Correlation between structural disorder and electric properties in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO)

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Abstract. The degradation of the surface resistance $R_s$ of YBCO material by ion milling is usually supposed to be linked to oxygen loss and crystallographic defects. To study this effect, the structural and physical analysis of the milled YBCO thin film has been carried out using Ion Beam Analyses and SQUID measurements. The cationic composition and the oxygen quantity measured in the disordered layer on the top of the film are the same on milled and reference samples. An increase of the bulk defect concentration, especially in the oxygen sub-lattice, is observed in the layer underlying the disordered layer. From SQUID measurements, the milled sample shows a degradation of susceptibility vs temperature $X(T)$ compared to the reference sample. This observation is in a good agreement with the structural analysis and the $R_s$ measurements. After an oxygen annealing at 450°C on the milled samples, the cationic disorder decreased and the bulk defect concentration has not been affected. The $X(T)$ characteristic has improved for the milled film showing its correlation with the evolution of the disordered layer. However the $R_s$ value of the annealed material is not restored.

1. Introduction

The patterned devices in a superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) thin film, prepared by an ion milling, exhibit a degradation of the surface resistance $R_s$ of the material at the microwave frequencies [1]. During ion milling, the edges of the patterned devices are not protected by the resist and are bombarded by the argon ions. According to the generally admitted idea this effect is supposed to create oxygen losses and crystallographic defects in YBCO material causing the degradation of $R_s$ and a decrease of the critical current density $J_c$. To avoid the contributions of the other technological steps (resin, masking, development), we used the interaction of the Ar beam with YBCO bare film. To study this effect, the structural and physical analysis of the YBCO thin films was carried out using Ion Beam Analyses (IBA) and SQUID measurements.

2. Composition and structure
The detection and the analysis in energy of the products of close interactions (Backscattering Spectrometry) between the He ions in the MeV energy range and the atoms of the sample supply precise quantitative information on the atomic composition with a resolution in depth of 10 to 30 nm and on the material crystalline quality on some microns depth. The IBA techniques included the measurements in the random and channeling geometries in order to measure the atomic composition and defects. Two techniques based on the analysis in energy of ions backscattering by atoms of the target were used with a measurement accuracy of 3 %:

- The Rutherford Backscattering Spectrometry (RBS) with a 2 MeV \(^{4}\text{He}^+\) beam to determine cation composition and to characterize crystal defects in the cation sub-lattice of YBCO film.
- The elastic \(^{16}\text{O}(\alpha,\alpha)^{16}\text{O}\) scattering resonance at 3.045 MeV to measure the oxygen concentration profiles (quantity) and to characterize the defects in the oxygen sub-lattice.

A 650-nm-thick YBCO thin film grown on a MgO (100) substrate by coevaporation [2] is used for this analysis. A sample serves as reference. The second one is milled by Ar beam (30°, 500 V, 0.8 mA.cm\(^{-2}\), 10 mn) to remove a 200-nm-thick layer in order to preserve an YBCO thickness sufficient for the electric characterizations.

Before any processing, the surface resistance \(R_s\) of these two samples was measured at 0.3 m\(\Omega\) by the dielectric resonator method (77 K, 10 GHz) [3]. After ion milling, the \(R_s\) was measured at 0.49 m\(\Omega\) and the intrinsic value is calculated to 0.4 m\(\Omega\) by taking into account the reduced thickness [4].

2.1. Cations.
By comparing the spectra of milled and reference YBCO films, we observe that (table 1):

- The cationic composition, determined by using the RUMP simulation, is \(\text{YBa}_2\text{Cu}_3\text{O}_{6.9}\) for the two samples. The value of oxygen composition is confirmed by the Xrays measurement of \(c\) axis value at 11.695Å [5].
- The analysis of the peak of surface of Ba allows to determine the number of displaced atoms in the sub-lattice of the superficial layer. The number of displaced atoms is defined as being the subtraction between the integral of the measured Ba surface peak and the Ba theoretical one. An equivalent perturbed layer is associated to this number of moved atoms. After ion milling, the value of the Ba surface peak increased which corresponds to a 20-nm-thick equivalent disordered layer on the top of the milled YBCO film.
- The Ba \(\chi_{\text{min}}\) of the milled YBCO film increased which means that the structural quality of the YBCO film is degraded.

| Sample          | reference | milled | milled + annealed |
|-----------------|-----------|--------|-------------------|
| \(\chi_{\text{min}}\) Ba | 6.8 %     | 10.1 % | 10.6 %            |
| Disorder Ba / cm\(^{2}\) | 2.7 \(10^3\) | 21.7 \(10^3\) | 18.03 \(10^3\) |
| Equivalent disorder layer | 2.5 nm     | 21.4 nm | 17.8 nm           |

| Analyzed slice  | 34 nm at 25 nm depth |
|-----------------|----------------------|
| Peak O          | 1 (ref)              | 1.03                | 1.02                |
| \(\chi_{\text{min}}\) O | 44 %               | 52 %                | 51 %                |

| Analyzed slice  | 39 nm at 73 nm depth |
|-----------------|----------------------|
| Peak O          | 1 (ref)              | 1.02                | 1.01                |
| \(\chi_{\text{min}}\) O | 51 %               | 57 %                | 56 %                |

Table 1 : Cations and oxygen data in reference, milled and annealed samples by IBA techniques.

2.2. Oxygen.
A disorder layer estimated at 20 nm has been revealed by RBS. The analyses of oxygen were investigated in depths located at 25 ± 17 nm, largely in the disorder layer and at 73 ± 18.6 nm in the film YBCO underlying the top disorder layer. To make analyses in these slices, the initial energy of
the analysis beam was increased so that the oxygen resonance took place in 25 and 73 nm of depth. The results are presented in the table 1. We observe that:

- the concentration of oxygen is the same in the bulk part of the two samples (the concentration of oxygen in the reference sample was normalized to 1).
- the concentration of oxygen is the same in and out the disordered slice for the two samples.
- for the two analyzed slices, the $\chi_{\text{min}}$ of the oxygen in the milled sample is superior to that of the reference layer showing an increase of defects in the oxygen sub-lattice.
- the $\chi_{\text{min}}$ of the oxygen increases with the depth of the analyzed slice. This is a predictable effect which is inferred from the de-channeling of the analysis beam with the depth.

Figure 1. $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ resonance at 3.045 MeV in random (a) and channeling (b) geometries on reference (black) and milled sample (red).

3. SQUID results
The ion milling of the YBCO layer does not cause oxygen loss, additional measurements were carried out to observe the evolution of the critical temperature $T_c$ and the critical current density $J_c$.

A 650-nm-thick YBCO film grown on LaAlO$_3$ (100) substrate by coevaporation with a measured RS identical to samples of the IBA studies, is used for this study [2]. As for the nuclear analyses, we used a reference sample and a milled sample (Ar, 500 V, 0.8 mA.cm$^{-2}$, 10 mn).

The experiment was carried out in a Quantum Design SQUID magnetometer. After stabilization of the temperature of the sample at 20K and application of a 100 gauss magnetic field perpendicular to the sample, the signal was recorded during warming up to 95K. We define the critical temperature $T_c$, as being the temperature of the end of transition "superconductor - normal".

The susceptibility dependence on temperature $X(T)$ for both samples, shown in figure 2.a, is normalized to $-1$ at 20K. $T_c$ is 87K and does not vary after ion milling which corroborates the nuclear analyses. The milled sample shows a degradation of diamagnetism compared to the reference sample. This observation is in good agreement with the structural analysis and the $R_s$ measurements.

At the temperature of 81K, the diamagnetism is weaker for the milled layer. This difference means that the critical current density decreased after the ion milling, probably because of the perturbed layer and disorder in the crystalline sub-lattice.

4. Influence of the annealing under oxygen
To reorganize the cations and the atoms of oxygen in order to improve the electrical properties of the superconducting material, an annealing at 450°C during one hour in a flow of pure oxygen was carried out on the two milled samples. We have shown previously that this annealing has improved the microwave properties of a patterned resonator according to the modeled quality factor [1].
4.1. YBCO composition and structure

After the annealing under oxygen, the $R_s$ intrinsic value is 0.38 mΩ and is not restored as for the patterned resonator. From nuclear analyses, we determine the annealing changes neither the cationic composition nor the oxygen ratio of the milled sample (table 1). It does not change, in a significant way, either the thickness of the perturbed layer or the atoms organization in the sub-lattice. After the annealing the Ba and O $\chi_{mss}$ do not vary. The annealing does not allow to restore the structural properties before ion milling in agreement with the $R_s$ value.

4.2. Electrical results

The $T_c$ is 87 K and does not vary after the annealing (figure 2.b). However at 81 K, the X(T) has improved for the annealed milled film back to its value before ion milling.

![Figure 2. Magnetic susceptibility versus temperature after ion milling (a) and annealing (b).](image)

5. Conclusion

By studying the effect of Ar beam milling (30°, 500 V, 0.8 mA.cm$^{-2}$) on the electric properties of YBa$_2$Cu$_3$O$_{7-\delta}$, we confirmed that this technological step induces a degradation of $R_s$ and $J_c$ as established before during the realization of devices [1]. The nuclear analyses point out that the ion milling creates defects in the sub-lattice without variation of the composition while an annealing under oxygen (450°C, 1 h) does not allow the recrystallisation of the sample surface. After annealing, the $R_s$ (77K, 10 GHz) behavior of superconducting material is different between patterned device and bare sample. Different clues can be recalled: (i) the YBCO material, protected by the resist mask, is damaged only on its edges while the bare material is on its full area. The irradiation levels (energy, dose) are different and consequently, the quantity and nature of created defects can vary. (ii) the crystal orientations of edges and top surface are respectively ab-plane and c-axis, and can have different diffusion coefficients. This work will be pursued by using submicronic analytical techniques.

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