The Preparation of $YBa_2Cu_3O_{7-x}$-Films by Plasma Flash Evaporation

B. Michelt, G. Lins, and R.J. Seeböck

Siemens AG, Corporate Research and Development, Plasma and
Switching Technology, Postfach 3220, D-91050 Erlangen

Abstract - Plasma flash evaporation, a process using a high-power, inductively coupled thermal plasma to vaporise fine powders, was employed to deposit high-temperature superconducting $YBa_2Cu_3O_{7-x}$ films on $SrTiO_3$ and YSZ substrates. The films were c-axis oriented and had transition temperatures around 90 K. Their critical current density exceeded 200 kA/cm^2 in the case of $SrTiO_3$ substrates, but was considerably lower for YSZ. The deposition rate of up to some hundred nm/min makes plasma flash evaporation a competitive process as compared to sputtering and pulsed laser deposition. It is expected that the process can be scaled up to enable large-area deposition at high rates.

Introduction

Thick films of a few micrometers of high-temperature superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) deposited by different methods up till now, typically exhibit critical current densities j_c of the order of 100 kA/cm^2 at the temperature of liquid nitrogen (77 K) and moderate magnetic fields ($B \leq 10$ T). Their future application in devices such as superconducting cables, transformers, fault current limiters, and inductive energy storage systems depends on the availability of a deposition process which enables the production of large quantities of superconducting film in a reasonable time at a competitive price.

If a rated current I_{rms} is supposed to be carried by a film with critical current density j_c and thickness d, deposited on a tape of width b it can readily be shown that the deposition speed v_d, i.e. the coated length per unit time, is given by

$$v_d = \frac{l \cdot b \cdot r_d \cdot j_c}{\sqrt{2} I_{rms}} \tag{1}$$

where l is the length of tape which can be treated simultaneously and r_d is the deposition rate. If, for example, $d = 4$ µm, $b = 3.5$ cm, $l = 10$ cm, $r_d = 200$ nm/min, $j_c = 100$ kA/cm^2, and $I_{rms} = 100$ A, then $v_d = 30$ cm/h, such that it would take more than 300 hours to produce 100 m of superconducting tape. As a consequence, a high-rate, large-area deposition process is needed which works reliably and stable over an extended period of time. Plasma flash evaporation (PFE) [1], has a great potential to fulfil these requirements.

PFE is a plasma-assisted CVD technique similar to the one described in [2], but starting from a solid rather than from a liquid precursor. A high-power, inductively coupled thermal plasma is used to completely evaporate YBCO powder and to decompose it down to its atomic constituents. In a sheath close to the substrate the vapors of Y, Ba, and Cu react with oxygen to form a YBCO film. It is an intrinsic advantage of the technique that the oxygen content of the working gas can be set to enhance the stoichiometric growth of the YBCO films by the presence of a favourable amount of oxygen radicals, and that the gas pressure and the substrate temperature can be chosen such that the YBCO films are generated immediately in the superconducting orthorhombic phase without any further treatment [3].

Experiment

The design and operation of the plasma torch (Fig. 1) used in the experiments have been described in great detail by Boulos [4]. An induction coil which is powered by an r.f. generator delivering up to 40 kW at a frequency of 4 MHz concentrically surrounds two coaxial tubes. Between the outer plasma confinement tube and the inner tube which serves to establish the desired gas flow pattern, oxygen is introduced as a sheath gas which cools the walls of the plasma confinement tube and also plays an important role as a reactant in the deposition process. Argon, the central or plasma gas, is made to flow through the inner tube with a swirl as well as an axial velocity component. A third gas stream carries as an aerosol the powder to be evaporated and is injected through an axially mounted powder injection probe. Typical gas flow rates are 40 slm O_2 as sheath gas, 25 slm Ar as central gas and 4 slm Ar as carrier gas. The powder feeding rate is of the order of 10 mg/min.

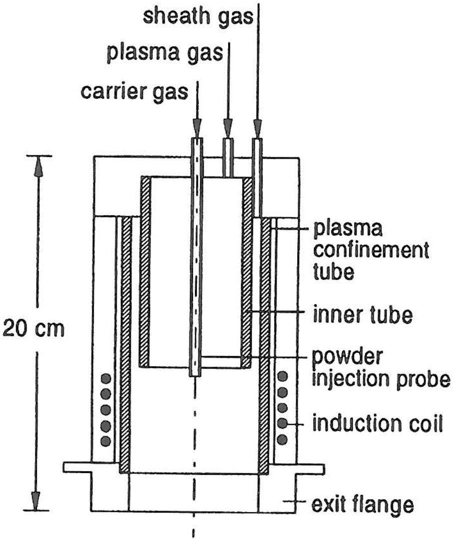

Figure 1. Cross-sectional view of plasma torch

The flame of the plasma torch is directed into a reaction chamber where the substrate is mounted on a water-cooled substrate holder. The chamber is fitted with one end-on and three side-on windows to enable optical diagnostics. A throttled water ring pump is adjusted so as to maintain a pressure of 275 mbar throughout the deposition process.

The temperature in the coil region of the plasma torch rises to values of up to 10 000 K [4], [5]. However, since the residence time of the powder inside this hot region is only of the order of milliseconds [5], the grain size of the powder must not exceed a limiting value of the order of 10 μm, to achieve complete evaporation. Thus great care has to be taken to feed the powder at a constant low rate and to prevent agglomerations of powder grains from getting into the plasma flame which owing to their size cannot be evaporated and form droplets which solidify as splashes on the substrate.

The constancy and reproducibility of the powder feeding rate were studied using Mie scattering of HeNe laser light in the absence of a plasma. When the deposition plasma was present, the metal vapor concentration was monitored by observing the intensity of the transition $6^2S_{1/2}$ - $6^2P_{3/2}$ of singly charged barium ions at $\lambda = 455.4$ nm. The Mie-scattered signal indicated that the powder entered the vaporisation zone of the plasma torch free from any agglomerations and at a sufficiently constant rate. Similarly, the intensity of the Ba^+ line did not show much variation during a deposition cycle.

It is well known that YBCO forms immediately in its superconducting orthorhombic phase only if the partial pressure of oxygen and the substrate temperature lie between 200 and 1000 mbar and 600 and 700 °C, respectively [6]. Hence in order to obtain acceptable deposition results it is of vital importance to carefully control the substrate temperature. To do so the temperature on the substrate surface was measured pyrometrically while the temperature of the substrate holder was monitored by a thermocouple mounted less than 1 mm below its surface.

Fig. 2 shows the substrate temperature and the temperature of the substrate holder measured during preheating of a $SrTiO_3$ substrate and the subsequent deposition process. Two minutes after the plasma torch has been switched on, both temperatures are about the same and amount to 200 °C. When the substrate is heated, its temperature rises slightly faster than that of the substrate holder because the substrate is not as strongly thermally coupled to the cool-water flow inside the substrate holder as the substrate holder itself. After 15 minutes the substrate has reached a constant temperature of 700 °C. When, at $t = 23$ min, powder is fed into the torch the pyrometer readout starts rising again. This increase, however, does not necessarily indicate a real rise in temperature, but can be essentially attributed to a change in the optical properties of the substrate while it gets coated with YBCO. The uncoated substrate has a transmission of roughly 25 % at the working wavelength of 4.8 μm of the pyrometer [7]. As a consequence the radiation received by the instrument is influenced to a certain extent by the temperature of the substrate holder. When the substrate gets coated with YBCO its translucency further decreases, and at the same time its surface emissivity changes. Both effects lead to an increase in the

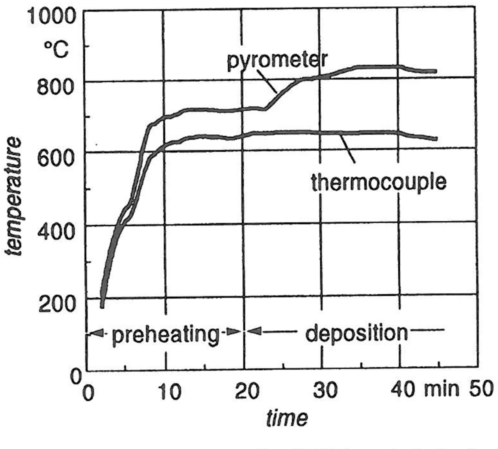

Figure 2. Temperatures of a $SrTiO_3$ substrate (pyrometer) and of the substrate holder (thermocouple) during a deposition cycle.

temperature indicated by the pyrometer. The emissivity stops changing when the substrate is completely opaque which in principle offers the opportunity of an in-situ measurement of the deposition rate. In the present work the deposition rate was, however, determined from a profilometer measurement of the film thickness *d* and the deposition time.

The substrate temperature results from a balance of the energy input from the plasma on the one hand and energy losses due to radiation, heat conduction and convection, on the other hand. Hence it appears useful to know the plasma temperature near the substrate. If thermal equilibrium prevails (which is not necessarily the case in the plasma we are dealing with [8]) the rotational temperature of molecular oxygen is equal to the plasma temperature.

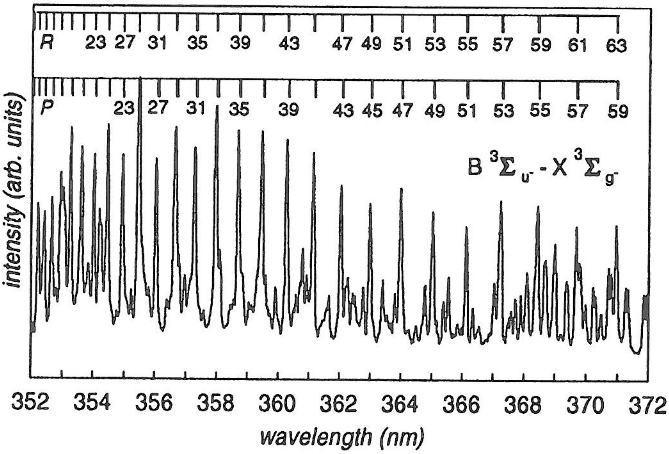

Figure 3. Rotational spectrum of O_2 taken with an optical multichannel analyser connected to a 1m-monochromator with 0.1 nm spectral resolution. Only the positions of the strongest lines are indicated in the upper part of the graph. They belong to the *R*- and *P*- branches of the band $v' = 0 \rightarrow v'' = 15$, respectively, of the Schumann-Runge system.

Several rotational bands of the $B\,^3\Sigma_{u^-}$ - $X\,^3\Sigma_{g^-}$ Schumann-Runge system [9], [10] of molecular oxygen were identified in spectra which were taken without feeding powder in order to avoid interference with spectral lines of Ba, Cu, Y and their compounds. The spectrum shown in Fig. 3 was obtained at a position 1 cm above the substrate. The rotational temperature inferred from this spectrum amounts to 2250 K.

Deposition Results

YBCO films were grown on monocrystalline (100) $SrTiO_3$ (STO) substrates as well as on polycrystalline substrates made of yttria-stabilized zirconia (YSZ), i.e. ZrO_2 with an addition of Y_2O_3. The substrate sizes are given in Table 1. At the highest deposition rate the powder feeding rate was of the order of 30 mg/min. The grain size distribution of the YBCO powder was always such that average and maximum grain size amounted to 4 μm and 12 μm, respectively. More than 99 per cent of the powder particles were smaller than 8 μm.

Table 1
YBCO films on STO and YSZ substrates

Substrate Material	Size mm³	d μm	T_{con} K	T_{coff} K	j_c kA/cm²	r_d nm/min
STO	10×10×1	0.24	90.3	88	480	8
STO	10×10×1	1.3	88.5	87.5	230	43
STO	10×10×1	3.0	89.5	89.0	270	150
YSZ	10×10×2	3.5	89	85	0.5	350
YSZ	10×10×2	3.3	89	87	0.9	330
YSZ	50×10×0.1	1.0	89	85	1.0	100

The superconducting films were characterised by measurements of their thickness d, their transition temperatures T_{con} and T_{coff}, and their critical current density j_c. The onset temperature T_{con} is the temperature at which the transition into the superconducting state begins; at T_{coff}, the superconductivity is fully developed. Both temperatures were obtained by an inductive measurement of the Meissner-Ochsenfeld effect. The critical current density was measured according to [11] using a magnetic field to induce a critical current in the superconducting film.

Monocrystalline substrates of STO are favourable for the deposition of YBCO in so far as the lattice constants of STO are particularly well adapted to those of YBCO. As a consequence, critical current densities in excess of 100 kA/cm² are readily achieved as can be seen in Table 1. The technical applications mentioned in the introduction require substrate materials such as YSZ which are available as flexible tapes or in large-area formats. Although YSZ substrates are, in general, polycrystalline, and do not match as favourably with the YBCO crystal structure as STO, superconducting films can be grown also on this material. Up till now, however, the critical current densities are considerably lower as can be inferred from Table 1.

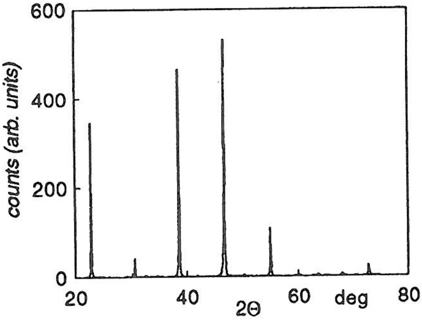

Figure 4. X-ray diffractogram of the first film of Table 1. Each peak corresponds to a particular order of Bragg diffraction from c-axis oriented YBCO crystals.

Since superconductivity of YBCO is anisotropic, it is necessary that the individual YBCO crystals which combine on the substrate to form a film be aligned such that their crystallographic c-axes are parallel to each other and perpendicular to the substrate surface. This property which is referred to as c-axis orientation can be confirmed by x-ray diffraction. The x-ray diffractogram of Fig. 4 was taken for the first film of Table 1. It clearly reveals that the desired c-axis orientation is present. The same is true for all of the films of Table 1.

Conclusions

Plasma flash evaporation (PFE) was used to deposit superconducting $YBa_2Cu_3O_{7-x}$ films on STO and YSZ substrates at deposition rates of up to some hundred nm/min. With these deposition rates, PFE is competitive with respect to other high-rate deposition methods for YBCO films, such as sputtering and pulsed laser ablation. Future work will aim at the optimisation of deposition on materials such as YSZ, in particular to enhance the critical current density. Furthermore, the substrate size will be increased in order to take advantage of the large cross section of the plasma flame to coat large areas in a short time.

Acknowledgments

The skilful technical assistance of Mr. J. Verleger and the evaluation of spectra by Mrs. R. Hughey are gratefully acknowledged. The work was supported by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie under contract number 13N6482.

References

[1] K. Terashima, H. Komaki, T. Yoshida, *IEEE Trans. Plasma Sci.*, **18**, 980-984 (1990)

[2] E. Pfender, H. Zhu, Y.C. Lau, *Mat. Sci. Engng.* **A139**, 352-355 (1991)

[3] Y. Takamura, Y. Hirokawa, H. Komaki, K. Terashima, T. Yoshida, *Physica C* **190**, 122-123 (1991)

[4] M.I. Boulos, *Pure & Appl. Chem.* **57**, 1321-1352 (1985)

[5] T. Yoshida, *Materials Transactions, JIM*, **31**, 1-11 (1990)

[6] R. Feenstra, T.B. Lindemer, J.D. Budai, M.D. Galloway, *J. Appl. Phys.*, **69**, 6569-6585 (1991)

[7] Data kindly provided by C. Staniewicz, Heimann Optoelectronics, Wiesbaden, Germany

[8] D.V. Gravelle, M. Beaulieu, M.I. Boulos, A, Gleizes, *J. Phys. D: Appl. Phys.* **22**, 1471-1477 (1989)

[9] P.H. Krupenie, *J. Phys. Chem. Ref. Data*, **1**, 433-534 (1972)

[10] W. Lochte-Holtgreven, G.H. Dieke, *Ann. Phys. Lpz.*, **3**, 937-977 (1929)

[11] H. Behner, W. Rauch, E. Gornick, *Rev. Sci. Instrum.*, **63**, 4373 (1992)