PII: S0955-2219(98)00182-4

Textured YBCO-Film Formation by Sol–Gel Process and Post Annealing

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Abstract

Thick YBCO-films were prepared on single crystalline $SrTiO_3(001)$ and $LaAlO_3(001)$ substrates by the dip-coating process starting with Y-, Ba- and Cu-acetylacetonates. When a characteristic temperature during transformation of the precursor into $YBa_2Cu_3O_x$ is exceeded a strong biaxial texture with FWHM = 1·2° for 1 μm thick fims results. When the O_2 partial pressure of the annealing atmosphere is lowered the characteristic temperature decreases and films with increased current density (j_c) are obtained. The values of J_c achieved for films deposited onto $SrTiO_3(001)$ at 77 K in self field are as high as 50·000 A cm^{-2} with T_cs of 90K. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

The sol–gel method promises an effective fabrication of YBCO-films on a large scale with a relatively low technological expenditure.[1,2] One prerequisite for the technical use of sol–gel YBCO-films is a competitive current carrying capacity. As known from former results[3,4] the possibility for fabrication of high current carrying YBCO-fims by the sol–gel method is available. However, the principles of textured YBCO-film formation from sol–gel precursors have to be better understood to utilize sol–gel technology in YBCO-film production. Hence it is necessary to investigate the dependence of the crystallization behaviour of the 123-phase on the annealing conditions.

2 Experimental

Precursor films were produced by dip-coating on single crystalline $SrTiO_3$ and $LaAlO_3$ substrates. Coating solutions of two different Y:Ba:Cu ratios, 1:2:3 and 1:1.6:3·4, were fabricated from Y-, Ba- and Cu-acetylacetonates as described in Ref. 5. The film thicknesses were controlled by varying the lifting speed and viscosity. The films were then dried and pyrolysed at 600°C in air. The coating procedure can be repeated so as to increase the film thickness. Phase transformation into the 123–phase occured by heating the precursor films at temperatures of 740 up to 925°C under N_2/O_2–atmospheres with an oxygen partial pressure between 20 and 500 Pa. Thereafter, the films were slowly cooled down to room temperature in a pure O_2-atmosphere. The film morphologies have been investigated by SEM. For orientation measurements X-ray diffraction methods have been used.

3 Results and Discussion

The successful fabrication of high quality YBCO films by the sol–gel method has resulted in J_c values up to 10^6 A cm^{-2}. These films were annealed in low oxygen partial pressures below 100 Pa.[3,4] Therefore we started our investigations by variation of the annealing temperature between 740°C and 850°C under oxygen partial pressures of 20 and 30 Pa. At this p_{O2} the experiments have been carried out simultaneously for films with Y:Ba:Cu ratios of 1:2:3 and 1:1.6:3·4. The latter Y:Ba:Cu ratio was given in Ref. 6 and is apparently very effective for good superconducting properties of YBCO-films that have been made by MOCVD. This chemical method of YBCO-film deposition could be comparable with the sol–gel process regarding the formation of the 123-phase.

In each film prepared by sol–gel processing the 123-crystals are only present in two shapes. Firstly,

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the majority are platelike shaped with the *c*-axis perpendicular to the surface of the substrate. Secondly the 123-crystals are needle shaped and grown together at a right angle. In this case the a-axis of the crystals is perpendicular to the surface of the substrate. Taking this into account it is possible to estimate roughly the orientation of a large fraction of 123-crystals within the film.

In the case of films with starting composition 1:2:3 all annealing temperatures result in a fraction of randomly oriented 123-phase. When the temperature rises in the range between 780 to 800°C the randomly oriented 123-fraction strongly decreases with reduction of film thickness. This phenomenon is demonstrated in Fig. 1. It shows the morphology of films with different thickness (500 and 100 nm),
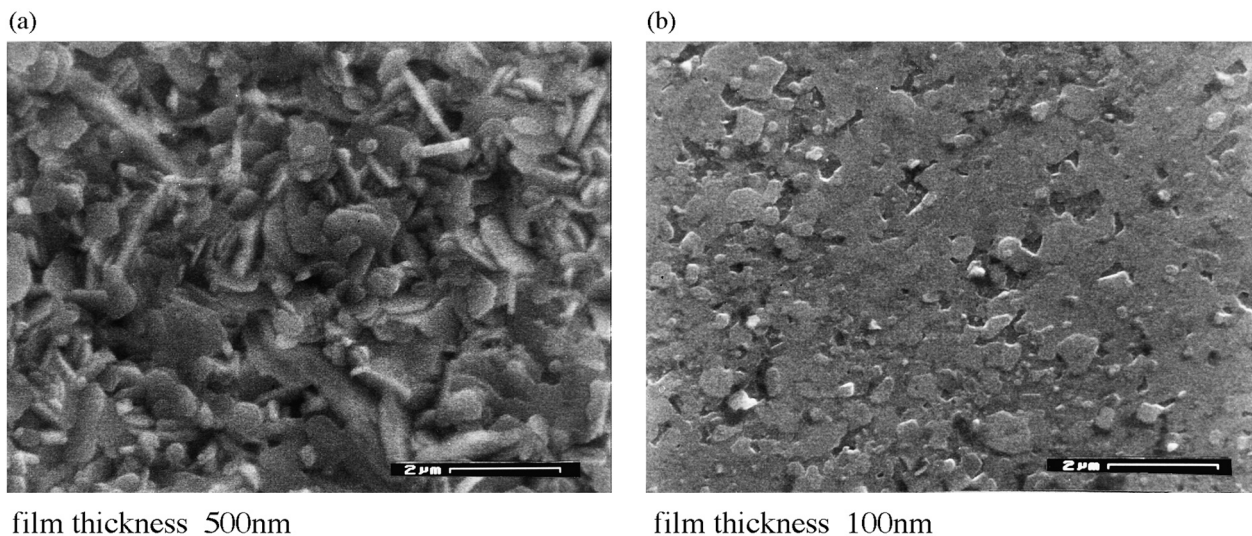
(a)

(b)

film thickness 500nm

film thickness 100nm

Fig. 1. Scanning electron micrographs of YBCO-films (starting composition 1:2:3) with different thickness (500 nm and 100 nm), heat-treated at 800°C under $p_{O2} = 30$ Pa
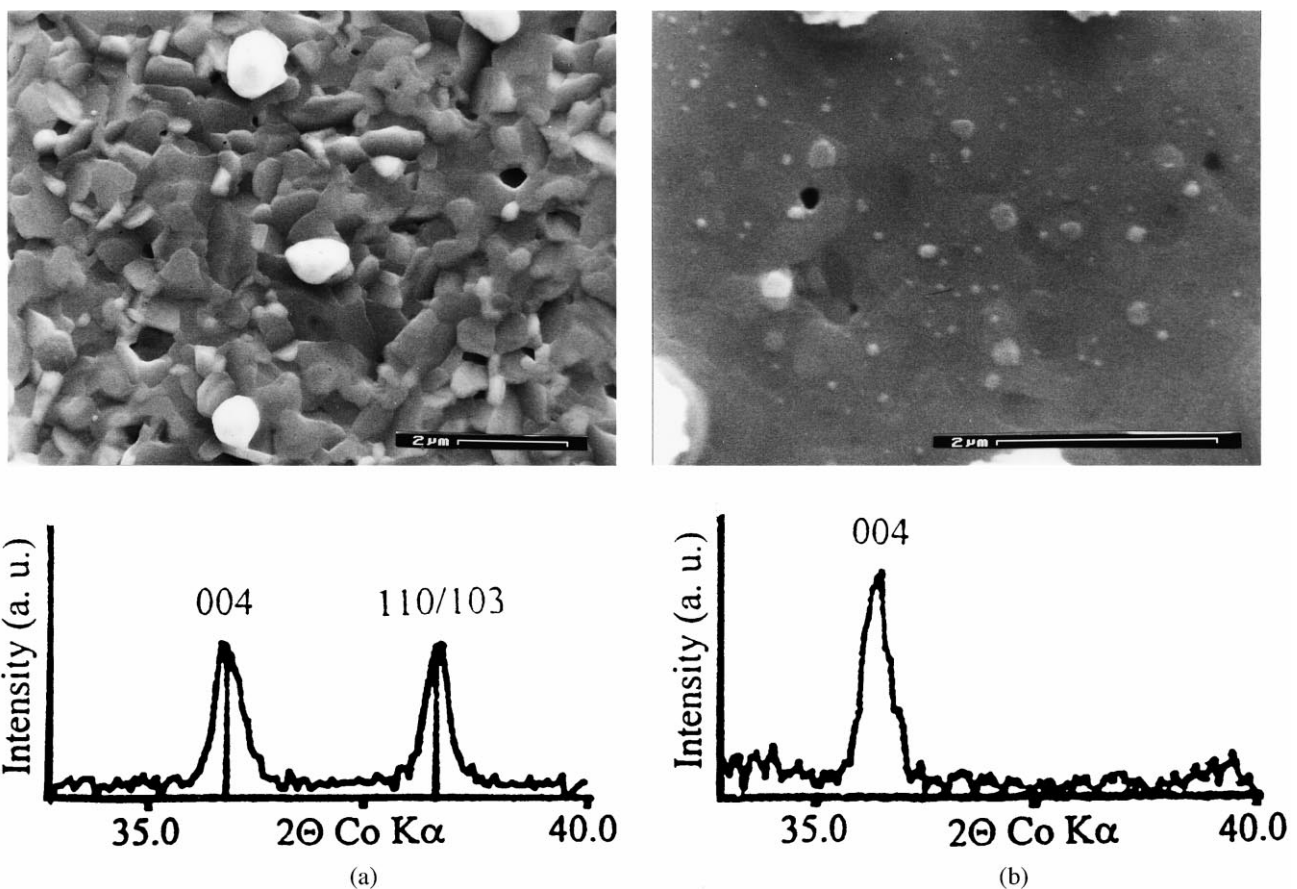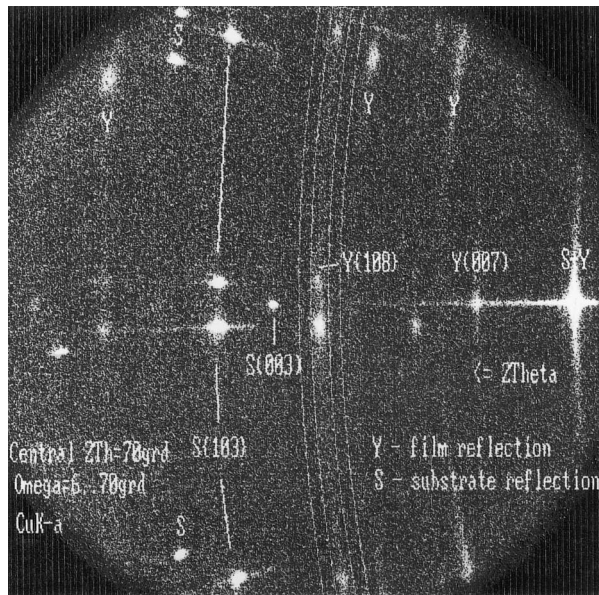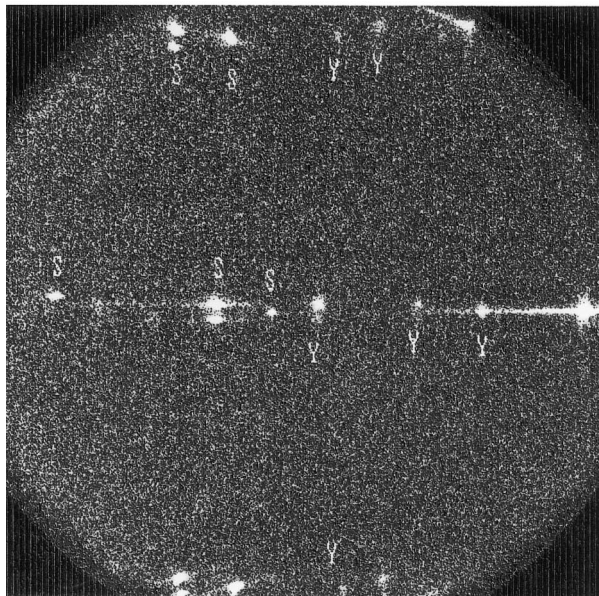
(a)

(b)

Fig. 2. Scanning electron micrographs and X-ray diffraction patterns of YBCO-fims with starting composition 1:1·6:3:4 annealed under $p_{O2} = 30$ Pa at (a) 770°C and (b) 780°C showing the increase of texture of the 123-phase with temperature.

(a)

(b)

Fig. 3. Omega-scan images of films with the same thickness (1 μm) with starting composition (a) 1:2:3 and (b) 1:1·6:3·4 made by a microdiffractometer with area detector. The weak Debye–Scherrer lines in (a) prove the presence of a randomly oriented 123-phase fraction. The omega-scan image in (b) shoes only reflection spots and does not contain Debye-Scherrer lines.

which were annealed under the same conditions at 800°C. The surface smoothness of the very thin film is clearly higher. Above 800°C the beginning of the local decomposition of the films was observed.

Figure 2 demonstrates the most important results of the morphology and texture investigations of films with starting composition 1:1·6:3.4. By heating at 770°C platelike 123-crystals are formed, but predominantly in a random orientation, which can be seen in Fig. 2(a) and is also confirmed by X-ray analysis. The X-ray pattern of these films shows

the 110/103 reflection at 38·33°. A film heat-treated under $p_{O2} = 30$ Pa at 780°C [Fig. 2(b)] consists of platelike 123-crystals that are all positioned in one plane parallel to the substrate surface. The complete c-axis orientation (00l-texure) of this film is indicated by the absence of the 110/103 reflection in the X-ray diffraction pattern.

Figure 3(a) shows the omega-scan image of a film with starting composition 1:2:3 that was made by a microdiffractometer with area detector. The Debye–Scherrer lines prove the presence of a randomly oriented 123-phase fraction. A comparable film with starting composition 1:1.6:3·4 with the same thickness (1 μm) has a complete in-plane alignement. The omega-scan image of this film [Fig. 3(b)] shoes only reflection spots and does not contain Debye–Scherrer lines. The FWHM-value along omega of the 1 μm thick film is 1·2°. The micro-diffractometer used in the X-ray investigations works with an irradiated spot of about 0·2–2·0·2 mm^2. Thus it is possible to obtain information about differences in orientation of small areas of the film. It is found that the orientation of these sharply textured films is very homogeneous. Due to this behaviour of precursor films with starting composition 1:1·6:3·4, these have further been used for experiments with a stepwise increase of the temperature of 10K, from 750 to 850°C under an oxygen partial pressure of 60 Pa, and from 800°C to 920°C under 500 Pa oxygen partial pressure. The aim of these experiments is the comparison of morphology and superconducting properties of textured films that are obtained at different temperatures. In these series of annealing experiments under higher oxygen partial pressures an analogous phenomenon as under $p_{O2} = 30$ Pa was observed, but in higher temperature ranges. This is demonstrated in Fig. 4(a)–(b). The transition from random orientation of the 123-phase to 00l-texture occurs between 790°C and 800°C under $p_{O2} = 60$ Pa and between 840°C and 850°C under $p_{O2} = 500°$Pa. There exists a clear change in crystallization behaviour of the 123-phase with rising temperature at a characteristic temperature that we call T_{ch}. For films that are heat-treated below T_{ch}, a fraction of randomly oriented 123-phase is found. In the case of films with starting composition 1:1·6:3·4, annealing at T_{ch} or higher causes the randomly oriented 123-phase to disappear completely and only 00l-textured 123-phase remains. T_{ch} increases with increasing oxygen partial pressure. In Fig. 5 the T_{ch} values determined in this work are presented versus p_{O2}. The distance of the T_{ch}/p_{O2}-line from the 123-decomposition line makes it clear that 123-crystallization from sol-gel precursor films is not based on the peritectic reaction between the 211-phase and a molten phase. On the other hand
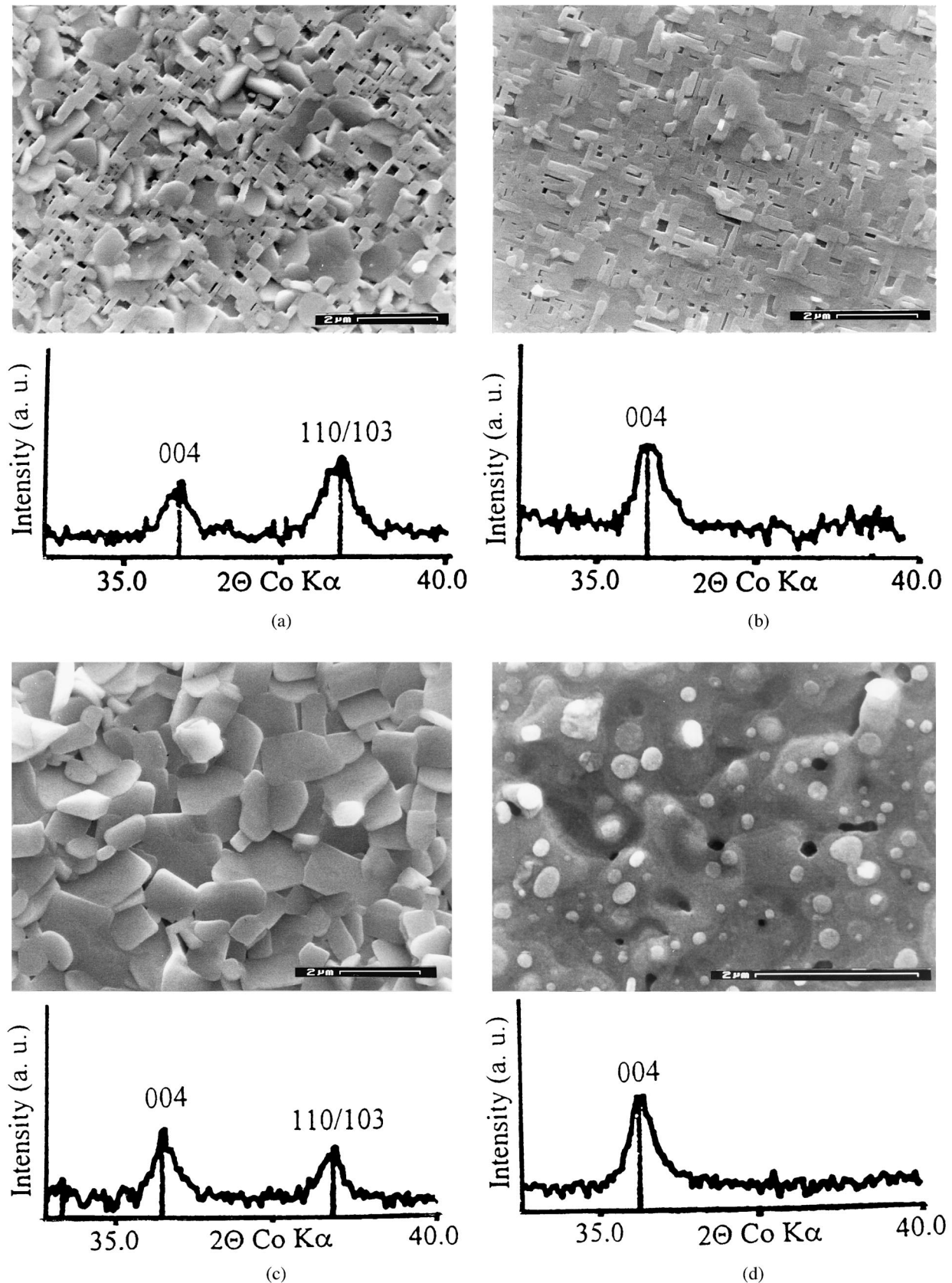
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Fig. 4. Scanning electron micrographs of YBCO-fims with 1:1·6:3·4 heat-treated at different oxygen partial pressures; annealing conditions: (a) 500 Pa O_2; 840°C, 1 h; (b) 500 Pa O_2, 860°C, 30 min, (c) 60 Pa O_2, 790°C, 80 min,(d) 60 Pa O_2, 805°C, 80 min.

the sharp texture of relatively thick YBCO-films indicates the presence of a molten phase, which starts to play a role as a transport phase for the epitactic 123 growth when T_{ch} is reached. This assumption is supported by the reaction path for the annealing of sol–gel YBCO-films in N_2-atmosphere proposed by Chu and Buchanan.[7] Thereafter, 123-phase crystallization slightly starts at 620°C. At 800°C a molten phase with the composition $Ba_2Cu_3O_{3.5}$ is formed by the reaction of Cu_2O with

$BaCO_3$ under annealing conditions in the thermodynamical stability range of Cu(I)-oxide. By lowering the oxygen partial pressure this reaction is forced to the right side which enhances the liquid phase formation. An intensive 123-phase formation follows due to the reaction of the molten phase with Y_2O_3.

The presence of the molten phase can be effective as a transport medium for the 123-phase formation, enabling a fast epitactic 123-growth. Taking into account the relationship between Cu(I)/Cu(II)-oxide balance and liquid phase formation, the p_{O2} dependence of T_{ch} becomes understandable. T_{ch}s which have been determined are located near the Cu(I)/Cu(II)-coexistence line in the thermodynamical stability range of Cu(I)-oxide as can be seen in Fig. 5.

Investigations concerning the reaction between Cu_2O and $BaCO_3$ have been carried out by means of DSC, thermobalance and mass spectrometry (see Fig. 6). They are in agreement with the reaction path proposed by Chu and Buchanan. Formation of CO_2 caused by the reaction between Cu_2O and $BaCO_3$ is observed around 600°C and above 800°C.

4 Superconducting properties

Figure 7 shows R/R_{300} (T)- and j_c (T)-curves of YBCO-films that were annealed at different oxygen partial pressures. It is found that films which were annealed at lower p_{O2} and corresponding lower temperatures show improved superconducting properties.

Figure 8 shows j_c in dependence on the temperature. Maximum values of j_c measured at 77 K in zero-field for films with 0·5 μm thickness that were annealed at 780°C under $p_{O2} = 30$ Pa was 50 000 A cm^{-2} and for 1 μm films 30 000 A cm^{-2}.
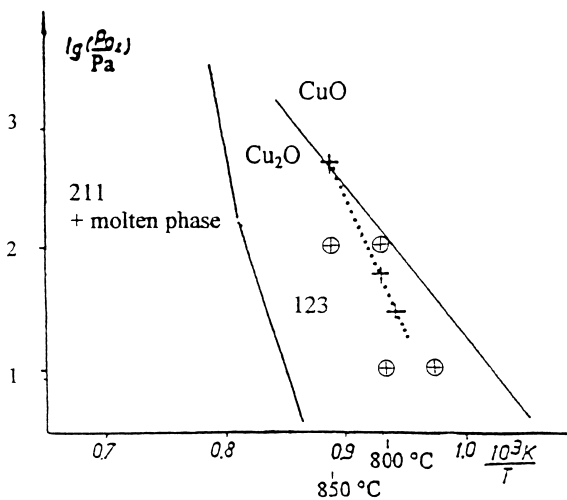

Fig. 5. 123-phase stability line as given in Ref. 2: characteristic crystallization temperature (T_{ch}) dependence on oxygen partial pressure (dotted line); $\otimes$, temperature ranges as shown in Ref. 8 where a considerable increase of the 123-crystallization rate was determined; Cu_2O/CuO-coexistence line.
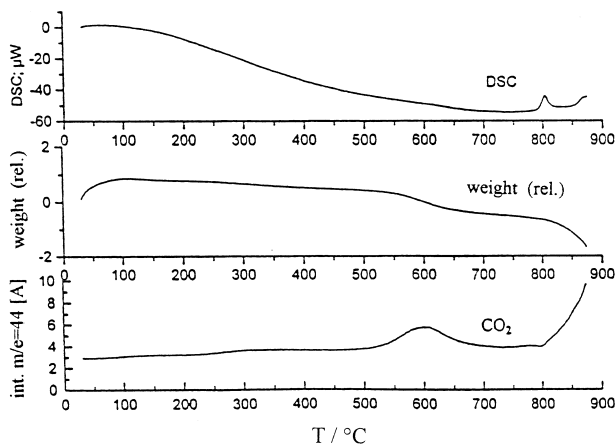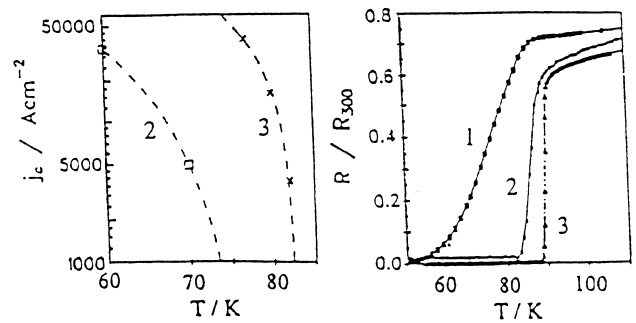

Fig. 7. R/R_{300} (T)- and j_c (T)-curves of YBCO-films annealed at different oxygen partial pressures. Annealing conditions: (1) (500 Pa O_2) 860°C, 30 min; (2) (60 Pa O_2) 805°C; 80 min; (3) (30 Pa O_2) 780°C; 80 min
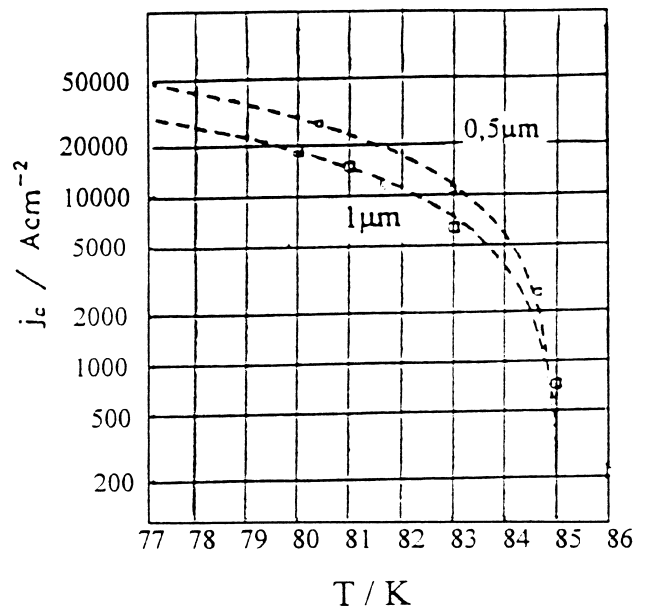

Fig. 6. DSC-curve, mass reduction (by thermobalance) and CO_2-formation (by mass spectrometer)—dependence on temperature, measured for sol–gel YBCO powder with Y:Ba:Cu = 1:2:3.

Fig. 8. j_c dependence on temperature for YBCO-films with 0·5 and 1 μm thickness on $SrTiO_3$(100).

5 Conclusions

The potential of the sol–gel process so as to fabricate YBCO-films with good superconducting properties has still not been reached. Although a very good texture was achieved, the best values for j_c does not exceed $5 \cdot 10^4$ A cm^{-2}. Investigations concerning the reaction behaviour of $BaCO_3$ indicate that one reason could be an incomplete $BaCO_3$ decomposition. Thus it is further necessary to investigate the processes and conditions that are important for the conversion of $BaCO_3$. The reaction kinetics of $BaCO_3$ in the films as well as the reaction behaviour of the molten phase, need also to be considered.

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