Journal of Alloys and Compounds, 195 (1993) 555–558
JALCOM 7526

Effect of oxygen deficiency and disorder on microwave losses of epitaxially grown $YBa_2Cu_3O_{7-\delta}$ films

S. Orbach, S. Hensen, G. Müller, H. Piel
Fachbereich Physik, Bergische Universität Wuppertal, 5600 Wuppertal, Germany

M. Lippert, G. Saemann-Ischenko
Physikalisches Institut, Universität Erlangen, 8520 Erlangen, Germany

S.A. Wolf
Naval Research Laboratory, Washington, DC 20375-5000

Abstract

We have investigated the influence of oxygen content and disorder on the surface impedance of epitaxial $YBa_2Cu_3O_{7-\delta}$ (YBCO) films at 87 GHz. For this purpose, five films prepared by DC-sputtering on MgO substrates were annealed for 1 h at 500° C in different oxygen pressures between 80 and 1000 mbar. The degree of oxygen disorder was varied by a change of the cooling procedure or a subsequent annealing at 250° C. The absolute values as well as the slope of the resistivity in the normal conducting state and the penetration depth in the superconducting state are continuously increasing with δ. The transition temperatures change only slowly and a maximum in T_c vs. δ occurs. As a main result, we observe a strong influence of δ on the surface resistance below $0.8T_c$ which first increases at the maximum of T_c and then decreases for higher oxygen deficiencies. Oxygen disorder leads to a degradation of all measured quantities, but R_s was found to be most affected. These observations can be explained in the context of a recent model by Kresin and Wolf which proposes two conductive subsystems and, as a result, a two-gap structure of YBCO. Charge transfer between the Cu-O planes and chains leads to an induced superconducting state in the chains. Oxygen content and order affect the value of the smaller energy gap of the chains, which in turn has a large impact on R_s. However, T_c changes only slowly, reflecting its main correlation to the large energy gap given by the planes.

1. Introduction

In contrast to classical superconductors, for most of the YBCO films a high and only slightly temperature dependent surface resistance R_s has been measured at temperatures below $0.8T_c$ [1, 2]. Recent observations of a weak exponential decrease of R_s at temperatures below 50 K [2, 3] for films with improved structural properties as well as a decrease of R_s after ^{16}O-ion irradiation [4] indicate that the high residual losses are not intrinsic. Several experimental results [5, 6, 7] and recent theoretical studies [8, 9] demonstrate that oxygen content and order are important parameters which affect the superconducting properties of YBCO.

In the test series reported here, we started to investigate the surface impedance of films with different oxygen deficiency and disorder in order to clarify the role of oxygen for the microwave losses of YBCO. First, we describe the details of the preparation and the annealing procedure. In the main part, the results of the surface impedance measurements are presented and discussed in the frame of a recent theoretical model by Kresin and Wolf [9].

2. Preparation and characterisation of the films

Five epitaxial, c-axis oriented YBCO films were deposited in situ on single-crystalline $1\times1\ cm^2$ substrates of ⟨100⟩ MgO by high oxygen pressure DC-sputtering and cooled to room temperature in 1 h. The oxygen was partially removed by annealing the films in a vacuum chamber for 1 h at 500° C (T_H) in different oxygen pressures $p(O_2)$ (Tab. 1). The samples were slowly cooled (sc) in 2 min down to 250° C and in 20 min to room temperature. In a second test series, sample #1 was annealed stepwise. First (#1b), it was annealed in the same way as #2 but fast cooled (fc) in 4 s down to 250° C and in 20 s to room temperature. In the second step (#1c), this film was annealed for 0.5 h at 250° C at 1000 mbar and cooled slowly. Finally (#1d), the annealing and cooling procedure of #4 was repeated.

After each step, the surface impedance was measured (Sec. 3) and the length of the c-axis was determined from the evaluation of up to seven (00ℓ) reflections. As oxygen is removed, the (00ℓ) peaks remain sharp, indicating that the oxygen content is uniform in the samples. For state d of sample 1 and for sam-

0925-8388/93/$06.00

Tab. 1: Overview of the structural and microwave data of the YBCO films. All symbols are explained in the text.

#	d [nm]	$p(O_2)$ [mbar]	T_H [°C]	c [Å]	δ (upper limits)	T_c [K]	$R_s(4.2\,K)$ [mΩ]	$R_s(0.85T_c)$ [mΩ]	$\lambda(0)$ [nm]	$\rho(100\,K)$ [μΩcm]	$\partial\rho/\partial T$ [μΩcm/K]
1	300	not annealed		11.689	0.15	89.5	4	23	150	80	1.3
2	330	1000	500, sc	11.704	0.25	92	22	54	200	116	2.3
3	290	300	500, sc	11.710	0.27	91	6	24	210	151	2.8
4	280	150	500, sc	11.716	0.3	87	5	33	240	168	3.1
5	300	80	500, sc	11.729	0.4	59	100	102	290	215	-
1b	300	1000	500, fc	11.705	0.25	89.5	71	68	290	154	2.8
1c	300	1000	250, sc	11.705	0.25	89.5	21	72	290	175	4.3
1d	300	150	500, sc	11.72	0.33	80	6	77	310	182	5.0

ple #5, we observe a peak broadening, which can be explained with a distribution of c-axis values.

According to a correlation between c-axis length and oxygen deficiency [10], we determine rather high values of δ (Tab. 1). They are not consistent with δ values obtained from a T_c-δ-correlation [7], which are about 0.07 lower. Since this problem does not occur for films on $LaAlO_3$ or $SrTiO_3$, we assume that films on MgO exhibit an additional shift in the c-axis length which is due to the large lattice mismatch. Therefore, we present our data versus c-axis length as a relative measure for the oxygen content. Detailed information about the samples as well as structural and microwave data are summarized in Tab. 1.

3. Surface impedance measurements

The effective surface impedance was measured at low magnetic surface fields ($\lesssim 20\,A/m$) between 4.2 K and 150 K. The films were mounted as an endplate of a cylindrical cavity, which is excited near 87 GHz in the TE_{013}-mode for $R_{eff} \lesssim 1\,\Omega$ and in the TE_{021}-mode for $R_{eff} \gtrsim 1\,\Omega$ [11]. The absolute accuracy of the effective surface resistance R_{eff} of the films is limited by the losses of the copper host cavity to about $\pm 3\,m\Omega$. Changes in R_{eff} and in the effective penetration depth λ_{eff} can be detected with a sensitivity of $0.3\,m\Omega$ and 1 nm respectively. The intrinsic values, R_s and λ, depend on the relative film thickness d/λ and were determined by an analysis of the film-substrate sandwich, based on impedance transformations [12]. The variation of the film thickness d, which was measured by an α-stepper to be about 10 % over the sample area, contributes to additional 5 % uncertainty in the determination of R_s and λ.

The average resistivity ρ of the films was determined from R_s by means of the normal skin effect formula. The absolute values of ρ as well as the slope of the resistivity $\partial\rho/\partial T$ up to 150 K increase linearly with δ (Tab. 1, #1...#5), in good agreement with other experiments [6, 13]. The linear $\rho(T)$ behaviour is observed for all films, except for film #5 where a strong increase of the slope above 120 K occurs. By comparison of the films #2 and #1b, it is seen that fast cooling leads to slightly higher values of ρ and $\partial\rho/\partial T$. Subsequent low-temperature annealing (#1c) results in a further enhancement of both quantities.

It can be seen from Fig. 1 that T_c, determined from the onset of the microwave transition, is not monotonic with δ but shows a maximum at $c = 11.704\,Å$. This peak within the "90 K-plateau" has been observed by several authors [6, 13]. After fast cooling (#1b), the maximum disappears (Tab. 1) and is not recovered by low-temperature annealing (#1c).

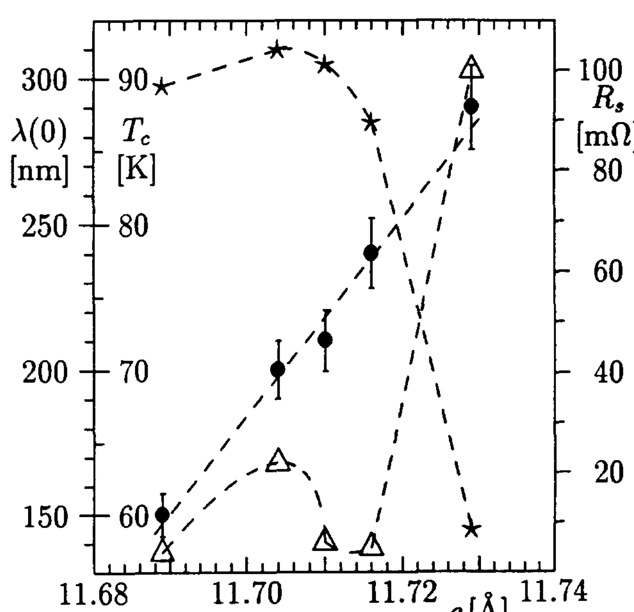

Figure 1: T_c (⋆), $\lambda(0)$ (•), and $R_s(4.2\,K)$ (△) versus c-axis length for the films #1...#5. The lines are included to guide the eye.

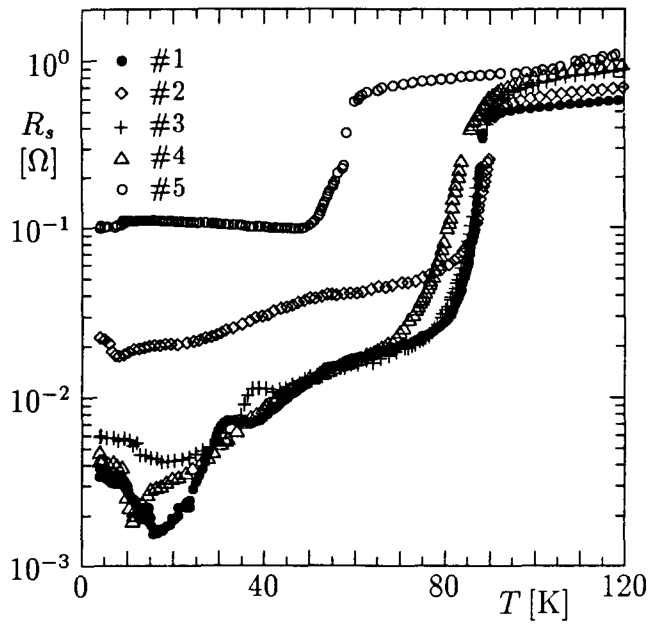

Figure 2: $R_s(T)$ as a function of the oxygen content.

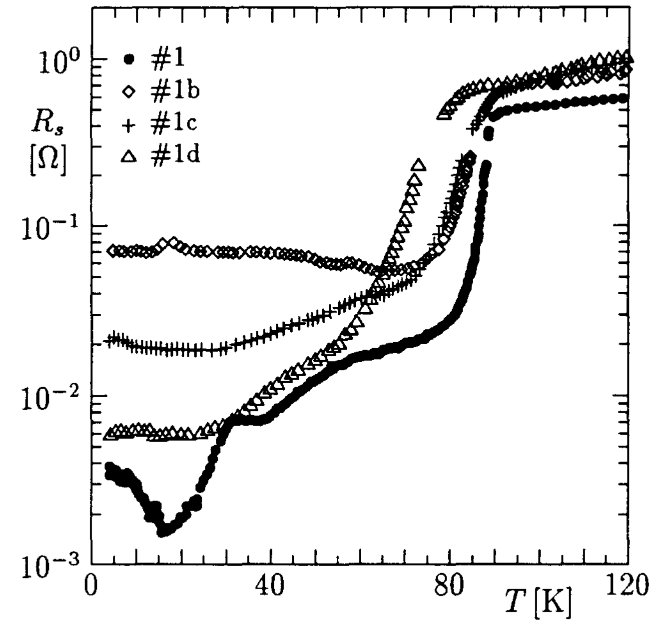

Figure 3: $R_s(T)$ as a function of oxygen content and order.

From the measurement of the resonant frequency shift we obtain the change of the penetration depth with temperature. The absolute $\lambda(0)$ values were determined from fits to the weak-coupling BCS-theory in the clean limit. The penetration depth increases linearly with increasing δ (Fig. 1) and is enhanced after fast cooling (#1b). This change is not recovered after low-temperature annealing (#1c).

In contrast to ρ and $\lambda(0)$, the surface resistance in the superconducting state exhibits a more complicated dependence on the oxygen content (Figs. 1, 2). The small maxima and minima in the $R_s(T)$ curves at low temperatures are sometimes observed, but not understood yet and will not be discussed in this contribution. Instead, we want to focus on the absolute level of the residual losses. Below $0.8T_c$, R_s first increases (#2) and then decreases for higher oxygen deficiencies within the "90 K-plateau" (#3,#4). There, R_s is similar to that of the film with the highest oxygen content, but the transition is broadened. At $c = 11.729$ Å (#5), the residual losses are drastically increased. Another important result is the strong effect of the annealing procedure on R_s (Fig. 3). After fast cooling, film #1b shows significantly higher R_s values than film #2, although they exhibit the same c-axis value. After a subsequent annealing at 250° C (#1c) this difference vanishes and the R_s-values of #2 are recovered. Further oxygen depletion (#1d) leads to an improvement of R_s below $0.8T_c$ and confirms the results of the first test series (#4). However, for film #1d as well as for #5, the microwave transitions are very broad, and there exists a discontinuity of the R_s-data near T_c, where the microwave field distribution is switched from the TE_{013}- to the TE_{021}-mode. These results appear to be consistent with the observed (00ℓ) peak broadening (Sec. 2), indicating that the oxygen contents are not uniform.

4. Discussion

In the model of Kresin and Wolf [9], the YBCO compound is described as containing two conductive subsystems, i.e. Cu-O planes and chains, and correspondingly, having two energy gaps. Charge transfer between these subsystems can be provided by two channels: 1. intrinsic proximity effect and 2. phonon-mediated coupling. Both make a positive contribution to the induced energy gap in the chains, whereas T_c is affected in opposite ways by these two channels. The main result is that the chain gap is reduced, and even made gapless, if oxygen is depleted from the chains. The gapless state arises when the average length of the Cu-O chain fragments is less than the estimated coherence length $\xi = 25$ Å of the chains [9]. For random oxygen defects, this should occur somewhere between $\delta = 0.1$ and 0.2. However, if the oxygen defects order, the average chain fragments are longer than ξ for the same δ, and the system does not become gapless.

The results of R_s below $T_c/2$, which is governed by the smaller chain gap [14], appear to be consistent with this model. The initial sample #1 with an oxygen content of about 6.85 might have still a small gap. A much more pronounced exponential decrease was observed for other films [2, 3, 14], which exhibit a higher oxygen content. When the sample is heated and fast cooled (#1b), random oxygen defects are produced, with a resulting oxygen content below 6.8. Therefore, the gap is suppressed, leading to the observed drastically enhanced losses. Low-temperature annealing and slow cooling (#1c) do not alter the oxygen content [5] but allow oxygen ordering, causing an increase in the size of the chain segments and possibly the reappearance of a gap on some of the chain segments and a decrease in R_s. In fact, R_s is improved in good agreement with the result of sample #2, where the same oxygen content and ordering was achieved in one step. The positive effect of low-temperature annealing has been confirmed by N. Klein et al. [14].

As the oxygen content is further decreased, two ordered orthorhombic phases OIII (at $\delta = \frac{1}{3}$) or OII (at $\delta = \frac{1}{2}$) can be formed [5, 8], where every third or second chain contains no oxygen, while the other chains are filled. In this context, the improvement of R_s after further oxygen depletion (#3, #4, and #1d) can be understood. The oxygen content of these films is close to 6.7 and the OIII phase might be formed at least to some extent. This leads to a decrease of R_s, according to the mechanism described above. We observed a similar behaviour earlier: films irradiated with higher ^{16}O-ion fluences, which exhibit higher c-axis values, show less losses than more weakly irradiated films [4]. Sample #5 exhibits very high losses which could be attributed to the less ordered state between the OIII and OII phases.

Within this model, we can also understand two further observations: 1. The pronounced exponential decrease of R_s at low temperatures [2, 3, 14] weakens a few weeks after film preparation, as expected for reduction of the oxygen content. 2. For samples with initially higher losses, we found an improvement of R_s after a few months, which could be explained by ordering due to "room-temperature annealing".

The other quantities investigated in this contribution, i.e. T_c, $R_s(0.85T_c)$, $\lambda(0)$, $\rho(100\,\mathrm{K})$, and $\partial\rho/\partial T$, are mainly correlated to the Cu-O planes and therefore less influenced by changes of oxygen content and disorder. Nevertheless, the distribution of oxygen in the chains determines the coordination number of the chain copper atoms, which is believed to affect the charge transfer and, therefore, changes the carrier concentration in the planes [5]. This leads to the observed small and monotonous increase of λ and ρ with increasing δ. However, T_c is nearly unchanged and exhibits a maximum in the "90 K-plateau". This behaviour can be explained by the assumption that T_c is affected in opposite ways by the two channels which provide the charge transfer [9].

Although oxygen ordering, indicated by a decrease of R_s, affects T_c, ρ, and λ only slightly, a negative influence of fast cooling has been found for all quantities. This is not yet understood, but we often found that $R_s(4.2\,\mathrm{K})$ is not strongly correlated with the other quantities [2, 4]. Especially in this case, the improvements of R_s take place without improvements of λ, indicating that changes in the quality of weak links [15, 16] are not the dominating mechanism.

In conclusion, we point out that microwave losses of YBCO films depend strongly on oxygen content *and* order. The number of Cu-O chain fragments seems to be the key parameter which determines the chain gap and therefore R_s below $T_c/2$. Further microwave measurements on films with systematically varied oxygen contents and annealing procedures, especially close to $\delta = 0$, $\delta = \frac{1}{3}$, and $\delta = \frac{1}{2}$ are planned. Accompanying electron diffraction experiments would be helpful to investigate the relationship between atomic structure and superconducting behaviour.

For fruitful discussions, we thank V.Z. Kresin from Lawrence Berkeley Lab. and N. Klein from Forschungszentrum Jülich. We wish to acknowledge the friendly support of M. Hein, M. Lenkens, and A. Both from University of Wuppertal and W. Dorsch from University of Erlangen. This work has been funded in part by the German Federal Minister for Research and Technology (BMFT) under the contract numbers 13N5502A and TK0336 0.

References

1 H.Piel, G.Müller, IEEE Trans. MAG-27,854(1991).
2 S.Orbach et al., Proc. of the IV Soviet-German Seminar on HTSC, St. Petersburg, 438 (1991).
3 N.Klein et al., J. Supercond. 5, 195 (1992).
4 S.Orbach et al., in "High T_c Superconductor Films", ed. L.Correra, North Holland, 107 (1992).
5 B.W.Veal et al., Phys. Rev. B42, 6305 (1990).
6 H.Claus et al., Physica C198, 42 (1992).
7 J.D.Jorgensen et al., Phys. Rev. B41, 1863 (1990).
8 R.McCormack et al., Phys. Rev. B45, 12976 (1992).
9 V.Z.Kresin, S.S.Wolf, Phys. Rev. B46, 6458 (1992).
10 M.E.Parks et al., J. Sol. St. Chem. 79, 53 (1989).
11 N.Klein et al., Appl. Phys. Lett. 54, 757 (1989).
12 N.Klein et al., J. Appl. Phys. 67, 6940 (1990).
13 R.Feenstra et al., Phys. Rev. B45, 7555 (1992).
14 N.Klein et al., subm. to IEEE Trans. Supercond..
15 J.Halbritter, J. Appl. Phys. 71, 339 (1992).
16 M.Hein et al., J. Magn. Magn. Mat. 104–107, 529 (1992).