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Pulsed laser deposition of $YBa_2Cu_3O_{7-x}$ superconducting thin films : correlation between preparation conditions and structural and electrical properties.

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Abstract

$YBa_2Cu_3O_{7-x}$ thin films were obtained on MgO single crystals using pulsed laser deposition with a KrF excimer laser (248 nm) operated at 10 Hz with a laser fluence of 3 J/cm^2. Substrate temperature was monitored at 790°C with an halogen lamp and oxygen pressure was maintained at 0.3 mbar. Structural parameters were systematically investigated by X-ray diffraction. Electrical properties were characterized using a dc four probes method (25 to 300 K).

In order to understand parameters which may lead to epitaxial thin films with high superconducting properties (i.e. transition temperature as high as 90 K, low transition width and critical current density of about 10^5 to 10^6 A/cm^2), the role of cooling process was studied for purely c-axis oriented films using different cooling gases (oxygen or argon) and different cooling pressures. The effects of cooling process were checked by systematic study of cell parameters, rocking curves, critical temperature and transition width. Optimum cooling pressure led to thin films with a transition width of about 0.5 K and critical current density of about 10^6 A/cm^2 at 80 K.

1 Introduction

Since the discovery of superconductivity /1/, numerous investigations have been devoted to the preparation of superconducting thin films. Comparatively to the different deposition techniques /2-7/, pulsed laser deposition rapidly appeared to be the most suitable technique to obtain the correct cationic stoichiometry /8/. However, to produce reproducible high quality YBaCuO thin films suitable for practical applications, not only appropriate cationic stoichiometry but also oxygen stoichiometry control is necessary because YBaCuO is a non stoichiometric oxide /9, 10/. In addition, physical properties of YBaCuO, particularly conductivity, are very anisotropic /11/. So it is very important to obtain oriented thin films and to try to obtain epitaxial material.

However, crystallographic orientation, cationic and oxygen stoichiometry depend on simultaneous control of many parameters during deposition and cooling steps. The influence of preparation conditions have been reported in precedent papers /12, 13/, so we report here the influence of the cooling step for samples prepared with parameters leading to purely c axis oriented films, because only few work has been devoted to the influence of cooling conditions for YBaCuO thin films prepared by this technique /14/.

2 Thin films elaboration

YBaCuO thin films were obtained on MgO (100) single crystals using pulsed laser deposition, with a KrF excimer laser (λ = 248 nm) operated at 10 Hz with a laser fluence of about 3 J/cm^2. During deposition process, substrate can be heated by an halogen lamp and its temperature is kept at 790°C. Pure oxygen is introduced in the vacuum chamber at a pressure of 0.3 mbar. Deposition process takes about 10 minutes to obtain 300 nm thick film.

After deposition, the vacuum chamber is filled with the selected gas (see table 1) and samples are allowed to cool down without any control of cooling speed.We systematically studied the effects of different cooling atmospheres using oxygen or argon and different cooling pressures (10^{-6} mbar to 1065 mbar). This process leads to black mirror like films purely c axis oriented.

3 Sample characterization

Immediatly after deposition, structural properties are investigated using a standard $\theta/2\theta$ diffractometer (Cu K_α). Thin films obtained by this process are purely c axis oriented, so only (001) lines are detected by X-ray diffraction. Computation of these different lines gives the c parameter and the value of the oxygen content x /10, 15/. Rocking curve of the (005) YBaCuO line gives an idea of the mosaicity of the film.

The thermal evolution of electrical resistivity is measured by a standard dc four probes method in a closed cycle helium cryostat (25-300 K). Transition width ΔT is defined using the 90% - 10% criterion. Critical current density is measured on a 0.5 mm x 25 μm etched line, using a 1 μV criterion.

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N°	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11
Substrate	MgO (100) single crystals, 0.5 mm thick										
Deposition parameters	10 minutes, 10 Hz, F ≈ 3 $J.cm^{-2}$, T = 790°C, P_{O_2} = 0.3 mbar										
Cooling gaz	/	O_2								Ar	
Cooling pressure (mbar)	10^{-6}	2	30	160	330	345	665	930	1065	330	1040
c cell parameter (nm)	1.185	1.174	1.1705	1.1692	1.1693	1.1684	1.1688	1.1688	1.1685	1.1747	1.1758
Jc (A/cm^2) at 80 K	/	/	/	2.3 10^5	/	/	6.7 10^5		6.10^3	/	/

Table 1 : Elaboration conditions and cooling parameters of the YBaCuO thin films.

4 Cooling process

Previous studies /12, 13/ gave evidence for the achievement of purely c axis oriented films for particular values of oxygen pressure and temperature during deposition, but oxygen deficiency, as measured by X-ray diffraction and superconducting properties (ΔT = 6 K), were not optimum. Some authors /14/ reported that deposited material was tetragonal with an oxygen content close to 6, and that oxygen incorporation was occuring by in-diffusion during cooling down under oxygen. They reported too that increasing oxygen pressure during cooling was leading to an improvement of YBaCuO oxygen content, as measured by decrease of c cell parameter. So we tried to improve oxygen content and superconducting properties by a systematic study of cooling process.

Eight samples were cooled under oxygen using different total pressures (samples D2 to D9, see table 1). In order to give evidence for the necessity of an oxygen atmosphere during cooling, one sample was cooled under vacuum (D1) and two samples were cooled down under argon (D10 and D11).

5 c lattice parameter

X-ray diffraction spectra show only (00l) lines. For sample cooled under vacuum, the c cell parameter is high, giving an oxygen deficiency of about x ≈ 0.8 /10, 15/. c decreases rapidly with increasing oxygen cooling pressure (fig. 1), indicating that oxygen deficiency is decreasing too, from x ≈ 0.8 to x ≈ 0.2 /10, 15/, according to Ohkubo values /14/.

For argon cooled samples, oxygen deficiency is about 0.6-0.7, less than the value obtained for vacuum cooled sample. So we can consider, as Ohkubo did, that during cooling, oxygen diffusion occurs from gazeous phase into the film. Equilibria conditions determine final oxygen content of samples.

Argon cooled samples could not increase their oxygen content during cooling because there was no oxygen in gazeous phase. So we can consider that before cooling, they were oxygen deficient, but oxygen deficiency is lower than reported by Ohkubo /14/. These results show clearly that during deposition, YBaCuO grows epitaxially with an oxygen deficiency of about 0.6-0.7, indicating a structure close to the orthorhombic to tetragonal transition /10, 15/.

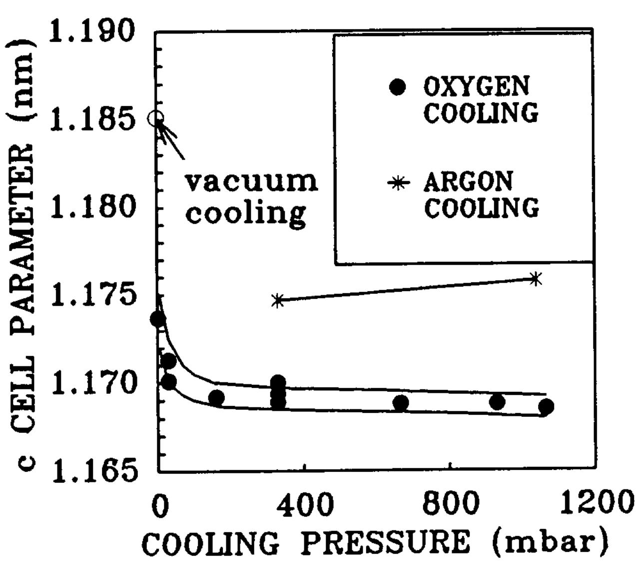

Fig. 1 : Evolution of c cell parameter with cooling pressure for samples cooled under oxygen or argon.

6 Mosaicity of the films

X-ray diffraction rocking curves were systematically measured for (005) YBaCuO line. Evolution of full width at half maximum (FWHM) of the measured diagram clearly shows an evolution of the mosaicity of the film with cooling pressure (fig. 2). First, mosaicity decreases with increasing pressure, from 0.65° for 10^{-6}mbar to about 0.5° for 100-150 mbar. Then, it increases to reach a constant value of 0.7°above about 200 mbar.

This evolution could be due to an increase of lattice mismatch between YBaCuO and MgO with increasing oxygen content, and consequently, an increase of interfacial stress accomodated by structural defects like dislocations.

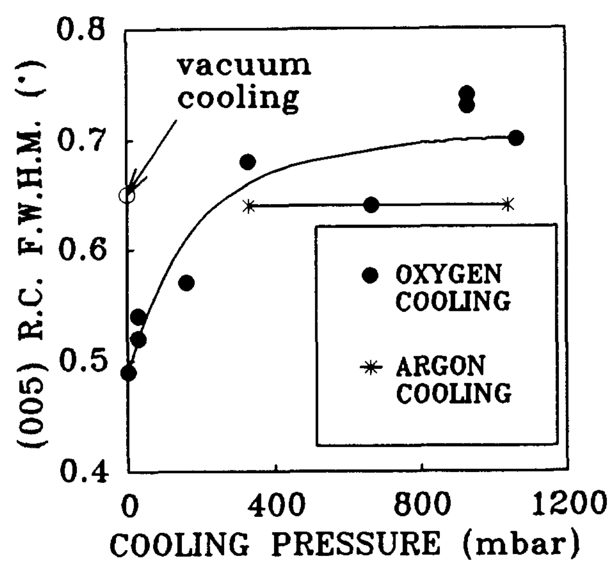

Fig.2 : Evolution of (005) YBaCuO rocking curve FWHM. with cooling pressure.

7 Electrical properties

Electrical properties were measured between 25 and 300 K. Vacuum cooled sample is perfectly semi-conducting (Fig. 3 a). Samples cooled under oxygen are all superconducting (fig. 3 a and b). Transition temperatures increase and transition width decreases with increasing cooling pressure (fig. 4). The curve suggests that an optimum cooling pressure exists, with a value between 100 and 300 mbar of oxygen.

Argon cooled samples are superconducting with lower transition temperatures (fig. 3 a) and very large transitions. This clearly indicates that for these films, YBaCuO is not tetragonal but orthorhombic because only orthorhombic YBaCuO is superconducting /10, 15/.

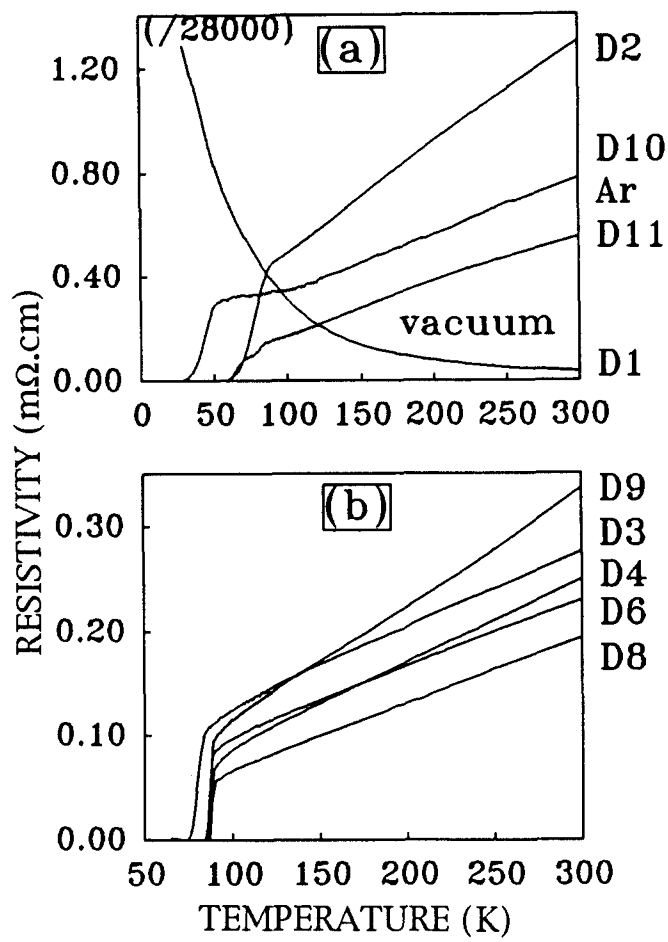

Fig. 3 : Evolution of resistivity versus temperature characteristics : (a) D1 (vacuum cooled), D10 and D 11 (Argon cooled) and D2 (2mbar oxygen)

(b) samples D4 to D9 cooled under increasing oxygen pressure.

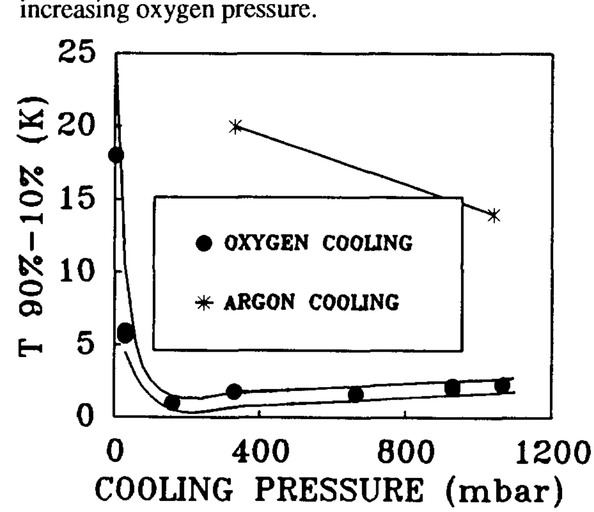

Fig. 4 : Evolution of superconducting transition width with cooling pressure.

8 Critical current density

Three samples only were characterized (see table 1). Critical current densities of two samples are slightly lower than those reported before (10^6 A/cm^2). The abnormaly low value obtained for sample D9 is up to now unexplained. Further measurements are in progress in order to confirm both these values and the possible occurence of an optimum oxygen cooling pressure.

9 Conclusion

In situ growth of superconducting thin films depends on many interdependant parameters. For particular values of substrate temperature and oxygen pressure, deposited material is purely c axis oriented (X-ray diffraction pole figures, which are not reported here, clearly showed epitaxy of YBaCuO on MgO substrate). During deposition, superconducting YBaCuO grows epitaxially on MgO, with an oxygen deficiency of about $x = 0.6$, indicating a structure close to the orthorhombic to tetragonal transition. So we can considere that oxygen incorporation during deposition is not sufficient.

During cooling step, oxygen incorporation depends on oxygen partial pressure. If partial pressure exceeds equilibrium value, oxygen can diffuse into the film and so the oxygen content increases. This evolution leads to improvement of electrical properties.

Evolution of rocking curves, transition width and critical current density seems to indicate that an optimum cooling pressure exists. Further experiments are in progress, in order to determine this optimum value.

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