

Oxygen diffusion in laser deposited YBaCuO thin films

Hans-Ulrich Krebs, Christian Krauns and Frank Mattheis
Institut für Metallphysik, University of Göttingen, Hospitalstraße 3-7, 3400 Göttingen,
Germany

Abstract

YBaCuO thin films were deposited on polycrystalline Zr sheets ($T_c = 89$ K) and single-crystalline MgO ($T_c = 90$ K) by KrF laser ablation. The oxygen loading was studied by resistance measurements. In the case of films on Zr the oxygen diffusion coefficients are similar to values determined for sintered pellets by thermogravimetric measurements. For films on MgO, the values are reduced by a factor of more than 100. These differences can be understood by the different microstructures of these films. In the case of films on Zr-sheets, the *c*-texture is not perfect and large-angle grain boundaries are 'open channels' for the diffusion of oxygen. The diffusion into the grains occurs parallel to the YBaCuO planes in *a/b*-direction. On the other side, in the case of high quality films on MgO with critical densities $j_c(77\text{K}) = 3 \cdot 10^6$ A/cm², the grain boundaries seem to be 'dense' and, therefore, the oxygen diffusion has to take place in *c*-direction, which increases the loading times by a factor of about 100 due to the anisotropic oxygen diffusion in the layered YBaCuO structure.

1. Introduction

Since a few years $Y_1Ba_2Cu_3O_Y$ (YBCO) thin films with superconducting transitions of about 90 K and critical current densities of more than 10^6 A/cm² at 77 K are obtained by almost every deposition method used so far. Especially, the pulsed laser deposition is found to be a suitable method for the preparation of high quality YBCO films from stoichiometric targets due to a 1:1-concentration transfer between target and film.^{1,2,3} In order to reach high superconducting transition temperatures the films have to be carefully prepared at high temperatures of about 750 °C and loaded with oxygen after deposition at lower temperature. For this reason, it is important to know the loading times for thin films prepared on different substrates.

In this paper we describe our results of the oxygenation of YBCO thin films grown on polished polycrystalline Zr-sheets and on single-crystalline MgO substrates. From the obtained results we propose a model, which correlates the different loading velocities to the anisotropic diffusion coefficients in the *a/b*- and the *c*-direction.

2. Experimental Procedures

Thin YBCO films were *in situ* deposited at temperatures between 700 and 800 °C and an oxygen partial pressure of about 0.3 - 0.5 mbar on polished Zr-foils and on single-crystalline (100) MgO substrates by KrF excimer laser ablation (Lambda Physik LPX110i) as earlier described.⁴ The structure and microstructure of the deposited films were examined by X-ray diffraction and scanning electron microscopy. T_c -measurements were performed by a conventional four-probe method.

The oxygen loading was directly monitored by resistance measurements at high temperatures. For these measurements the resistance of the films was measured by a four-probe method with silver painted contacts pressed on the film. At constant temperature the oxygen content was changed by varying the oxygen partial pressure from 10^{-4} to 1 bar.

3. Results and Discussion

The quality of the crystal structure,

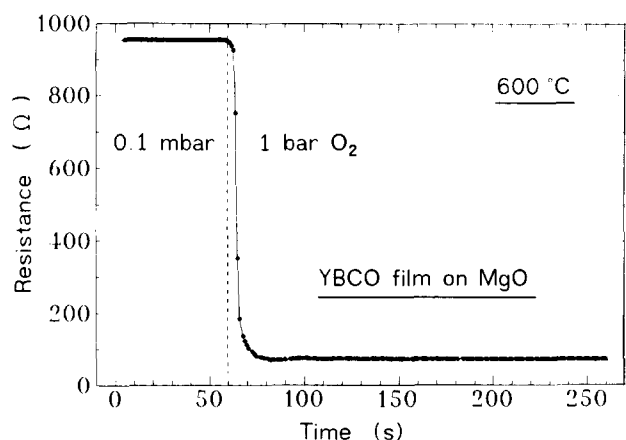


Figure 1. Resistance vs. time during oxygen loading of YBCO on MgO

the grain orientations and the superconducting properties of the YBCO films on Zr foils strongly depend on the surface roughness of the substrate, the used substrate temperature and oxygen partial pressure during deposition.⁵ The best superconducting properties ($T_c = 89$ K and $j_c(10\text{K}) > 10^4$ A/cm²), the sharpest rocking curves of the (006)-reflection of about 2.7° full width at half maximum (FWHM) and a c-lattice parameter of 11.68 Å were obtained in highly c-textured films grown on polished Zr sheets at 750 °C and 0.3 mbar O₂. These values are close to the stability limit of the perovskite structure.⁶

The superconducting properties of YBCO films deposited on single-crystalline MgO at 780 °C and an oxygen partial pressure of 0.5 mbar are characterized by a $T_{c,0} = 90.5$ K, a resistivity at 100 K of $\rho(100\text{ K}) = 150$ μΩ cm, a resistivity ratio of $\rho(300\text{ K})/\rho(100\text{ K}) = 2.8$, $j_c(4.2\text{ K}) = 10^7$ A/cm² and $j_c(77\text{ K}) > 3 \cdot 10^6$ A/cm².⁷ In these films the rocking curves of the (006) reflection are sharp (FWHM < 0.3°) indicating that these films are strongly epitaxially grown with 'perfect' c-texture.

In order to determine the oxygenation times for the thin films grown on the different types of substrates the resistance of the films was monitored during the loading process at different fixed temperatures. A typical resistance measurement performed at 600 °C is shown in Fig. 1 for a 80 nm thick film grown on MgO. As can

be followed, at this temperature the resistance drops within a few seconds by a factor of about 10 after changing the oxygen pressure from 1·10⁻⁴ to 1 bar. The resistance is constant after loading indicating that the thermodynamic equilibrium is reached. In Fig. 2 it can be followed that for thin films on Zr foils loading times (determined by 95 % of the resistance decrease) of a few seconds are obtained at a much lower substrate temperature of 400 °C, although the thickness of these films of about 500 nm was much larger compared with the film on MgO.

For each of the used substrates such experiments were performed at different substrate temperatures. The results are summarized in the time-temperature-transformation (TTT) diagram shown in Fig. 3. Obviously, the loading times for films grown on MgO strongly increase with decreasing temperature from about 10 s at 700 °C to about 25 min at 400 °C. On the other side, the loading times on polished Zr-foils are about two orders of magnitudes lower than those for the films on MgO.

4. Conclusions

In order to understand the differences in the loading times of the thin films on Zr foils compared with the results for the films on MgO, one has to compare the different textures and microstructures of the YBCO samples.

As earlier described^{7,9} it can be con-

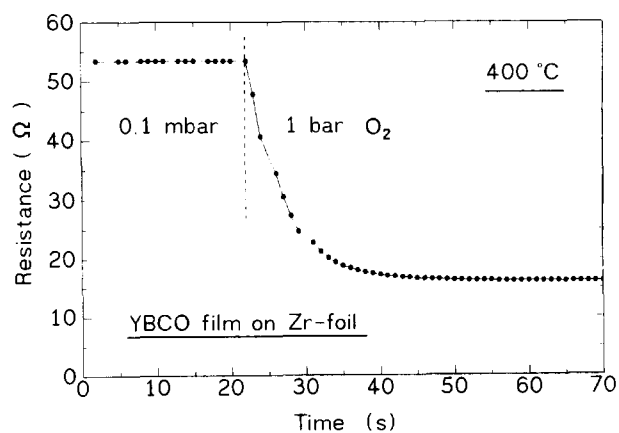


Figure 2. Resistance vs. time during oxygen loading of YBCO on a Zr foil

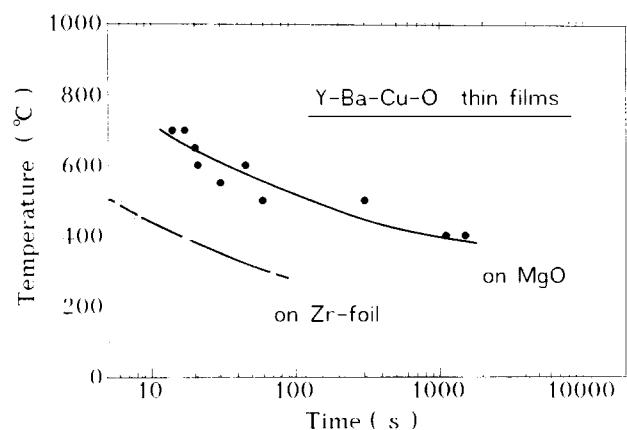


Figure 3. Time-temperature-transformation diagram for the loading of YBCO thin films on Zr foils and on MgO

cluded from texture measurements using a four circle diffractometer and from scanning tunneling measurements that the YBCO films grown under 'optimal' preparation conditions on Zr foils are not only c-textured, but also a partial alignment of the a/b-directions induced by the rolling texture of the Zr sheet occurs. Due to an island growth in the early stage of the film growth the incomplete alignment of the c- and a/b-directions leads to a large number of large-angle grain boundaries in the films on Zr. On the other side, the epitaxy on the MgO substrates leads to completely aligned a/b directions and a perfect c-texture. Therefore, only small-angle grain boundaries occur, although the early stages of the film growth on MgO are also characterized by an island growth. On both substrates the grain size of the obtained films is similar and the surface topography can be characterized by a large number of growth steps and growth spirals.

All the obtained results can be understood by the following model, which correlates the strongly different oxygen loading times with the differences in the film textures and microstructures:

(1) In the case of films on Zr-sheets, the large-angle grain boundaries are 'open channels' for the diffusion of oxygen and, therefore, the diffusion into the grains can occur parallel to the film planes in a/b-direction.

(2) On the other side, in the case of high quality films on MgO the small-angle grain boundaries seem to be 'dense', although the growth steps and growth spirals seen in scanning tunneling experiments probably lead to a complicated structure of these grain boundaries. Obviously, the oxygen uptake has to take place in c-direction, which reduces the loading times by a factor of more than 100 due to the anisotropic oxygen diffusion in the layered YBCO structure, which is well known from measurements on single crystals.¹⁰

The diffusion coefficients for the thin films on the different substrates can be compared with values obtained for sintered bulk pellets. The diffusion coefficients can be calculated by a random walk model by $\langle x^2 \rangle = 2 \cdot D \cdot t$ with the loading time t . In the case of thin films on Zr foils the grain radius determined by scanning electron microscopy was used for x , while in the case of films on MgO the film thickness has to be taken. The obtained diffusion coefficients are shown in Fig. 4. In this figure, the results of the increase in weight measured on bulk pellets with a density of about 75 % by thermogravimetric measurements (see Ref. 8) are included. As expected from the model discussed above, the diffusion coefficients for thin films grown on Zr foils are the diffusion coefficients in a/b direction $D_{a/b}$ and, therefore, are

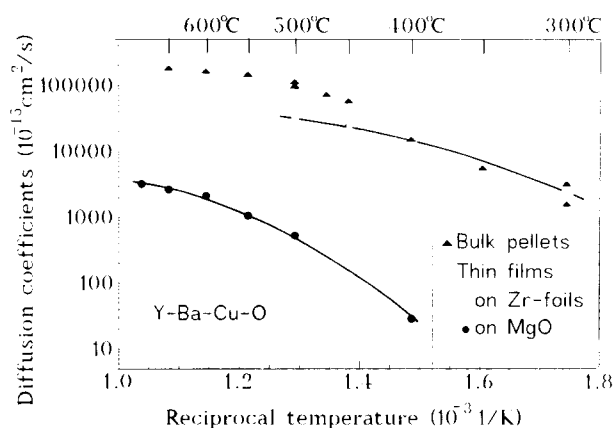


Figure 4. Diffusion coefficients for YBCO films grown on Zr and MgO substrates and on sintered pellets

similar to those of the bulk pellets. In both cases the oxygen atoms can easily reach the a/b-planes of the grains due to the 'open channels' of the large-angle grain boundaries of the films and the low density of the sintered material, respectively. On the other side, the diffusion coefficients along the c-direction D_c measured for films grown on MgO are reduced by two orders of magnitudes due to the anisotropy of the oxygen diffusion in the layered perovskite structure.

From these characteristic differences in the diffusion behaviors one can conclude that a determination of a slow oxygen uptake in thin films by resistance measurements can be taken as a crucial indicator for a high quality of the thin films with complete c-texture and only a small number of large-angle grain boundaries.

This work was supported by the BMFT under Grants No. FKZ 13N5493 and 13N5493A.

References

1. X.D. Wu, A. Inam, T. Venkatesan, C.C. Chang, P. Barboux, J.M. Tarascon, and B. Wilkens, *Appl. Phys. Lett.* **52** (1988) 754.
2. S. Witanachchi, H.S. Kwok, X.M. Wang, and D.T. Shaw, *Appl. Phys. Lett.* **53** (1988) 1557.
3. B. Roas, L. Schultz and G. Endres, *Appl. Phys. Lett.* **53** (1988) 1557.
4. H.U. Krebs, M. Kehlenbeck, M. Steins, and V. Kupcik, *J. Appl. Phys.* **69** (1991) 2406.
5. F. Mattheis and H.U. Krebs, this conference.
6. R. Bormann and J. Nölting, *Appl. Phys. Lett.* **54** (1989) 2148.
7. H.U. Krebs, Ch. Krauns, X.G. Yang, and U. Geyer, *Appl. Phys. Lett.* **59** (1991) 2180.
8. Ch. Krauns and H.U. Krebs, submitted to *Zeitschrift für Physik B*.
9. M. Steins, F. Mattheis, R. Gaebel, K. Bente, and H.U. Krebs, accepted for publication in *J. Cryst. Growth*.
10. S.J. Rothman, J.L. Routbort, and J.E. Baker, *Phys. Rev.* **B40** (1989) 8852.