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Compositional effects in $Y_xBa_yCu_zO_{7-\delta}$ thin films prepared by metal-organic chemical vapour deposition

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Abstract

We report on effects of composition onto superconducting and structural properties of Y-Ba-Cu-O thin films, prepared by a carrier-gas free MO-CVD technique. Although high quality $YBa_2Cu_3O_{7-\delta}$ thin films with $T_c^{ind} \geq 90\,K$, $\Delta T_c \leq 1\,K$ and $j_c^{trans}(T=77\,K,B=0\,T) \geq 10^6\,A/cm^2$ can be prepared by this method, one finds a strong dependence of the inductively measured $T_c(50\%)$ on the ratio of Ba/Cu. The surfaces show CuO-precipitates for Ba/Cu < 2, increasing in quantity and size with increasing concentration of CuO. An excess of yttrium leads to coherent inclusions of cubic Y_2O_3 shown by X-ray diffraction and TEM-investigations. A ratio of Ba/Y > 2 causes an expansion of the c-lattice parameter, which qualitatively could be explained by a "cation-disorder"-model. To investigate the influence of Y_2O_3- and CuO-precipates on the pinning potential, the resistive transition in magnetic fields up to 12 T were measured and interpreted by a thermal activated flux-creep model. These measurements indicate the inefficiency of both, inclusions and precipitates, to enhance the pinning potential.

1. Introduction

HTC-films with smooth surfaces and high quality superconducting properties are needed for the reproducible production of electronic devices, but these demands on the films' properties seem to contradict each other. On one hand there is a need of defectless surfaces and on the other hand defects are made responsible by some authors for the high critical current density in the presence of a magnetic field in MO-CVD films [2][3]. The composition of the films is of great importance for their morphology and superconductivity [1][3]. In the present work we study the critical temperature, the surface morphology, the microstructure and the activation energy, obtained by resistance measurements in a magnetic field up to 12 T, as a function of composition. We will show that the carrier-gas free MO-CVD technique is able to produce films with smooth surfaces and high quality superconducting properties too.

2. Experimental

The Y-Ba-Cu-O films were prepared with a carrier-gas free MO-CVD technique described in detail elsewhere [4]. As source materials the well-known $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$ β-diketonates were used. We synthetisize the precursors in our own laboratories to ensure a high quality, e.g. a controlled water content. To adjust the composition of the films the evaporation temperatures of the Ba-source were fixed to 230° C. The temperatures of the Y- and Cu-sources were varied in the range of 120° C - 130° C, and 112° C -120° C, respectively. All films were deposited on single-crystalline (100)-$SrTiO_3$ substrates at 800° C and 1 hPa O_2 partial pressure. After the deposition the films were cooled down to room temperature in 900 hPa O_2 atmosphere within 50 minutes. The thicknesses of all films of 200 nm are achieved within 60 minutes. This technique allows for suitable compositions the preparation of high quality thin films with $T_c(50\%) \geq 90\,K$, and critical current densities up to $j_c(T=77\,K,B=0\,T) = 3 \cdot 10^6\,A/cm^2$.

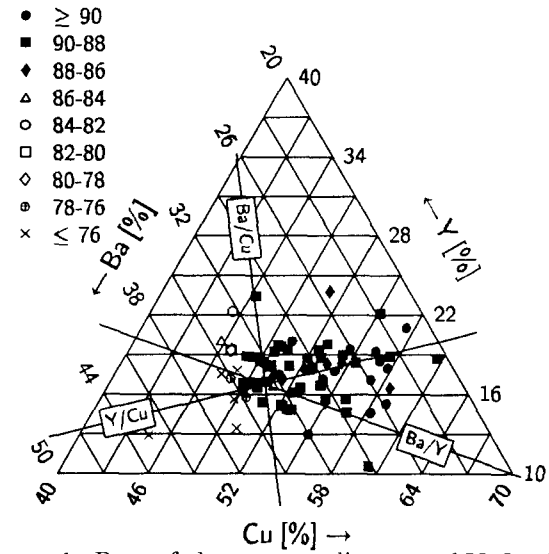

Figure 1: Part of the ternary diagram of Y_2O_3, BaO and CuO. The different symbols represent the ranges of the inductively measured $T_c(50\%)$ of MO-CVD thin films, scaled at the top left. The lines correspond to Ba/Y=2/1, Ba/Cu=2/3, and Y/Cu=1/3.

The composition of the films was determined by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). The great advantage of this method is its

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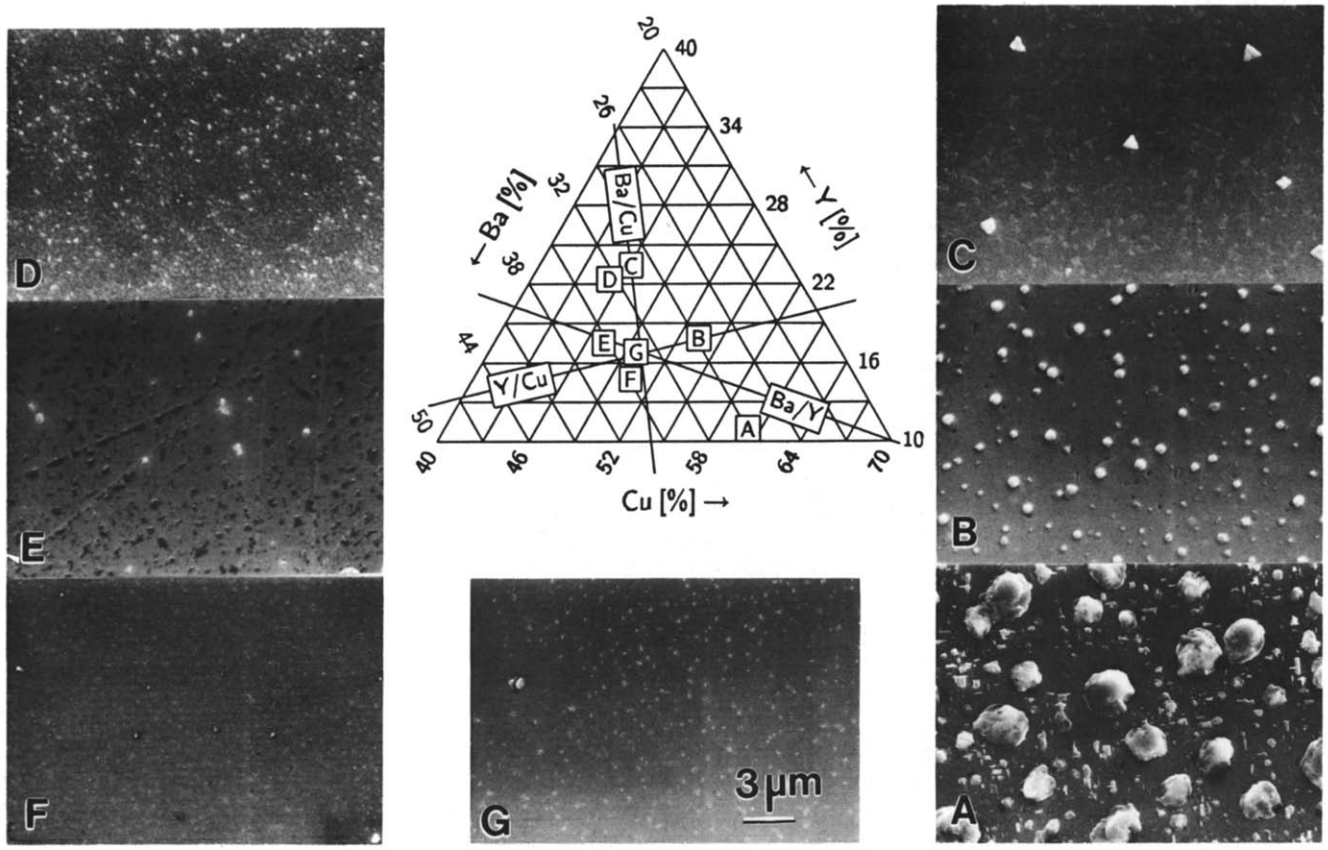

Figure 2: Dependence of surface morphology of $Y_xBa_yCu_zO_{7-\delta}$-thin films on the composition, prepared by carrier-gas free MO-CVD. The magnitude of all micrographs is given on film G. For details see text.

high accuracy (< 1 atomic percent). This analysis, on the other hand, results in incorrect compositions if the films are patterned. Using conventional photolithography of off-stiochiometric films, precipitates may resist the patterning since they are not as effectively etched by strongly diluted acids (for example 0.5% H_3PO_4) as $YBa_2Cu_3O_{7-\delta}$. Determining the composition of such a film by means of ICP-AES, the film and the remaining precipitates get completly resolved, and the latter causes an systematic error. To avoid this problem, the composition of the films was determined by the quantity of the evaporated $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$ precursors. This quantity was obtained by the loss of weight of the crucibles. The relation between loss of weight and the composition was calibrated by ICP-AES analysis of 10 unpatterned films. This calibration resulted in a linear relation between the composition of the films and the evaporated precursors. For example a composition Y:Ba:Cu=1:2:3 requires a molar ratio of 1 : 2.74 : 2.15 of evaporated precursors.

3. Results and Discussion

3.1. Critical Temperature

Using this relationship the composition can be plotted (Fig. 1) into a ternary diagram. The edges of the diagram represent the three metals Y, Ba and Cu in atomic percent. Lines corresponding to Y/Ba=1/2, Y/Cu=1/3, and Ba/Cu=2/3 are additionally included. Accordingly, the diagram is divided into six regions of excess or deficit of yttrium, barium, and copper compared to stoichiometric $YBa_2Cu_3O_{7-\delta}$. The critical temperature T_c was determined by ac-susceptibility measurements. This method is more sensitive to inhomogenities in superconducting state than resistive measurements. In Fig. 1 the inductively measured values of $T_c(50\%)$, scaled into steps of $\Delta T = 2\,K$, are shown by different symbols. With the exception of films very close to the stoichiometric composition, we can divide the samples into two groups of quality by the line corresponding to $Ba/Cu = 2/3$. In the area of $Ba/Cu \leq 2/3$, all measured films have $T_c \geq 86\,K$ (full symbols) and T_c seems not affected by the ratio of Cu/Y and Ba/Y. In the complementary area with ratios of $Ba/Cu > 2/3$, all films except the ones very close to 1:2:3 have $T_c < 86\,K$ (open symbols and crosses), particularly in the region of deficit of both, yttrium and copper. In this region T_c is drastically reduced. Concerning T_c, similar observations have been reported for plasma enhanced MO-CVD films [3].

3.2. Surface Morphology

The film morphology was characterized by scanning electron microscopy (SEM). The micrographs of seven exemplary films and their positions in the ternary diagram are given in Fig. 2. The dependence of the film morphology on the composition is also strongly affected by Ba/Cu. Films with excess of Cu in proportion to Ba always show precipitates (pressumably CuO) on the surfaces. These precipitates increase in quantity and size with increasing excess of CuO. Accordingly, film A exhibits many CuO-precipitates up to large sizes. They are reduced by decreasing Cu-content (film B) and seem to disappear at Ba/Cu = 2/3 (film C). Film C, on the other hand, shows excess of yttrium, causing weak surface roughness between CuO-outgrows. Films with less excess of yttrium show a smoother surface between the CuO-precipitates (film B).

Films with a deficit of Cu in proportion to Ba are completly free of precipitates on the surface, but are rather rough. Films with a deficit of both yttria and copperoxide are rather smooth (film F) or show holes caused by island growth mechanism [1]. A film very close to 1:2:3 has smooth surface without precipitates (film G).

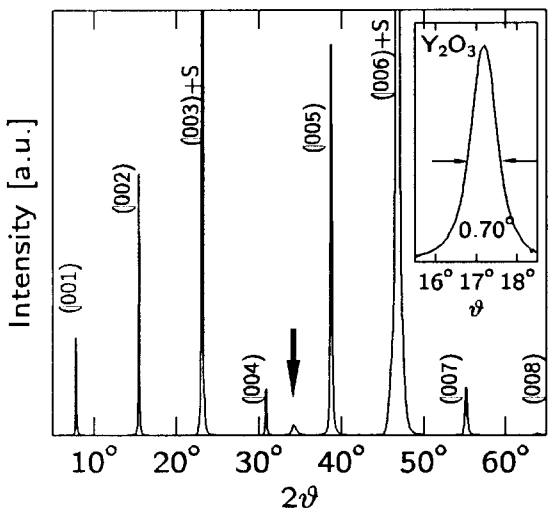

Figure 3: Bragg-Brentano x-ray diffraction pattern of a $Y_{1.55}Ba_2Cu_{3.06}O_{7-\delta}$-thin film. The arrow indicates the (400)-peak of cubic (100)-Y_2O_3 at $2\Theta \approx 34°$. Inset: Rocking curve of the (400)-peak of cubic (100)-Y_2O_3.

3.3. Microstructure

3.3.1. Excess of Y

Due to the SEM-observations, we assume that excess Y_2O_3 are incorporated into the film. This can be confirmed by x-ray diffraction. The Bragg-Brentano $\Theta/2\Theta$-diffraction pattern is plotted in Fig. 3. Besides the (00ℓ)-peaks of $YBa_2Cu_3O_{7-\delta}$ and the peaks of the (100)-$SrTiO_3$ substrate, there is an additional peak at $\Theta \approx 34°$ (marked by an arrow) which is not related to $YBa_2Cu_3O_{7-\delta}$. This peak is indentified as the (400)-peak of cubic Y_2O_3 [5]. The high degree of alignment of the cubic Y_2O_3 inclusions relative to the $YBa_2Cu_3O_{7-\delta}$-lattice is shown by the rocking-curve of the (400)-Y_2O_3 reflex (inset of Fig. 3), having a full width at half maximum (FHWM) of 0.70°. Accordingly, the Y_2O_3 impurity phase forms strongly textured (100) oriented inclusions in the 1-2-3 matrix. In comparison, the rocking-curve of (005)-$YBa_2Cu_3O_{7-\delta}$ has FHWM = 0.18°. This indicates that the epitaxial growth of $YBa_2Cu_3O_{7-\delta}$ is not affected by Y_2O_3-precipitates as has recently been shown by HREM-investigations [6].

3.3.2. Excess of Ba

On the other hand, films with increasing excess of Ba in proportion to $YBa_2Cu_3O_{7-\delta}$, show an increasing c-lattice parameter up to c=1.1875 nm for a film with composition of 1 : 3.3 : 3.5 as presented in Fig. 4 (full symbols). In the same figure the results of Matijasevic et al. [7] (open symbols) are displayed. This enlargement of the c-axis parameter cannot be explained by oxygen deficit because all films are prepared under high oxygen partial pressure (1 hPa), with the same annealing procedure as described before. A cation-disorder model is proposed in Ref. [7] to explain the c-axis expansion in films with increasing Ba-content. This model assumes a substitution of Ba on Y-sites with increasing Ba concentration. This solubility of Ba in the yttrium-layer is additionally enhanced with decreasing oxygen partial pressure during film growth. This qualitatively explains that the lowest c-lattice parameter given in Ref. [7] (open symbols in Fig. 4) is nearly 0.004 nm higher than in our MO-CVD films, because the films in Ref. [7] were prepared by reactive coevaporation under rather low oxygen partial pressure (0.01 hPa). Furthermore, the model explains that the c-lattice expansion of the coevaporated films begins at ratios of $Ba/Y \approx 1.7$, and the ones of MO-CVD films at $Ba/Y \approx 2.0$.

3.3.3. Excess of Cu

As shown in Fig. 2 excess of Cu forms precipitations on the surface of the films. Saeman-Bohlin x-ray diffraction analysis identify the structure of these precipitates as CuO-Tenorit and the CuO-precipitates are non-oriented.

3.4. Pinning

Investigating the effects of precipitates on the superconducting properties in magnetic fields, measurements of the critical current density are problematic,

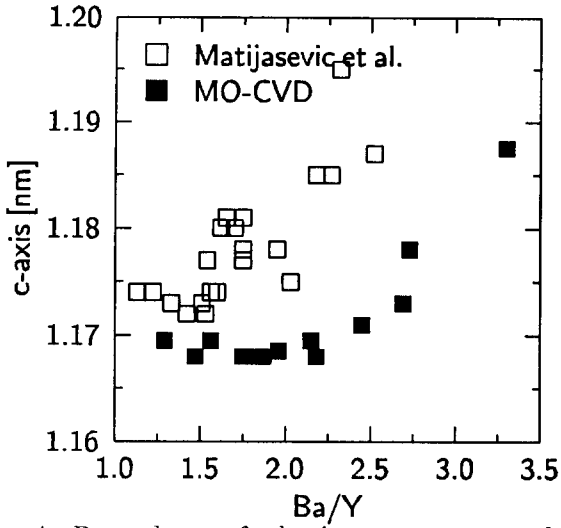

Figure 4: Dependence of c-lattice parameter on the ratio of Ba/Y. The filled symbols stand for MO-CVD films, the open symbols for reactive coevaporated films of Matijasevic et al. The curves are plotted to guide the eye.

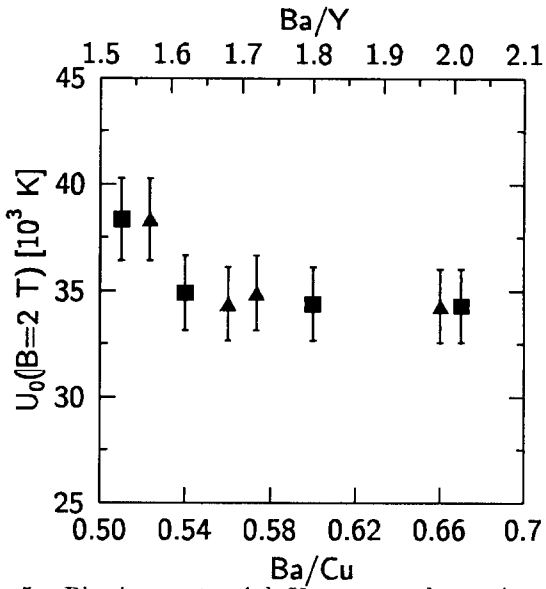

Figure 5: Pinning potential U_0 versus the ratio of Ba/Cu (squares) and Ba/Y (triangles), upper axis).

since the effective superconducting cross-section of a microbridge may be reduced by precipitates. Therefore we measured the resistive transitions to the superconducting state in magnetic fields up to $B = 12\,\mathrm{T}$ ($B \parallel \mathrm{c}$) in a conventional four-probe arrangement. In the course of this measurement we obtained the influence of Y_2O_3-inclusions and CuO-precipitates on the pinning potential U_0. In all films T_c^0 decreases from $T_c^0(B = 0\,\mathrm{T}) > 90\,\mathrm{K}$ to $T_c^0(B = 12\,\mathrm{T}) > (75 \pm 1)\,\mathrm{K}$. From this data U_0 was evaluated by a thermal activated flux-creep model ($\rho = \rho_0 \cdot \exp(-U/kT)$). Assuming a temperature dependence of the activation energy

$$U_0(t) = U_0(0)\frac{(1-t^2)^q}{(1+t^2)^{q-2}}, \quad q = 1.5, \quad t = \frac{T}{T_c} \qquad (1)$$

as given in [8], the flux-creep regions of the resistive transition can be fitted by only one parameter $U_0(0)$. This pinning potential $U_0(0)$ is plotted in Fig. 4 versus the Ba/Y and Ba/Cu ratios. Within the accuracy of the model, there is no effect of Y_2O_3-inclusions and CuO-precipitates on the pinning potential U_0. Therefore we find no evidence for higher pinning in yttrium-rich films as described in [3]. Films with a nearly exact composition of 1:2:3 posess high activation energies too (see fig. 4).

4. Summary

We have shown that both T_c^{ind} and the morphology of thin films prepared by a carrier-gas free MO-CVD technique depend strongly on the metal composition. $T_c(50\%) \geq 86\,\mathrm{K}$ is obtained for films having Ba/Cu < 2/3, leading to CuO-precipitates on the surface. Films with Ba/Cu > 2/3 are free of precipitates but T_c is drastically reduced. The excess of Y and Ba is incorporated into the films. One forms well textured, nearly coherent cubic Y_2O_3-inclusions, and the other causes a c-lattice parameter expansion, which may be explained by a cation-disorder model. In the region of high T_c values, U_0 is neither affected by Y_2O_3-inclusions nor CuO precipitates. To prepare smooth films with excellent superconducting properties, it is important to approach Ba/Cu = 2/3 as close as possible.

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