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STRUCTURE AND MORPHOLOGY OF $YBa_2Cu_3O_{7-x}$ LPCVD LAYERS

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Thin films of $YBa_2Cu_3O_{7-x}$ have been grown by chemical vapor deposition at 825 °C (5 Torr). The starting materials are tetramethylheptanedionates of Y, Ba and Cu. The superconducting properties of the films obtained on monocrystalline MgO have been studied by AC resistivity, AC susceptibility and magnetization measurements. Superconducting layers with zero resistance at 85 K and a transition width lower than 2 K are obtained. This communication will address more specifically the structural properties as well as the morphology of the layers. The films are highly orientated with their c-axis perpendicular to the substrate plane, and the pole figures show a very good in-plane orientation. The morphology of the layers has been investigated by scanning electron microscopy: we do observe a strong correlation between the roughness of the surface and the composition of the gas phase.

1. INTRODUCTION

There has been a very intense activity in the field of high-T_c thin films over the last four years (it would be impossible to quote all the significant contributions; a good review paper is to be found in ref. 1). The great majority of the films are made by a physical vapor deposition technique. There is, however, a growing number of studies on the deposition of superconducting oxides by Chemical Vapor Deposition[2-4] (CVD).

The properties of the films achieved so far by CVD are good with respect to the transport properties. This is unfortunately shadowed by the great difficulty to control the morphology of the layers. This is a key point, however, if stacked layers are to be used as Josephson junctions. Moreover, the parameters which control the critical currents in thin films are still poorly known. The highly anisotropic character of the superconducting properties points to the importance of the orientation both perpendicular and parallel to the surface of the substrate. The structural assessment generally done by most groups is, however, limited to x-ray diffraction from planes which are parallel to the substrate surface.

This paper will concentrate on the morphology and the structure of thin films of $YBa_2Cu_3O_{7-x}$ (further on abbreviated as YBCO) deposited by low pressure CVD from metalorganic complexes, on MgO crystals (the high quality of the films deposited on $SrTiO_3$ is rather well established[1]).

2. EXPERIMENTAL PROCEDURES

The experimental set-up has been fully described elsewhere[4]. The growth takes place at a temperature of 825°C and at a total pressure of 5 torr. Argon is used as a carrier gas which is passed over solid precursors of yttrium, barium and copper whose temperatures are controlled in three different sublimators; oxygen is feeded independently. After the deposition the films are cooled down to room temperature under one atmosphere of pure oxygen.

The precursors are tetramethyl-heptanedionates

(tmhd) of yttrium, barium and copper. Whereas the yttrium and copper diketonates have been purchased from STREM inc., the barium compound has been synthetised from pure barium *via* the alkoxide route. Our experience is that it is crucial to optimize the reproducibility of the $Ba(tmhd)_2$ vapor pressure. Furthermore, in order to reduce[5] the decomposition of the barium complex a vapor pressure of tetramethyl-heptanedione is maintained above the solid during the sublimation process: this is achieved by passing argon over liquid H(tmhd) at about 30°C. The gas phase composition was modified by changing the temperature of the sources. In our reactor, the best superconducting layers have been obtained for source temperatures which are 130 °C, 205°C and 110°C, respectively for $Y(tmhd)_3$, $Ba(tmhd)_2$ and $Cu(tmhd)_2$.

For the experimental conditions described above and for a total deposition time of 30 minutes the thickness of the layers is of the order of 2000 Å. The substrates used throughout this study were (100) oriented MgO single crystals. Analysis was carried out by Scanning Electron Microscopy (SEM) and x-ray diffraction. The latter was performed routinely in the Bragg-Brentano geometry; in-plane texturing was also investigated with a pole figure goniometer in the Schultz geometry[6]. The superconducting properties of the layers were measured by AC four point probe resistivity and AC susceptibility measurements down to liquid helium temperatures.The magnetization of the films was measured with a vibrating sample magnetometer.

3. RESULTS AND DISCUSSION

3.1. Morphology

Because the stability of $Ba(tmhd)_2$ is by far the major concern with the MOCVD of YBCO, we have investigated the effect of intentionally varying, within broad ranges, the $Ba(tmhd)_2$ gas phase concentration. In these experiments the $Ba(tmhd)_2$ temperature was varied between 220°C and 200°C while the other parameters were kept constant.

Two secondary electrons images are displayed in figure 1. The top photograph is characteristic of barium-poor films. The layer is very rough and the composition as determined by electron probe microanalysis is very rich in copper, barely indicating the presence of barium. An x-ray $\theta - 2\theta$ scan performed on this kind of film shows, nevertheless, the presence of YBCO with a strong c-axis (perpendicular to the substrate surface) preferred orientation. A cross-sectional observation of such a sample resolves this apparent paradox: a continuous layer (between 1000 and 2000 Å thick) of

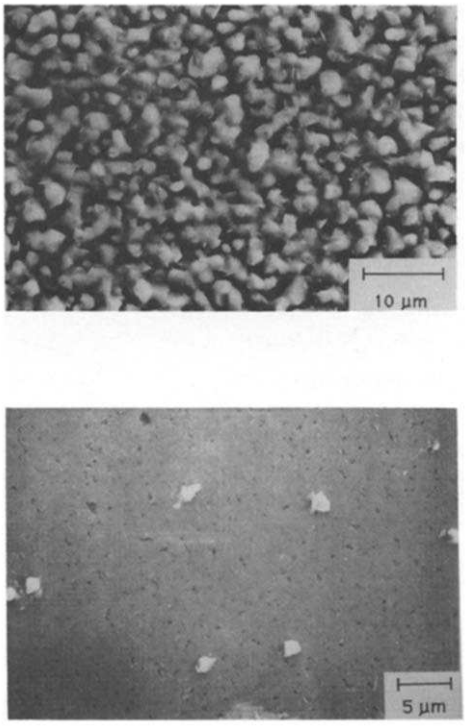

FIGURE 1
Scanning electron micrographs of CVD layers deposited with different barium concentrations in the gas phase.

YBCO is present at the interface; this allows the film to appear superconducting as a whole, as evidenced by resistance measurements (figure 2 - curve C). The superconducting transition temperature of these barium poor films are not affected by this large off-stoechiometry: films deposited on MgO exhibit zero resistance at 82 K and a transition width of 3 K. On the other hand the normal state resistance is rather high and do not extrapolate to zero at 0 K.

Increasing the barium content leads to the gradual appearance of the superconducting YBCO layer connected with a decrease in the density of the copper-rich precipitates (see figure 3 in ref. 4).The YBCO film consists of many rectangular platelets with parallel edges, a strong indication for in-plane orientation. The layer which appears at the lower part of figure 1 belongs to this composition range; here the Cu/Ba ratio has been kept low enough in order to have a low density of precipitates on the surface. Pitting is also observed in a similar way as what has been reported for coevaporated layers[7]; we do observe, however, the coexistence of

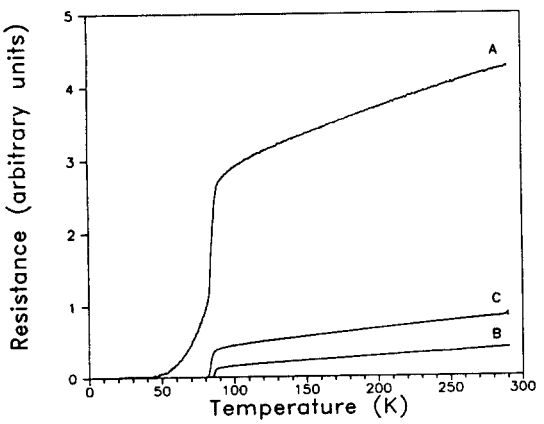

FIGURE 2

Resistance versus temperature for three films deposited with different barium gas phase concentrations (the Ba concentration is lowered in going from A to C).

precipitates and pitting, at variance with what was observed by Edwards *et al*[7]. The superconducting properties of these layers are good: Tc = 85 K and ΔT_c = 2 K from resistance measurements (figure 2-curve B); now the normal state resistance extrapolates to zero at 0 K. The zero field critical current derived from magnetization measurements[8], assuming the Bean model to apply, lies between 1.7 10^5 A cm^{-2} and 1.5 10^6 A cm^{-2} at 10 K.

Still increasing the barium content drastically reduces the critical temperature, as is evidenced on the resistance vs temperature plot of figure 2 (curve A): Tc = 43 K and ΔT_c = 22 K.

3.2. Structure

The indexation of a diffractogram, from a diffraction experiment performed in the Bragg-Brentano geometry, gives generally for these thin layers only a complete set of 00l lines from YBCO. Unfortunately this technique probes only the planes parallel to the substrate surface and gives no information on the in-plane texture. This latter information can be obtained using the Schultz geometry.

Three pole figures which refer to the (007), (013) and (113) planes are displayed in the stereographic projection drawn in figure 3. β refers to the rotation around the normal to the plane of the sample and ϕ around an axis which is the intersection of the incidence plane and the sample's plane. For each diffraction peak the dark area encloses 60% of the intensity and the outer line represents the level of 15% intensity.

The extension of the 007 spot shows that the c-axes of the crystallites are perpendicular to the substrate with a dispersion of about 2°. The (013) and (113) pole figures clearly show a strong in-plane texturing; the spot widths indicate a total angular spread around the common direction of about 2° (a similar dispersion is found in the plane as well as perpendicular to the substrate surface). The existence of a four-fold symmetry in this orthorombic compound is a clear evidence for twinning which

appears when crossing the tetragonal-orthorombic transition.

In agreement with what has already been reported[9] we find that the YBCO crystals have their [100] (or [010]) direction parallel to the [100] direction of MgO. The pole figures from figure 3 do not indicate the presence of any crystals oriented differently; Zheng *et al*[9] do find a small proportion of the crystals with their [100] direction parallel to the [110] direction from MgO. A careful examination of our S.E.M. micrographs leads to a proportion of 45°-oriented platelets of about 1 to 2 %.

4. CONCLUSION

We have shown that MOCVD films deposited on MgO have a strong preferred orientation in the plane of the substrate. This explains the high critical currents of these layers:

J_c (0 T, 10 K) = 1.5 10^6 A cm^{-2}.

The occurrence of both high critical temperature and low surface roughness, in CVD films, requires a careful control over the gas phase composition. This is a difficult task because of the low thermal stability of barium tetramethyl-heptanedionate.

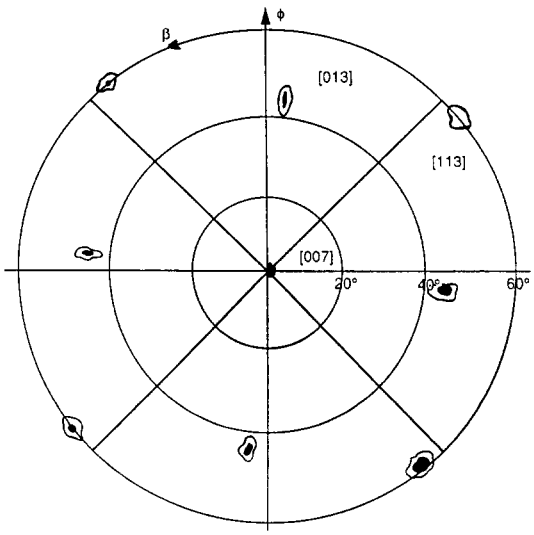

FIGURE 3

Stereographic projection for the density of the normals to the (007), (013) and (113) planes. The projection plane is the film plane.

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