)	700	7.9×10^{-15}	NA
p4Ca (pellet)	870	1.4×10^{-12}	NA

shown in Fig. 2. The values of the Ca chemical diffusion coefficient as well as the grain boundary diffusion coefficient are given in Table II.

The Ca-diffusion coefficient in the bulk pellet is about 20 times higher than in PLD films. This discrepancy is attributed to the much higher Ca diffusion along the a-b

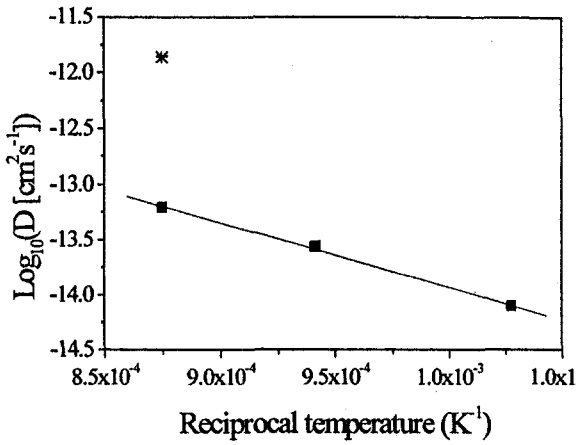

Fig. 2. Arrhenius plot of Ca diffusion coefficient in $YBa_2Cu_3O_{7-x}$ thin films (') and polycrystalline ceramics (*). Solid line is a linear fit of the data.

planes in $YBa_2Cu_3O_{7-\delta}$ (randomly oriented grains in polycrystalline pellets) as compared with diffusion along the c-direction (c-oriented grains in the thin films). Analogous anisotropy in the diffusion along the a-b planes and the c-direction was observed for oxygen [4] and barium diffusion [3] in $YBa_2Cu_3O_{7-\delta}$.

From the fits to the diffusion profiles, the temperature dependence of the Ca chemical diffusion coefficient along the c-axis in $YBa_2Cu_3O_{7-\delta}$ can be described as

$$D_{bulk} = 8.9\times10^{-9}\exp\left(-\frac{113\text{kJ/mol}}{RT}\right) \quad (5)$$

where R is gas constant, T is annealing temperature in K. The activation energy for Ca chemical diffusion is ~ 113 kJ/mole. This value is significantly smaller than the activation energies of tracer diffusion of Ba and Y in $YBa_2Cu_3O_{7-\delta}$, 890 kJ/mol and 1000 kJ/mol, respectively [3]. It is thought that this discrepancy is due, in part, to the fact that chemical diffusion coefficient is measured in this work as oppose to the tracer diffusion in [3]. At the same time, the activation energy for the chemical diffusion of Ag and Co in $YBa_2Cu_3O_{7-\delta}$ has been measured at 240 and 275 kJ/mol, respectively [3].

The grain boundary diffusion coefficient was calculated assuming the width of the grain boundary to be of the order of 1 nm [12] the value was 3.1×10^{-11} cm^2s^{-1} for the film annealed at 798°C. Diffusion enhancement factors ($D_{bulk}/D_{g.b.}$) are roughly estimated to be of the order of 10^3. Thus Ca diffuses much faster along the grain boundaries in $YBa_2Cu_3O_{7-\delta}$ than through the bulk. Consequently,

preferential doping of the grain boundaries appears to be possible.

T_Cs of all the thin films were in the range 90 – 93 K without any correlation with the duration of the Ca anneal (Table I). We note that Ca doping in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ decrease T_C from 88.7K at x=0 to 73.9K at x=0.3 [13].

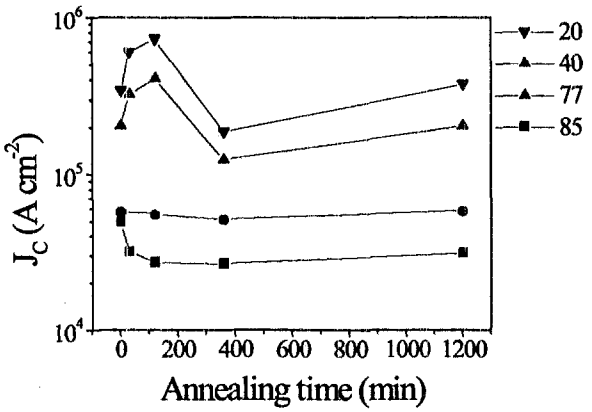

Fig. 4. Effect of annealing time on the critical current densities. Data at 20, 40, 77K were measured at 1.2 T and data at 85K at 0.17 T. Solid lines are guides to eye.

Consequently, in our work, Ca incorporation into samples has been limited to the grains only near the surface but to the grain boundaries throughout the film for long annealing conditions.

For the films, at low temperatures (20 K and 40 K), the current carrying lengths were of the sample dimensions and no difference between the undoped and the Ca doped samples was observed. However, at 85K, and 0.3 T the length scale of undoped sample was about 5 times larger in the undoped sample compared to the Ca-doped sample.

The effect of the Ca annealing time on J_C at 20, 40, 77 K (1.2 T) and 85K (0.17 T) are shown in Fig. 3. It is clear that Ca doping decreased J_C at high temperatures 85K and 77K. However Ca doped film annealed at 870°C for 2 hrs, showed an increase of J_C by a factor of two. At prolonged annealing times, J_C appears to decrease. This decrease of the J_C is thought to be related to the overdoping of the grains with Ca supplied from the grain boundaries leading to a decrease of T_C in the grains close to the grain boundary. A sudden drop of the J_C value for the sample annealed for 6 hrs (YE105) is thought to be caused by significant overdoping of the film as a very deep diffusional profile was measured by SIMS. The reason for this overdoping is unclear at present.

IV. Conclusions

Ca chemical diffusion was studied in $YBa_2Cu_3O_{7-\delta}$. Ca-diffusion along the c-axis grains was slow as compared with the randomly oriented grains. The activation energy of Ca diffusion was ~ 113 kJ/mol. Fast diffusion along the grain boundaries was observed in c-oriented thin films.

The optimum duration of Ca annealing increased of J_C by a factor of 2 in epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films at 20 K. The doping /diffusion technique developed in this work allows preferential doping of grain boundaries in $YBa_2Cu_3O_{7-\delta}$.

ACKNOWLEDGMENT

We would like to thank C. Shaw for the help with SIMS measurements and Y. Bugoslavsky for helpful discussions and assistance with VSM measurements.

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