

Orientation of the BSCCO films prepared by low-pressure single-aerosol source metallorganic chemical vapour deposition

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Thin films (0.7–0.8 μm) of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ were deposited by low-pressure metallorganic chemical vapour deposition with a single aerosol source. The influence of the deposition parameters on the orientation of the films was studied. It was established that low deposition rate, high deposition temperature and the presence of the liquid phase resulted in films with predominant *c*-orientation.

1. Introduction

The preparation of thin superconducting films with various types of orientation is of special interest for the construction of different electronic devices [1]. Some dependences of the type of the film orientation on the metallorganic chemical vapour deposition (MOCVD) process conditions were revealed for YBCO thin films [2]. It was established, for example, that a low deposition temperature and a high deposition rate promoted the formation of *a*-oriented films. The influence of the deposition parameters on the orientation of 2212 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$) thin films has not been studied before in detail. Only the preparation of the 2212 films with predominant *a*-orientation has been reported elsewhere [3].

The main difficulties of the MOCVD of the 2212 thin films are the low rate of HTSC phase formation and the limited field of the high temperature superconductor (HTSC) phase existence [4]. This limits the deposition rate and the possibility of varying process parameters, especially the deposition temperature within a wide range.

In the present work we tried to study the influence of the different parameters (deposition temperature, stoichiometry, substrate material and deposition rate) on the orientation of 2212 films.

2. Experimental procedure

To obtain the 2212 films, metallorganic chemical vapour deposition with a single aerosol source was used. This modification of MOCVD has already been successfully applied for the preparation of YBCO thin films [5]. Volatile compounds containing metallic components of the films were dissolved in the organic solvent. Earlier it was found [5] that diglyme is an appropriate solvent for this purpose. Complexes of

TABLE I Parameters of the deposition process

Parameter	
Deposition temperature	740–800 °C
Total pressure	30 mbar
Partial pressure of oxygen	25 mbar
Total gas flow	30 l h ⁻¹
Concentration of the solution	0.01–0.1 mol metal/l
Substrate material	(1 0 0) YSZ, (1 0 0) MgO, (1 0 0) SrTiO ₃
Deposition rate	0.25–3 $\mu\text{m h}^{-1}$

strontium, calcium and copper with 2,2,6,6-tetramethylheptandion-3,5 and triphenylbismuth were used as precursors. An aerosol produced from this solution by the ultrasonic nebulizer was transported by argon to the heated zone where the evaporation of the precursors took place. Vapour thus obtained reached the heated substrate where the film was formed. The “cold-wall” vertical reactor with r.f.-heater was used to reduce the combustion of the solvent. Parameters of the deposition process are summarized in the Table I.

X-ray diffraction (four-circle diffractometer “Siemens D5000”), and energy dispersive X-ray (EDX) analyses (electron microscope “CamScan 4” with electron probe microanalyser) were used to determine the phase and chemical composition of the films. Critical temperature and critical current density were measured by the techniques described elsewhere [6].

3. Results and discussion

3.1. Deposition temperature and deposition rate

An anisotropy of the superconducting properties of HTSC means that only films with a definite type of orientation may be of great interest for the application.

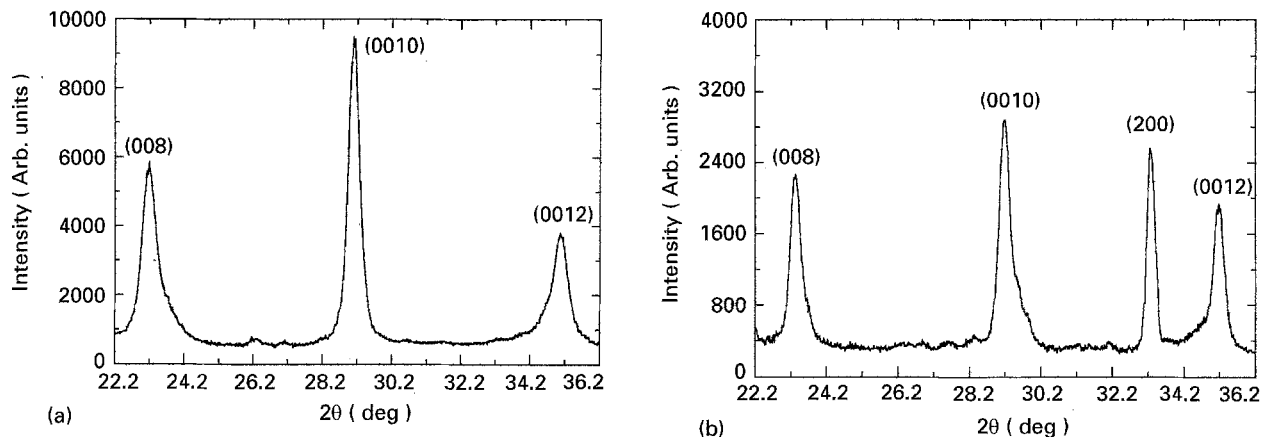


Figure 1 XRD patterns for the 2212 films deposited on (a) (1 0 0) MgO and (b) (1 0 0) YSZ, ($T_d = 780^\circ\text{C}$).

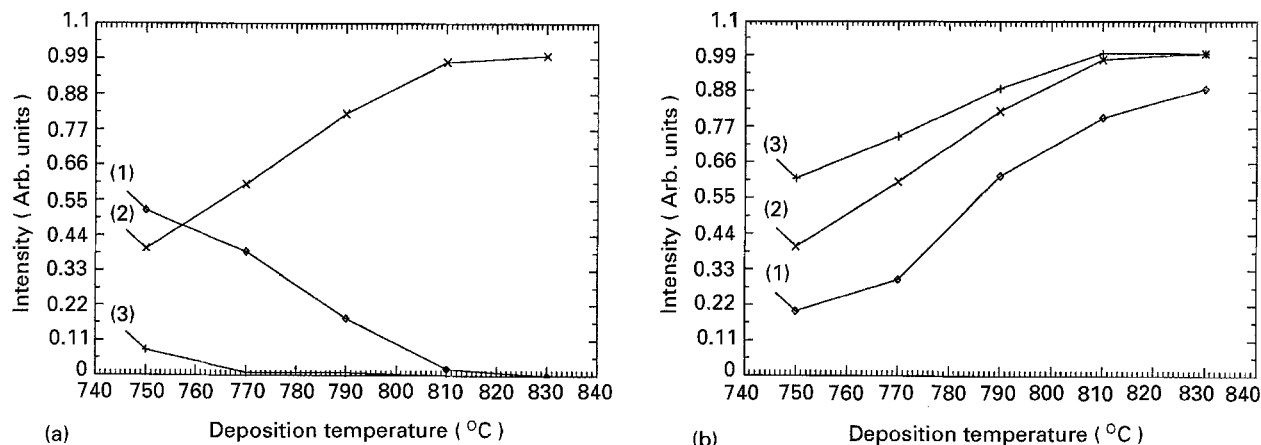


Figure 2 Dependence of film orientation on the deposition temperature. Intensity = $I_x / (I_{200} + I_{113} + I_{115} + I_{008} + I_{0010})$. (a) (1) $I_x = I_{200}$, (2) $I_{008} + I_{0010}$, (3) $I_{113} + I_{115}$. (b) $I_x = I_{008} + I_{0010}$; substrates (1) (100) YSZ, (2) (100) MgO, (3) (1 0 0) SrTiO₃.

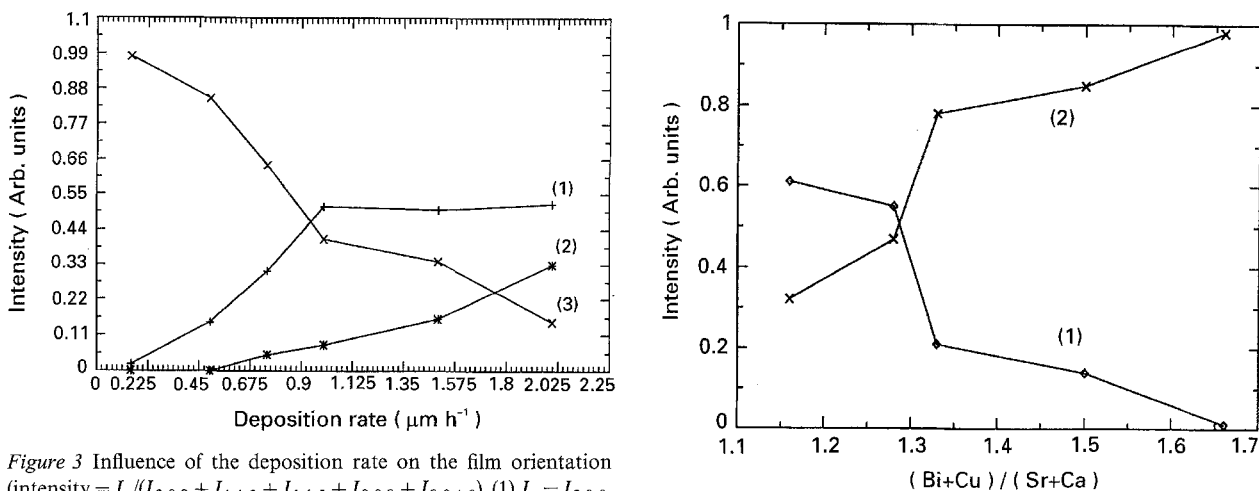


Figure 3 Influence of the deposition rate on the film orientation (intensity = $I_x / (I_{200} + I_{113} + I_{115} + I_{008} + I_{0010})$, (1) $I_x = I_{200}$, (2) $(I_{113} + I_{115})$, (3) $(I_{008} + I_{0010})$).

Figure 5 Influence of the film stoichiometry on the film orientation. (Intensity = $I_x / (I_{200} + I_{113} + I_{115} + I_{008} + I_{0010})$, (1) $I_x = I_{200}$, (2) $(I_{008} + I_{0010})$, $T_d = 780^\circ\text{C}$, substrate (1 0 0) MgO).

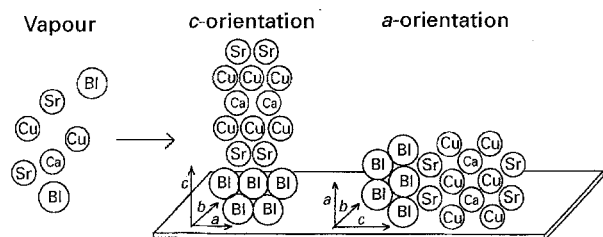


Figure 4 Formation of the blocks corresponding to the different types of the film orientation. Positions of the 2212 phase unit cell are shown relative to the substrate surface. Atoms of oxygen are omitted.

The deposition temperature had a strong influence on the film's orientation. At a low deposition temperature (700–770 °C), randomly oriented films of stoichiometry 2212 were prepared on all substrates used. In this case the reflections 00 *l*, 11 *l* and 200 were present in the XRD spectra (Fig. 1). The intensity of the 200 and 11 *l* peaks decreased with increasing

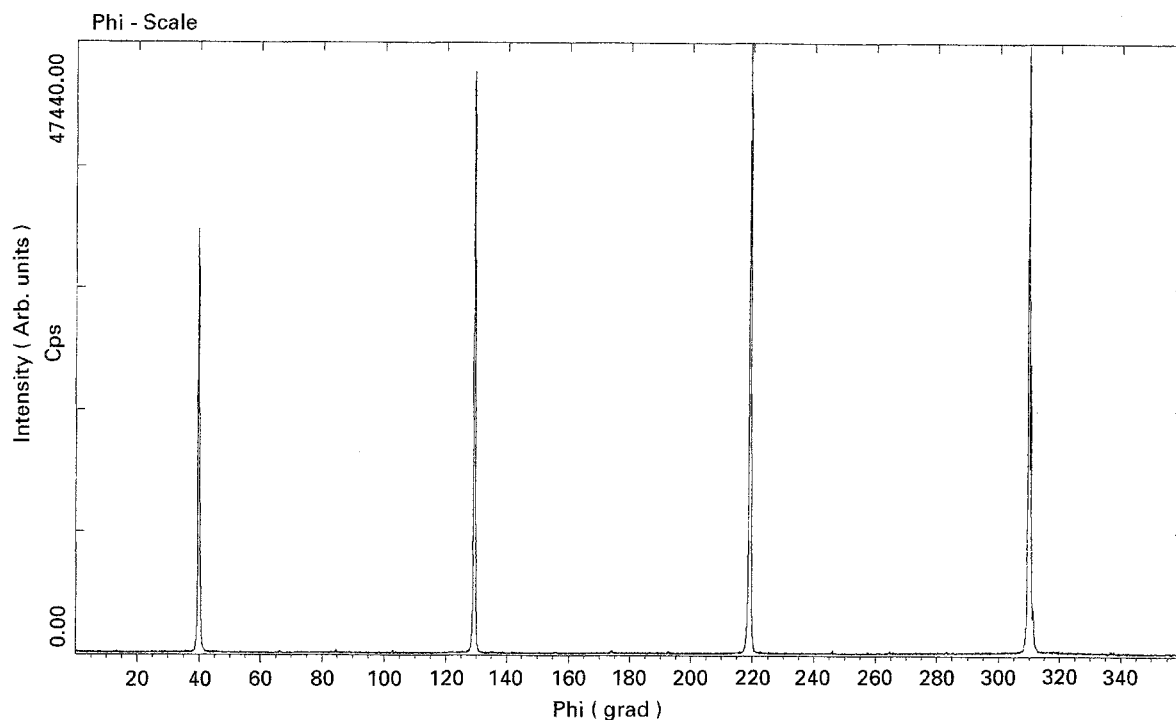


Figure 6 Phi-scanning diagram for the (1 1 7) reflection of 2212 film deposited on (1 0 0) SrTiO₃ ($T_d = 800^\circ\text{C}$).

deposition temperature (Fig. 2). At a temperature higher than 780°C , only *c*-oriented films were obtained on (1 0 0) MgO and (1 0 0) SrTiO₃. However, *c*-oriented films can be prepared on YSZ only at a temperature higher than 810°C .

The deposition rate also affected the orientation. 0 0 *l*-oriented 2212 films were grown on (1 0 0) MgO and (1 0 0) SrTiO₃ at a rate lower than $0.9 \mu\text{m h}^{-1}$ (Fig. 3) and at a deposition temperature higher than 780°C . Thin films with considerable contribution of *h* 0 0 and 1 1 *l*-orientation were obtained as a result of the increase of the deposition rate: the higher deposition rate, the greater was the amount of *h* 0 0 and 1 1 *l* oriented grains. Possible reasons for such behaviour are discussed below.

These results are in agreement with the fact that *c*-orientation of HTSC phases is thermodynamically preferable [7] because the free energy of *c*-oriented grain formation is smaller than that of *a*-oriented ones.

It was also found [7] that *a*-orientation is more favourable kinetically. According to the data obtained by RHEED [8], chaotic distribution of the metal atoms on the surface of the substrate takes place at the first moment of the deposition. The formation of the two-dimensional net corresponding to the *a*-*b* facet can be reached by smaller displacements of the atoms than the formation of a two-dimensional net corresponding to the *a*-*c* (*b*-*c*) facet. This is due to the structure of the facets: the *a*-*b* facet is built by atoms of only two elements, while the *a*-*c* (*b*-*c*) facet is built of atoms of four elements (Fig. 4).

Moreover, atomic layers parallel to *a*-*b* or *a*-*c* planes are not electrically neutral. So HTSC cannot grow layer by layer but by blocks containing neutral piles of the atomic layers. In the case of 2212 phase, such piles would include 2 or 7 atomic layers for the growth in the *a* and *c* directions, respectively. Thus at high deposition rate, the growth of predominantly

a-oriented films is preferable. At the same time, the necessary conditions for *c*-orientation are low deposition rate and high diffusion mobility of the components of the film. Generally high mobility can be provided at the high temperature and/or in the presence of the liquid phases.

3.2. Composition of the films

We found that excess bismuth and alkaline earth elements ($\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{2.2}\text{Cu}_2\text{O}_x$) led to the formation of non-textured thin films with low T_c values (20–40 K) and with poor morphology. Films of 2212 phase with the best properties ($T_c = 84 \text{ K}$, $j_c = 10^4 \text{ A cm}^{-2}$, ($H = 0.1 \text{ Oe}$, $T = 60 \text{ K}$)) contained excess copper and $\text{Ca}(\text{Bi}_2\text{Sr}_{1.85}\text{Ca}_{1.3}\text{Cu}_{2.15}\text{O}_x)$.

A variation of the stoichiometry which can promote the formation of the liquid phase also resulted in the growth of predominantly *c*-oriented HTSC films. The presence of the liquid phase makes transport of the components easier and favours the growth with a thermodynamically preferable orientation. It is very important in the case of Bi-HTSC, because the equilibrium liquid phase can exist at the deposition temperature [9].

It was established that excess bismuth and copper increased the contribution of *c*-orientation in comparison with stoichiometric 2212 films (Fig. 5).

The influence of excess copper and bismuth may be treated from two points of view. Firstly, an additional amount of copper and/or bismuth can induce the formation of non-equilibrium, as well as equilibrium, liquid phases. Secondly, an excess of copper and/or bismuth, which are considered to be the most mobile components in this system, favours the formation of a two-dimensional net corresponding to the facet *a*-*b* because this facet can be built only by atoms of copper and oxygen or by atoms of bismuth and oxygen.

3.3. Substrate material

The predominant orientation is determined also by the material of the substrate. It was found that *c*-oriented films can be prepared on (1 0 0) MgO at a lower temperature than on (1 0 0) YSZ, and on (1 0 0) SrTiO₃ at a lower temperature than on (1 0 0) MgO (Fig. 2).

The presence of the nearly coincident lattice sites is a necessary condition for the appearance of a definite type of film orientation. For example, substrates with lattice parameters close to a 2212 phase favour the *c*-orientation of the films. From this point of view, (1 0 0) SrTiO₃ (lattice mismatch is less than 2%) is the best substrate of those used for the growth of the *c*-oriented films of 2212 phase. Epitaxial films were deposited on (1 0 0) SrTiO₃ at 800 °C at a rate 0.5–0.7 μm h⁻¹.

The absence of additional peaks on the phi-scanning diagram for the reflection 115 indicates an epitaxial character of the films thus obtained (Fig. 6). The epitaxial films of the 2212 phase were deposited under the same conditions on (1 0 0) MgO. It is difficult to explain this fact as above because the lattice mismatch for MgO seems to be rather high (10%). It was impossible to prepare an epitaxial film on (1 0 0) under the conditions used.

4. Conclusions

It was established that the type of 2212 thin film orientation depends strongly on the deposition temperature, deposition rate, substrate material and stoichiometry of the films. The conditions favouring the *c*-orientation of 2212 films may be summarized as follows:

1. low deposition rate (less than 0.9 μm h⁻¹);
2. high mobility of the components of the film which can be provided by the increase of the deposition temperature or by variation of the stoichiometry;
3. a substrate with the small lattice mismatch relative to the *a*(*b*) lattice parameter of the 2212 phase.

References

1. F. SCHMADERER, R. HUBER, H. OETZMANN and G. WAHL, *Appl. Surf. Sci.* **46** (1990) 53.
2. H. YAMANE, M. HASEI, H. KUROSAWA and T. HIRAI, in "Proceedings of Symposium A1", ICAM 1991, edited by L. Corraera (Elsevier, Amsterdam 1992) p. 319.
3. T. SUGIMOTO, M. NAKAGAWA, Y. YOSHIHARA and S. TANAKA, *Phys. C* **192** (1992) 108.
4. V. N. FUFYIGIN, A. R. KAUL and S. A. POZIGUN, *J. Phys. IV* (1993) Coll. C3, suppl. *J. Phys. II* **3** (1993) 361.
5. G. WAHL, W. DECKER, A. NÜRNBERG, A. KAUL, R. STOLLE and M. PULVER, in "Proceedings of the International Symposium CVD-XII", Honolulu 1993, edited by K. F. Jensen and G. W. Cullen (The Electrochemical Soc., Pennington, NY) pp. 264–76.
6. O. YU. GORBENKO, A. R. KAUL, I. V. POGOSOVA and S. POLYAKOV, *Mater. Sci. Eng.* **B17** (1993) 157.
7. C. P. BURMESTER, L. T. WILLE, and R. GRONSKY, in "Proceedings of Symposium A1," ICAM 1991, edited by L. Corraera (Elsevier, Amsterdam, 1992) p. 313.
8. T. KAWAI, M. KANAI, T. MATSUMOTO and M. KOINUMA, *ibid.*, p. 287.
9. J. C. TOLEDANO, P. STROBEL and D. MORIN, *Appl. Supercond.* **1** (1993) 581.

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