Preparation of Y–Ba–Cu–O thin films by laser evaporation with near-infrared radiation

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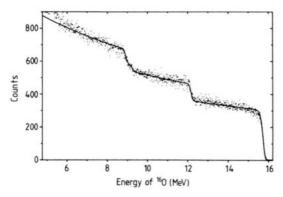‡ Physikalisches Institut der Universität Erlangen-Nürnberg, 8520 Erlangen, FRG

Abstract. We report preparation of Y–Ba–Cu–O thin films by laser evaporation with near-infrared radiation. Pulsed radiation of a Nd–YAG laser (wavelength 1.06 μm) was used for evaporation of material from the surface of a $YBa_2Cu_3O_7$ ceramic sample. Thin films, deposited on Al_2O_3 single-crystal substrates, became conductive after a heat treatment in oxygen atmosphere. One of our films, with a room-temperature resistivity of 1 mΩ cm, showed onset of superconductivity at 100 K and had T_c values of 94–76 K (90%–10%) for the resistive transition. The films were characterised by RBS analysis, SEM and x-ray diffraction.

Thin films of high-T_c superconductors have been prepared by various techniques. Superconducting Y–Ba–Cu–O films with onset of superconductivity at 105 K and zero resistance at 90.2 K were obtained, by Chaudhari et al [1], by electron beam evaporation from Y, Ba and Cu metallic sources on $SrTiO_3$ substrates; these films had critical current densities of 10^6 A cm^{-2} at 4.2 K [1]. Similar values for the critical current and T_c values of 93–90 K (90%–10%) for the resistive transition have been found by Oh et al [2], also using an electron beam evaporation technique. Multilayer deposition techniques [3, 4], various sputtering methods [5–7], and molecular beam epitaxy [8] have meanwhile been applied for preparation of thin films of high-T_c superconductors on a number of different substrates. In a laser evaporation experiment [9], Y–Ba–Cu–O thin films have been prepared by pulsed excimer laser evaporation from a bulk target, making use of the high absorptivity of $YBa_2Cu_3O_7$ for UV radiation. Onset of superconductivity at 95 K and zero resistance at 75 K for a thin film on a sapphire substrate (and 85 K for a film on a $SrTiO_3$ substrate) were reported [9]. Recently, films have also been produced by TEA CO_2 laser evaporation using $SrTiO_3$ substrates [10]. Zero resistance at 86 K was reported. In another laser evaporation experiment radiation of a pulsed YAG laser (wavelength 1.06 μm, pulse duration 0.1 ms) was used for preparation of films on MgO- and ZrO_2-coated sapphire substrates [11]. An onset at 90 K and a midpoint temperature of 60 K were obtained. The resistivity curves show values of 78 K and 33 K (90%–10%) for the resistive transition; zero resistance is not

reached for $T > 20$ K. In this paper we report preparation of Y–Ba–Cu–O films on sapphire substrates using a pulsed Q-switched YAG laser. After annealing, our best film showed T_c values of 94 K and 76 K (90%–10%) for the resistive transition. By measurement with increased sensitivity we found that the resistance was near zero (10^{-2} of the resistance at 100 K) at 60 K and no more measurable ($<10^{-4}$ of the resistance at 100 K) for $T < 50$ K. Our films were, in addition to the resistivity measurements, characterised by RBS analysis, SEM and x-ray diffraction.

Substrate and target were mounted in a vacuum chamber with a pressure of 5×10^{-6} Torr; during evaporation the pressure increased to 2×10^{-5} Torr. As substrates we used optically polished sapphire single-crystal plates (diameter 15 mm) heated to a temperature of typically 450 °C. The target consisting of a ceramic $YBa_2Cu_3O_7$ pellet (diameter 13 mm), mounted under an angle of 45° with respect to the substrate, was rotated during the evaporation process to obtain uniform abrasion; the distance between the centre of the target and the substrate was 2 cm. The beam of a Nd:YAG laser (wavelength 1.06 μm, pulse duration 50 ns, maximum pulse energy 0.4 J) was focused through an optical window of the vacuum chamber on the target at an angle of incidence of 45°. The energy density on the target was about 10 J cm^{-2}. The heated spot, near the centre of the rotating target, had a diameter of 2 mm. From the focus region intense light emission was observed with each laser shot. With each shot about 10 nm of target material was removed. For a typical evaporation procedure the laser was run for

Figure 1. RBS analysis of a film grown at 450 °C on sapphire (points). The full curve is a simulation of a 3 μm thick film with composition $Y_{1.3}Ba_{1.8}Cu_3$.

Figure 3. Micrographs of a Y–Ba–Cu–O film, laser evaporated on an Al_2O_3 substrate.

half an hour at a repetition rate of 3 Hz. Then, the sapphire substrate was covered with a black, homogeneous film that had a thickness of the order of 1 μm. The film had a very good mechanical contact and could not easily be removed. After evaporation the film composition was examined by RBS analysis with a 25 MeV ^{16}O beam. In figure 1 an RBS spectrum is shown, together with a simulated spectrum for a film of $Y_{1.3}Ba_{1.8}Cu_3$ composition and of 3 μm thickness. The analysis shows that the composition of the films produced with the YAG laser from targets of 1, 2, 3 stoichiometry was Y-rich and Ba-deficient; by modifying the target composition [10, 11] we should be able to use our technique to produce films with the 1, 2, 3 stoichiometry.

After laser evaporation films did not show conductivity; the resistance was larger than 20 MΩ over a distance of 1 mm between silver contact points. Conductivity was observed after annealing in oxygen atmosphere. The superconducting properties depended critically on the annealing procedure. Our best film had been heated up quickly to a maximum annealing temperature of 900 °C and then cooled down in oxygen atmosphere with a rate of 5 °C per minute. The crystalline quality of the film was examined by x-ray diffraction (Cu Kα source). Essentially all peaks of the orthorhombic phase are obtained (figure 2) comparable to the x-ray pattern of polycrystalline $Y_1Ba_2Cu_3O_7$ [12]. Our film consists mainly of the desired superconducting phase. The film shows strong intensity of the 110 peak which is characteristic for
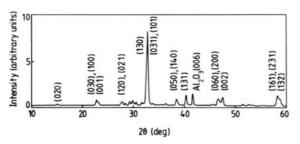
films with low room-temperature resistivity annealed at 900 K [13].

For additional characterisation of the film we have made scanning electron micrographs (figure 3). The pictures show that the film had a grain structure with voids of typical diameter of a few μm. The formation of voids seems to be enhanced by a tendency to columnar growth indicated in figure 3; columnar growth was also reported recently for Y–Ba–Cu–O films on ZrO_2 substrate [3].

The resistance was measured with a four-point technique, contacts being made with silver epoxy paint. The distance between contacts for voltage measurement was 1 cm and the width of the film also about 1 cm; the contact resistance was about 1 Ω. The experimental resistivity curve for the film is shown in figure 4 (full curve). The resistivity increased from about 1 mΩ cm at room temperature to 1.3 mΩ cm at 100 K and decreased strongly at lower temperatures and became small (10^{-2} of the resistivity at 100 K) at 60 K
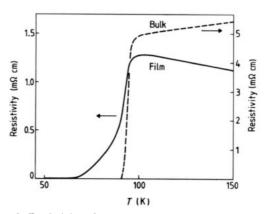

Figure 2. X-ray diffraction pattern of an annealed film.

Figure 4. Resistivity of a laser-evaporated Y–Ba–Cu–O thin film and of the bulk (sintered) target material.
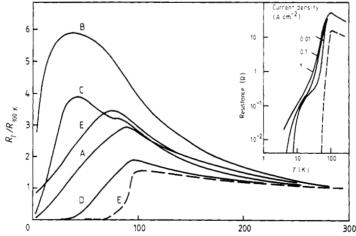
Table 1. Film preparation and properties.

Sample	Substrate orientation	Substrate temperature (°C)	Cooling rate (°C min⁻¹)	Maximum annealing temperature (°C)	Resistivity at 300 K (mΩ cm)	T_c (90%–10%) (K)
A	a	400	2	900	3	74–10
B	a	400	0.8	900	8	15
C	c	400	2.7	930	6	29–5
D	c	450	2.5	900	3	87–45
E	c	450	5	900	1	94–76
F	c	450	1.2	900	7	58

and almost zero ($<10^{-4}$ of the resistivity at 100 K) at 50 K. The film had an onset of superconductivity at 100 K and T_c values of 94–76 K (90%–10%), i.e. the transition width was 18 K. For comparison we have also shown (figure 4) the resistivity of the target sample (broken curve), with an onset of superconductivity at 100 K and a transition width of 3 K. As a result, we find that the resistivity of the film showed the main features of the bulk material, but with a resistance tail towards smaller temperatures. By a far-infrared reflection experiment we found that the film contained both superconducting $YBa_2Cu_3O_7$ and non-conducting Y_2BaCuO_5 in the ratio of about 4:1 [14]; this is consistent with the result of the RBS analysis. We suggest therefore that the tail of the resistivity curve was due to the stoichiometry.

We have also studied resistivities of films obtained by slightly different preparation procedures. Details on film preparation and film properties are summarised in table 1. We have varied substrate temperature, annealing procedure, and have used two different crystal orientations (with a or c axis perpendicular to the substrate surfaces). A change of substrate temperature by 50 °C (from 400 °C to 450 °C) did not lead to a measur-

able change of the stoichiometry. The annealing procedure of our best film (E on figure 5) is characterised by a relatively short annealing time at high temperatures corresponding to a fast cooling rate (table 1). Slow cooling rates resulted in films of worse quality in that these films had a larger room-temperature resistivity and the onset of superconductivity occurred at lower temperatures. Thus, a short annealing time at high temperature was essential for films of reasonable quality. Film degradation for long annealing times at high temperatures can most likely be attributed to diffusion of aluminium atoms from the substrate into the films, as is also known from other studies [3]. While the resistance of our best film (E) increased only slightly with decreasing temperature, the resistances of the other films increased strongly (figure 5). These films showed, as already mentioned, smaller onset temperatures for superconductivity and some of them remained normally conducting down to low temperatures (figure 5).

The resistances for the low-quality films depended strongly on the curent densities in the films, as shown in the inset of figure 5 for one of our films (D). This behaviour may be due to low critical current regions

Figure 5. Resistances of Y–Ba–Cu–O films prepared under different preparation conditions (R_T = resistance at temperature T, measured with a current density of 10^{-2} A cm⁻²); inset, dependence of the resistance on the current density for film D (full curves) and resistance of our best film (broken curve).

at grain boundaries. The resistance of our best film, (E, broken curve in the inset of figure 5) was independent of current density for the densities (up to $1\,A\,cm^{-2}$) applied in our experiment. We have not measured the critical current for this film; because the film was composed of a phase mixture no large critical current was expected. Compared with a recent experiment with YAG laser evaporation [11] we obtained improved film quality. We attribute the improvement to both substrate heating and use of shorter pulses (of 50 ns duration instead of 0.1 ms). The stoichiometry of the films was different (1.3:1.8:3 instead of 1.6:2.7:3 in [11]). In a recent study [15] of evaporation with YAG laser radiation (pulse duration 15 ns and 150 ns) films with stoichiometric composition were obtained by evaporation from a $YBa_2Cu_3O_7$ target. For films on sapphire substrates, T_c was below 50 K. The reason for the different result with respect to film stoichiometry is not clear. We note that a comparison with UV laser evaporated films (on sapphire substrates) shows that evaporation with a pulsed YAG laser leads to films of similar quality. Thus, evaporation with near-infrared radiation may have no advantage over UV laser evaporation.

In summary, we have demonstrated that by laser evaporation with a pulsed Q-switched YAG laser superconducting Y–Ba–Cu–O films can be produced; films with a resistive transition comparable to UV laser-produced films (on sapphire substrates) can be obtained. We found that films evaporated from a stoichiometric sample are slightly Y-rich and Ba-deficient. Further studies are necessary for optimisation of the evaporation and annealing procedures.

Acknowledgment

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