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EXPERIMENTAL WORKSHOP ON HIGH TEMPERATURE SUPERCONDUCTORS & RELATED MATERIALS (BASIC ACTIVITIES)

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DEPOSITION OF SUPERCONDUCTING YBaCuO THIN FILMS BY PSEUDOSPARK ABLATION

C. SCHULTHEISS

Kernforschungszentrum Karlsruhe
KFK
Box 3640
D-Karlsruhe
Federal Republic of Germany

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Deposition of Superconducting YBaCuO Thin Films by Pseudospark Ablation

M. Höbel, J. Geerk, G. Linker, C. Schultheiss [a]

Kernforschungszentrum Karlsruhe
Institut für Nukleare Festkörperphysik (INFP)
P.O.B. 3640, D-7500 Karlsruhe
Federal Republic of Germany

a) Kernforschungszentrum Karlsruhe
Institut für Neutronenphysik und Reaktortechnik (INR)

ABSTRACT

Thin YBaCuO films have been deposited on ZrO_2 (Y) and $SrTiO_3$-substrates by a novel ablation method, using a pulsed intense electron beam generated by a pseudo-spark source. Films with zero resistance around 85 K were grown at substrate temperatures of 820°C with high reproducibility. X-Ray analysis indicates highly textured growth on both substrates. J_c values were 6×10^6 A/cm^2 at 4.2 K and 1.1×10^5 A/cm^2 at 77 K. Because of the high simplicity of the deposition system and the variety of changable parameters it represents an interesting alternative to existing laser ablation methods.

In the last two years a variety of methods to produce HTSC-films has been investigated [1-5]. Among them, especially laser ablation has proved to be a very successful way to deposite stochiometric, epitaxially grown YBaCuO-films with excellent superconducting properties[6,7]. Most laser ablation systems today use excimer lasers, which require high capital expenditures for the hardware. Therefore, there is still great interest in alternative and perhaps simpler ablation methods. In this paper we propose a novel ablation technique in which we make use of a pulsed high-intensive electron beam emitted from a speudo spark chamber[8].

The pseudospark is an axially symmetric high voltage gas discharge operating on the left side of the Paschen-curve at pressures below 100 Pa. The main feature of a pseudospark chamber is the combination of a hollow cathode, producing high electron currents, with an accelerator system consisting of parallel electrodes separated by insulators. The special arrangement of hollow cathode and electrodes leads to an electrical field configuration that focusses electrons in the central axis. At a given pressure dependent breakdown voltage the low pressure gas discharge escalates into a very fast sparklike discharge characterized by an overexponential current rise. The discharge leads to the formation of a pulsed high intensive electron beam in the central axis (pulse width ≈ 100 ns, ≈ 5000 A/cm^2) which can be extracted out of the chamber by a bore-hole in the anode.

We show in Fig. 1 a schematic drawing of the deposition system. The principal similarity to existing laser ablation devices is evident. At a distance of several cm from the anode the electron beam hits a rotating YBaCuO-target. The ablated material is deposited on a heated substrate positioned typically 30 - 40 mm away from the target. The electrical energy of the pseudospark chamber is stored in a variable number of solid high voltage capacitors which can supply up to 7 Joule per shot. In most cases we operated with an applied voltage of 20 kV at pulse frequencies of 1 - 2 Hz. The corresponding pressure (pure oxygen) in the deposition chamber was approximately 3 Pa. Calorimetric measurements showed that under these conditions each pulse transfers an energy of about 100 mJ to a 0.1 cm^2 spot on the target. It is interesting to note the flexibility of the operation mode. Besides a variation of the stored electrical energy, the control of the applied voltage allows to change the penetration depth of the electron beam in the target. The application of drift tubes with different bore-holes provides an easy way to keep the beam focused on its way to the target and to control its diameter.

In the experiments we generally observed deposition rates of several Å/s. The presence of small spherical particles on the substrate with dimensions up to 10 µm suggests an explosive like material removal in form of liquid droplets[9,10]. The YBaCuO-films were deposited in the usual two step procedure described in earlier publications[1]. The substrate temperature was monitored independently with a chromel / alumel thermocouple and an optical pyrometer. After the deposition of the film, the pressure in the chamber was raised to a few torr for two minutes, followed by a 10 minute anneal at 400°C in 150 torr O_2.

Fig. 2 represents a typical resistance versus temperature curve of a film grown on a (100) $SrTiO_3$ substrate. Films on $SrTiO_3$ and ZrO_2(Y) show almost identical transitions: in both cases we observe reproducibly complete superconductivity around 85 K, metallic behaviour (R(273 K) / R(100 K) ≈ 2.0 - 2.3) and resistivities of 200 µΩ × cm at 100 K. The effect of the substrate temperature during the first deposition step on T_c is depicted in Fig. 3. Complete superconductivity is only achieved at substrate temperatures above 650 °C. In the temperature range of 700°C to 800°C we obtain shiny black films exhibiting metallic behaviour and zero resistance values between 70 K and 80 K. In order to obtain higher transition temperatures, the substrate temperature has to be raised to 820°C. We attribute these rather high deposition temperatures to the very pronounced explosive material

removal. As the energy concentration in the top layers of the target is lower in comparison to laser ablation, the fraction of atomically evaporated material should be smaller. Therefore the substrate has to provide more energy in form of heat to allow the crystallization of the rather big clusters, arriving at the substrate. Fig. 3 also demonstrates the upper limit for the deposition temperature. At substrate temperatures above 850° C we observe severe substrate-film interactions starting presumably at the grain boundaries which lead to the deterioration of superconductivity.

An even simpler way to produce superconducting films is deposition in air followed by the usual intercalation step. Under these simplified conditions where no special security measures, e. g. for O_2-pumping have to be taken, we get metallic, shiny films with zero resistance values around 80 K. However, in this case reproducibility is not as good as for depositions in pure O_2 atmosphere.

One of the main advantages of pseudo spark ablation is the very good conservation of the target stochiometry. Within a large parameter range the composition of the target is well reproduced. From Rutherford backscattering (RBS) measurements we can deduce that in most cases deviations are below 10 %. Contrary to laser ablation, a variation of the energy density at the target doesn't influence the film composition, provided that the energy concentration is high enough for eruptive removal of target material. Very small energy densities resulted in very low deposition rates. Instead of crater formation we observed in this case only a visual colour change of the target spots hit by the beam. RBS measurements of these spots on the target revealed Yttrium excess. This means that Yttrium, the component with the highest melting and vaporization temperatures had been removed less effectively than the other components. Therefore fractionated material removal at low energy densities is probable. Films produced with higher energy density from such target spots showed large deviations from the nominal target stochiometry. In this case a change of the point of impact was sufficient to re-establish the correct film composition. We believe that the very good reproduction of the target composition is related to the special interaction between the pulsed electron beam and the target. The eruptive removal of molten target material takes place in form of liquid droplets, reflecting the target composition. Moreover this leads to equal spatial distributions of all target components. In fact, in the angular range of ± 30° to the target normal there was no evidence for deviations in film stochiometry. The characteristic feature of pseudospark ablation to reproduce exactly the target composition may also be of interest with regard to future applications in the ablation of more complicated compounds (e.g. high T_c Bi- or Tl- superconductors).

In addition to the RBS measurements, X-ray analysis were carried out to investigate the crystalline structure of the films. Fig 4 illustrates the results obtained in different diffraction geometries for a film grown under optimum conditions on a (100) $SrTiO_3$ substrate. In the Bragg-Brentano focussing geometry only sharp (00ℓ) - lines appear in the spectrum (Fig 4a). This indicates textured growth with the c-axis oriented normal to the substrate surface. The presence of faint peaks in the spectrum of the same film, investigated in the Seemann-Bohlin arrangement shows, however, that at least a small fraction of the film remains polycrystalline (Fig 4b). Omega scans through the (005)-line reveal a small mosaic distribution of the crystal grains of only 0.65° (Fig 4c) underlining the highly textured growth of the YBaCuO films on $SrTiO_3$. X-ray analysis of films on ZrO_2(Y) substrates yield similar results. As before, in Bragg-Brentano geometry only (00ℓ)-lines appear, whereas in the Seemann-Bohlin spectrum other lines of small intensity are present. The mosaic spread of films on ZrO_2(Y) - substrates, however, is somewhat larger than for $SrTiO_3$- substrates (1.7°).

Fig 5 illustrates the results of critical current density (J_c) measurements for a film on $SrTiO_3$ - substrate in zero magnetic field. 200 µm long and 25 µm wide bridges were obtained by Ar^{++}- irradiation of films which were covered with a special mask. The energy of the Ar^{++}-ions and the fluences were chosen such, that the irradiated part of the film was completely transferred into an isolating phase. For the determination of the critical current we made use of the 1 µV criterium. The measurements resulted in J_c- values of 6×10^6 A/cm² at 4.2 K and 1.1×10^5 A/cm² at 77 K. Higher J_c's should be attainable if we succeed to suppress the polycrystalline fractions in the films.

In summary, we propose a simple novel ablation technique that is capable of producing YBaCuO-films with good superconducting properties. The present results appear motivating enough to continue research in the field of pseudo spark ablation. Improvements should be achieved with increasing the O_2-pressure during the deposition step by differential pumping at the cathode side of the pseudospark chamber. There also exists the possibility of a plasma assisted deposition processus. Because of the 5 to 10 times lower capital investment required for setting up a pseudospark ablation device, pseudospark ablation offers already at the present level of development an interesting alternative to existing laser ablation devices.

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FIGURE CAPTIONS

Figure 1: Schematic representation of the pseudospark ablation device.

Figure 2: Resistance versus temperature curve of an YBaCuO film deposited on (100) $SrTiO_3$ - substrate by pseudospark ablation.

Figure 3: Transition temperatures as a function of the deposition temperature. All films were deposited on ZrO_2 (Y) - substrates.

Figure 4: X-ray diffraction spectra of a film grown on (100) $SrTiO_3$- substrate.
a) Bragg-Brentano geometry : only (00ℓ)- lines appear in the spectrum
b) Seemann-Bohlin geometry: several peaks of low intensity are present indicating that a fraction of the film remains polycrystalline.
c) Omega-scan through the (005) - planes of the film. The full width at half maximum $|\Delta\Psi|$ of the rocking curve gives the mosaic spread of the crystal grains and is therefore a criterion for the degree of texture.

Figure 5 : J_c- values in zero magnetic field versus temperature for a film deposited on (100) $SrTiO_3$

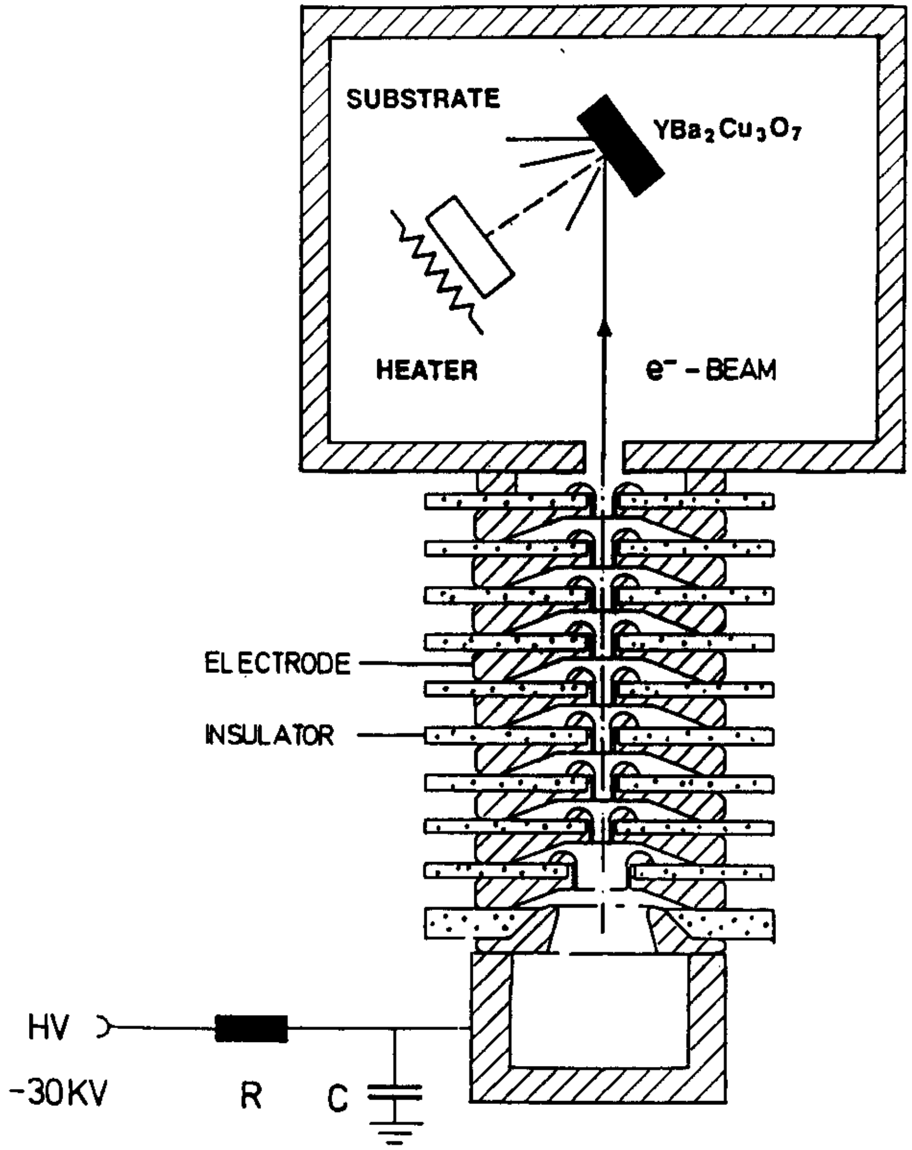

SUBSTRATE
$YBa_2Cu_3O_7$
HEATER
e⁻ - BEAM
ELECTRODE
INSULATOR
HV
-30KV
R
C

Fig 1

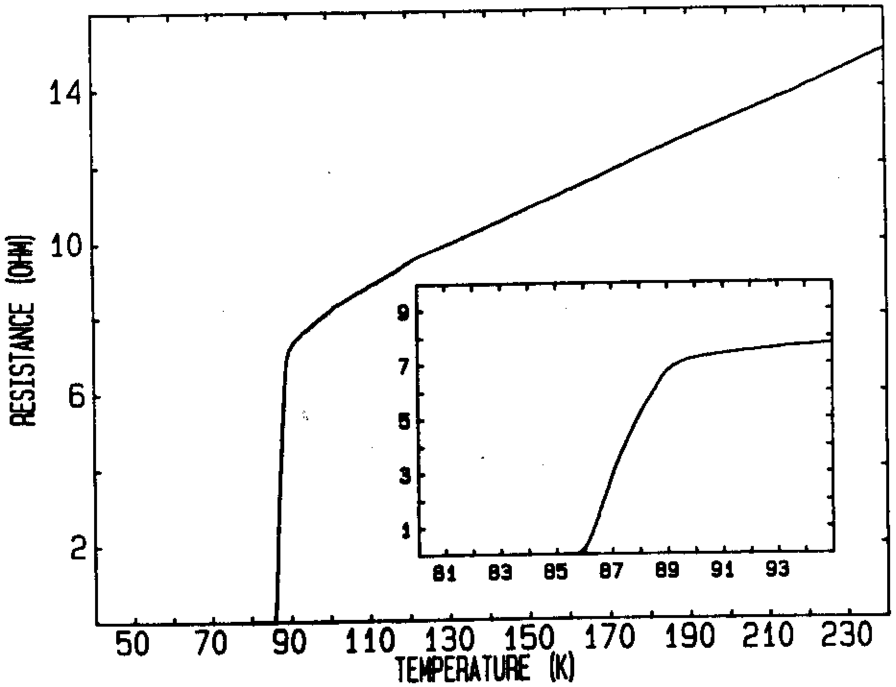
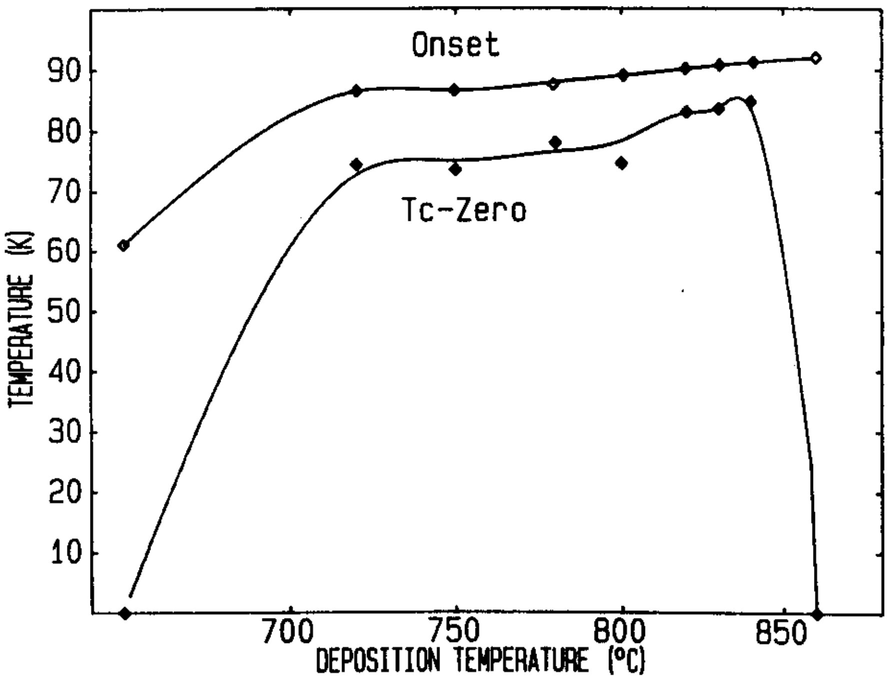
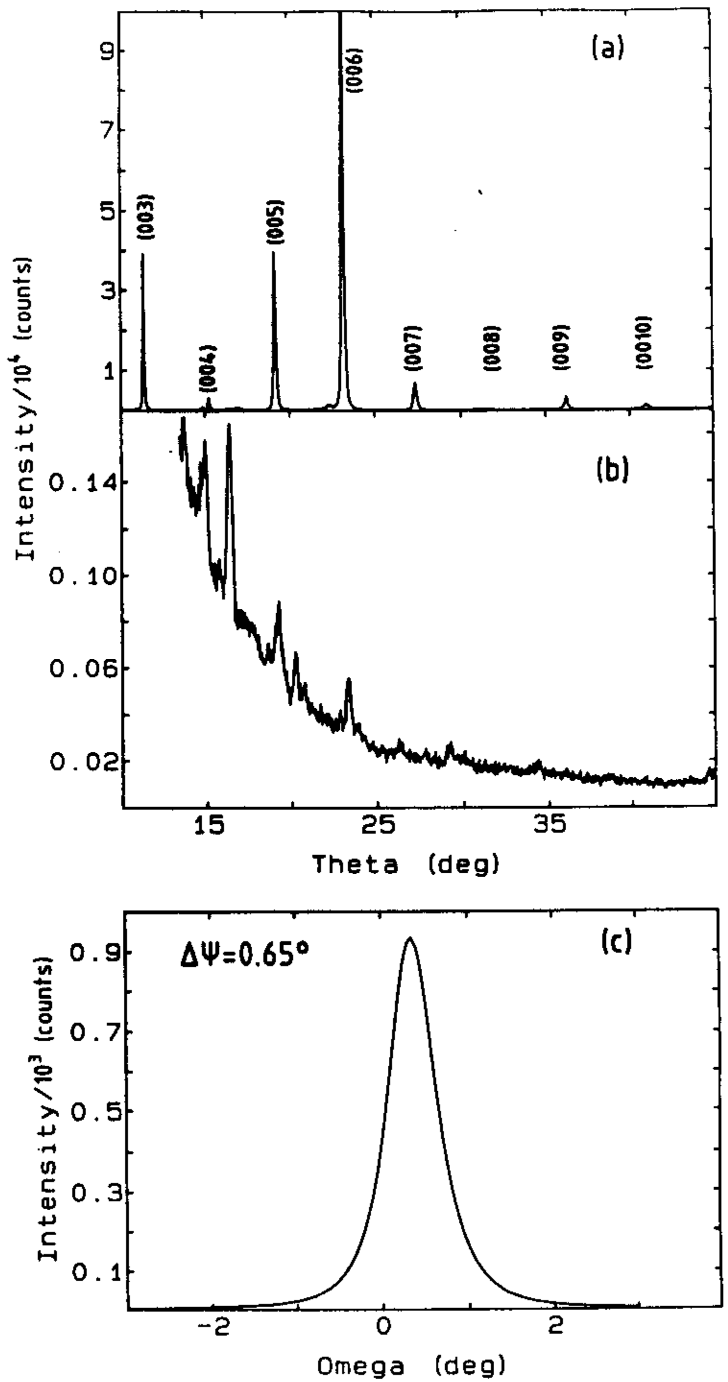

RESISTANCE (OHM)
14
10
6
2
50 70 90 110 130 150 170 190 210 230
TEMPERATURE (K)
9
7
5
3
1
81 83 85 87 89 91 93

Fig.



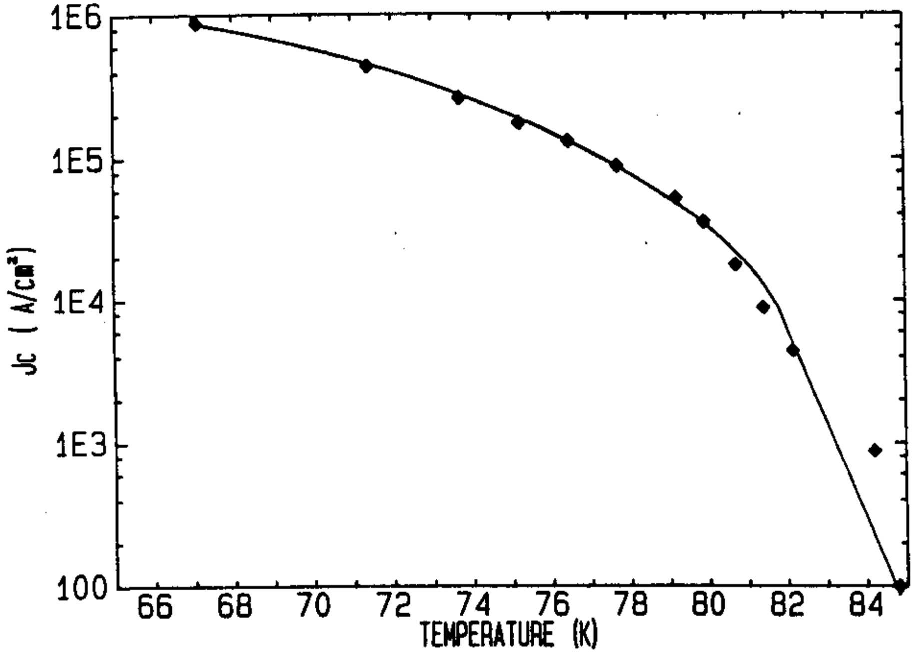
Onset
Tc-Zero
TEMPERATURE (K)
90
80
70
60
50
40
30
20
10
700
750
800
850
DEPOSITION TEMPERATURE (°C)

Fig. 3



(a)
(b)
(c)
Intensity/10⁴ (counts)
(003)
(004)
(005)
(006)
(007)
(008)
(009)
(0010)
9
7
5
3
1
0.14
0.10
0.06
0.02
15
25
35
Theta (deg)
ΔΨ=0.65°
Intensity/10³ (counts)
0.9
0.7
0.5
0.3
0.1
-2
0
2
Omega (deg)

Fig. 4



1E6
1E5
1E4
1E3
100
Jc (A/cm²)
66
68
70
72
74
76
78
80
82
84
TEMPERATURE (K)

Fig 5