Chemical vapor deposition of the superconducting YBa2Cu3O7−x phase using halides as metal sources

M. Ottosson, T. Andersson, J.O. Carlsson, A. Hårsta, U. Jansson, P. Norling, K. Niskanen, and P. Nordblad

Citation: Applied Physics Letters **54**, 2476 (1989); doi: 10.1063/1.101540
View online: http://dx.doi.org/10.1063/1.101540
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/54/24?ver=pdfcov
Published by the AIP Publishing

Chemical vapor deposition of the superconducting $YBa_2Cu_3O_{7-x}$ phase using halides as metal sources

M. Ottosson, T. Andersson, J.-O. Carlsson, A. Härsta, and U. Jansson
University of Uppsala, Department of Inorganic Chemistry, Thin Film and Surface Chemistry Group, Box 531, S-751 21 Uppsala, Sweden

P. Norling, K. Niskanen, and P. Nordblad
University of Uppsala, Department of Solid State Physics, Box 534, S-751 21 Uppsala, Sweden

(Received 1 March 1989; accepted for publication 18 April 1989)

It is shown for the first time that the superconducting $YBa_2Cu_3O_{7-x}$ phase can be deposited by chemical vapor deposition using the halide precursors YCl_3, BaI_2, and CuCl as metal sources and an O_2/H_2O gas mixture. Sintered calcium stabilized zirconia plates were used as substrates. The superconductor was obtained upon deposition without the need for post-annealing. An ideal (001) texture was always found to prevail.

A high T_c superconducting phase, $YBa_2Cu_3O_{7-x}$, was recently discovered in the Y-Ba-Cu-O system.[1] The critical temperature of this new phase was found to exceed that of liquid nitrogen (77 K). The superconductors are expected to find early applications in the thin-film area. Among the thin-film preparation techniques, chemical vapor deposition (CVD) seems to have many attractive features for growth of high T_c materials. With CVD usually dense, well-crystallized and textured films are obtained. The texture can be varied with growth conditions and controlled by, for instance, adsorption. The CVD films can also be grown under a well-defined oxygen activity in the vapor, yielding superconducting films without any post-annealing procedure. This might be of importance for optimization of current densities since a post-annealing procedure, starting with the binary oxides and yielding the superconducting phase, may result in a negative specific volume change and hence pore formation. Finally, CVD is known to have a high throwing power with a capability of forming on complex-shaped substrates.

A key point in CVD is the selection of source materials. With metalorganic precursors for Y, Ba, and Cu, respectively, the risk of carbonate formation, affecting current densities, cannot be excluded. Nevertheless, metalorganic precursors have been used to deposit films which contained the superconducting phase $YBa_2Cu_3O_{7-x}$ after a subsequent anneal in an oxygen atmosphere.[2–4] Recently the superconducting phase was reported to form upon deposition from metalorganic compounds.[5]

The risk of carbonate formation mentioned above can be eliminated by using halides instead of metalorganics. The halides are then evaporated at appropriate temperatures and brought to react with some oxygen source immediately before the deposition zone. In complex systems such as CVD of $YBa_2Cu_3O_{7-x}$ from metal halides, thermodynamic calculations can be used as a guide to select the deposition parameters. Such calculations suggested that YCl_3, BaI_2, and CuCl were attractive metal source substances and that the presence of both oxygen and water would be advantageous for deposition of the superconducting phase.[6] A mixture of oxygen and water was, therefore, chosen as oxygen source. Since the ratio between the metal halides and the oxygen source as well as the O_2/H_2O ratio can be varied independently, the oxygen activity in the vapor can be controlled in such a way that post-annealing is not needed. This is the first report on the use of metal halides to grow thin films of $YBa_2Cu_3O_{7-x}$ by CVD.

A low-pressure CVD system with a hot-wall reactor was constructed for the deposition experiments. The deposition apparatus was made of fused silica and consists of three parallel evaporation tubes connected to a larger deposition tube. The temperature of each tube can be monitored independently giving maximum possibilities to control vapor composition. The separate evaporation tubes have also the advantage of eliminating cross-contamination problems with the metal sources. The leak rate of air into the system corresponds to an air contamination level of less than 1 ppm.

The purity of the gases was 99.9997% for argon and 99.998% for oxygen. All gas flows were monitored by mass flow controllers. The chemicals used were yttrium trichloride (Aldrich Chemicals, Milwaukee, with a claimed purity of 99.9%) and barium iodide, BaI_2, and copper(I)chloride (Merck, Darmstadt, Germany). The barium iodide was obtained as a hydrate and was heated to 150 °C prior to the deposition experiments in order to evaporate the water. Calcium stabilized zirconia plates (sintered) were used as substrates.

Ar was used as a carrier gas for all the metal halides. The amount of the different metal halides admitted into the reactor was controlled by the temperature of the evaporation zones and by the Ar flow through the evaporation tubes. The oxygen/water mixture was obtained by passing a flow of oxygen through boiling water and letting the temperature of an attached reflux condenser determine the partial pressure of water, and hence the oxygen/water ratio.

The experimental parameters were as follows: total pressure 20 Torr, linear gas flow velocity 67 cm s^{-1}, deposition temperature 750–950 °C, and deposition time 2–4 h. The evaporation temperatures of the halides were 820, 950, and 340 °C, respectively, for YCl_3, BaI_2, and CuCl and the corresponding flows of argon were 300, 150, and 100 sccm. The flow of oxygen was 200 sccm and the temperature of the reflux condenser was 20 °C, corresponding to an oxygen/water ratio of 1/7. By assuming equilibrium evaporation

 0003-6951/89/242476-03$01.00

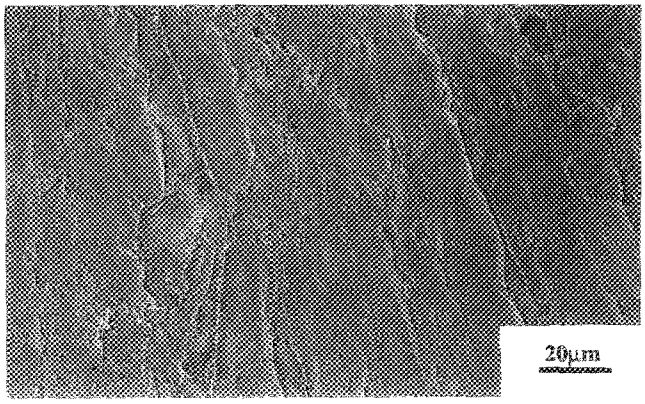

FIG. 1. SEM micrograph showing the front side of a deposited film.

conditions, the flows of the halides can be calculated to be 6.1 sccm for YCl_3, 5.0 sccm for BaI_2, and 0.4 sccm for CuCl. However, from the weight losses of the halides in the evaporation tubes, the actual flows were found to be considerably smaller especially for YCl_3 and to a lesser extent also for BaI_2. Hence, the relationship between the flows of the metal halides might correspond more closely to the 1:2:3 composition of the superconducting phase.

Phase analysis and texture investigation were performed by x-ray diffractometry using a Philips PW 1050 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The morphology of the coatings was studied by scanning electron microscopy (SEM) using a JEOL JSM 840 scanning electron microscope. The critical temperature T_c was measured by conventional four-point probe resistance measurements.

The superconducting phase $YBa_2Cu_3O_{7-x}$ was obtained without any post-annealing in the temperature range 870–910 °C. A typical growth rate was about 5 nm/min. The substrate was positioned perpendicular to the main gas stream in a so-called impingement flux arrangement. The superconducting phase, illustrating the throwing power of CVD, was grown on the front side as well as on the back side of the substrate. However, the growth conditions were not exactly the same on the two substrate sides. The front side films revealed a microstructure (Fig. 1) indicating partial melting, while the back side films show a vapor growth microstructure (Fig. 2). This shows the strong influence of the

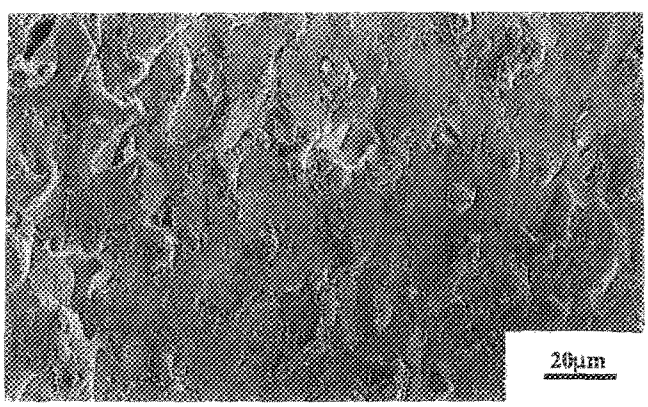

FIG. 2. SEM micrograph showing the back side of a deposited film.

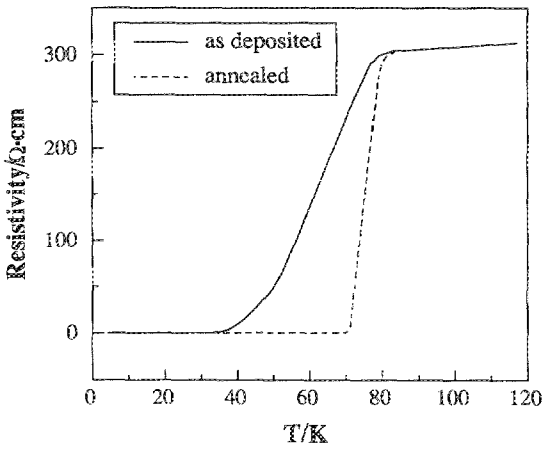

FIG. 3. Resistivity curves for a typical film, before and after annealing in oxygen.

oxygen activity in the vapor on the melting point of $YBa_2Cu_3O_{7-x}$. As for the Bi-Sr-Ca-Cu-O system,[7] the melting point is expected to increase with increased oxygen activity in the vapor. Because of differences in mass transport properties in the vapor between different gas molecules, a somewhat higher oxygen activity, explaining the difference in microstructure between the two substrate sides, can be expected on the back side. In this work the ratio between the metal halides and oxygen source was 1/140. Upon checking the melting of $YBa_2Cu_3O_{7-x}$ by using sintered samples and practically the same oxygen activity as during the deposition, a partial melting with a small fraction of melt of the sintered sample was obtained in the temperature range used in this work.

The films had a strong (001) preferred orientation and only the 00*l* reflections were visible on the diffractograms. The texture was the same for both unmelted and partially melted samples. No reflections other than those attributable to the $YBa_2Cu_3O_{7-x}$ phases were detected. The resistivity of the films was found to decrease abruptly below 80 K. Zero resistivity was obtained at about 40 K. When the films were annealed in oxygen at a temperature of 475 °C for 48 h, the temperature where zero resistivity was obtained increased to about 70 K. However, the onset temperature was not affected. Both curves are shown in Fig. 3. For other samples the onset temperature was 90 K with a zero resistivity at about 60 K. Finally, the resistivity curve was the same for the front side and the back side samples.

In summary, it has been shown that it is possible to deposit the superconducting $YBa_2Cu_3O_{7-x}$ phase by CVD using halides as metal precursors. The superconducting phase was obtained upon deposition without any need for a subsequent annealing in oxygen. The deposited superconductor was, furthermore, found to possess a strong (001) preferred orientation.

The financial support from the Swedish Natural Science Research Council and the Swedish Board for Technical Development is gratefully acknowledged.

[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).
[2] H. Yamane, H. Kurosawa, and T. Hirai, Chem. Lett. **6**, 939 (1988).

[3]H. Suhr, Ch. Ochr. H. Holzschuh, F. Schmaderer, G. Wahl, Th. Kruck, and A. Kinnen, Physica C **153-155**, 784 (1988).
[4]T. Nakamori, H. Abe, T. Kanamori, and S. Shibata, Jpn. J. Appl. Phys. **27**, L1265 (1988).
[5]H. Abe, T. Tsuruoka, and T. Nakamori, Jpn. J. Appl. Phys. **27**, L1473 (1988).
[6]M. Ottosson, A. Härsta, and J.-O. Carlsson (unpublished).
[7]U. Endo, S. Koyama, and T. Kawai, Jpn. J. Appl. Phys. **27**, L1476 (1988).