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Abstract

In situ YBaCuO thin films are deposited on MgO single-crystal by pulsed laser ablation using an excimer laser (KrF, 248 nm). Deposition and cooling conditions are investigated in order to obtain *c*-oriented samples. The influence of substrate temperature and oxygen pressure during both deposition and post-deposition processes on the structural (orientation, lattice parameters) and electrical (resistivity at 300 K, critical temperature, transition width) film properties is analyzed. These studies lead to reproducible high quality *c*-oriented thin films which exhibit a critical temperature of 90 K, a superconducting transition width less than 1 K and a good behavior in the normal state.

1. Introduction

Since the discovery of high-T_c superconductivity in 1987 [1], the elaboration of superconducting thin films has led to numerous investigations. Among the different deposition methods [2-5], the pulsed laser deposition (PLD) appears to be the most successful technique because of its ability to transfer the stoichiometry from the target to the substrate. However, to produce reproducible high quality YBaCuO thin films suitable for practical applications or basic physics studies, not only appropriate stoichiometry but also good crystallographic orientation is necessary. All these characteristics depend on simultaneous control of several physical parameters during both deposition and cooling steps. In this paper, we report the influence of the substrate temperature, the oxygen pressure during deposition and the environment (gas nature and pressure) during cooling on the structural and electrical properties of in situ laser-deposited YBaCuO thin films.

2. Experimental details

2.1. Target preparation

YBaCuO bulk targets are prepared from a corresponding mixture of 99.9% pure copper and yttrium oxides (CuO, Y_2O_3) and barium carbonate ($BaCO_3$). The powders are carefully mixed, ground and then calcined in an electrical furnace as follows: rise up to 850°C at 300°C/h, first dwell at 850°C for 20 h, second dwell at 950°C for 6 h and natural cooling. After crushing and sifting, the powders are pressed to a shape of a 2 cm diameter pellets, which are sintered at 975°C for 20 h under oxygen atmosphere. The superconductivity of the samples as-made is verified at 77 K by magnet levitation.

2.2. Deposition system

Deposition experiments are performed in an ultra-high vacuum cell equipped with an introduction chamber for targets and substrates manipulation. The beam of a pulsed excimer laser (248 nm, pulse duration 14 ns, repetition rate 10 Hz, energy per pulse 20-300 mJ) is focused by a tetrasyl quartz lens onto a rotating bulk superconducting YBaCuO target. According to the 35° incidence angle, the laser spot is elliptical and its size is typically 2.3 mm^2. The vaporized material, ejected normally to the target surface is deposited on a single-crystal (001) oriented MgO substrate placed opposite the target at 3.8 cm. The substrate can be heated up to about 820°C by a halogen lamp. Its temperature is estimated with a pyrometer in combination with a chromel alumel thermocouple mounted at the edge of substrate holder. Several gas inlets allow the control of the deposition and cooling atmospheres.

2.3. Deposition parameters

The structural properties of the deposited thin films are investigated by X-ray diffraction using a standard $\theta/2\theta$ diffractometer (Cu Ka radiation) in order to determine crystalline orientation. The detection of lattice planes parallel to the substrate surface allows a computation of lattice parameters. The electrical resistivity is measured by a standard DC four probes method in the 25-300 K range using a closed cycle helium cryostat. Temperature is monitored and given by a silicon diode.

3. Results

3.1. Substrate temperature

It is well recognized [8] that substrate temperature is one of the most important parameters for the growth of high quality superconducting thin films. In order to analyze its influence, several films are prepared at different substrate temperatures (T_s), as listed in table 1. All these films are mirror-like but their color evolves from brown at low temperatures (T_s < 620°C) to black at high temperature. The X-ray analysis (fig. 1) shows that the sample crystallinity changes with temperature. At low temperature (430-620°C), the films are amorphous. Then an increase of the deposition temperature improves the quality of the film crystallization and phase orientation. At 690°C, the strong diffraction peak at about 33° corresponds to the randomly oriented phase (103 / 013 / 110). At 725°C, this peak is no longer observed and the films are perfectly *a*-oriented. With increasing T_s, the intensity of the (h00) diffraction peaks decreases while that of (001) peaks increases. The room temperature resistivity of these films decreases from a few kΩ. cm (T_s < 620°C) to a few mΩ.cm and their electrical characteristics versus temperature evolve from semiconducting (at 690°C) to superconducting behavior (at 790°C), as shown in fig. 2. These results are in agreement with the structural properties of the films and prove the important role of substrate temperature on the film structural properties.

3.2. Deposition oxygen pressure

The previous results show that substrate temperature during deposition should not the only parameter to be studied in order to improve high-T_c superconducting film quality. According to the previous experiments and our aim (*c*-oriented films), the selected substrate temperature is 790°C. The oxygen pressure will vary in the range of $6x10^{-3}$ - 0.3 mbar. The other deposition parameters are identical as previously, that is to say: the laser fluence is 3 J/cm^2 and repetition rate 10 Hz. After deposition, samples are cooled under oxygen at 30 mbar. Fig. 3 shows the change of the resistivity versus temperature curves with the deposition pressure. All the films are superconducting. The critical temperature (T_{onset}) increases (from 80 to 86 K) and the transition width decreases (from 32 to 6 K) when the deposition pressure increases. These electrical properties are in agreement with the structural ones. Indeed, the mixture of (h00) and (00l) orientations which is observed at low deposition pressure disappears on behalf of the single orientation (001), at the highest pressures (fig. 4). The improvement of the critical temperature and transition width can be attributed to a more effective oxygen incorporation in the material at high pressures. This hypothesis is confirmed by the values of the lattice parameters *c*. In the present case, the *c* values, are respectively equal to 1.183 and 1.171 nm for 0.1 (sample D6) and 0.3 mbar (sample D8). Indeed, the lowering of the *c*-lattice parameter corresponds to an increase of the number of oxygen atoms in $YBa_2Cu_3O_x$ [9]. In fact, these two parameters *c* and $_x$ are linked by the relation

$$x = (1.2736 - c(\text{ nm})) /0.01501$$

established for bulk samples by Ohkubo et al. [10].

3.3. Choice of gas and pressure during cooling step

The former studies emphasize the influence of the substrate temperature and the deposition oxygen pressure on the crystalline orientation. When the temperature is 790°C and the pressure 0.3 mbar, *c*-oriented superconducting thin films are obtained, but their electrical properties are not optimal (transition width 6 K). That is why the influence of the nature (vacuum, argon and oxygen atmosphere) and the pressure of the gas present during cooling is investigated. The deposition conditions are reported in table 2. The films are found highly-*c* oriented independently on the nature and the pressure of the gas present during cooling. This observation demonstrates that the deposition conditions themselves (substrate temperature, oxygen pressure, laser fluence, target-substrate distance, etc.) determine the crystalline orientation. Fig. 5 shows the temperature dependence of resistivity for the films of this experiment. We notice that the film cooled down in vacuum is semiconductive, while those cooled down in argon or oxygen atmospheres are superconducting. This is attributed to the difference in *c* lattice parameter and, therefore, in the oxygen content $_x$ (in $YBa_2Cu_3O_x$). Indeed, the sample D12, cooled in vacuum condition, is oxygen deficient (x = 5.9). This result, in agreement to Ohkubo's observations [10], leads to the two following hypotheses:

- the oxygen incorporation during the deposition process is insufficient,
- the oxygen contained in the film at the end of the deposition process has outdiffused from the film during the cooling process in vacuum.

In order to try to conclude, we can examine the sample D13, which is cooled down in argon pressure of 330 mbar. Its oxygen content, greater than in the case of cooling in vacuum, yields to a superconducting behavior, as shown in fig. 5. The transition width, of about 20 K, indicates that the incorporation of oxygen into the film during deposition is certainly not sufficient, according to the first hypothesis. But, it is not possible now to confirm or cancel the second hypothesis. Indeed, oxygen can outdiffuse, like in the case of cooling in vacuum, from the film to the gaseous phase (argon).

However, this experiment shows that the superconducting YBaCuO phase grows epitaxially on MgO during the deposition. This result, evident from our experiment, disagree with the conclusions of Ohkubo et al. [10] and Ying et al. [11]. These results show that cooling in oxygen is primordial to obtain high quality superconducting thin films. So, we have grown several films samples which were cooled down in different oxygen pressures (table 2). All these films are superconducting (fig. 5) and have a good metallic behavior above the transition (ratio of the resistivities at 300 and 100 K of about 3). The transition width varies from 18 to 1 K and presents an optimum for the oxygen pressures during cooling in the range of 160-330 mbar.

4. Conclusion

In situ growth of high quality superconducting thin films depends not only on the deposition parameters but on the cooling process. The determinant role of the substrate temperature and the oxygen pressure during deposition on the crystalline orientation, has been shown. The optimization of the electrical properties needs adequate oxygen pressure during the cooling process.

Acknowledgement

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Table 1

Deposition temperatures of the YBaCuO thin films on single crystal MgO(00l) samples (oxygen pressure $6x10^{-3}$ mbar. laser fluence 3 J/cm^2, natural cooling with 30 mbar of oxygen)

Sample	Temperature (°C)
D1	430
D2	620
D3	690
D4	725
D5	790

Table 2

Deposition parameters, structural and electrical properties of YBaCuO thin films deposited on heated single crystal MgO (001) substrates at 790°C (oxygen pressure 0.3 mbar and cooled down in different environments)

Sample	Cooling gas	Cooling pressure (mbar)	c (nm)	x (in YBa_2Cu_x)	ρ (300 K) (m$\Omega \cdot$ cm)	T_{onset} (K)	T_{offset} (K)	ΔT (K)
D12	Vacuum	–	1.185	5.9	1200	–	–	–
D13	Argon	330	1.175	6.59	0.55	85	56.6	20
D7	Oxygen	2	1.174	6.65	1.3	88	58	18
D8	Oxygen	30	1.171	6.81	0.28	86	75.5	6
D9	Oxygen	160	1.169	6.95	0.25	89	87	1
D10	Oxygen	330	1.170	6.91	0.35	89	86.4	1.3
D11	Oxygen	930	1.169	6.98	0.2	89.2	86.2	2

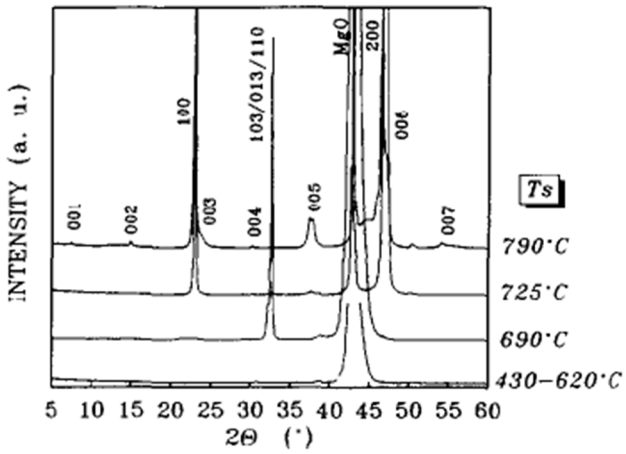

Fig. 1. X-ray diffraction patterns of YBaCuO films on MgO as functions of the substrate temperature.

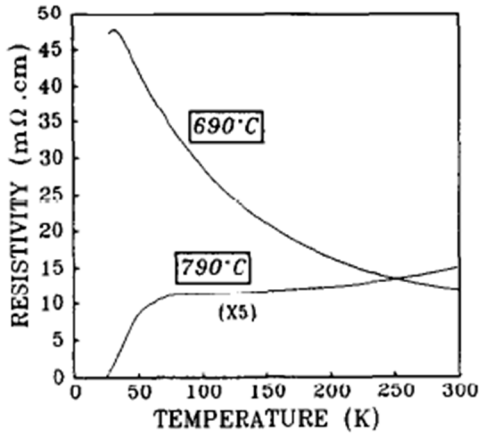

Fig. 2. Resistivity versus temperature curves for samples D3 (T_s = 690°C) and D5 (T_s = 790°C).

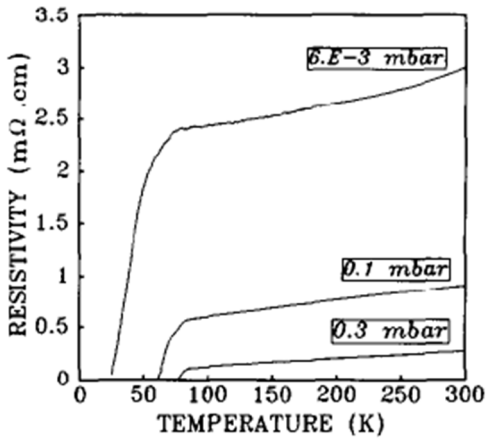

Fig. 3. Resistivity versus temperature curves for different deposition oxygen pressures.

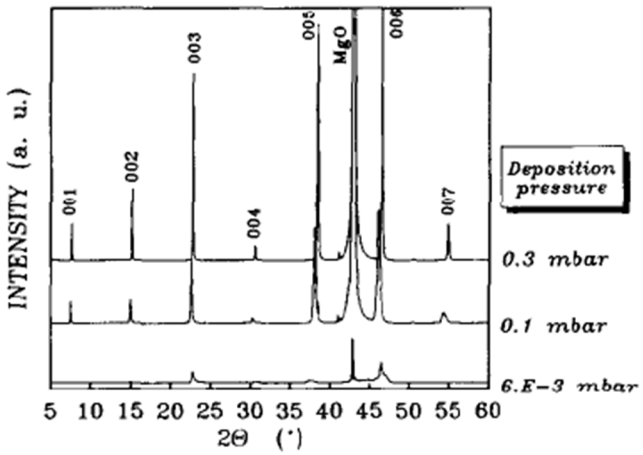

Fig. 4. X-ray diffraction patterns of YBaCuO films deposited on MgO at T_s =790°C as functions of the deposition pressure.

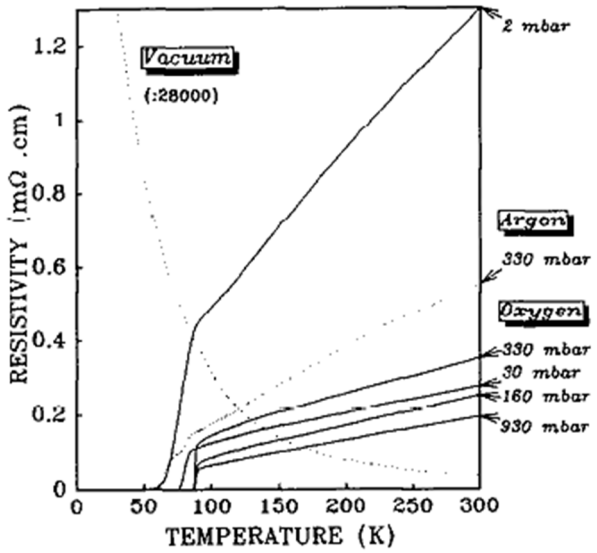

Fig. 5. Resistivity as a function of temperature for films cooled at different residual ambient gas.