Grain growth and biaxial texture of chemically deposited La$_2$Zr$_2$O$_7$ buffer layers for YBCO-coated conductors

L Molina$^1$, S Engel$^2$, K Knoth$^2$, R Hühne$^2$, B Holzapfel$^2$, O Eibl$^1$

$^1$ Institute of Applied Physics, University of Tübingen
Auf der Morgenstelle 10, D-72076, Tübingen, Germany

$^2$ IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany

E-mail: leopoldo.Molina-luna@uni-tuebingen.de

Abstract. Chemically deposited La$_2$Zr$_2$O$_7$ (LZO) thin films are crucial for coated conductor production since they transfer the texture from a highly biaxially textured nickel substrate to the YBCO superconducting layer and act as nickel diffusion barriers. The misfit of LZO with respect to Ni is 7.6%. The LZO buffer layers studied in this work were deposited on biaxially textured Ni-5at%W substrates by chemical solution deposition (CSD) using the same precursor starting solutions and were annealed at temperatures ranging from 600 to 1000°C for 1 h. Samples were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) in plan-view and cross-section. By combined TEM and XRD investigations on the same samples we found a clear difference in the microstructure of the LZO thin films: (i) a nanocrystalline state for T < 800°C with grains 5-10 nm in size (ii) and a polycrystalline state for T > 800°C with an average grain size of up to 200 nm. Thus, the LZO grain size is much smaller than the Ni grain size and the LZO buffer layers are highly biaxially textured, but no epitaxial growth occurs. Grain growth started at 800°C and nanovoid formation and growth occurred during the grain growth process. The nanovoid size was determined to be 10-20 nm and small-angle grain boundaries were observed in the LZO buffer layers. The facetting of the LZO grain boundaries play an important role in the grain growth process, samples annealed at higher temperatures had less strongly facetted grain boundaries than at lower temperatures. On top of the LZO buffer layers YBCO thin films were deposited by PLD and CSD yielding critical current densities of > 1 MA/cm$^2$ at 77 K.

1. Introduction

Second generation (2G) high-temperature superconductor (HTS) wires, known as coated conductors, consist of highly biaxially-textured YBCO thin films. A nickel tungsten alloy with biaxial cube texture is coated with one or more buffer layers and a thin film of superconducting YBCO [1]. The biaxial texture is transferred from the substrate to the superconducting thin film and the grains in the YBCO film are highly biaxially textured, forming a small-angle grain boundary network. The LZO buffer layers studied in this work were prepared by chemical solution deposition (CSD): a Ni-5%W substrate is successively dip-coated in a LZO precursor solution at room temperature followed by a heat-treatment. CSD is a promising technique for the fabrication of low-cost long scale YBCO-coated conductors for industrial applications [2]. The misfit of LZO with respect to Ni is 7.6% (compressive), a tilting mechanism is believed to play an important role for strain relief in this highly strained system [3]. LZO on YSZ has a similar (compared to LZO on Ni) misfit of 5% and growth of LZO films on (001) YSZ was investigated by Lu C J et.al. [12]. The arrangement of misfit dislocations and the formation of slightly tilted domains was analysed in the LZO pyrochlore islands grown on YSZ substrates. Also in this case misfit yielded tilting of neighbouring domains/grains.

2. Experimental

2.1 Sample preparation

Biaxially-textured Ni-5at.%W tapes were dip coated using a 0.15 M solution, pyrolyzed and annealed at temperatures ranging from 600-1000°C. The pyrolysis was performed at 600°C with a heating rate of 10K/min. After the pyrolysis the samples were brought to room temperature and annealed with a
2. Heating rate of 10 K/min. Annealing time was 60 min and cooling was done at 2-3 K/min. For details on preparation procedures see [2,11]. The LZO film thickness was between 150 to 170 nm for all samples investigated in the temperature series.

The sample preparation and superconducting properties of the full YBCO(PLD)-coated conductor shown in this work is described in [10].

A Zeiss 912 Omega EF-TEM operating at 120 keV and equipped with an EDX detector (Oxford) was used in this study, all images shown here were energy-filtered (EF). The EDX spectra were acquired for 100 s with a spot size of 10-40 nm. The Cliff-Lorimer method was used for quantitative analysis of the spectra no absorption correction was applied.

2.2 TEM specimen preparation

Samples were prepared for TEM investigations by conventional mechanical polishing and grinding methods followed by ion milling using a Res 100 Baltec ion milling machine operated at 4.5 kV and 3.5 mA for several hours. Plan-view samples were ion milled from one side only at an angle of 12°. Cross-section samples were prepared by the method described in [7] and then ion milled from both sides using angles of ±12°.

3. Results and discussion

3.1 XRD and SEM characterization.

Figures 1 (a-f) show XRD pole figures and secondary electron images (SEM) at high magnification of LZO buffer layers annealed at 900°C and 1050°C. Preparation details of these two samples are given in [3]. In figure 1(c) individual grains of 100 nm in size are found (denoted by numbers in the image). At T=1050°C the LZO grain size increases reaching ~200 nm. Although XRD suggests epitaxial growth, SEM shows a much smaller grain size (200 nm) for the LZO films than the Ni grain size (40 µm) which contradicts epitaxial growth. Therefore, TEM investigations should clarify the microstructure and the process of biaxial texturing.

Figure 1. (a-b) XRD pole figures of a sample annealed at 900°C and (c) corresponding secondary electron diffraction. (d-e) XRD pole figures (d,e) and (f) corresponding secondary electron diffraction image of a LZO buffer layer annealed at 1050°C. The scale bar in the upper image is 500 nm and in the lower 200 nm.

3.2 TEM characterization

Understanding the biaxial texturing of the buffer layer is of key importance for coated conductor preparation technology. Therefore, detailed TEM diffraction contrast studies were preformed to image small misorientations of the LZO grains with respect to the underlying Ni substrate. TEM diffraction contrast is more sensitive to small misorientations of the grains than electron diffraction patterns.
Electron diffraction patterns are useful to obtain diffraction rings of the nanocrystalline microstructure prior to annealing, and spot patterns of individual grains that are 100-200 nm in size after grain growth occurred. Figure 2 shows a tilt series of an LZO thin film in plan view annealed at 900°C, the LZO film thickness was 80 nm. The sample was tilted such that two-beam diffraction conditions were established in a number of grains of the area that appear in dark contrast (fig. 2 top left). From this position the sample was further tilted and different grains were brought into diffraction condition. By such experiments small tilts of neighbouring grains can be determined and the grain size was found to be 100-200 nm. The contrast in these images is sensitive to the out-of-plane tilt of the crystallites. Within the grains the diffraction contrast is determined by nanovoids, which were determined to be 10-20 nm in size [3].

Figure 2. Diffraction contrast under two beam conditions. Bright-field images in plan-view of a LZO thin film heat-treated at 900°C showing the same area with varying tilt angle. The scale bar in all images is 100 nm.

Figures 3 (a-c) show a bright-field TEM tilt series from $\theta = -5.0^\circ$ to $-6.3^\circ$ of the same sample area shown in figure 2, but at higher magnification. Figures 3 (d-f) show the corresponding electron diffraction patterns where the (200)Ni and the 440(LZO) reflections can be indexed. Due to the overlapping of the LZO film and the Ni substrate in the electron beam direction Moiré contrast is observed, note the different orientations of the fringes in the image (white bars in 3 c).

Figure 3. (a-c) TEM Bright-field tilt series of a LZO sample heat-treated at 900°C showing the same sample area in plan-view with varying tilt angle. Moiré fringe contrast is observed. (d-f) corresponding electron diffraction patterns. The scale bar in all images is 20 nm.
This Moiré contrast magnifies the misorientation of LZO grains with respect to the underlying Ni grain by a factor of ~13 and small rotations of the LZO grains of less than 3° can be determined [9]. The bright contrast in the images is due to the nanovoids present in the film. The Moiré fringe imaging is sensitive to the in-plane-rotation of the crystallites. The splitting of the (200) Ni and the (440) LZO reflections is the reason for the Moiré fringe contrast to appear and shows that the lattice parameter for LZO is close to the intrinsic value. The misfit of the film with respect to the substrate was compensated by strain relaxation, misfit dislocations that were expected to be arranged in a two-dimensional grid were, however, not observed in these images. Figure 4 (a-d) shows XRD pole figures, TEM bright field images and corresponding electron diffraction patterns at different annealing temperatures. For T= 700°C no LZO(222) reflection in the pole figure can be observed and nm sized LZO grains are observed in the bright-field TEM image.

Figure 4. XRD pole figures, TEM bright-field images and corresponding electron diffraction patterns (both in plan-view) for samples annealed at T= 700-1000°C. The scale bar in all the TEM BF images is 100 nm.

The electron diffraction pattern shows a ring that corresponds to LZO (222). At T= 800°C grain growth and biaxial texture started as seen in the pole figure where LZO(222) reflections are observed. In the BF-TEM image grains of ~100 nm grain size are found. At T=900°C and T=1000°C the grain size increases to 100-200nm, pole figures yield less background and more defined peaks and corresponding electron diffraction patterns show distinct spots instead of rings [8].

The microstructure of the of the films prior to the annealing was studied in detail. Figures 5 (a-b) show bright and dark-field TEM images in plan-view and (c) the corresponding electron diffraction pattern of the sample annealed at T=600°C. In the electron diffraction pattern rings corresponding to LZO(222), LZO(422) and LZO(444) can be identified indicating that the sample is nanocrystalline. The LZO grains were found to be ~5 nm in size by dark field images. Figure 5 (e) shows a single LZO grain of ~100 nm and the corresponding dark-field image 5 (f) in a sample annealed at 800°C. Within the LZO grain nano-granularities of 10-20 nm can be identified. The electron diffraction pattern, figure 5 (g), shows a diffraction ring corresponding to LZO(222). Within the ring diffraction spots can be identified. The ring segment circled was used to obtain the dark-field image shown in figure 5 (f). Figure 5 (d and h) show EDX spectra from which the cation mole fraction and the C mole fraction were determined. Table 1 summarises data obtained by TEM for all samples. The nanocrystalline state appeared at T< 800°C with grains of ~5 nm and polycrystalline grain growth starts above 700°C where LZO grain boundaries were found to be strongly faceted at T =800°C and 900°C. In samples prepared at T=1000°C grain boundaries were less strongly faceted (fig.6).
Figure 5. (a) TEM bright-field image in plan-view of the sample heat treated at 600°C. (b) corresponding dark-field image. (c) electron diffraction pattern (d) EDX spectrum. (e) Bright-field image of the sample annealed at 800°C where a single LZO grain is shown. (f) corresponding dark-field image and (g) corresponding electron diffraction pattern. (h) EDX spectrum obtained within a single LZO grain.

| Temperature | 600°C | 700°C | 800°C | 900°C | 1000°C |
|-------------|-------|-------|-------|-------|--------|
| Grain size  | 5nm   | 5nm   | 50-100nm | 50-100nm | 100-200nm |
| Grain boundaries | -      | -      | strongly facetted | strongly facetted | less facetted |
| Voids      | -      | -      | -      | 10nm | 10nm |
| Bright and dark areas | yes | yes | yes | yes | dark only |
| Diffraction patterns | ring | ring | ring + spots | ring + spots | spots only |

Table 1. Microstructural parameters of the LZO films annealed at different temperatures.

Figure 6. Schematic image of grain boundary facetting in LZO grains with increasing annealing temperature.

After having identified the various structural defects in LZO buffer layers, the growth of PLD-YBCO films on these buffer layers was studied [5,10]. Figure 7 (a) shows a YBCO coated-conductor in cross-section, in which the various layers could be identified. The critical current density obtained was 0.84 MA/cm² at 77 K. Nanovoids are visible within the LZO buffer layers. Figures 6 (b-d) are the corresponding electron diffraction patterns, fig.6 (e-f) are TEM-EDX spectra obtained within the LZO and CeO₂ buffer layers.
5. Conclusions

Although XRD pole figures of the LZO samples annealed at $T \geq 800^\circ$C suggest epitaxial growth of the LZO film it has been shown by TEM that epitaxial growth does not occur. The grain size in LZO films was found to be 100-200 nm by TEM and SEM and grains are misoriented with respect to the underlying Ni. The biaxial texture of LZO observed in the pole figures comes from averaging over large areas of the sample. It was shown that plan view bright- and dark field images under two-beam conditions are sensitive to image the in-plane and out-of-plane tilt of LZO grains. The LZO lattice parameter was close to its intrinsic value, however, misfit dislocations were not observed in the Ni/LZO interface. The tilting of LZO grains with respect to the underlying Ni grain might be a mechanism for misfit compensation. LZO films annealed at temperatures between 600$^\circ$ and 1000$^\circ$C were systematically studied by TEM and detailed results were presented.

Acknowledgments

Authors acknowledge financial support from the "Chemically deposited YBCO superconductors" Virtual Institute of the Helmholtz-Gemeinschaft.

References

[1] Obradors X et al 2004 Supercond. Sci. Technol. 17 1055
[2] Knoth K, Hühne R, Oswald S, Schultz L and Holzapfel B 2005 Supercond. Sci. Technol. 18 334
[3] Molina L, Knoth K, Engel S, Holzapfel B and Eibl O 2006 Supercond. Sci. Technol. 19 1200
[4] Schowalter L J, Hall E L, Lewis N and Hshimoto S 1989 Mater. Res. Symp. Proc. 130 171
[5] Molina L, Eibl O, Knoth K, Engel S, Hühne R, Holzapfel B Physica C Vol 460-462 (2007) 1407-1408
[6] Eyidi D, Croitoriu M D, Eibl O, Nemetschek R, Prusseit W J. Mater. Res. 18 (2003)
[7] Eyidi D, Eibl O 2002 Micron 33 499
[8] Molina L, Engel S, Knoth K, Hühne R, Holzapfel B, Eibl O. Microscopy and microanalysis (2007), 13: 412-413 Cambridge University Press
[9] Molina L, Knoth K, Engel S, Holzapfel B, Eibl O. TEM analysis of biaxially textured La$_2$Zr$_2$O$_7$ thin films by the Moiré technique. Poster presented at the DPG conference 2007, Regensburg
[10] Hühne R, Selbmann D, Eickemeyer J, Hänsich J, Holzapfel B. Supercond. Sci. Technol. 19 (2006) 169
[11] Knoth K, Hühne R, Oswald S, Molina L, Eibl O, Schultz L, Holzapfel B. Thin solid films (2007), doi:10.1016/j.tsf.2007.08.130
[12] Lu C J, Senz S, Hesse D Philosophical Magazine Letters, 2002 Vol.82, No.4, 167-174