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LA-UR -89-3963

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DE90 003655

DEC 0 4 1989

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TITLE PARTIAL REDUCTION RE-OXIDATION PROCESSING OF Y-Ba-Cu-O SPUTTERED THIN FILMS

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SUBMITTED TO Materials Research Society Proceedings Fall Meeting 1989

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Partial Reduction Re-oxidation Processing of Y-Ba-Cu-O Sputtered Thin Films

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Abstract

Thin films of Y-Ba-Cu-O were produced by RF sputtering of $YBa_2Cu_3O_{7-x}$ ceramic targets, using a variety of plasma compositions, RF power levels, and substrate temperatures. Post annealing of these films in oxygen produced superconducting films with T_c values between 40-60 K, broad transition widths and semiconductor-like electrical behavior above T_c. Subsequent annealing at 850°C in an inert gas with a residual oxygen partial pressure of ≤10 ppm followed by an oxygen anneal produced high quality thin films: T_c> 85 K with narrow transition widths. The structure and morphology of these films during reduction-oxidation processing were monitored using X-ray diffraction and electron microscopy.

Introduction

RF sputtering of $YBa_2Cu_3O_{7-x}$ from a single composite oxide target is a potentially attractive method for producing high temperature superconducting thin films [1-5]. The process is well adapted for large area coverage and is a less complex deposition technique than multi-target sputtering, coevaporation, chemical vapor deposition or laser ablation. To become a preferred deposition method it must be capable of producing superconducting films of comparable or better electrical and morphological quality than the other techniques.

Deposition and Annealing

Y-Ba-Cu-O was deposited onto 1 cm^2 (100) $SrTiO_3$ substrates by RF sputtering of 15 cm composite oxide targets (MRC 17-34-49 and 15-29-45 atom % Y-Ba-Cu) in an Ar/O_2 atmosphere of 21μm of Hg total pressure. Single crystal substrates were mounted either perpendicular or parallel to the electrodes. Film compositions were measured using energy dispersive X-ray microanalysis and/or Rutherford backscattering spectroscopy. X-ray diffraction and scanning electron microscopy as shown in Fig. 1, revealed that the films deposited at ambient temperature were amorphous in structure. A post-anneal in O_2 at 850°C for 1 hour then a hold at 400°C for 2 hours was initially used to crystallize the material.

Structure Morphology and Electrical Properties

The electrical quality of the post-annealed material was poor; four-point DC conductivity measurements illustrated in figure 2, typically displayed semiconductor like pre-transition behavior and broad superconducting transitions with depressed T_c values ranging from 40-70 K . The diffraction patterns of the post annealed material displayed in Fig.4 suggest the formation of a tetragonal (no orthorhombic splitting of the (103) (013) (110) reflections)

$YBa_2Cu_3O_{7-x}$ related structure of random crystallographic texture along with other impurity phases. The ratio of the intensities (002)/(110) reflections were much lower than the intensities calculated from the hypothetical diffraction pattern and the absence of the (001) reflection, both suggest considerable disorder along the c axis. Further annealing at 850°C for 72 hours followed by 400°C for 2 hours did not significantly alter the diffraction patterns (Fig.4) or the electrical behavior (Fig.2). The possibility of chemical contamination arising from the deposition system was investigated; previous dopant studies indicate that some foreign cations favor the growth of tetragonal rather than orthorhombic phase material.[6] This hypothesis was discounted as X-ray microprobe and Auger surface analysis did not reveal the presence of any extraneous metal species.

Reduction/Oxidation Processing

Another explanation proposed for the poor film quality was that low concentrations of trapped Ar from the sputtering process may be affecting the superconductor growth. Because phase decomposition of the material in a non-argon containing atmosphere would liberate any entrapped gases, films were consequently reduced in a He atmosphere followed by a re-oxidation in O_2. An 850°C anneal for four hours in He with a residual oxygen partial pressure of $\leq 10^{-5}$ atm followed by an oxidation in O_2 at the same temperature for 10 hours dramatically improved the crystal structure and the electrical behavior and of the thin films. This effect also has been independently observed by other investigators [7]. A series of X-ray diffraction and SEM measurements were performed to investigate what morphological and structural modifications were occurring during the reduction and oxidation processing steps. The diffraction patterns of the partially reduced thin films indicated that the tetragonal structure was totally decomposed. Complete phase identification from powder x-ray diffraction was not possible in this system due to the large number of potential phases with overlapping reflections and possible epitaxial effects eschewing the relative intensities of the peaks. One of the new phases that appeared after He annealing is probably $Y_2Ba_4O_7$. This pervoskite-related structure has a lattice spacing of ~5.8Å closely matched to c/2 -5.75Å of the 123 compound. The Y-Ba-O phase may recombine with copper rich phases to form 123 directly upon re-oxidation. The diffraction pattern of the re-oxidized material shows the presence of c and a epitaxial orthorhombic $YBa_2Cu_3O_{7-x}$ plus minor quantities of second phases, thermodynamically consistent with the starting composition 21-32-47 atom % Y-Ba-Cu that deviated slightly from ideal stoichiometry. The morphology of the these films (Fig.1) was a granular platelet on edge and platelet lying parallel to the substate structure typical of mixed a c epitaxy thin films [8]. The electrical response of the thin films after re oxidation displayed in Fig.3, exhibits metallic pretransition behavior, a ratio of 100 K/300 K DC conductivity of 0.59, $T_{c\ 0}$ at

85 K and narrow transition widths. This conductivity behavior is similar to thin films deposited by coevaporation techniques of similar composition on (100) strontium titanate substrates.

Conclusions

The RF sputtering process and oxygen post-anneal creates a possibly c axis disordered "123 like" structure that does not arise from metallic impurities. The structure exhibits strong kinetic stability; long term anneals in oxygen do not significantly alter the X-ray diffraction patterns or the superconductive properties. The compound can decomposed in a reducing He atmosphere at 850°C. Upon re-oxidation epitaxial orthorhombic $YBa_2Cu_3O_{7-x}$ with good electrical properties forms in accordance with the equilibrium phase diagram.

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Figure 1.
Scanning electron micrographs of films of Y-Ba-Cu-O on (100) $SrTiO_3$ processed under different atmospheric conditions.

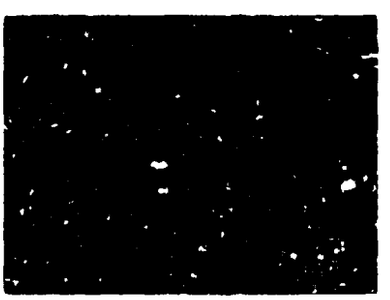
Figure 2.
The upper trace plots DC resistivity versus temperature behavior for films processed in oxygen for 1 hour at 850°C followed by 2 hours at 400°C in O_2. Lower trace: 72 hours at 850°C followed by 2 hours at 400°C in O_2.

Figure 3.
DC resistivity versus temperature behavior for a film processed in oxygen for 72 hours at 850°C followed by 2 hours at 400°C in O_2 (upper trace) and for the film subsequently annealed 4 hours at 850°C in He, then re-oxidized for 10 hours at 850°C in O_2 and held for 2 hours at 400°C (lower trace).

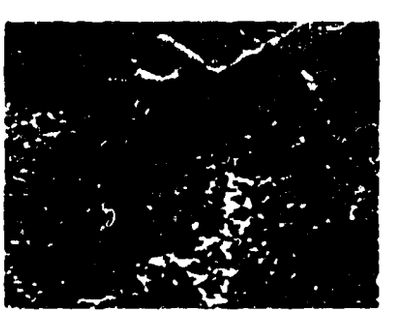
Figure 4.
X-ray diffraction patterns (Cu K_α radiation) for RF sputtered Y-Ba-Cu-O films sequentially processed: *a*) 1 hour at 850°C then 2 hours at 400°C in O_2 , *b*) followed by 4 hours at 850°C in He, *c*) re-oxidized for 10 hours at 850°C in O_2 then annealed for 2 hours at 400° C. Stars indicate 123 reflections, $Y_2Ba_4O_7$ reflections are marked x.

EFFECT OF ANNEALS

AS SPUTTERED



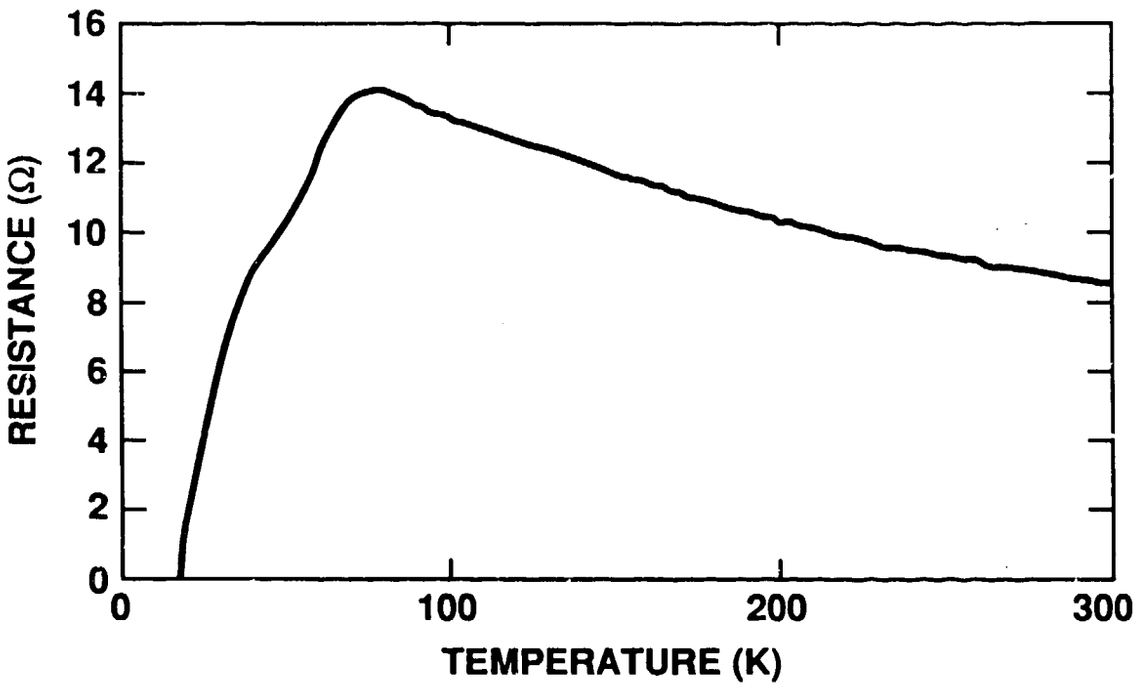
O_2 ANNEAL



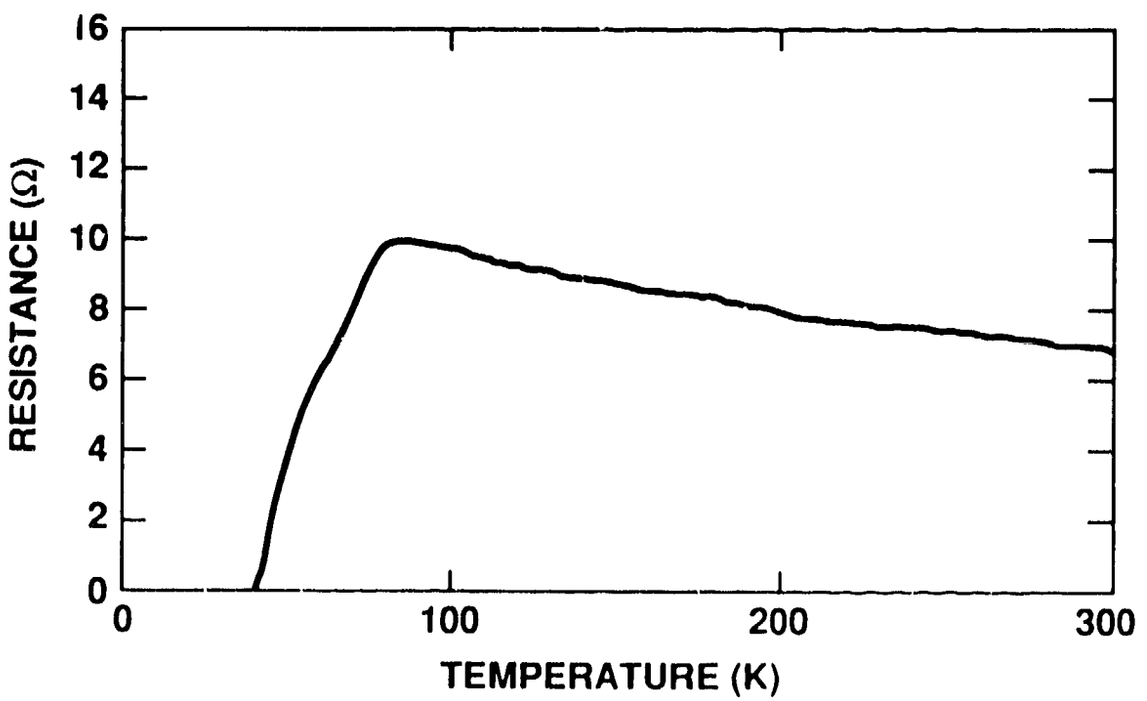
He/O_2 ANNEAL

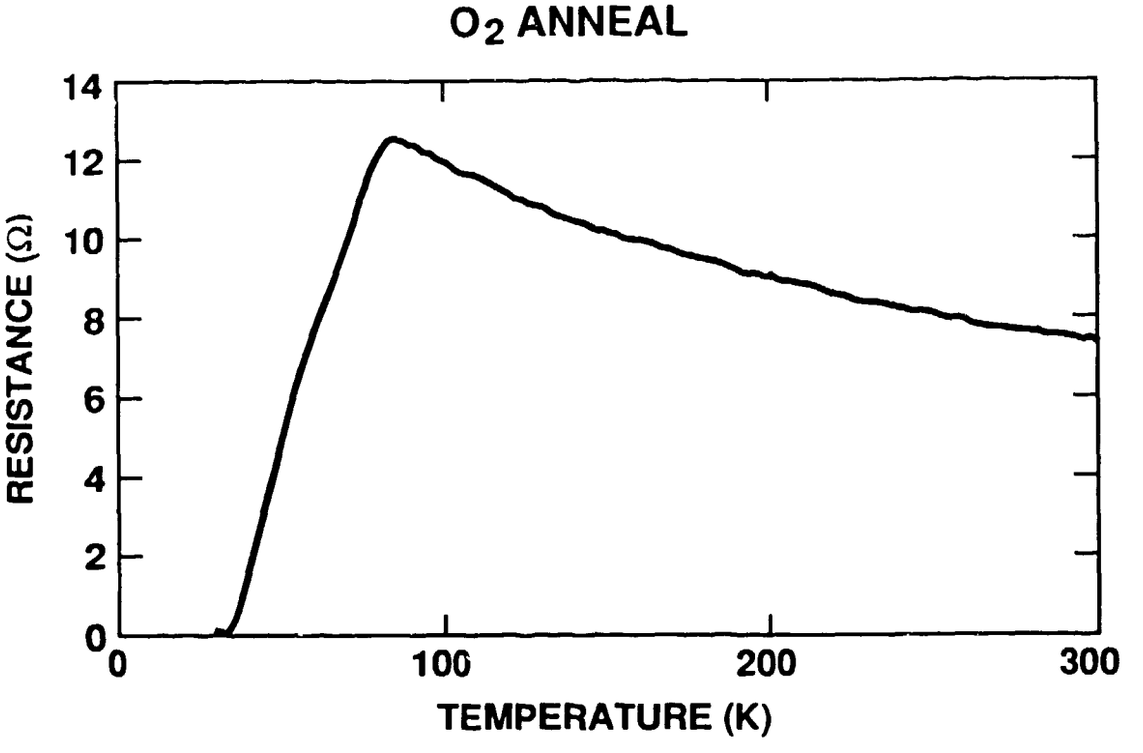
Fig. 1

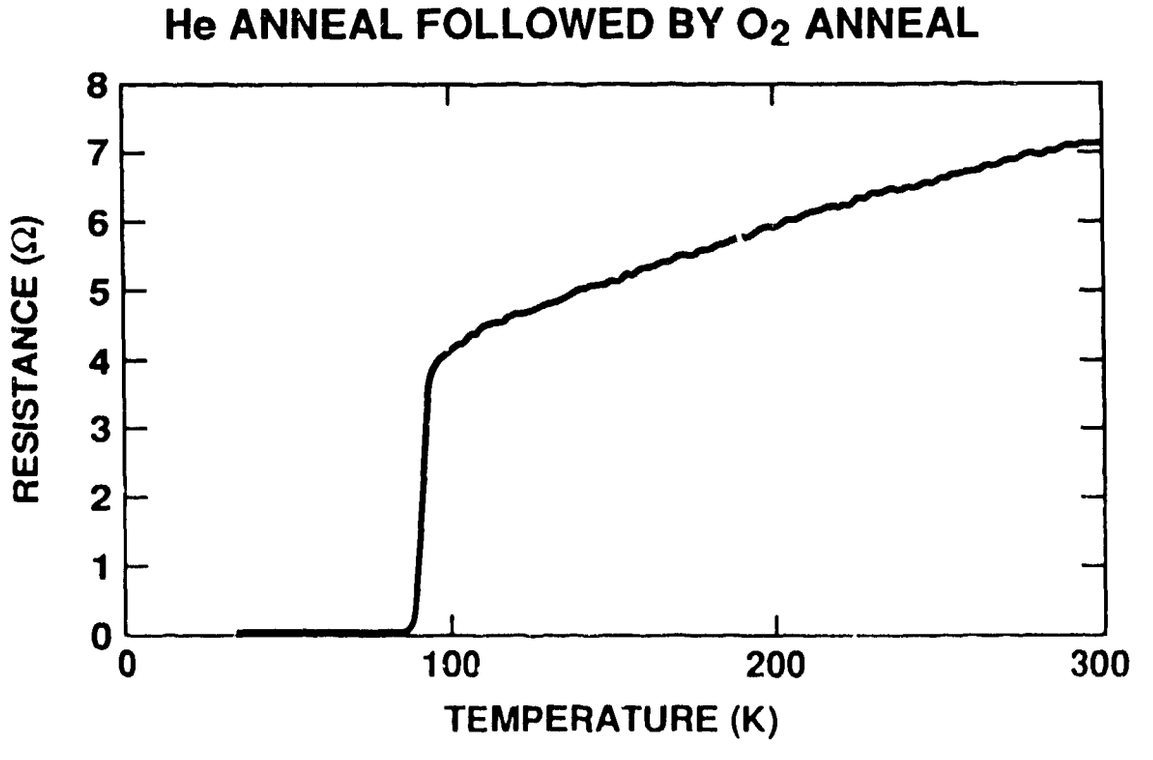
SHORT O_2 ANNEAL



ADDITIONAL 72 HOURS O_2 ANNEAL




O_2 ANNEAL
RESISTANCE (Ω)
14
12
10
8
6
4
2
0
0
100
200
300
TEMPERATURE (K)


He ANNEAL FOLLOWED BY O_2 ANNEAL
RESISTANCE (Ω)
8
7
6
5
4
3
2
1
0
0
100
200
300
TEMPERATURE (K)

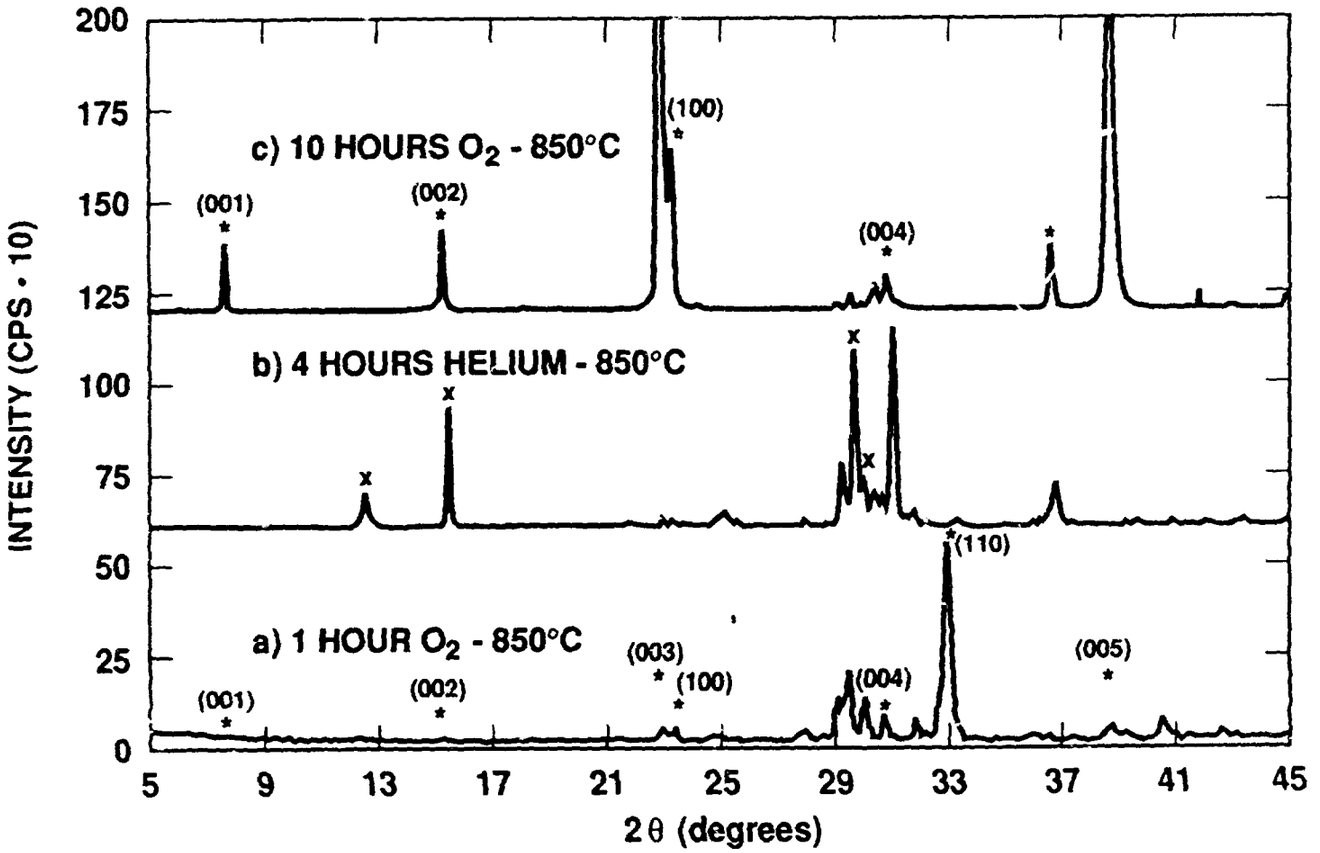

200
175
150
125
100
75
50
25
0
INTENSITY (CPS • 10)
c) 10 HOURS O_2 - 850°C
(001)
(002)
(100)
(004)
b) 4 HOURS HELIUM - 850°C
x
a) 1 HOUR O_2 - 850°C
(003)
(110)
(005)
5
9
13
17
21
25
29
33
37
41
45
2θ (degrees)

Figure 4.