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Growth and properties of MOCVD $YBa_2Cu_3O_{7-x}$ thin films

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Abstract

Epitaxial thin layers of $YBa_2Cu_3O_{7-x}$ are synthesised by thermal decomposition (750 - 830 °C) of tetramethylheptanedionates of yttrium, barium and copper in the presence of oxygen. Argon is used as a carrier gas and the partial pressures of the different precursors are monitored via a careful control of the sources temperatures. The superconducting films with thicknesses ranging between 40 nm and 200 nm are grown on (100) $SrTiO_3$, (012) $LaAlO_3$ or (100) MgO. The growth rate varies between 2.7 nm/min and 4 nm/min. The layers are analysed by scanning and transmission electron microscopy, x-ray diffraction and Rutherford backscattering spectrometry. The normal - superconductor transition is investigated via DC and AC resistance, magnetization and AC susceptibility measurements as a function of temperature. Magnetisation hysteresis loops recordings, I-V measurements on microbridges and non linear susceptibility analysis are used to explore the irreversible properties of the layers. Typical parameters for MOCVD films grown on $LaAlO_3$ are as follows:
T_c = 90 K, ΔT_c = 0.4 K and J_c (77 K) = 2 10^6 A cm^{-2}.

1. Introduction

The complicated structure of high Tc oxides offers a great challenge for crystal growers. The synthesis of epitaxial $YBa_2Cu_3O_{7-x}$ layers imposes the monitoring of three cation fluxes together with the control of the in-plane orientation. The occurrence of stacking faults [1,2] in this compound has still to be related to the physical properties and it is not very clear yet what are the best conditions (p_{O2}, T, composition) to control them.

This communication addresses some of the specific problems associated with the Chemical Vapor Deposition from Metal Organic precursors (MOCVD) of $YBa_2Cu_3O_{7-x}$ (YBCO) thin films. The structure, the composition and the electrical as well as the magnetic properties are presented.

2. Growth control

The deposition zone has been fully described [3] earlier. One important difference compared with the setup described in [3] is the presence of an additional by-pass line which allows for a better control of the deposition parameters. The reactor is of a horizontal hot wall type. Film deposition takes place between 825 and 750 °C and the total pressure (mostly Ar + O_2 - see below) is 5 Torr. Full oxygenation takes place in the reactor by simply switching off the power supply under 760 Torr of pure oxygen.

A careful design of the precursors delivery system is essential for a good control and reproducibility of the gas phase composition. Each source consists of a horizontal furnace (heat pipe) with a tight temperature control (~ 0.3 °C). In each furnace the tetramethylheptanedionate is loaded in an alumina crucible whose surface is flushed with a monitored argon flow (mass flow control). Under these conditions, provided the carrier gas flow is low enough [4], the gas phase composition downstream is directly related to the solid vapor pressure. At the temperatures we are using ($Y(tmhd)_3$: 113 - 116 °C, $Ba(tmhd)_2$: 200 -220 °C, $Cu(tmhd)_2$: 98 - 115 °C) the equilibrium vapor pressures [5] are about 10^{-2} Torr; that means that the gas phase above the substrate is very diluted (~ 1%).

In Figure 1 the sublimation rates of the tetramethylheptanedionates of Y, Pr and Gd, as measured by mass losses, are compared with the deposition rates for individual oxides at 825 °C on MgO as measured by Rutherford Backscattering Spectrometry (RBS). The direct relationship between the sublimation and the growth rates is a clear indication that growth is controlled by mass transport. This is evidenced also in Figure 2 where the growth rate is plotted against the evaporation rate for individual oxides of Y, Ba, and Cu from their tetramethylheptanedionates. The growth efficiencies scale

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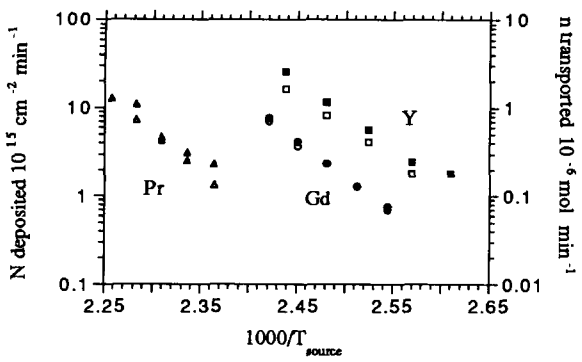

Figure 1 - Mass losses (Ar flow: 50 sccm, P_{source} = 10 Torr), open symbols, and deposition rates (825 °C, P_{tot} = 5 Torr), full symbols, as a function of the reciprocal source temperature for the tetramethylheptanedionates of Y, Gd, and Pr.

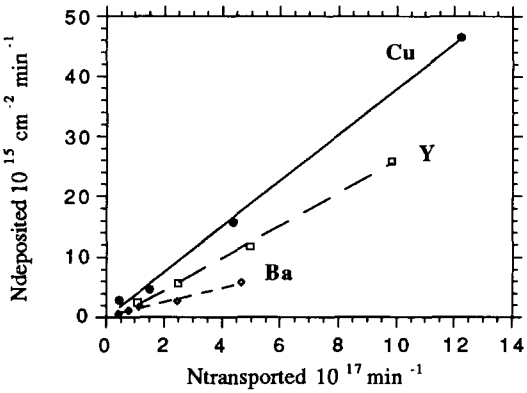

Figure 2 - Growth rates versus sublimation rates for individual oxides of Y, Ba, and Cu from their tetramethylheptanedionates at 825 °C and 5 Torr.

in the order of the vapor pressures (Cu>Y>Ba); which is a fact already noted by Kim *et al* [6] with a similar experimental arrangement.

The stability vs time and temperature of $Ba(tmhd)_2$ is a major concern for the MOCVD community. Some stabilization has been achieved by adding tetramethylheptanedione [7] or tetrahydrofuran [8] vapors above the solid. Another way to circumvent this problem is to keep precursor at room temperature and only bring to high temperature [9-10] the amount necessary to grow the film. We have found that using a carefully prepared [11] $Ba(tmhd)_2$ and keeping it above 200 °C for less than five hours gives a good reproducibility of the deposition rate, as checked by RBS.

3. Structure and properties of the films

AC screening measurements performed by sandwiching the sample between a driving and a sense coil is a rapid and non destructive method to analyse the superconducting transition. In Figure 3 a and b the third harmonic responses of two films (about 120 nm thick) deposited in similar conditions on $LaAlO_3$ and MgO are plotted versus temperature. The applied field was 20 mOe at a fundamental frequency of 800 Hz. This nonlinear behaviour is a very good way to characterize the onset of irreversibility close to T_c. Indeed , the peak temperature lowering when the applied field is increased may be

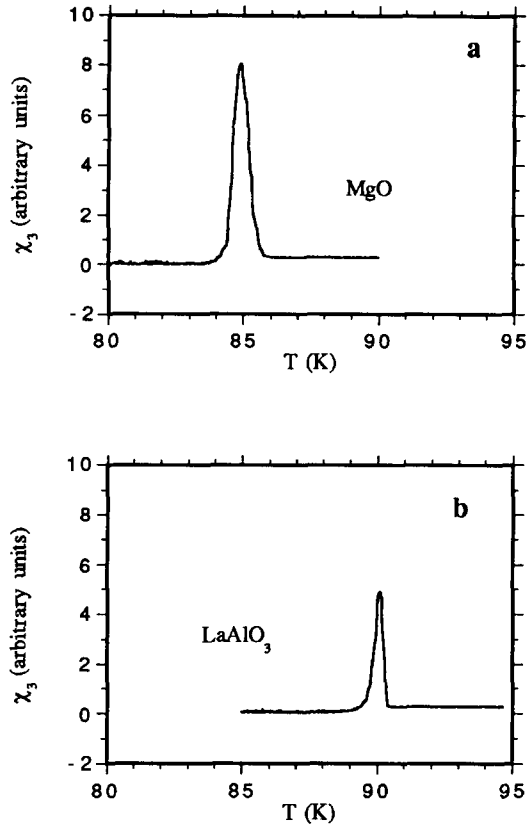

Figure 3 - Third harmonic component of the AC susceptibility for two films deposited at 825 °C on MgO (a) and $LaAlO_3$ (b).

correlated [12] to the variation of the critical current density as a function of temperature. The absolute critical current densities at 77 K of our MOCVD films, as obtained from direct transport measurements lie between 1 and 3 10^6 A cm^{-2}. These measurements were performed on microbridges (30 x 200 μm^2) defined by photolithography and argon ion-milling. The current densities that one can deduce from the remanent magnetization in a vibrating sample magnetometer,

utilizing the Bean's model [13] are about a factor 2 lower at 77 K (Figure 4). The films exhibiting the best superconducting properties show a room temperature resistivity between 290 and 420 mWcm and a resistance ratio $\frac{R(300K)}{R(100K)}$ between 2.4 and 3. The thickness of these layers, measured by a - step, range from 40 to 120 nm depending on the deposition time. Films deposited on MgO show generally inferior properties (T_c, J_c) compared to layers grown on (100) $SrTiO_3$ or (012) $LaAlO_3$ (see figure 3). The fact that it was not possible to obtain 40-nm-thick superconducting films on MgO may be indicating that there is some interdiffusion between MgO and YBCO.

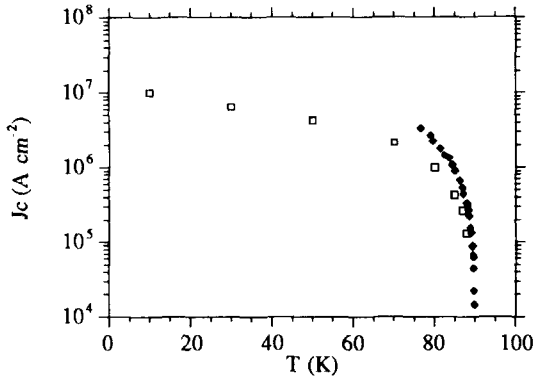

Figure 4 - Critical current density of a 150-nm-thick layer deposited on $LaAlO_3$. The full symbols refer to transport measurements and the open ones to magnetization measurements.

The origin of the very high critical currents in "epitaxial" thin films is still being debated upon. The discussion that follows focuses on the different types of defects that may be present in the layers.

A necessary condition for a high J_c is the absence of large angle grain boundaries as was shown earlier by Dimos *et al* [14] (some special orientations, however, proved to be favorable [15] for the transport of current). X-ray diffraction performed in the Bragg-Brentano geometry shows a strong c-axis orientation in the MOCVD layers. X-ray pole figures [16] indicate a high degree of in-plane orientation. The 4-fold symmetry of the 103/013 pole figure shows the presence of YBCO grains rotated by 90 ° (twinning). Under our growth conditions the tetragonal to orthorhombic transition occurs during cooling down. Moreover, the cubic symmetry of the single crystal substrates we are using probably cannot favor $[100]_{YBCO}$ over $[010]_{YBCO}$. Thus the best films contain at least one type of defect: Twin boundaries along (110) planes.

The samples with the best properties have a Ba/Y composition ratio around 1.5, measured by RBS. This was already noticed by Li *et al* [17]. It has been demonstrated that this Y-rich composition [17] corresponds to a distribution of coherent Y_2O_3 precipitates that could very well act as pinning centers. On the other hand the Cu/Ba ratio can be varied in a wide range (1.5<Cu/Ba<4.5) without any important degradation of the superconducting properties. The copper-rich samples exhibit large micron sized CuO grains. The very short coherence lengths of YBCO make these precipitates poor candidates for flux pinning. Indeed, smooth layers (see Figure 5) with very high critical current densities can be obtained under controlled growth conditions. The sample whose surface is shown in Figure 5 was prepared at a low growth rate (2.7 nm min^{-1}) and at 750 °C on (012) $LaAlO_3$.

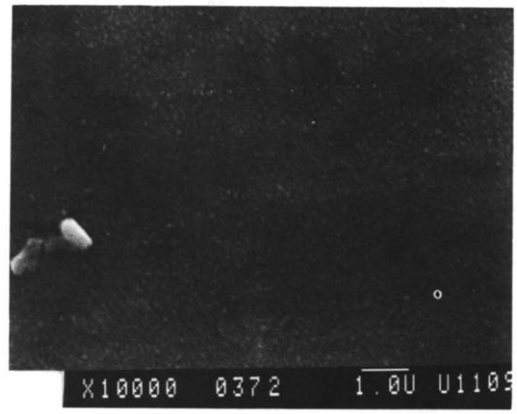

Figure 5 - S.E.M micrograph of a 80 nm film deposited on single crystal (012) $LaAlO_3$. (T_c = 87 K).

A number of authors (see e.g. [18]) report the measurements of an expanded c-lattice parameter in YBCO thin films. This unit cell distortion has been attributed [18] to cation disorder. We do not find any expansion and the c - lattice parameters of our superconducting layers lie between 1.168 nm and 1.170 nm for a wide range of average compositions; this is an indication that off-stoichiometry results in the precipitation of extra phases.

A cross sectional observation, by Transmission Electron Microscopy (TEM), of a c-axis oriented film deposited on MgO shows a sharp interface. High resolution imaging with an incident electron beam direction along [110] reveals the presence of planar defects perpendicular to the c-axis: on both sides of the defect the fringes parallel to the [001] direction are mutually displaced by half of a period along the $[1\bar{1}0]$ direction. Moreover the c lattice parameter is 0.21 nm larger when one fault is included, in perfect agreement with Matsui *et al* [19]. One may therefore hypothesise that these defects are stacking faults resulting from the addition of an extra

CuO layer and a $\frac{b}{2}$ translation. The ordering of such defects along the [001] direction yield superstructures such as $YBa_2Cu_4O_8$ [20] or $Y_2Ba_4Cu_7O_{14+x}$ [21] with well defined critical temperatures. In our sample the mean distance between the faults is about 7 nm, a frequency higher than the one (20 nm) reported by Gao *et al* [2] in a MOCVD film. Further work is needed to clarify the influence of these faults on the transport properties of YBCO layers.

4. Conclusion

Thin YBCO films (40 - 150 nm) with smooth surfaces and high critical current densities (up to 3 10^6 A cm^{-2}) may be obtained by MOCVD. The origin of these high critical current densities is not clear yet and it is not possible to tell whether they are intrinsic or not. The large off-stoichiometry of these layers (Ba/Y ~ 1.5) tends to favor an extrinsic origin. A detailed analysis of the microstructure is needed to understand the relationship between off-stoichiometry and defects (precipitates, stacking faults, point defects, ...) in these thin films.

Acknowledgments

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