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FLUORINATION UNDER NF_3 FLOW OF OXYGEN DEFICIENT $YBa_2Cu_3O_x$ THIN FILMS DEPOSITED ON VARIOUS TYPES OF SUBSTRATE

P. Massiot, C. Perrin and M. Guilloux-Viry, A. Perrin and M. Sergent

Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS 1495
Avenue du Général Leclerc, 35042 Rennes Cédex, France

Oxygen deficient YBaCuO thin films, *c*-epitaxially grown by laser ablation on different substrates such as (100)MgO, (100)$SrTiO_3$ and (100)$LaAlO_3$, were fluorinated by an *ex situ* solid/gas reaction with NF_3 (3% NF_3 diluted in N_2) at 280°C. The kinetics of the reaction depends on the type of the substrate. After reaction the superconducting behaviour of the films is improved without degradation of their crystallinity, whatever the nature of the substrate. The stability of the fluorinated films under oxygen or nitrogen gas was studied. All these results will be compared with those previously obtained for fluorination of oxygen deficient YBaCuO ceramics.

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1. Introduction

The superconducting properties of YBaCuO compounds have been shown sensitive both to the charge transfer and to the microstructure [1–4], which can be modified by replacing oxygen atom by halogen one, for instance the fluorine. In previous works we have shown the possibility to fluorinate $YBa_2Cu_3O_x$ ($x = 6, 6.7$ and 7) ceramics without decomposition, via a solid/gas reaction using diluted NF_3 (3% NF_3 in N_2) at temperature around 300°C [5, 6]. After fluorination, the T_c of $YBa_2Cu_3O_{6.7}$ is greatly improved: T_c increases from 62 K up to 90 K. Structural determinations by powder neutron diffraction had shown an increase in the 0 1/2 0 and 1/2 0 0 sites occupancy, which was attributed to the presence of the fluorine in these sites [7]. These results are in good agreement with theoretical calculations which indicated that these two sites are favoured for the fluorine occupancy [8].

We have extended this work concerning the fluorination of ceramics to the fluorination of oxygen deficient YBaCuO thin films [9, 10]. Following first experiments on thin films deposited on (100)MgO, we have studied the fluorination of films deposited on other types of substrates in order to determine the influence of the nature of the substrate on the kinetics of reaction and on the characteristics of the microstructure of the fluorinated films. In this paper we report our recent results obtained with (100)$LaAlO_3$ substrate and we discuss them in comparison with the ones that we have previously obtained for (100)$SrTiO_3$ and (100)MgO substrates.

2. Experimental

The YBaCuO thin films were intentionally oxygen deficient grown on various substrates ((100)MgO, (100)$SrTiO_3$, (100)$LaAlO_3$, 5×5 or 5×10 mm^2 in dimensions), using a pulsed laser deposition technique previously described [11]. All these films have the *c* unit-cell parameter perpendicular to the plane of the substrate and *a* and/or *b* axes aligned with the substrate axes.

These thin films, about 1500 Å thick, were *ex situ* treated under a diluted NF_3 (3% NF_3 in N_2) flow, during various reaction times, in a similar way as for ceramics [5]. However, the temperature was chosen slightly lower (280°C) in order to avoid their degradation. Other treatments under nitrogen and oxygen were performed in the same conditions on the starting films and on the fluorinated films.

Before and after fluorination, the films were characterized by $\theta - 2\theta$ X-ray diffraction patterns, θ-scans ($\Delta\theta$), electron channeling patterns (ECP), oscillating single crystal technique using a Weissenberg camera; the evolution of their superconducting behaviour was studied by a.c. susceptibility. Energy-dispersive X-ray (EDX) spectroscopy analyses were performed to confirm the presence of the fluorine in the films after NF_3 treatments.

3. Results

3.1. Improvement of the inductive transition after fluorination

It was shown that a long time of fluorination (24 hours) was necessary to obtain a homogeneous thin film with a good superconducting behaviour in the case of the film deposited on (100)MgO (T_c increased from 54 K up to 86 K, narrow inductive transition: 1.2 K), while only one hour is sufficient for such a result with a (100)$SrTiO_3$ substrate as shown in Fig. 1a. The crystallinity of all these films was maintained after fluorination. The results obtained with a film deposited on (100)$LaAlO_3$ are very similar to those observed for (100)$SrTiO_3$ substrate. An increase in T_c (defined as the beginning of the inductive transition) is observed after only a short time of fluorination. As an example, in Fig. 1b is reported the improvement of the superconducting behaviour of such a type of film after one hour of treatment under NF_3: increase in T_c from 85 K up to 88 K and an important narrowing of the inductive transition attesting a homogenization of the film under NF_3 treatment. After fluorination the crystallinity of the films is maintained as shown by X-ray diffraction (for instance, $\Delta\theta = 0.17°$ for a fluorinated film deposited on a (100)$LaAlO_3$ substrate) and ECP patterns.

3.2. Stability of the fluorinated films under O_2 and N_2

The stability of the fluorinated thin films under O_2 and N_2, at the temperature of fluorination, was investigated for films deposited on (100)$SrTiO_3$ and (100)$LaAlO_3$ substrates.

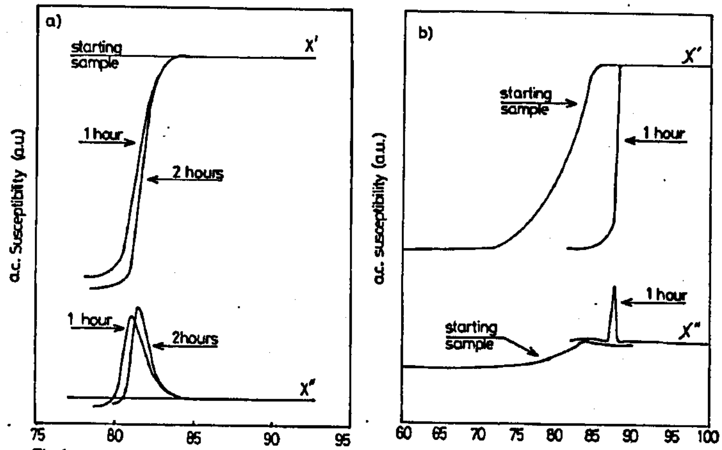

Fig. 1

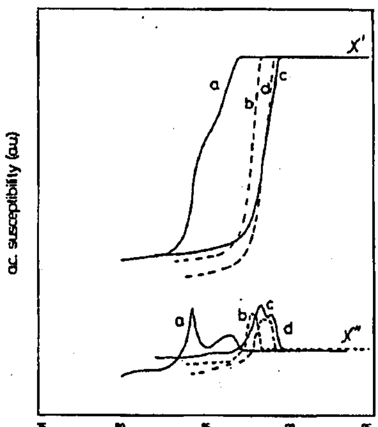

Fig. 2

Fig. 1. Inductive transition for oxygen deficient YBaCuO thin films before and after successive treatments under NF_3 at given times: (a) (100)$SrTiO_3$ substrate and (b) (100)$LaAlO_3$ substrate.

Fig. 2. Inductive transition for an oxygen deficient thin film deposited on (100)$LaAlO_3$ substrate for the following successive treatments: *a* — starting sample, *b* — 3 h 15 under NF_3, *c* — 1 h under N_2, *d* — 2 h under NF_3.

After one hour of treatment under O_2 at 280°C, no significant evolution of inductive transition of the fluorinated film was observed: only a very slight decrease in the T_c while no significant broadening of the transition is noted. A successive treatment under NF_3 of this oxygenated film does not produce a great change. It must be noticed that the same treatment under O_2 performed on a starting non-fluorinated film highly degradates its inductive properties; indeed, after one hour of oxygenation, an important decrease in T_c and a broadening of the inductive transition is observed, which can be greatly improved by a further treatment under NF_3.

A similar N_2 treatment at 280°C was performed on fluorinated films. In that case, a slight increase in T_c is observed, but the transition becomes broader and a double χ'' peak appears (Fig. 2). A further treatment under NF_3 does not change greatly the T_c, but the two χ'' peaks get together. The same N_2 treatment performed on a starting non-fluorinated film produced an important broadening of the inductive transition (about 10 K) with no significant T_c variation, while further treatment under NF_3 improved the transition width.

4. Discussion

The observed evolution of the superconducting behaviour of thin films under NF_3 treatments is consistent with our previous works on the fluorination of YBaCuO ceramics, in good agreement with the modification of charge transfer related to the fluorine insertion in the YBaCuO oxygen vacancies. The kinetics of the fluorine insertion is greatly slower for thin films deposited on (100)MgO substrate than on (100)$SrTiO_3$ one. It was attributed to the influence of the nature of the substrate on the thin film growth and then to the nature of the grain boundaries [10]. Indeed, the films deposited on (100)MgO in most cases contain an array of high angle grain boundaries [12]. This is not the case for the films deposited on (100)$SrTiO_3$ for which the mismatch is considerably smaller. This hypothesis is confirmed by the results obtained for (100)$LaAlO_3$ substrate which give similar kinetics as for (100)$SrTiO_3$, these two substrates leading to a similar growth mechanism in spite of the twins which always are present in the (100)$LaAlO_3$ substrate. Other works have also shown a significant oxygen diffusion dependence on the microstructure and the orientation of the films: the diffusion is very anisotropic with values along $a-b$ planes several orders of magnitude larger than those along the c axis inside the crystal lattice [13]. A study of this orientation dependence of the films on the NF_3 diffusion is now in progress.

The fluorinated films exhibit a good stability under O_2 treatment, but are sensitive to N_2 treatments in the same conditions, mainly producing inhomogeneities. In comparison, the fluorinated ceramics are not degraded under the same N_2 treatment attesting their greatest stability when compared to fluorinated thin films. It is possible that during N_2 treatment of thin film, the fluorine can move easily in the oxygen vacancies and/or leave the YBaCuO structure leading to the observed inhomogeneities, while the O_2 treatment does not favour this mobility. Further treatment under NF_3 allows to reorganise or to fill with fluorine the vacancies so created and then to improve again the inductive transition.

Finally, it is important to mention that in any case (for starting oxygen deficient YBaCuO thin films or for fluorinated films further treated under O_2 or N_2) the treatment under NF_3 improves significantly the inductive transition. Then, this *ex situ* solid/gas reaction with NF_3, performed in mild conditions, could be a promising way to improve the superconducting behaviour of some oxygen deficient YBaCuO thin films.

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