

*Rapid Communication*

## Preparation of Tl-Ba-Ca-Cu-O Thin Films by Diffusion of Tl into Laser Evaporated $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ Films

H. Lengfellner, J. Betz, and K. F. Renk

Fakultät Physik, Universität, D-8400 Regensburg, Fed. Rep. Germany

Received 9 March 1989/Accepted 20 March 1989

**Abstract.** Preparation of superconducting Tl-Ba-Ca-Cu-O thin films by diffusion of Tl into laser evaporated  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  thin films is reported. From a sintered  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  bulk sample we prepared using a pulsed Nd:YAG laser, Ba-Ca-Cu-O thin films on sapphire and  $\text{SrTiO}_3$  single-crystal substrates. Subsequently the films were loaded with Tl by simultaneously annealing the films together with a sintered  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  sample both enclosed in a small stainless steel box; in our procedure Tl contamination was reduced to a minimum.  $T_c$  values near 100 K and critical currents of  $5 \cdot 10^3 \text{ A/cm}^2$  at 77 K were obtained.

PACS: 74.70, 74.75

After the discovery of superconductivity in Tl-Ba-Ca-Cu-O compounds [1], thin films of this material have been obtained by electron beam evaporation [2] and sputtering techniques [3-5]; critical currents of  $10^4$ - $10^5 \text{ A/cm}^2$  at 77 K have been reported [2-5]. Tl-Ba-Ca-Cu-O films have also been prepared by rf sputtering of a Ba-Ca-Cu-O film and a subsequent heat treatment for diffusion of Tl into the film [6]. As a Tl source a piece of metallic Tl was used, and zero resistance was reached at about 75 K [6]. We have developed a similar film preparation method, using, however, a laser evaporation technique and a modified Tl diffusion procedure. We obtained films with a superconducting transition temperature near 100 K and critical currents of about  $5 \cdot 10^3 \text{ A/cm}^2$  at 77 K.

For the preparation of Tl-Ba-Ca-Cu-O thin films used was made of a standard sintered  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  sample and a sintered  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  sample. The (nonmetallic)  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  sample was prepared by using and grinding appropriate amounts of  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and CuO, pressing to a pellet (with  $2 \text{ tons/cm}^2$ ) and sintering at  $900^\circ\text{C}$  for 10 h in oxygen atmo-

sphere. From this pellet, a thin film was laser evaporated onto sapphire and  $\text{SrTiO}_2$  single crystal substrates (heated to  $400^\circ\text{C}$ ). The substrate was located in the evaporation cone at a distance of about 2 cm from the pellet. The slightly focused beam (diameter:  $\approx 2\text{mm}$ ) of a pulsed Nd:YAG laser (pulse duration: 50ns, pulse energy: 200mJ) was directed onto the slowly rotating target pellet mounted in a vacuum system ( $5 \cdot 10^{-5}$  Torr during evaporation). Material from the target evaporated perpendicular to the target surface. Our arrangement is described in more detail elsewhere [7]. In the next preparation step the film and a  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  bulk sample were placed in a small stainless steel box ( $3 \times 2 \times 2 \text{ cm}^3$ ); a stainless steel ring (diameter: 10mm, thickness: 1mm) served as a spacer between film and bulk sample. The (closed) box was put into a preheated tube furnace (at  $880^\circ\text{C}$ ) for 5 min and then taken out and quickly cooled to room temperature. Our film had a diameter of about 6 mm and a thickness of about  $1 \mu\text{m}$  (after 5000 laser shots). We note here that we also tried the Tl-loading step with a small amount of  $\text{Tl}_2\text{O}_3$  powder instead of the  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  bulk

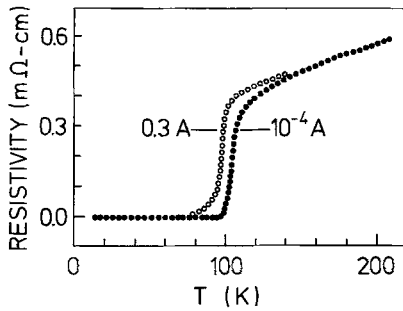


Fig.1. Resistivity versus temperature for a Tl-Ba-Ca-Cu-O film on SrTiO<sub>3</sub>, for currents of 10<sup>-4</sup> A and 0.3 A, respectively

sample, but did not succeed in obtaining superconducting films.

Conductivity and critical current measurements were performed by a standard four-point technique; contacts were made with silver epoxy paint. The resistivity at room temperature was about 0.7 mΩ-cm for a film on a (100) SrTiO<sub>3</sub> substrate. The resistivity decreased almost linearly between 300 and 150 K, a deviation from this behavior was observed below 140 K (Fig.1). We obtained  $T_c$  values of 100-117 K (10-90%) for the resistive transition, with  $T_c^{R=0}$  at 96 K. Similar results with respect to resistivity values have been obtained for a film on a sapphire substrate;  $T_c^{R=0}$  was 93 K for this film.

The resistivities were measured with small currents (10<sup>-4</sup> A). For a measurement of the critical current, we increased the current through the film. In Fig.1, the slope of the resistivity obtained with a current of 0.3 A (dotted line) is

also shown. The film showed non-zero resistance for temperatures above 77 K. We increased the current, with the film immersed in liquid helium, up to 0.5 A. At a higher current the film was destroyed, probably due to incomplete cooling of the contact regions. From these observations we obtained lower limits for the critical currents of about 5·10<sup>3</sup> A/cm<sup>2</sup> at 77 K and of 10<sup>4</sup> A/cm<sup>2</sup> at 4.2 K.

In conclusion, we have shown that Tl-Ba-Ca-Cu-O films with high values for  $T_c$  and for the critical current can be produced using a laser evaporation technique for the production of a Tl-free Ba-Ca-Cu-O film and a subsequent Tl diffusion step to load the film with Tl. The use of Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> bulk samples as a Tl source in an enclosed environment seems to be important for the diffusion procedure.

#### References

1. Z.Z. Sheng, A.M. Hermann: Nature 332, 138 (1988)
2. D.S. Ginley, J.F. Kwak, R.P. Hellmer, R.J. Baughman, E.L. Venturini, B. Morosin: Appl. Phys. Lett. 53, 406 (1988)
3. Y. Ichikawa, H. Adachi, K. Setsune, S. Hatta, K. Hirochi, K. Wasa: Appl. Phys. Lett. 53, 919 (1988)
4. M. Hong, S.H. Liou, D.D. Bacon, G.S. Grader, J. Kwo, A.R. Kortan, B.A. Davidson: Appl. Phys. Lett. 53, 2102 (1988)
5. W.Y. Lee, V.Y. Lee, J. Salem, T.C. Huang, R. Savoy, D.C. Bullock, S.S.P. Parkin: Appl. Phys. Lett. 53, 329 (1988)
6. C.X. Qiu, I. Shih: Appl. Phys. Lett. 53, 1122 (1988)
7. H. Lengfellner, K.F. Renk, P. Fickenscher, W. Schindler: J. Phys. D 22, 323 (1989)