

Analysis of $Y_1Ba_2Cu_3O_{7-y}$ thin films on sapphire substrates made by electron beam evaporation

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Received October 12, 1987

We have analyzed the structure and properties of $Y_1Ba_2Cu_3O_{7-y}$ films on (012) sapphire substrates. The films were obtained by evaporation of the metals in a UHV system with an oxygen beam directed at the substrate. Analysis was performed by X-ray diffraction and electron probe microanalysis [EPMA], after annealing in addition by scanning electron microscopy [SEM] and Auger electron spectroscopy. Without annealing no superconductivity was obtained although sufficient oxygen could be incorporated during growth. The copper does not oxidize. After annealing in oxygen superconductivity is found with an onset temperature of 80–90 K and zero resistance at 30–40 K. A grain-like pattern of 3–5 µm typical size is seen. Chemical reactions between layer and substrate are observed.

Introduction

After the discovery of Bednorz and Müller [1] of superconductivity at high temperatures in materials with perovskite-type structure, followed by the rapid increase of T_c observed in $Y_1Ba_2Cu_3O_{7-y}$ by Chu et al. [2], there has been an explosion in the number of publications on high T_c superconductors. The fabrication of thin films of Y1Ba2Cu3O7-v was soon successful. The best results have been obtained on single crystal SrTiO₃ substrates, with films having a narrow resistive transition and a high T_c of 91 K (Chaudhari et al. [3], Naito et al. [4]). Films on sapphire have a much broader transition [4]. With e-beam evaporation no superconductivity is obtained without annealing in oxygen after the actual evaporation. As sapphire substrates are much more generally available than strontium titanate it is important to understand why the use of sapphire leads to films of much lower quality. We report our results with on $Y_1Ba_2Cu_3O_{7-y}$ films on sapphire substrates, both before and after annealing.

Fabrication

The films were fabricated in a UHV system which is drawn in Fig. 1. The copper and yttrium were evaporated with two electron beam guns, the barium with an effusion cell (purity Cu 99.99%, Ba 99% and Y 99.9%). The flux of the three metals was measured with the aid of a cross-beam mass spectrometer, which operated in a three channel time-multiplexed mode.



Fig. 1. Schematic drawing of the UHV-system. X = X-tal, SH = substrate holder, IC = mass spectrometer (Balzers QMG 511), E = effusion cell and*e* $-guns, <math>O_2 = oxygen$ beam

The output of the mass spectrometer was demultiplexed and the signals used to stabilize the evaporation rate of the three metals. The aim was to make the high T_c superconductor with the composition $Y_1Ba_2Cu_3O_{7-y}$. The evaporation rate of the Ba was about 0.3 nm/s and the other rates were adjusted to obtain the ratio 1:2:3 for Y, Ba and Cu. The evaporation time was about 40 min for a film thickness of about 1 µm, adapted to the typical depth of analysis in normal electron probe microanalysis [EPMA] practice.

The oxygen was sprayed onto the substrates during evaporation to get locally a high effective pressure. The oxygen flow was measured to be 2 ml/min, which resulted in a system pressure before evaporation of 1.10^{-2} Pa. Five outlets were used at about 5 cm from the substrates. The oxygen flux was large enough to allow $Y_1Ba_2Cu_3O_7$ to be formed with the evaporation rate used if the oxygen were to react in the right way. The strong gettering of oxygen by Ba and Y reduced the pressure as measured with the ion gauge during evaporation to 2.10^{-4} Pa. One has to realize that the pressure reading is strongly influenced by the location of the ion gauge. The maximum oxygen flow was limited by the mass spectrometer, as its sensitivity and baseline were influenced when the system pressure was increased too much.

The system contained a heated and a non-heated substrate holder, consequently during every evaporation run we obtained films deposited at different substrate temperatures. Concentration differences due to the beam profile of the evaporating metals were small. The substrate material was (012) sapphire. No buffer layers were used.

Results before annealing

The fabricated films were smooth and shiny and had a dark brown appearance. When exposed to humid air the samples slowly degraded in about half an hour. No observable changes occurred in pure oxygen, pure carbon dioxide or pure nitrogen on the time scale of one day. The films deposited on heated substrates seemed more stable. The resistance of the films was always very high, of the order of megaohms.

Analysis of the layers was performed with an EPMA-instrument of Jeol (Superprobe 733) using an $Y_3Fe_5O_{12}$ standard for Y analysis, a K-458 glass (31.93 mass % of O_2 , 23.08 mass % of Si, 3.07 mass % of Zn, 41.92 mass % of Ba) for the Ba and O analysis and pure Cu for the Cu analysis. As a reference small grains high- T_c $Y_1Ba_2Cu_3O_{7-y}$, made by powder technology, were analyzed. After application



Fig. 2. Wide angle Debye-Scherrer X-ray photograph, Cu radiation. The spots arise from the sapphire substrate. The X-ray photo shows the copper rings and a faint diffuse ring from an amorphous material

of corrections for matrix effects this analysis yielded a composition $Y_{1.0}Ba_{2.0}Cu_{3.0}O_{6.3}$.

The analysis of the films as evaporated always showed a higher oxygen concentration than needed to oxidize the Ba and Y. In some films, in particular with high substrate temperatures, we even found a higher concentration of oxygen than necessary to form $Y_1Ba_2Cu_3O_7$, so it seemed that enough oxygen was incorporated in the films during evaporation.

X-ray diffraction performed on films, evaporated with substrate temperatures from room temperature to 400 °C, indicated amorphous material with two diffuse rings. Films fabricated at temperatures between 600 °C and 800 °C showed, apart from the diffuse rings, the crystal structure of fcc Cu (Fig. 2). So these films contained small precipitates of pure Cu. To investigate the oxidation properties of copper we evaporated pure copper under conditions similar to those during the $Y_1Ba_2Cu_3O_{7-y}$ runs. The copper was not oxidized at room temperature, which is in agreement with measurements by Yu et al. [5]. We found we could achieve successful oxidation to CuO with a 100 eV oxygen ion beam directed at the substrate. The ion flux at the substrate was larger than the copper flux. Similar results have also been obtained by Guarnieri et al. [6].

The equilibrium pressure of oxygen as a function of temperature is given for CuO by Smyth and Roberts [7] and for Cu₂O by Allmand [8]. These equilibrium diagrams indicate that it is difficult to evaporate CuO or Cu₂O under vacuum conditions, as was experienced by Naito et al. [4], because the oxides dissociate when heated. Judging from the equilibrium oxygen pressure, only formation of Cu₂O is likely between 600 and 800 °C at the effective local oxygen pressure in our system. For oxidation to CuO in this temperature range a much higher oxygen pressure is required, about 10^{-1} Pa at 600 °C. The intensities of the X-ray diffraction lines for films evaporated at temperatures higher than 600 °C indicated that the major fraction of the copper in our film was not oxidized. We expect the same is true for the copper in films fabricated at temperatures below 600 °C, although metallic copper could not be observed there by X-ray diffraction. As the copper remained largely unoxidized in our films, the preparation of $Y_1Ba_2Cu_3O_{7-y}$ in the proper crystal structure seems impossible in our system. An extra anneal in oxygen at higher pressures to form the high T_c phase is necessary. The high oxygen content in our films as inferred from the EPMA data can be explained by incorporation of oxygen in the films in the form of Ba peroxides.

Results after annealing

After annealing in pure oxygen the films became superconducting. The typical annealing procedure was: An increase from room temperature to 800 °C in 3 h, 4 h at 800 °C, followed by a decrease to room temperature in 8 h. Typical resistive transitions are given in Fig. 3. The superconducting onset occurs at 80 to 90 K, but the transition width is always very broad, about 40 K. All curves have a resistive tail, which is strongly influenced by a transverse magnetic field. Positive as well as negative temperature coefficients are observed. The substrate temperature during evaporation has very little influence on the final resistive transition obtained after annealing. The films remained smooth and shiny after the annealing procedure. Figure 4 shows a secondary electron image made with a scanning electron microscope (SEM) (JEOL 840). The pattern in the layer is made by ion beam etching with Ar.

The X-ray diffraction yields the orthorhombic (high T_c) or tetragonal structure. The lines are considerable broadened, therefore the actual splitting which distinguishes between these two structures can not be observed. Preferential orientation of the small crystallites (≈ 20 nm as determined from line width) is not observed. There are always some X-ray lines which cannot be identified and hence the material is not single phase.

The I-V characteristic of a narrow line of 20 μ m width, made with ion beam etching, is shown in Fig. 5. The calculated ρ_{225K} is 140 $\mu\Omega$ m. A line with a width of 5 μ m, etched in the same film, had a ρ_{225K} which was 10 times higher. This line did not become superconducting, the resistance decreasing with only 30% on cooling from 80 K to 4.2 K.

When the layers were inspected with the SEM and the backscattered electrons were used for image formation, a grain-like structure with dimensions much larger than the inferred X-ray grain size is ob-



Fig. 3. Resistive transitions of films of $Y_1Ba_2Cu_3O_{7-y}$ on sapphire substrates. The resistances at 150 K are 58 Ω (upper curve), 501 Ω and 25 Ω (lower curve). The dashed line is a transition in a transverse magnetic field of 0.2 T (lower curve). This field has a marked effect on the low resistance part of the resistive transition



Fig. 4. Argon ion beam etched structure in a film of $Y_1Ba_2Cu_3O_{7-y}$ on a sapphire substrate. The bar is 1 µm. (V=35kV, substrate tilted with respect to beam)



Fig. 5. I–V characteristic of a line obtained with Ar ion beam etching. Dimensions of the line: $20 \ \mu m \times 2000 \ \mu m$. $T=1.3 \ K$



Fig. 6. Surface of an $Y_1Ba_2Cu_3O_{7-y}$ film after anneal. Backscattered electrons are used for image formation. In the right hand half of the figure, 90% of the film thickness has been removed by Ar etching. The bar is 10 µm. (V=25 kV, substrate perpendicular with respect to beam)

served in the films. Figure 6 shows a backscatteredelectron image, the left side shows the grain-like structure in the film. The part on the right in this figure was etched with an Ar ion beam until 10% of the thickness of the superconducting layer was left. The grain structure is seen to be continuous between the two halves of the figure, but the grain boundaries become thicker deeper in the film. The contrast in Fig. 6 between the two halves has been enhanced artificially. Figure 7 is a magnification of Fig. 6. The same area is given with backscattered and secondary electrons. Although the grain structure is visible in the secondary-electron image, the backscattered-electron image shows the grains more clearly. In the grain boundaries the presence of Si was detected with EPMA. In order to get an idea of the Si concentration in the boundaries Auger analysis was performed with a lateral resolution of the electron beam adapted to the dimensions of the boundaries. This resulted in an estimate of 30 at. % Si. The origin of the Si is not clear. A layer of Cu evaporated in the same UHV system contained no Si as determined by EPMA with a detection limit <35 ppm Si, so the UHV system itself and the Cu source are not suspected.

Efforts to improve the width of the resistive transition were not very successful. We believe this is caused by a chemical reaction of the evaporated material with the substrate. Our conclusion, which is in agreement with Hammond et al. [9], is based on several observations. EPMA before and after annealing yielded a different metal composition. The resistive transition was not much influenced by considerable changes in metal composition or annealing procedure



Fig. 7. Surface of an $Y_1Ba_2Cu_3O_{7-y}$ film after anneal. Detail from Fig. 6. Upper photograph is a secondary electron image (SE), the lower is a backscattered image (BE). The bar is 1 µm. (V=25 kV, substrate perpendicular with respect to beam)

for temperatures between 750 and 800 °C. With an annealing temperature of 900 °C the $BaAl_2O_4$ crystal structure could be identified by X-ray diffraction. After removal of the superconducting layer with a 10% solution of acetic acid, a thin transparent layer of about 30 nm thickness was found to remain. Although these observations show evidence for chemical reactions, we could not detect Al with EPMA in the films we used for our measurements. Also the relation between the resistive transition and the large grain structure detected in the films is not clear. Other measurement techniques are applied at present to obtain more information concerning the material inside the grain.

Conclusions

It seems unlikely that high- T_c Y₁Ba₂Cu₃O_{7-y} can be obtained during growth by straightforward evaporation of metals and the application of a beam of molecular oxygen. A minimum requirement to form high- T_c $Y_1Ba_2Cu_3O_{7-y}$ is the oxidation of copper, which does not occur at the attainable values of the effective oxygen pressure on the substrate. The use of an oxygen ion beam may be advantageous.

The magnetic field dependence and the strong increase of resistance in narrow lines indicate that the tail in the resistive transition is associated with the detected grain boundaries on a scale of several micrometers. The material within the grains has a reduced onset temperature and a broadened transition, as seen in the upper part of the R(T) curve. This might well be caused by impurity phases, for example due to chemical reactions with the substrate.

This work has been supported by the Dutch foundation for Fundamental Research (F.O.M.). We thank all those at our Delft University of Technology who made the fabrication and analysis of these films possible. We thank L. Demaegd and L. de Wulff of Bekaert Belgium for help with the scanning Auger analysis.

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Note Added in Proof

After completion of our manuscript we learned about additional work on YBaCuO films that is relevant to our paper: Kwo, J., Hsieh, T.C., Fleming, R.M., Hong, M., Liou, S.H., Davidson, B.A., Feldman, L.C.: Phys. Rev. B36, 4039 (1987); Li, H.C., Linker, G., Ratzel, F., Smithey, R., Geerk, J.: Appl. Phys. Lett.: (submitted for publication)