Superconducting depression in thin films of $YBa_2Cu_3O_{7-\delta}$ based on the variation of the relative humidity and the time

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Thin films of $YBa_2Cu_3O_{7-\delta}$ grown on $SrTiO_3$ (100) single crystal substrates by sputtering DC technique to high oxygen pressures were put under different conditions of relative humidity from 24 to 100% and different times of exposition. The electrical, morphologic and structural characteristics of the films by means of curves R-T, atomic force microscopy (AFM) and X-ray diffraction (XRD) were analyzed. The effect on structural and transport properties with the environmental conditions of relative humidity and with time were systematically studied. Samples under relative humidity around 24% measured just later of deposition showed a critical temperature (T_C) of 92 K, and thin films exposed around 90% of relative humidity with times greater to 10^4 s (1 day) showed a T_C of 16 K, while samples under a relative humidity 100% do not showed the superconductive phase. The degradation's causes of superconductive properties in this system were investigated.

Keywords: Relative humidity and time; D.C sputtering; $YBa_2Cu_3O_{7-\delta}$

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1. Introduction

Since the discovery of the $YBa_2Cu_3O_{7-\delta}$ high temperature superconductor compound [1] many of the difficulties have appeared in the process of bulk material conformation, as the handling and storage of this compound in form of thin film, due to their chemical high instability in aqueous environments, CO_2 atmospheres and physical phenomena that happen in the interface between substrate and film. The chemical instability of this superconducting phase both in high-humidity environments and in direct contact with water at temperatures ranging from 25 to 80 ^oC has been the subject of several studies appearing in the technical literature. [1],[2]

The mechanisms of degradation are relatively well understood for bulk specimens. [2],[3] In an X-ray diffraction and AFM study of the decomposition of the superconducting phase in water, [2] was found that the $YBa_2Cu_3O_{7-\delta}$ superconducting phase decomposes into Y_2BaCuO_5, $BaCO_3$, and CuO when exposed to aqueous and CO_2 environments by the following two-stage reaction:
(1) $2YBa_2Cu_3O_{7-\delta} + 3H_2O \rightarrow Y_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + 1/2O_2$ and
(2) $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$

On the basis of detailed microstructural, surface analytical and analytical chemical data. The two most important features of this model are that cation exchange will promote the formation of an amorphous layer, [3] while anion (OH^-) access will result in the formation of planar defects, lattice strain, micro-cracking, and ultimately total dissolution in the aqueous phase [4].

In another study, Fitch and Burdick [5] examined the microstructures of $YBa_2Cu_3O_{7-\delta}$ ceramics after 4 hr of exposure to 100 percent relative humidity at 80^{o}C. They found that the percent age of superconducting phase present had been reduced by approximately 60 percent and that secondary phases had developed in the grain boundaries. These secondary phases were identified as $BaCO_3$ and Y_2BaCuO_5 by X-ray diffraction. Furthermore, AFM analyses of the microstructures of the corroded specimens revealed the development of needle-like crystals both on the surfaces of the grains and along the grain boundaries. [6]

Table 1. Conditions of growth for the $YBa_2Cu_3O_{7-\delta}$ thin films.

Target	**$YBa_2Cu_3O_{7-\delta}$**
Deposition method	D.C sputtering
Target Current (mA)	150 A
Target Voltage (V)	260
Distance target – substrates (mm)	32
Work pressure (O_2 mbar)	$3.5x10^0$
Growth rate (nm/h)	100
Temperatura (^oC)	850

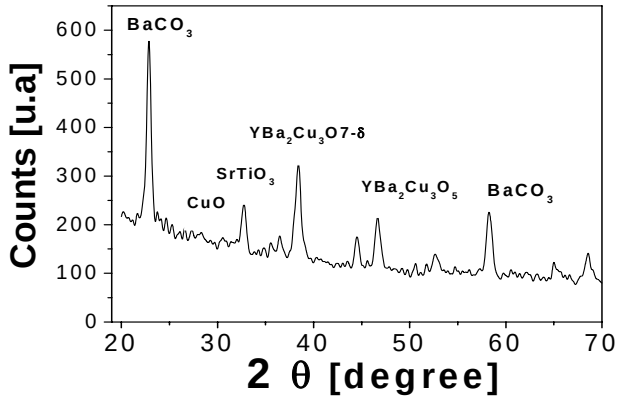

Figure 1. XRD pattern of Thin films specimen grown on $SrTiO_3$ substrate.

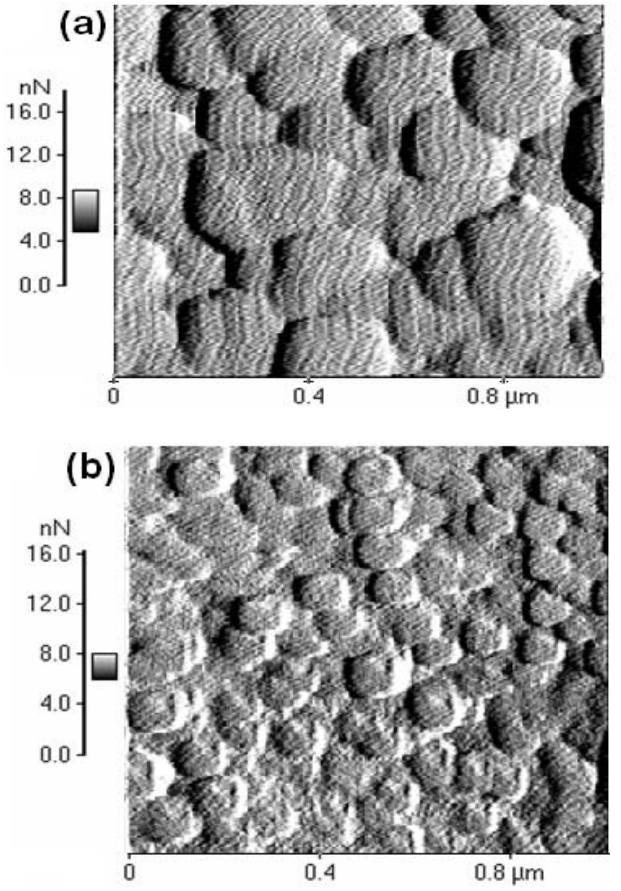

Figure 2. AFM images showing the typical grain for $YBa_2Cu_3O_{7-\delta}$ thin film with 90 percent of relative humidity. (a) time = 1 day, (b) time = 60 days.

The degradation of the superconducting aqueous phase and CO_2 means is thought [1],[2] to be due to the leaching of Ba^{2+} from the ceramic to form $Ba(OH)_2$ along the surface of the ceramic. As $Ba(OH)_2$ is produced, Y_2BaCuO_5 and CuO are simultaneously formed as the decomposition reaction proceeds. Upon exposure to atmospheric conditions, the $Ba(OH)_2$ present on the surface of the test specimens is converted to $BaCO_3$ by the interaction of the hydrated phase with CO_2 present in the atmosphere, as described by reaction (2) . [7]

The main motivation of this work is the qualitative study of the relation between the chemical degradation of $YBa_2Cu_3O_{7-\delta}$ thin films and their electrical properties that are demonstrated in the reduction of the superconductive phase. This ceramic material was evaluated in environments with high relative humidity levels and CO_2 atmosphere, running from 24 to 90 percent in times among 1 and 60 days to 25 ^oC and to determine this way the effects of long-term storage for these materials grown on $SrTiO_3$ substrates. After the time of exposure in humid environments, the superconductive films were evaluated by X-ray diffraction, atomic force microscopy and measures of resistance versus temperature.

2. Experimental Procedure

2.1. Thin film specimens

The films were grown insitu on polished 5×5 mm^2 $SrTiO_3$ (100) substrates by DC sputtering from a stoichiometric target such as is described in table 1.

2.2. Exposure to Humid Environments

Once produced, the $YBa_2Cu_3O_{7-\delta}$ thin films specimens in a dry environment subsequent to deposition, until the commencement of the exposure runs, in order to prevent adventitious degradation, after completing the total amount of films, these were stored in desiccators with controlled humidity level by means of the use of thermos- hydrometer Gonica MP 100 UV. Constant relative humidities of 24, 60, and 90 percent were produced by placing solutions with amounts of CO_2, in sealed desiccators. To determine the effects of excess percent relative humidity, $YBa_2Cu_3O_{7-\delta}$ specimens were stored in deionized water during the test period. Superconductive specimens were placed in constant temperature to 25 ^oC for times between 1 and 60 days as they are presented in table 2.

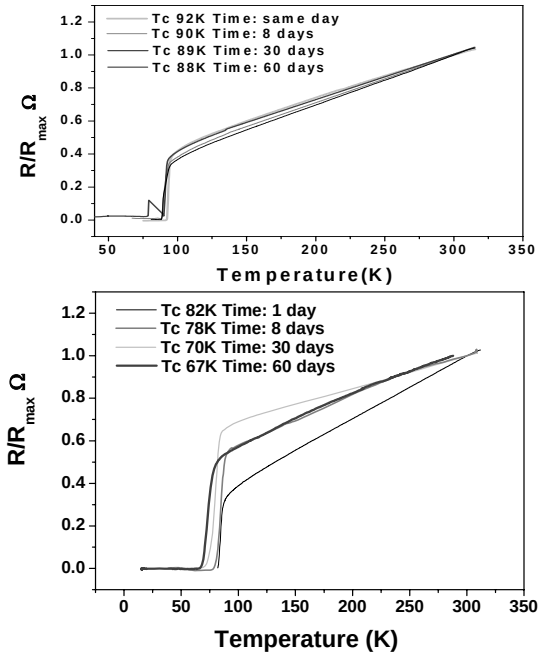

Figure 3. Resistence versus temperature plot of superconducting thin films. (a) stored at 24 percent relative humidity, (b) stored at 60 percent relative humidity.

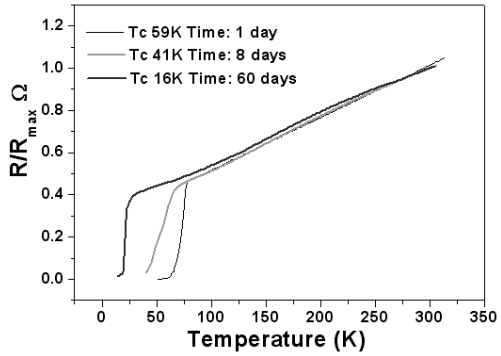

Figure 4. Resistence versus temperature plot of superconducting thin films stored at 90 percent relative humidity.

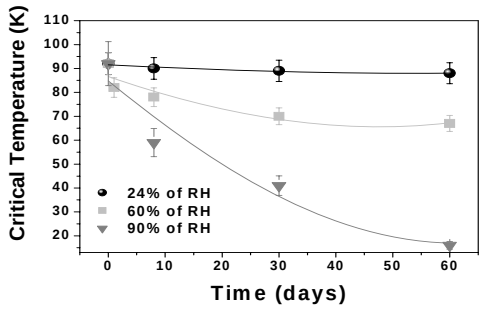

Figure 5. Critic temperature (Tc) obtaining R-T curves versus the storage time for diferent values of relative humidity (RH).

3. Experimental Results and Discussion

3.1. XRD Analyses of Aged Thin film Specimens

The XRD analyses of the superconducting thin films specimens stored at constant relative humidity of 90 percent indicate that after 60 days of exposure, great quantities of $BaCO_3$ were present such as is showed in the figure 1. In this instance, the most intense peak attributable to the presence of $BaCO_3$ (at diffraction angle 2θ = 22,9 and 58,2 degrees) the intense $YBa_2Cu_3O_{7-\delta}$ peak (2θ = 38,4 degrees), and the intense $SrTiO_3$ substrate peak (2θ = 32,8) The intensity of this peak was found to increase as the exposure time to this humidity level increased. [7]

In addition to the formation of $BaCO_3$, peaks attributable to the presence of Y_2BaCuO_5 and CuO were identified on the surface of the specimens aged around 60 days at 90 percent relative humidity. The relative peak intensities for these compounds were less than those attributable to $BaCO_3$, although the intensities of these peaks also increased as the time of exposure to the humid environment increased [7].

There are secondary phases that may have been produced during the exposure period. Particular emphasis was placed on the presence of $BaCO_3$ in the diffraction patterns, as Ba^{2+} is the most likely of the three metal ions in the superconductive compound to react with the humid environment and CO_2 atmosphere forming the $BaCO_3$. [7] The XRD pattern obtained for the as-produced ceramics was in agreement with those reported in the technical literature. [8].

3.2. AFM Analyses of Topography after degradation

AFM images were obtained with an Autoprobe CP Park Scientific Instrument. Several scanners (5x5μm) were used depending on the need for field-of-view and spatial resolution. The progress of the exposure experiments was monitored by optical microscopy; large degraded areas were readily identifiable. The investigations revealed that the degraded regions tended to "grow in" from the edges of the film; such as is showed figure 2. It is apparent that the degradation of the film was initiated at boundaries and edges. Also, features in the submicrometric range having the appearance of precipitates were found at random locations on apparently intact $YBa_2Cu_3O_{7-\delta}$ thin film. In figure 2a the apparently intact regions remained even after 1 day exposure to 90 percent relative humidity while the attack appeared to proceed from inhomogeneous nucleation, in the sense that regions of total decomposition occurred after 60 days exposure to 90 percent relative humidity as is showed figure 2b[6].

The consumption of OH^- is controlled in part by surface hydroxylation. More importantly, in the present context, is the ingress of OH^- along the Cu-O in the $YBa_2Cu_3O_{7-\delta}$ lattice, which is promoted by exchange of the hydroxyls with O^{2-} ions at the chain sites; the latter species is released as 0_2 gas, as described by reaction (2). [9] The decoration

Table 2. Saturation parameters for the $YBa_2Cu_3O_{7-\delta}$ thin films.

Specimen	Relative Humidity %	Time (days)	Temperature (oC)
(1) YBa2Cu3O7-d	~ 24	0 - 60	~ 25
(2) YBa2Cu3O7-d	~ 60	1- 60	~ 25
(3) YBa2Cu3O7-d	~ 90	1 - 60	~ 25

by submicrometric precipitates at random locations is most likely due to the release of Ba^{2+} species and formation of carbonate. It should be noted that the effective ratio of specimen surface area to to solution volume is very large, by the standards of dissolution experiments [6].

4. Results of Resistance versus Temperature Measurements

The resistance versus temperature measurements show that the exposure to each of the experimental conditions resulted in degradation of the superconductor thin films, such as were demonstrated by AFM and XRD results. At each relative humidity of superconductivity level tested the critic temperature of superconductivity (Tc) was reduced after several days of exposure to the humid environments.
The critic temperature of the films stored around 24 percent relative humidity among 1 and 60 days decreased from 92 to 88 K, although the superconducting transition temperature was unchanged. Specimen with 60 percent relative humidity among 1 and 60 days decreased from 92 to 67 K, After 60 days of exposure at 90 percent relative humidity level, the values of Tc were further decreased to 59 and 16 K. Resistance-versus-temperature plots for the thin films specimens are shown in figure 3a, 3b and figure 4 respectively. The specimens stored at 100 percent relative humidity or at direct contact with water did not exhibit a superconducting transition. This result was anticipated from the XRD an AFM studies, which show that these specimens are composed primarily of decomposition products. [7]

The decrease in the superconductive transition temperature is due to the deposition of insulating decomposition products along the grain boundaries, further reducing intergranular connectivity. [7]

4.1. Integrity of the $YBa_2Cu_3O_{7-\delta}$ Thin Films

The integrity of the thin films can be observed when it analyzes the reduction of the electrical properties like function of the relative humidity and the time, physical phenomenon this is attributable to the presence of these impurity phases in the grain boundaries,[10] which are already considered to be electrical "weak links" in the $YBa_2Cu_3O_{7-\delta}$ superconducting ceramic.[11]

The analysis between the degradation of the critic temperature evidenced in the reduction of electrical properties with increasing impurity phase concentrations may be best illustrated by plotting the critic temperature (Tc) obtaining R-T curves versus the storage time for different values of relative humidity among 24, 60 and 90 percent, as shown in figure 5. In this graph, the humidity level at which the specimens were stored is not taken into account. Nevertheless, the graph indicates that the reduction of the superconducting transition in the $YBa_2Cu_3O_{7-\delta}$ thin films is a function of the impurity phase concentration. [7]

5. Conclusions

The $YBa_2Cu3O_{7-\delta}$ thin films exposed to high relative humidity underwent a high degradation that produced compounds of decomposition like $BaCO_3$, CuO, and Y_2BaCuO_5 affecting the transport properties demonstrated in the reduction of the electrical properties.
The result of this study shows the direct dependency between the relative humidity like secondary compound precursor, that prevents the conductivity along the grain boundaries, being reflected in the reduction of the transition critic temperature of the superconductive phase, as function of the environmental increase agents and the temperature which was demonstrated by the analyses of XRD, AFM and resistance versus temperature curves.

The storage and handling of the $YBa_2Cu_3O_{7-\delta}$ thin films grown on $SrTiO_2$ substrates require a high care, due to the excessive reactivity of this ceramic compound with the humidity and the degradation in the time, demanding a new technology of protection or passivation of the surface by means of the use of a sacrifice electrode that does not react with this ceramic but which interacted with environment for offers the integrity of these thin films through time.

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