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Characteristics of epitaxial Y–Ba–Cu–O thin films grown by aerosol MOCVD technique

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Abstract. $YBa_2Cu_3O_{7-x}$/MgO(100) epitaxial films ($T_c^{off} \simeq 80$ K and $J_c \simeq 10^7$ A cm^{-2} at $T = 4.2$ K, $B = 5$ T) were prepared using an unconventional MOCVD technique. The method is based on the use of a solution of Y-, Ba- and Cu-β-diketonates, carried to the reaction zone in aerosol form. In the paper the essentials of aerosol MOCVD technique and the results of film characterization by x-ray diffraction analysis, scanning electron microscopy, Raman spectroscopy and critical current measurements are represented.

1. Introduction

Metalorganic chemical vapour deposition (MOCVD) is an attractive method of formation of high-T_c superconducting thin films. In comparison with a number of methods of physical deposition such as sputtering, laser ablation, co-evaporation etc it offers, in principle, the advantages of high deposition rates, soft processing conditions (i.e. low deposition temperatures, gas pressure from about 10 Pa up to atmospheric pressure in some cases), compatibility with substrates of complicated form and adaptability to wide scale fabrication.

In the conventional MOCVD technique [1–3] the multichannel gas transport apparatus is used that includes several (three or more) vaporizers of metalorganic precursors and corresponding gas channels. To secure stoichiometric composition of the compound on the substrate it is necessary to stabilize (or even control) the temperatures of the vaporizers and gas channels and to keep the transport gas flows at fixed levels with high accuracy.

We have succeeded in developing [4] an unconventional MOCVD technique for growing high-T_c epitaxial thin films. In our method, the metalorganic compounds solution is carried to the reaction zone in aerosol form so that the vapour phase formation occurs only just above the heated substrate.

The proposed technique is inexpensive and rather simple in operation. The following advantages of the method should be pointed out: epitaxial film growth at atmospheric pressure and lowered temperatures, the possibility of preparing homogeneous layers on large area substrates (tapes) and high reproducibility.

In this paper the aerosol MOCVD technique is described and the results of characterization of the films by means of x-ray diffraction analysis, scanning electron microscopy, Raman spectroscopy and critical current measurements are represented. Significant abilities of the method in question are illustrated by the data obtained for ultra-thin (10 nm thick) Y–Ba–Cu–O and other oxide epitaxial films.

2. Film preparation

The realization of MOCVD principles (vapour phase formation, decomposition of metalorganic molecules and film deposition on the substrate as a result of chemically active radicals assisting the reaction) in our case was as follows. A vapour phase was created just above the heated substrate as aerosol particles of metalorganic solution were carried to the reaction zone by O_2 gas flow. To prepare high-T_c films, β-diketonate chelates of Y, Ba and Cu, dissolved in a suitable solvent, were used as precursors. Film deposition was carried out at atmospheric pressure in the oxygen-containing gas medium at a substrate temperature of 550–650 °C and a growth rate of 2–30 nm min^{-1}. After deposition the reactor was slowly cooled to room temperature. The films had

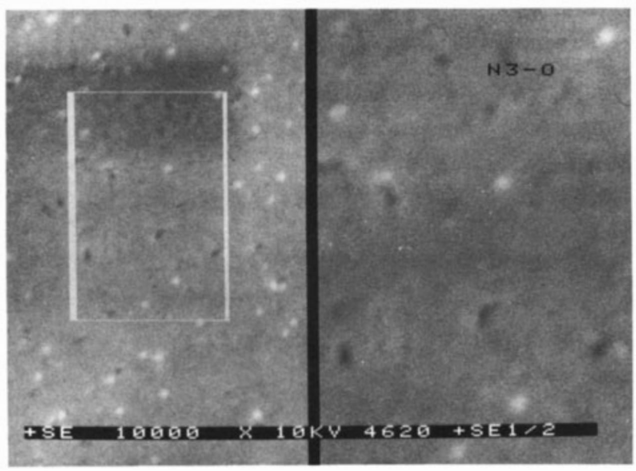

Figure 1. Scanning electron microscopy image of an 80 nm thick Y–Ba–Cu–O film on (100) MgO.

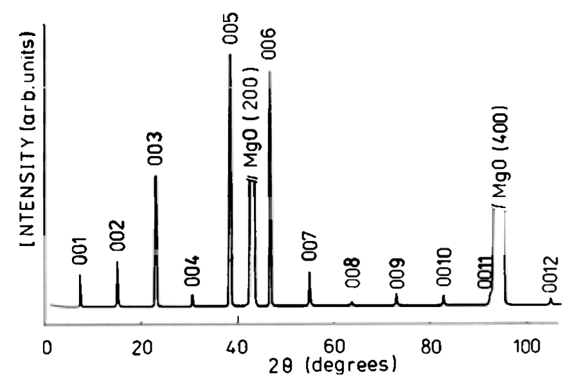

Figure 2. X-ray diffraction spectra for $YBa_2Cu_3O_{7-x}$/(100)MgO film.

superconducting properties at liquid nitrogen temperatures without the need for additional heat treatment. The films obtained seemed highly homogeneous, smooth and shiny.

Scanning electron micrographs of a film surface do not show (figure 1) the significant morphological defects such as pores, inclusions, cracks etc.

3. X-ray diffraction analysis

The XRD analysis of the films was made using a one-circle diffractometer (Cu Kα radiation, graphite monochromator) and a Weissenberg equi-inclined goniometer (non-monochromatized Cu K radiation, photoregistration).

The diffraction lines (figure 2) of the (00l) set of the $YBa_2Cu_3O_{7-x}$ reflection spectrum are very sharp (the peak halfwidth is about 0.1–0.15 deg on the θ scale). We could not find other sets of reflections at a higher registration sensitivity and higher incident beam intensity. This points to the high degree of texturing ($\bar{c}\perp$MgO(100)).

To find the co-orientations of film and substrate plane lattices (epitaxy) we used photographic registration of diffraction patterns (rotation and Weissenberg photographs of reciprocal lattice sections). On the rotation photographs around the $\bar{a}$ axis of MgO (figure 3) one can clearly see the layer lines formed by sharp reflexes, which are less intense than those of MgO. The translation vector $T_A = 3.86$ Å parallel to the rotation axis (i.e. the $\bar{a}$ of the MgO) corresponds to these layer lines. The data lead to the conclusion that,the film is a highly perfect pseudo-single crystal epitaxially grown from the (100) or (010) facet on (100)MgO (A-type epitaxy). The reflex sharpness of A-type epitaxy indicates that the misorientation of its mosaic blocks is even lower than that of the substrate. Weak and diffuse reflexes can also hardly be detected on the same rotation photograph. The translation vector, corresponding to this rotation layer line is $T_{[110]} = 5.43$ Å $\simeq a \times \sqrt{2}$, where a is the lattice parameter of the $YBa_2Cu_3O_{7-x}$ structure (B-type epitaxy when $\bar{c}_{film} \| \bar{c}_{MgO}$; $(\bar{a}/\bar{b})_{film} \| ([\bar{1}10]/[110])_{MgO}$). The evaluation based on total intensities of rotation layer line reflexes demonstrates the prevalence of A-type epitaxy ($m_A : m_B \geqslant 9:1$).

Additional information on the film structure has been obtained from the Weissenberg photographs of reciprocal lattice sections. The reflexes of the pseudo-

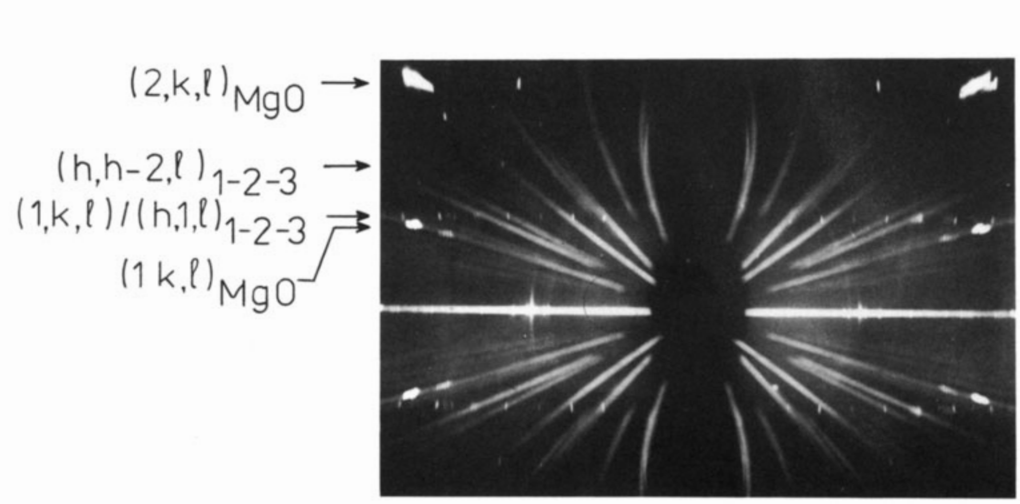

Figure 3. Rotation photograph around the *a* axis of MgO of the Y–Ba–Cu–O epitaxial film.

single crystal film are within the characteristic networks that correspond to the 0*kl* (or *h*0*l*) and 1*kl* (or *h*1*l*) cross sections of the $YBa_2Cu_3O_{7-x}$ reciprocal lattice (on the zeroth and first layer lines, respectively). In the vicinity of the *h*00 or 0*k*0 reflection pattern the reflexes are double split while the 00*l* reflexes do not show any splitting. The same picture is usual for the polydomenic Y–Ba–Cu–O crystals in the orthorhombic I phase.

The measured unit cell parameters of our films (a = 3.82 Å; b = 3.88 Å; c = 11.676 Å) and orthorhombic deformation $(a-b)/a = 0.013$ are close to those described elsewhere for Y–Ba–Cu–O single crystals.

Thus, the Y–Ba–Cu–O films prepared by the aerosol MOCVD technique are high quality pseudo-single crystals polysynthetically twinned along the (110) plane and forming a direct (A-type) epitaxy on MgO substrate.

4. Raman spectroscopy

Raman spectra analysis of Y–Ba–Cu–O thin films [5, 6] gives information about orientation, spatial homogeneity and structural perfection, as well as the presence of such impurity phases as $BaCuO_2$ and Y_2BaCuO_5. Raman spectra were measured at room temperature with backscattering geometry using the double spectrometer (excitation by Ar^+ laser: $\lambda = 514.5$ nm; incident beam power = 30 mW; laser spot on the sample surface = 30 μm).

Polarized spectra (shown in figure 4) of $YBa_2Cu_3O_{7-x}$/MgO(100) film were recorded for the backscattering geometries $z(x', y')\bar{z}$, $z(x', x')\bar{z}$, $z(x, y)\bar{z}$ and $z(x, x)\bar{z}$ (here, $x \parallel a$ axis, $y \parallel b$ axis, $z \parallel c$ axis of the MgO single crystal; x' and y' denote directions along the diagonals in the *ab* plane). It is seen that the Raman spectra are similar to those obtained from the *ab* plane of a high quality Y–Ba–Cu–O single crystal [6]. Indeed, the $\nu_1 \simeq 500$ cm^{-1} line, caused by valence vibrations of O(4)–Cu(1)–O(4) group along the $\bar{c}$-axis, is absent from $x'y'$ and xy spectra, while in the xx spectrum its intensity is small in comparison with the $\nu_3 \simeq 337$ cm^{-1} line, which corresponds to the out-of-phase vibrations of oxygen O(2) and O(3) atoms in CuO_2 planes.

This indicates that the $\bar{c}$-axis of the film is normal to the MgO (100) substrate plane. The presence of ν_3 line in the $x'y'$ spectrum shows that the $\bar{a}$ and $\bar{b}$ film axes are parallel to the [100] and [010] substrate axes. Thus, the polarized Raman spectra analysis confirms that the investigated films are epitaxial. Additionally, the good coincidence of Raman spectra obtained from different points of a number of samples shows the high spatial homogeneity of the films; at the same time the absence of lines other than ν_1 and ν_3 from the spectra shows the absence of other phases from the film.

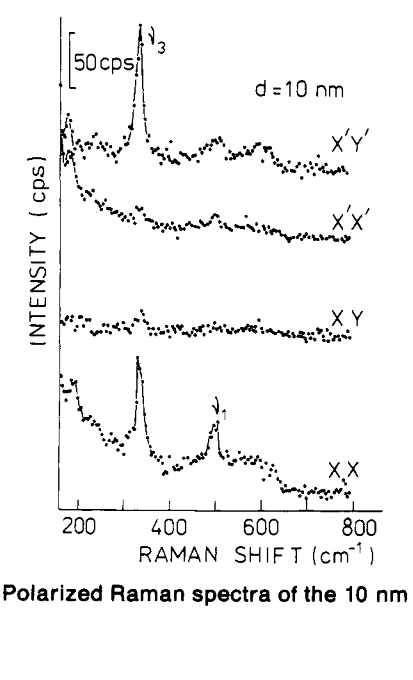

Figure 4. Polarized Raman spectra of the 10 nm thick film.

5. Parameters of the superconducting state

The temperature dependence of resistivity and field dependence of critical current density were measured using a four-probe method applied to a bridge $\simeq$100 μm wide 3 mm long, fabricated by laser etching.

Figure 5 shows the $\rho(T)$ dependences for several $YBa_2Cu_3O_{7-x}$/MgO films. The value of the transition temperature and width has been obtained $T_c(R = 0)$ = 78–80 K and $\Delta T_c \simeq 2$ K respectively for the films thicker than $d \geqslant 80$ nm. The ultra-thin film with $d = 10$ nm is characterized by $T_c(R = 0) = 50$ K ($\Delta T_c \simeq$ 13 K). One should note that low room temperature resistivity of the films $\rho(300\ K) \simeq$ 50–100 $\mu\Omega$ cm, which is close to the value typical for high quality single crystals of '123' phase, remains even for thicknesses down to 10 nm.

Though the critical current density is an important parameter for practical use, the results of J_c measurements will be considered here only as additional information on the quality of the grown epitaxial layers, because the strong dependence of J_c on the perfection of the superconducting material microstructure is well known.

Figure 6 shows $J_c(B)$ dependences for two orientations of magnetic field. The first orientation ($J \perp B$) is

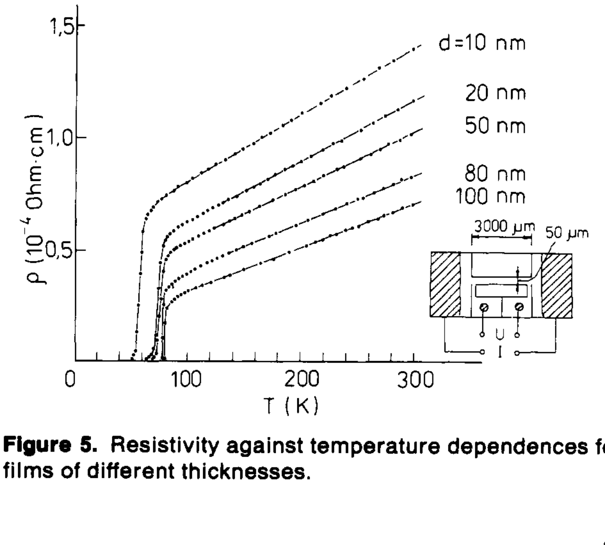

Figure 5. Resistivity against temperature dependences for films of different thicknesses.

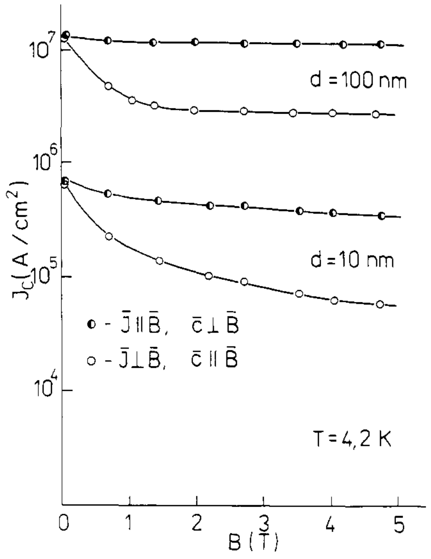

Figure 6. Magnetic field dependences of critical current density for the Y–Ba–Cu–O epitaxial films.

commonly used to investigate the flux pinning in thin layers, while the second one (longitudinal or so called 'force-free'—$J \parallel B$) has a configuration suitable for observing the highest values of the transport current in superconducting materials.

As seen from figure 6 the critical current densities for two orientations for a film of $d \simeq 100$ nm thickness are $J_{c\parallel} = 10^7$ A cm^{-2} and $J_{c\perp} = 3 \times 10^6$ A cm^{-2} in a field of $B = 5$ T. High values of J_c, and the fact that $J_{c\parallel}$ and $J_{c\perp}$ are comparable (taking into account the well known anisotropy of B_{c2} in these compounds) demonstrate the perfection of the microstructure (at least the absence of weak links and the availability of an efficient pinning centre system in these samples).

Of separate interest could be the investigation of flux pinning in ultra-thin ($d \leqslant 10$ nm) high T_c films. However, we would like to note here only the absolute value $J_c \simeq 10^6$ A cm^{-2} ($B = 0$, $T = 4.2$ K) we have observed in the epitaxial 10 nm thick films of $YBa_2Cu_3O_{7-x}$/MgO(100).

6. Summary

High T_c superconducting $YBa_2Cu_3O_{7-x}$ epitaxial thin films were prepared by a novel aerosol MOCVD technique. The advantage of this method over the conventional gas transport systems of vapour phase epitaxy consists in a considerable simplification and cost reduction of the apparatus. This advantage will be important in obtaining films of such complicated compounds as Bi- and Tl-containing high T_c materials.

Among other results, attention should be paid to the data obtained for ultra-thin Y–Ba–Cu–O films. The preparation of such samples demonstrates the attractive possibilties of this new technology. Some successful attempts were made also on the preparation of ultra-thin epitaxial films of other oxide systems (CuO, MgO, Eu_2O_3, $LaAlO_3$ and Y_2BaCuO_5), which can be used as the barrier layers in SIS tunnel junctions as well as buffer layers by deposition of the high T_c materials on semiconductors and other subtrates.

Acknowledgments

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