Physica C 162–164 (1989) 133–134
North-Holland

# SUPERCONDUCTING *Tl-Ca-Ba-Cu-O* THIN FILMS PREPARED BY DIFFUSION OF *Tl* INTO AN EXCIMER LASER ABLATED $Ca_2Ba_2Cu_3O_x$ FILM

J. BETZ, H. LENGFELLNER, E. DUSCHL, K. MEIDENBAUER and K.F. RENK

Institut für Angewandte Physik, Universität Regensburg, 8400 Regensburg, W.Germany

By laser ablation with an excimer laser (308 nm) cuprate films from a $Ca_2Ba_2Cu_3O_x$ sintered bulk target were deposited onto $SrTiO_3$ (100) single crystal substrates. Thallium was added by a diffusion process by simultaneously annealing of the cuprate films together with a sintered $Tl_2Ca_2Ba_2Cu_3O_{10}$ bulk sample both enclosed in a covered metal box; this film production method allowed to reduce the contamination by thallium. Scanning electron micrographs of the film surface show crystalline structures, i.e. a network of needle shaped crystallites laying in the film plane. For comparison, Nd:YAG laser produced films show rough surfaces consisting of clusters of grains.

Thin films of Tl-Ca-Ba-Cu-O compounds have been produced by several groups using electron beam evaporation [1] and sputtering techniques [2-4]. The use of thallium leads, however, to contamination of the film deposition system. This has been partially avoided by a film preparation procedure [5]: First, a Ca-Ba-Cu-O film was prepared by sputtering, then, by a heat treatment, thallium was diffused into the film from a metallic piece of thallium. Films with $T_c^{R=0}$ values of 75 K were obtained by this technique [5]. We have recently developed a technique [6] where thallium was brought into the film by a diffusion technique, too; a Nd:YAG laser was used for preparation of the Ca-Ba-Cu-O film. In the work described here we have used an excimer laser, thus reaching a largely improved film quality.

The film deposition system [7] consisted of a vacuum chamber with a base pressure of $5 \times 10^{-6}$ Torr. The excimer laser beam (308 nm, pulse duration 40 ns, pulse energy 450 mJ) was directed by a quartz optic into the vacuum chamber and focused onto a rotating $Ca_2Ba_2Cu_3O_x$ sintered bulk target. The energy density on the target was about 10 J/cm$^2$. The $SrTiO_3$ (100) single crystal substrates were heated to 400°C during the deposition procedure. To obtain structurized films a mask could be aligned in front of the substrate. Bridge-like structures could be easily obtained and were used for bolometric applications in optical response measurements.

In the next preparation step the film was loaded with thallium by a diffusion procedure: A standard $Tl_2Ca_2Ba_2Cu_3O_{10}$ bulk sample was placed upon the film, a stainless steel ring was used as a spacer between film and bulk sample. The whole arrangement was placed into a small covered stainless steel box, and was heated for about 5 min in a preheated furnace to 880°C, then taken off and cooled to room temperature.

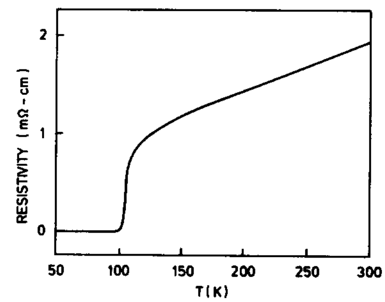


FIGURE 1
Resistivity of a 0.5 $\mu m$ thick Tl-Ca-Ba-Cu-O film on $SrTiO_3$.

For resistivity measurements a standard four point technique was used, contacts were made with silver epoxy paint. An experimental resistivity curve is shown in Fig. 1. We find $T_c$ values for the resistive transition of 100 K – 115 K (10% - 90%) and $T_c^{R=0} \sim 98$ K. Towards high temperatures the resistivity increases almost linearly. The slope of the resistivity including the $T_c$ values is very similar to films produced by the Nd:YAG laser ablation technique [6].

0921–4534/89/$03.50 © Elsevier Science Publishers B.V.
(North-Holland)

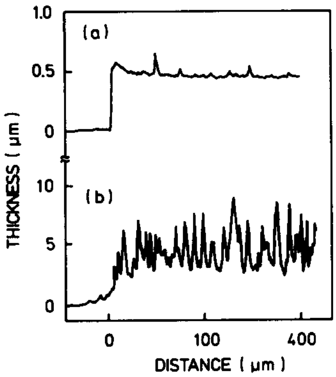


FIGURE 2
Surface profile scans of films produced by excimer (a) and Nd:YAG (b) laser ablation.

To compare the surface quality of Nd:YAG- and excimer laser produced films we made surface profile scans with a stylus equipment ($\alpha$-step). Fig. 2a shows a profile scan over the edge of a bridge-like structure of a film obtained by excimer laser ablation. After the steep increase in thickness to about 500 nm, the thickness remains quite constant; only a few structures are seen within a distance of 400 $\mu m$ from the edge. The film has a grey-metallic colour and shows a weak metallic reflection. In contrast, Nd:YAG laser produced films (Fig. 2b) are very rough and look dark black.

A further comparison is made by scanning electron micrographs. Fig. 3a shows a surface region of the excimer laser produced film. The surface is covered with a network of needle-shaped crystallites. This may indicate a certain loss of $Tl$ or $Ba$, whereas a closer achievement of the 2223 compound should result in a more terrace-like surface structure [4]. The surface of the Nd:YAG laser produced film (Fig. 3b) consists of an irregular arrangement of grains with different sizes. Similar observations were also made for surfaces of films of the Y-Ba-Cu-O compound obtained by Nd:YAG laser ablation [7,8].

An Auger electron spectroscopy depth profile for the excimer laser ablated film indicated that the $Tl$ concentration was largest at the free film surface and decreased to half the surface value within a surface layer of 50 nm. In the inner part of the film the $Tl$ concentration was almost constant. This gives evidence for sufficient $Tl$ diffusion.

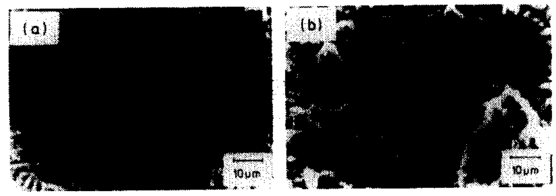


FIGURE 3
Scanning electron micrographs of films produced by excimer (a) and Nd:YAG (b) laser ablation.

In conclusion we have demonstrated that Tl-Ca-Ba-Cu-O films with $T_c^{R=0}$ values near 100 K can be produced by a combination of a laser evaporation procedure to obtain a thallium free Ca-Ba-Cu-O film and a diffusion technique to enrich the film with thallium. The surface quality of the film is strongly dependent on the wavelength of the laser radiation used for the ablation procedure; dependence of film properties on laser wavelength is well known for laser ablated $YBa_2Cu_3O_{7-\delta}$ films. Rough films made up of clusters of grains are obtained using 1.06 $\mu m$ radiation, smooth surfaces with a network of needle shaped crystallites are obtained using 308 nm radiation of an excimer laser.

[1] D.S. Ginley, J.F. Kwak, R.P. Hellmer, R.J. Baughman, E.L. Venturini and B. Morosin, Appl. Phys. Lett. 53 (1988) 406.
[2] Y. Ichikawa, H. Adachi, K. Setsune, S. Hatta, K. Hirochi and K. Wasa, Appl. Phys. Lett. 53 (1988) 919.
[3] M. Hong, S.H. Liou, D.D. Bacon, G.S. Grader, J. Kwo, A.R. Kortan and B.A. Davidson, Appl. Phys. Lett. 53 (1988) 2102.
[4] W.Y. Lee, V.Y. Lee, J. Salem, T.C. Huang, R. Savoy, D.C. Bullock and S.S.P. Parkin, Appl. Phys. Lett. 53 (1988) 329.
[5] C.X. Qiu and I. Shih: Appl. Phys. Lett. 53 (1988) 1122.
[6] H. Lengfellner, J. Betz and K.F. Renk, Appl. Phys. A 48 (1989) 501.
[7] H. Lengfellner, K.F. Renk, P. Fickenscher and W. Schindler, J. Phys. D: Appl. Phys. 22 (1989) 323.
[8] L. Lynds, B.R. Weinberger, G.G. Peterson and H.A. Krasinski, Appl. Phys. Lett. 52 (1988) 320.