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Fluorination of an epitaxial YBaCuO thin film with controlled oxygen vacancies

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Abstract

An intentionally oxygen-deficient thin film, epitaxially grown in-situ on a (100) MgO substrate by laser ablation at 750°C under a low pressure oxygen atmosphere, has been treated under NF_3 diluted in N_2 at temperatures not exceeding 280°C. During the fluorination process the epitaxy of the thin film is maintained ; its Tc onset progressively increases from 54K up to 85.6K and the width of the inductive transition is narrow at the end of treatment (1.2K). These results are discussed and compared to those obtained during the fluorination of oxygen-deficient $YBa_2Cu_3O_x$ ceramics.

1. Introduction

A number of results on $YBa_2Cu_3O_x$ compounds have shown the importance of oxygen stoichiometry on the superconducting properties. Replacing oxygen by a monovalent anion, like halogen, allows to control the charge transfer which greatly influences the superconductivity. From this point of view, we have started an important work on the halogenation of YBaCuO ceramics, using mild techniques of synthesis (1). An important enhancement of Tc has been observed under halogenation for oxygen-deficient compounds and even an insulating-superconducting transition in the $YBa_2Cu_3O_6$ phase (2). For fluorinated samples, structural determinations by powder neutron diffraction allowed us to correlate the sites of the structure occupied by the fluorine with the evolution of the superconducting properties (3).

However, in order to perform more specific studies of halogenated compounds, such as resistivity or optical measurements, other types of halogenated samples, like thin films, are necessary. In this work, we show that it is possible to obtain fluorinated films with a good crystalline quality, starting from an oxygen deficient film grown in-situ by laser ablation, and fluorinated ex-situ using the same technique of fluorination as for ceramics (2).

2. Experimental

2.1. Thin film growth

For this purpose, an oxygen deficient YBaCuO film has been specially grown in-situ by laser ablation (4). The film was deposited on a (100) MgO substrate heated by radiation, at a temperature estimated to 750°C. The growth is done as usually, under pure oxygen pressure of 0.3 mbar. However, during the cooling stage, the oxygen pressure was intentionally kept at a low value, typically the one used for deposition, in order to synthesize a phase deficient in oxygen ; in contrast, our standard $YBa_2Cu_3O_7$ films are cooled in 1 atm oxygen. The deposition parameters are summarized in Table 1.

Table 1. Deposition conditions of L246Y film

Substrate	(100)MgO
Laser	Excimer, XeCl, λ = 308 nm
Repetition rate	3 Hz
Energy density	3.6 J/cm^2
Deposition temperature	~750 °C
Deposition atmosphere	P (O_2) = 0.3 mbar
Cooling	~40 mn P (O_2) = 0.3 mbar
Film thickness	~1500 Å

The film was characterized by standard x-ray θ-2θ diffractometry and rocking-curves. It is highly c-oriented. The rocking-curve gives a $\Delta\theta$ of 0.40° for the film, compared to a $\Delta\theta$ of 0.33° for the substrate, which is characteristic of a high crystalline quality of the film.

The epitaxy of the film has been verified in-situ by reflection high energy electron diffraction (RHEED). The RHEED pattern, recorded at the same azimuth for the film and substrate (Fig. 1) shows that the crystalline axes of YBaCuO are aligned with those of (100) MgO in the plane of the sample, meaning an epitaxial growth.

2. 2. Fluorination of the thin film

To study the kinetic of fluorine insertion, the thin film prepared as described above was treated under diluted NF_3 (3% in N_2) gas flow during

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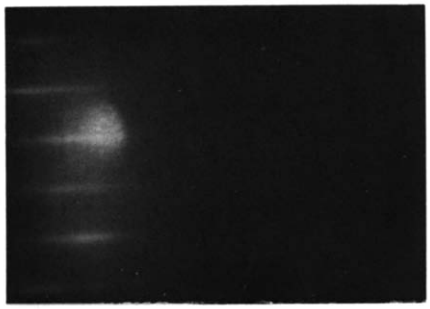

Figure 1. RHEED pattern of the starting film.

various times of reaction, at temperatures which we have optimized, not exceeding 280°C. For comparison, another YBaCuO thin film with the same characteristics was treated 2 hours at 300°C under N_2 : in that case, no change either in the x-ray patterns of the film or in the superconducting behaviour was observed. Thus the carrier gas has no influence on the evolution observed in our study.

2.3. Magnetic measurements

The influence of fluorination on the superconducting transition was monitored by a.c. susceptibility using miniaturized mutual inductance coils (5). The in-phase and out-of-phase components were recorded at each step of the reaction.

The superconducting properties of the film were further studied at the end of the fluorination, in particular by a.c. susceptibility as a function of the applied field and by d.c. magnetization. Results, fully described elsewhere (6), are summarized below.

3. Results

The epitaxy of the film is maintained at the end of fluorination: the Weissenberg pattern (7) shows that the axes of the film remain parallel to the axes of the substrate (Fig. 2), and there is no indication of any ring formation or even broadening of the diffraction spots of the film. Rocking-curves give for the film a $\Delta\theta$ of 0.48° which is very close to the initial value (Fig. 3). Thus, there is no significant variation of the crystalline quality of the film after treatment. X-ray diffraction patterns show a slight decrease of the c-parameter, in good agreement with the increase of Tc (8).

The evolution of the superconducting transition can be seen on Figure 4. Fig. 4 (a) shows the results obtained at the lowest temperatures of reaction, i.e., between 250 °C and 280 °C, for a total time up to 4 hours. The film was then treated at a fixed temperature of 280°C during different times (fig. 4 b), adding up to a total of 28.5 hours

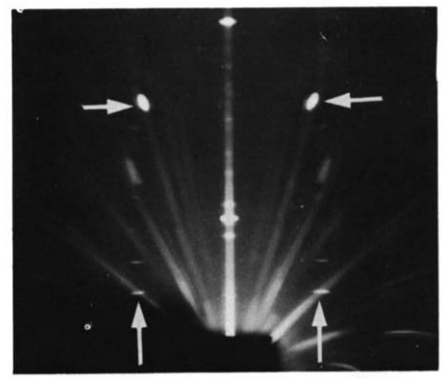

Figure 2. Weissenberg photograph of fluorinated film. The vertical arrows mark the rows of the diffraction spots due to the film, and the horizontal ones, those of the substrate.

of reaction. A progressive increase of Tc^{onset} is observed throughout the fluorination process, with a saturation limit at 85.6 K. Double transitions are observed at the beginning of reaction, presumably due to an inhomogeneous content of oxygen in the as-deposited film ; for instance, the as-grown film shows only one small transition at 54 K (by comparison with the results obtained after fluorination, we believe that the second transition must exist below 50K). A homogeneization process then takes place, since the double transitions

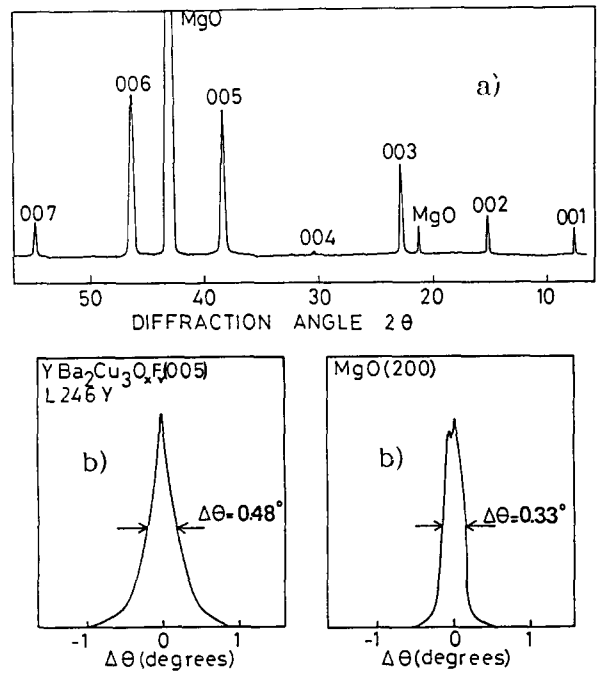

Figure 3. a) X-ray pattern of fluorinated $YBa_2Cu_3O_x$ film ; b) rocking curves of the substrate and of the film (005 reflection)

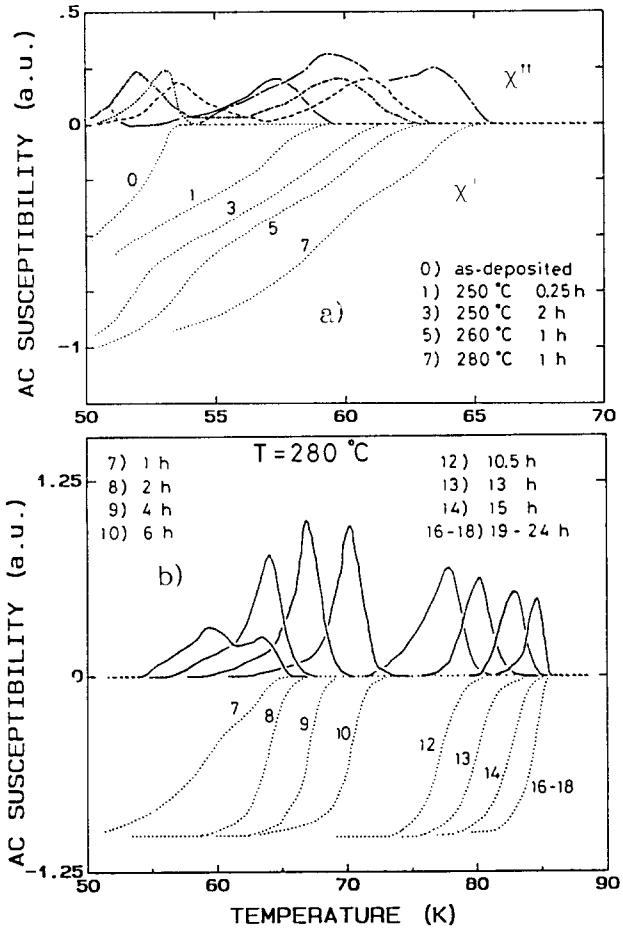

Figure 4. Real and imaginary parts of $\chi_{a.c.}$ after fluorination at temperatures between 250 and 280 °C at given times (a), and then as a function of reaction time at 280 °C (cumulative times) (b).

progressively collapse into one. The width of the transition FWHM decreases down to 1.2 K, while the amplitude of the $\chi'_{a.c.}$ component stays quite constant as a function of time (fig. 5), meaning that no significant change of the crystalline properties of the film occurs. A small decrease of the height of the $\chi''_{a.c.}$ peak is observed in figure 4 (b), perhaps also related to a better crystallinity and homogeneity of the film at the end of reaction.

A weak a.c.-field dependence of the inductive transition was observed, suggesting that granularity is not enhanced by fluorination and that, in fact, is not even an important parameter in this well-crystallized film. Secondly, a large irreversibility of the ZFC-FC cycle is observed, suggesting a large density of flux pinning centers ; the ratio M_{FC}/M_{ZFC} at 6 K of the Meissner-shielding branches is low (5×10^{-2}), more than one order of magnitude smaller than in fluorinated $YBa_2Cu_3O_{6.7}$ ceramics (9). These results indicate that the critical current density of the film at the end of the reaction must be

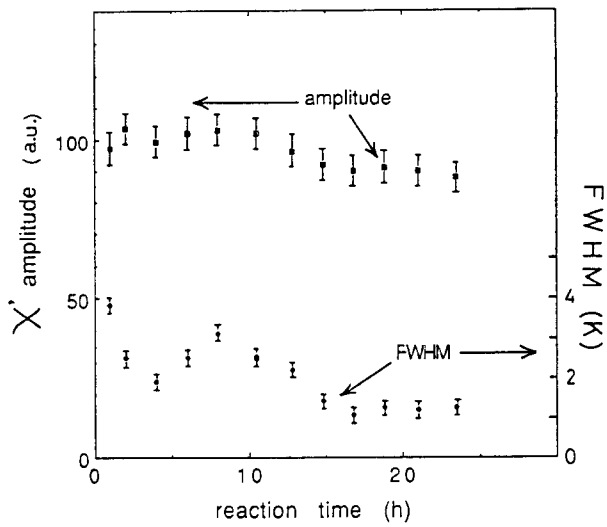

Figure 5. Amplitude of $\chi'_{a.c.}$ and FWHM of $\chi''_{a.c.}$, as a function of the fluorination time, for a temperature of reaction of 280 °C.

relatively high, as also suggested by the narrowness of the peak of the losses component. Indeed, it has been shown that the narrower is the χ'' peak, the higher is the critical current density (10, 11).

The critical current densities Jc were then evaluated from magnetic measurements performed at 5 K. Figure 6 shows the magnetization cycle for the film placed perpendicular to the applied field. The irreversible magnetization ΔM ($M^+ - M^-$) decreases very rapidly with field. The Jc densities, evaluated from the Bean model, are shown in figure 7, as a function of the applied magnetic field, and they are compared to a $YBa_2Cu_3O_7$ film grown on a MgO substrate having approximate the same superconducting (Tc^{onset} and FWHM)

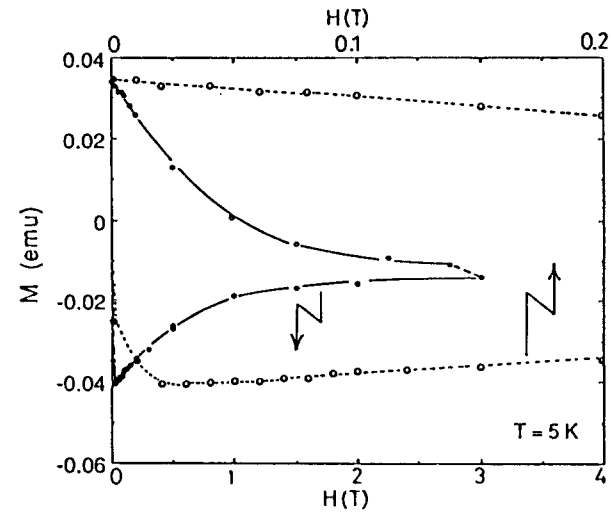

Figure 6. Magnetization cycle performed at 5 K at the end of fluorination (dotted line details the low field part)

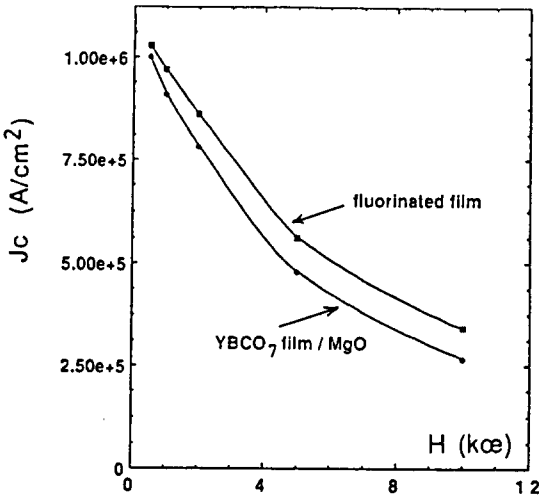

Figure 7. Critical current densities estimated from magnetic measurements at 5 K, compared to a $YBa_2Cu_3O_7$ material grown on a MgO substrate.

characteristics. Reasonable values for Jc are obtained, of the order of 10^6 (A/cm^2) at $H \leq 0.1$ T. Such values are not optimized, but they indicate that the film has not been degraded by the fluorination process. In fact, these values are only one order of magnitude smaller than in exceptionally well-crystallized thin films, epitaxially grown on $SrTiO_3$ or MgO substrates (12).

4. Discussion and conclusion

The Tc evolution observed for this fluorinated thin film closely compares to the one of fluorinated ceramics. In the latter case, fluorination of $YBa_2Cu_3O_{6.7}$ provokes an increase of Tc from 63K upto 90K and fluorinating the $YBaCuO_6$ insulator produces a superconducting phase with Tc of 56K (2). Fluorinated $YBa_2Cu_3O_{\sim 6.5}$ thin film interpolates well between these results : Tc increases progressively from 54K upto 85.6K. Moreover, very recent experiment confirms that observation : Tc of an even more oxygen deficient YBaCuO thin film increases from 45K upto 75K while keeping the film crystallinity. Another feature is the similarity of the decrease of the c-parameter under fluorination, for both thin films and ceramics. All these results suggest that the evolution of the charge transfer and crystallographic properties, for instance the occupation of the particular sites of the structure by fluorine, are similar in this fluorinated thin film and ceramics.

In contrast, it must be noticed that the fluorine is not inserted so easily in the thin film studied in this work compared to ceramics, even if the optimal temperature of reaction is 300°C in this latter case : after about 1 day of treatment (cumulative times) the thin film's characteristics do not change any more, while only a few hours were sufficient to obtain the fluorine saturation in the case of oxygen deficient bulks. This feature appears even more striking when considering the relative masses under reaction : about 150 mg for the bulk samples, less than 25 µg for the film. Taking into account the structural anisotropy of the material and the fact that the film is c-axis oriented, this feature may be understood in terms of difference in the diffusion rate along the c direction and in the (a,b) plane. Work is in progress, starting from a differently oriented films (e.g. (103) samples where the Cu-O planes are directly accessible to reagent) to compare their fluorination kinetics.

In conclusion, the fluorinated thin film prepared as described above, exhibits high quality. The structural and magnetic properties confirm its good crystallinity and its critical current density is relatively high. So, such sample is a good candidate for further physical investigations and will allow to extend our previous results on fluorinated ceramics, and to improve our comprehension of the mechanism of superconductivity in monovalent substituted (halogenated) YBaCuO compounds.

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