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# Room Temperature Oxidation of YBCO Thin–film by μs Pulsed Electrolysis in Aqueous Solution

M. Boutet, D. Di Gioacchino, F. Celani, A. Spallone, P. Tripodi
INFN – Laboratori Nazionali di Frascati, Via E.Fermi 40, I–00044 Frascati, (Roma) Italy

M. Polichetti
Phys. Dept., Univ. of Salerno, 84100 Baronissi (Sa), Italy

P. Cocciolo
Phys. Dept., II Univ. of Rome, Via della Ricerca Scientifica 00133 Rome, Italy

N. Sparvieri
Alenia Dir. Ric., Via Tiburtina Km. 12,400 Rome, Italy

**Abstract**

In this paper the oxygen deficiency of $YBa_2Cu_3O_{7-x}$ (YBCO) films has been decreased at room temperature by the anodic oxidation in an aqueous solution of LiOH (0.3 N). The anodic oxidation of the films has been performed by μs pulsed electrolysis by means of short (1.3 μs) and high current peak (up to 15.2 A) with a low duty cycle at 5 KHz. The very high oxygen equivalent pressure on the electrode surface allows to increase the oxygen stoichiometry with a simple experimental set–up.

The films have been characterized by the X–ray diffraction (XRD) and the temperature dependence of the dc resistivity.

It appears that the pulsed electrolysis allows to enhance the critical temperature with a corresponding transition from the "semiconducting" to the "metallic" behavior of the temperature dependence of the resistivity.

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## I. INTRODUCTION

Since the discovery of the superconducting oxides, the correlation between the oxygen stoichiometry and the superconducting properties has been extensively studied [2], [3], [4]. In fact, if the oxygen stoichiometry of the $YBa_2Cu_3O_{7-x}$ (YBCO) is lowered from 7 to 6, the crystalline structure goes from the orthorhombic to the tetragonal one [2], [3], [4] and the c–axis lattice parameter increases. At same time the critical temperature decreases and the normal state of the temperature dependence of the resistivity goes from the metallic behavior to the insulating one, until the superconducting properties disappear. However, high temperature treatments are usually involved in oxygen atmosphere to get the appropriate oxygen stoichiometry [1].

In this paper the μs pulsed electrolysis [7] has been explored to increase the oxygen stoichiometry of the oxygen deficient YBCO films at room temperature. The electrochemical method has the advantage to generate a very high equivalent gas pressure on the electrode surfaces and, as a consequence, to enhance the oxygen penetration at the sample surface [6]. We adopted the pulsed procedure because it appears ulteriorly to enhance the equivalent oxygen pressure [7].

Advantages in oxygen loading at room temperature arise from the absence of high temperature treatments, which often avoid the use of poisoning doping substrates or give problems in hybrid semiconductors–superconductors devices. Furthermore, without high temperature cycles, the pulsed procedure can restore the oxygen stoichiometry of the YBCO films damaged by their high reactivity with the ambient atmosphere [8], [9].

In the section II we briefly describe the sample preparation, the experimental apparatus and the electrochemical cell; further details are given elsewhere [7]. In the section III the loading procedure and the experimental results are reported and discussed.

## II. SAMPLE PREPARATION AND EXPERIMENTAL APPARATA

The films, 2000 Å thick, have been deposited on the MgO (100) substrate. They have been produced by laser ablation starting from a stoichiometric high density commercial target. The substrate temperature was equal to 730°C and the oxygen pressure to 500 mTorr. During the cooling, the film F015 has undergone a heat–treatment at 450°C in 1 atm oxygen pressure of for 30'. The temperature controller was turned off after the deposition of the sample F041, so it was grown with a oxygen deficiency.

The samples have been characterized by dc resistive measurements in the range between 30 and 300 K and, only in same cases, by XRD.

We performed the electrochemical loading by the set up described in a previous paper [7]. The charging is performed in an aqueous solution of LiOH (0.3 N in $H_2O$) at room temperature. The YBCO film is the anode and is polarized by a home–made power pulse generator, which supplies high peak power (up to 1.2 KW) with a high repetition rate (up to 20 KHz) and high peak current density on the YBCO surface. The cathode is made by a nickel–passivated network, connected to ground.

We have chosen 3 parameters to characterize the samples: the onset temperature of the resistive superconducting transition $T_{c,off}$ (where the sample resistance in the superconducting state starts to increase, increasing the temperature); the offset temperature $T_{c,on}$ (where the resistance in the normal state starts to decrease, decreasing the temperature) and the superconducting transition, defined as ($T_{c,on}$–$T_{c,off}$).

## III. EXPERIMENTAL RESULTS AND DISCUSSIONS

In figure 1 we show the resistance plotted as a function of the temperature of the sample F015, normalized as regards the 300 K resistence. After the deposition ($\alpha$ curve) the sample showed a $T_{c,off}$ equal to 88.3 K and a $T_{c,on}$ equal to 92.5, with a good metallic behavior in the normal state. After 6 months from the deposition ($\beta$), the sample showed a metallic behavior for T > 200 K, while, at lower temperature, a semiconducting one, without a superconducting transition down to 30 K. It clearly appears that the oxygen stoichiometry of the sample was decreased down to 6. We performed the electrolityc procedures imposing a current peak density between 6 and 10 A/cm$^2$ for 30'. After the oxidation of the sample, the resistivity dependence from the temperature of the film ($\gamma$) shows again a transition temperature ($T_{c,off}$ equal to 92.3 K) slightly lower than the $T_{c,on}$ measured just after the deposition; the $T_{c,off}$ is 75 K, i.e. the superconducting transition is broader than before. In the normal state we can observe on the plot a "hump", which could be correlated to a still poor oxygenation of the film [3]. We performed again the electrolysis and the result are shown on the plot ($\delta$), with a good metallic behavior in the normal state without the hump previously shown: it should confirm that it was due to a poor oxygenation of the sample. The $T_{c,on}$ is slightly decreased, while the $T_{c,off}$ is increased to 79.2 K.

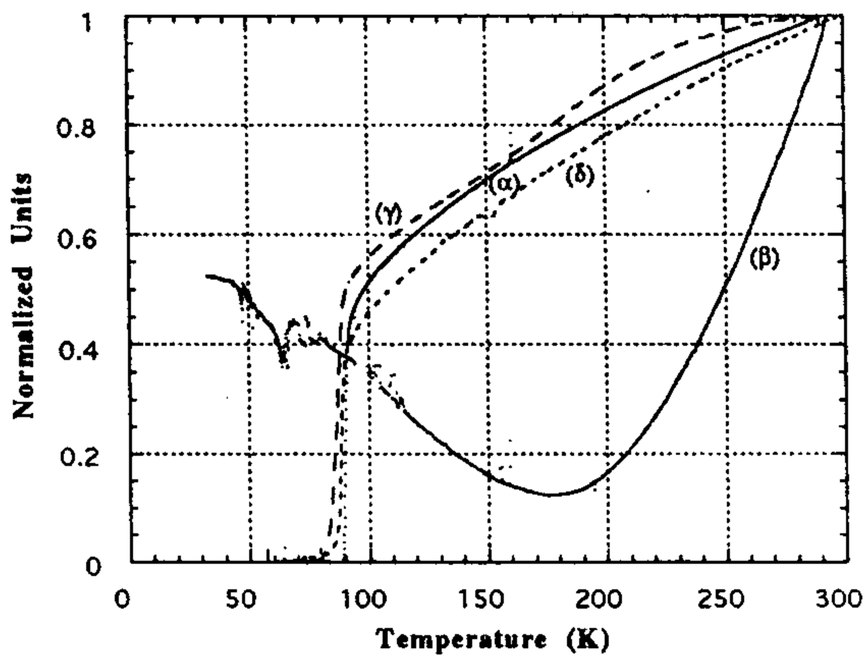


**FIG 1** – Temperature dependence of the dc resistivity of the sample F015 measured after the deposition ($\alpha$), after 6 months from the deposition ($\beta$), after the first electrolysis ($\gamma$) and after the second electrolysis ($\delta$).

In figure 2 we show the temperature dependence of the resistivity of the sample F041 deposited in oxygen deficiency. The plot ($\alpha$) correspond to the sample characterization after the deposition, it shows a $T_{c,off}$ = 43 K and a $T_{c,on}$ = 81.2 K, with a superconducting transition quite broad. We have characterized the deposited sample by the XRD too, they show

the presence of grains, oriented orthogonally to the film surface, both of the a– and/or the b–axis and of the c–axis (equal to 11.7 Å).

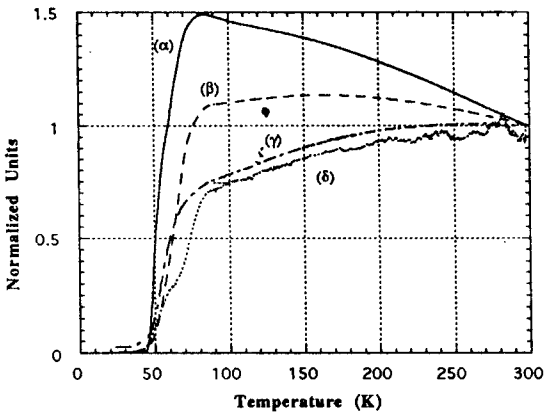


**FIG. 2** – Temperature dependence of the dc resistivity of the oxygen deficient sample F041 measured after the deposition (α), after the first (β), the second (γ) and the third electrolysis (δ).

After the first oxidation, we can observe on the plot (β) an enhancement of the $T_{c,on}$ to 88 K and a slight increase of the $T_{c,off}$ to 43.5 K. The normal state resistivity is changed from a semiconducting behavior to a metallic one. The next oxygenation (γ), while made worse the $T_{c,off}$ and the $T_{c,on}$, improved the metallic behavior of the normal state. The last electrolysis (δ), even if it increased the $T_{c,off}$ and the $T_{c,on}$ respectively to 36 and 87 K, seems that spoiled the sample F041: in fact the signal is quite noisy.

After the cycle of the electrochemical treatments, we could characterize the sample F041 by the XRD again. In figure 3 the XRD are plotted between 37 and 40 degrees in 2ϑ, before and after the oxidation. The c–axis seems to be unchanged. Before the oxygenations (α), the film is nearer to the tetragonal phases, in fact the 013 and 103 peaks are merged together: the evidence is that the peak intensity is higher than the peak 110. After the electrochemical treatments the peaks height is reversed, so the peak 013 is alone, while the peak 103 is merged with 110: the sample is in the orthorhombic phase [10].

## CONCLUSIONS

It seems that it is possible to increase the oxygen stoichiometry in YBCO film by the μs pulsed electrochemical method by means of an easy experimental set up. The electrolysis is performed at room temperature in an aqueous solution. We restored the superconducting properties of the film F015, spoiled by the adverse environment. In the sample F041, deposited in oxygen deficiency, we changed the conducibility in the normal state from a semiconducting behavior to metallic one and we increased the $T_{c,on}$, with a decrease of the $T_{c,off}$. Moreover, the XRD shows that the structural state has changed from tetragonal to orthogonal. The c–axis of the sample F041 did not change, this could be explained in the following way: in presence of grains grown orthogonally to the film surface in any direction, it is easier to oxygenate the a/b–axes because the oxygen diffusion coefficient is much faster along these axes than along

the c–axis [5]. We can affirm that the oxidation modalities depend also from the film orientation on the substrate.

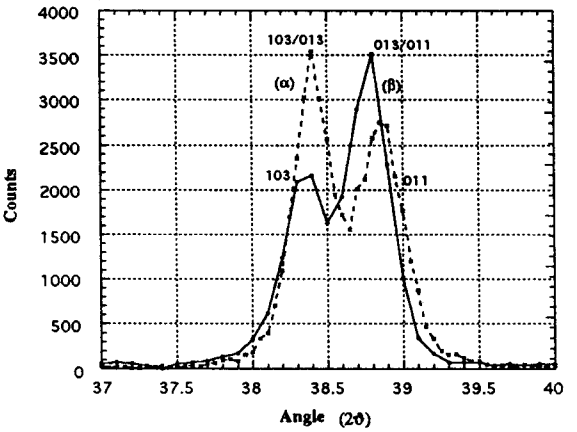


**FIG. 3** – X–ray diffraction pattern before (α) and after (β) the electrochemical treatments of the sample F041.

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