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Preparation of $Tl_2Ca_2Ba_2Cu_3O_x$ Superconducting Thin Films by DC Sputtering

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Thin films of the Tl-Ca-Ba-Cu-O system were prepared by a single-target dc sputtering system on YSZ substrates with postannealing. The effects of various annealing conditions on the films were studied. It was found that under suitable conditions, the $Tl_2Ca_2Ba_2Cu_3O_x$ thin films with a zero-resistance temperature of up to 97 K could be formed by sputtering from a target of the same composition. The X-ray diffraction patterns showed that the annealed films were preferentially *c*-axis oriented perpendicular to the substrates. It was also found that the films were highly resistant to *n*-butyl acetate, acetone and water.

KEYWORDS: superconductivity, high- T_c superconductor, $Tl_2Ca_2Ba_2Cu_3O_x$, thin film, dc sputtering

Since the discoveries of the rare-earth-free high- T_c superconductors of Bi-Ca-Sr-Cu-O¹⁾ and Tl-Ca-Ba-Cu-O²⁾ systems, a considerable amount of research has been carried out on these materials owing to their higher transition temperatures than those of the 1-2-3 rare-earth-based superconductors. Two superconducting phases with different T_c 's have been identified in both of these systems.³⁻⁶⁾ For the Tl-Ca-Ba-Cu-O compounds, the lower T_c phase is characterized by the 2-1-2-2 ratio and the higher T_c phase by 2-2-2-3 ratio. It is also reported that starting metal cation compositions of $TlCa_3BaCu_3$ and $Tl_2Ca_2Ba_2Cu_3$ gave rise to the largest percentages of the $Tl_2Ca_2Ba_2Cu_3O_x$ (2-2-2-3 phase) and $Tl_2CaBa_2Cu_2O_x$ (2-1-2-2 phase), respectively.³⁾ This characteristic has increased the difficulty of predicting the properties of the Tl-Ca-Ba-Cu-O thin films after postannealing. Recently, thin films of Tl-Ca-Ba-Cu-O superconductors showing a zero-resistance temperature, T_{co} , at ~ 100 K have been prepared by electron beam evaporation^{7,8)} and rf (magnetron) sputtering.^{9,10)} In this letter, we describe the synthesis of Tl-Ca-Ba-Cu-O thin films with a T_{co} up to 97 K by using a single-target dc sputtering system.

The sputtering system used here is a simple single-target system made by our group. The target diameter is one inch and the distance between the target and substrate is 5-8 mm. To prepare the target material, first we mixed an appropriate amount of $CaCO_3$ (99.98%), $BaCO_3$ (99.999%) and CuO (99.999%) powders in a molar ratio of 2:2:3, then calcined the mixture at 900°C in flowing oxygen for 16 h with several intermediate grindings. After the calcination, the mixture of Tl_2O_3 (99.5%) powders and the $Ca_2Ba_2Cu_3O_x$ compound obtained above with a nominal composition of $Tl_2Ca_2Ba_2Cu_3O_x$ was pressed into pellets, wrapped in gold foil, fired at 880°C for 12 min in flowing oxygen and then air quenched to room temperature to take precautions against loss of Tl. The sputtering was carried out in

an Ar/ O_2 mixture containing 10-20% O_2 at a pressure of ~ 300 mTorr. Films of 1.2 μm thickness were deposited at a typical deposition rate of 16 nm/min using a total dc input power of ~ 40 W. The film which was coated with the substrate heated to 350-650°C during sputtering gave a semiconductorlike behavior before and after postannealing, thus the films mentioned in the rest of this letter were all deposited without intentional heating. The final substrate temperature increased by the glow discharge was about 130°C. The substrate used was (100) yttrium-stabilized ZrO_2 (YSZ). The as-deposited films had smooth mirrorlike surfaces and all were nonconductive. A postannealing process was necessary to elicit the superconductivity. In such heat treatment experiments, the furnace temperature was raised to a temperature ranging from 870°C to 910°C and the oxygen was allowed to flow (200 ml/min). The deposited films which were wrapped in gold foil together with 0.2 g fragments of the target material were then pushed to the central zone of the furnace (1.5 cm from the head of the thermocouple) and kept there for 1-6 min. After the high-temperature treatment, the samples were furnace-cooled. The temperature decreased to ~ 600 °C within the first 30 min.

The electrical resistivity measurements were performed by a standard four-probe method with the constant current of 100 μA . Electrical contacts to the films were made with conductive silver paint. Details of the annealing schemes attempted, along the measured T_c 's, are listed in Table I; the annealing times shown in the table were estimated based on previous experiments. We assumed that the annealing temperature was the dominant factor of the structure of the film. In order to prevent an excess loss of Tl, the annealing times were decreased with higher temperatures. The T_{co} 's were promoted with the increasing annealing temperatures which varied in the range 870-900°C. Further heating at 910°C resulted in a superconducting transition with T_c (midpoint) close to that of the sample D in Table I, and with a lower T_{co} (see

Fig. 1). Figures 2(a) to 2(e) show the scanning electron micrographs taken from the five samples A-E, respectively. We can observe that as the postannealing temperatures were increased, the grains grew and contacts between them were apparently improved. However, heating to 910°C caused the film surface to melt and crystallize. The fine grains of 1–2 μm in diameter were grown with their c -axis oriented perpendicular to the substrate on a large area of sample D. We repeated the heat treatment at 900°C \times 3 min on many sputtered films, and the same T_c 's (midpoint) were always reproduced. The best T_{co} obtained was 97 K.

X-ray diffraction patterns obtained with Cu $K\alpha$ radiation of samples A–E in Table I are shown in Fig. 3. The diffraction peaks shown are dominated by a set of regularly spaced (00 n) reflections, which indicate that the films have a tendency for the c -axis to orient normal

Table I. Conditions of tested samples.

Sample No.	Annealing Condition	T_c (midpoint)	T_{co}
A	870°C \times 6 min	96 K	73 K
B	880°C \times 6 min	102 K	81 K
C	890°C \times 3 min	106 K	90 K
D	900°C \times 3 min	110 K	95 K
E	910°C \times 1 min	110 K	94 K

to the substrates. Postannealing at 870°C yielded mainly the 2-1-2-2 phase, and at 880–890°C allowed the formation of the 2-2-2-3 phase as well as the 2-1-2-2 phase.

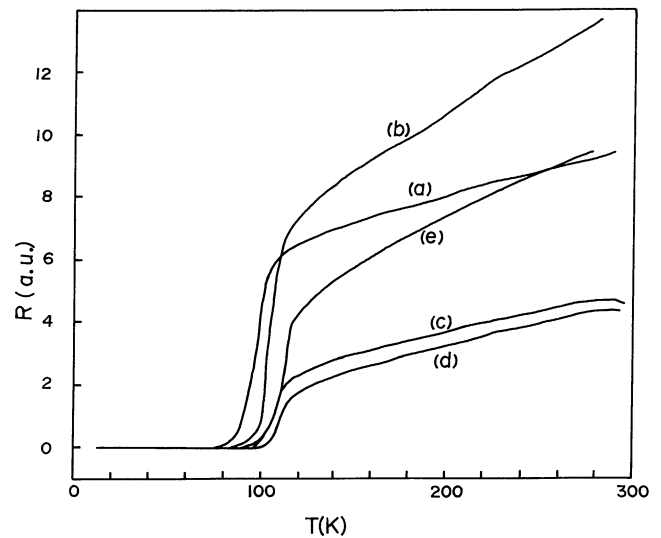
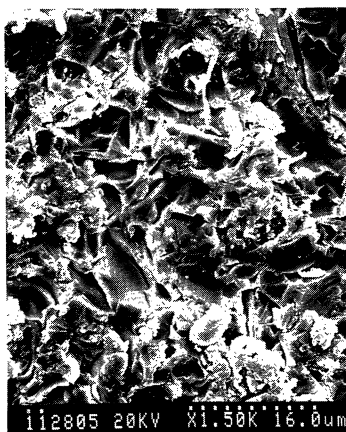
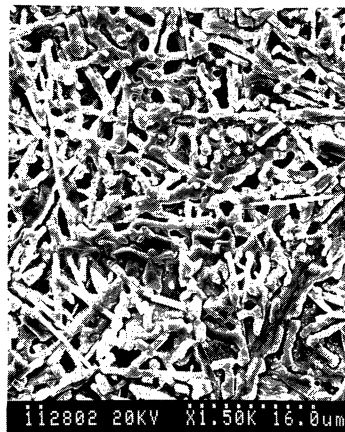


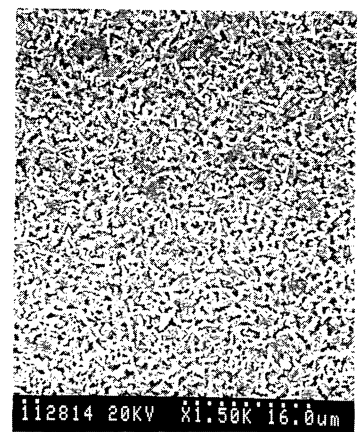
Fig. 1. Temperature-dependent resistivity of Tl-Ca-Ba-Cu-O thin films for annealing conditions of (a) sample A, 870°C \times 6 min (b) sample B, 880°C \times 6 min (c) sample C, 890°C \times 3 min (d) sample D, 900°C \times 3 min (e) sample E, 910°C \times 1 min.



(c)



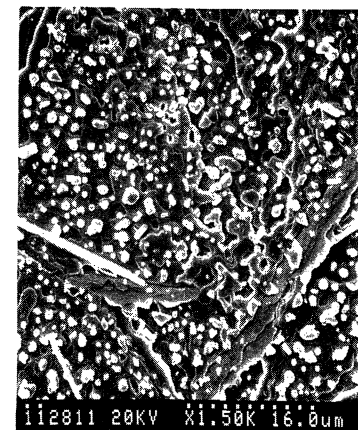
(b)



(a)



(e)



(d)

Fig. 2. SEM pictures of Tl-Ca-Ba-Cu-O thin films for annealing conditions of (a) sample A, 870°C \times 6 min (b) sample B, 880°C \times 6 min (c) sample C, 890°C \times 3 min (d) sample D, 900°C \times 3 min (e) sample E, 910°C \times 1 min.

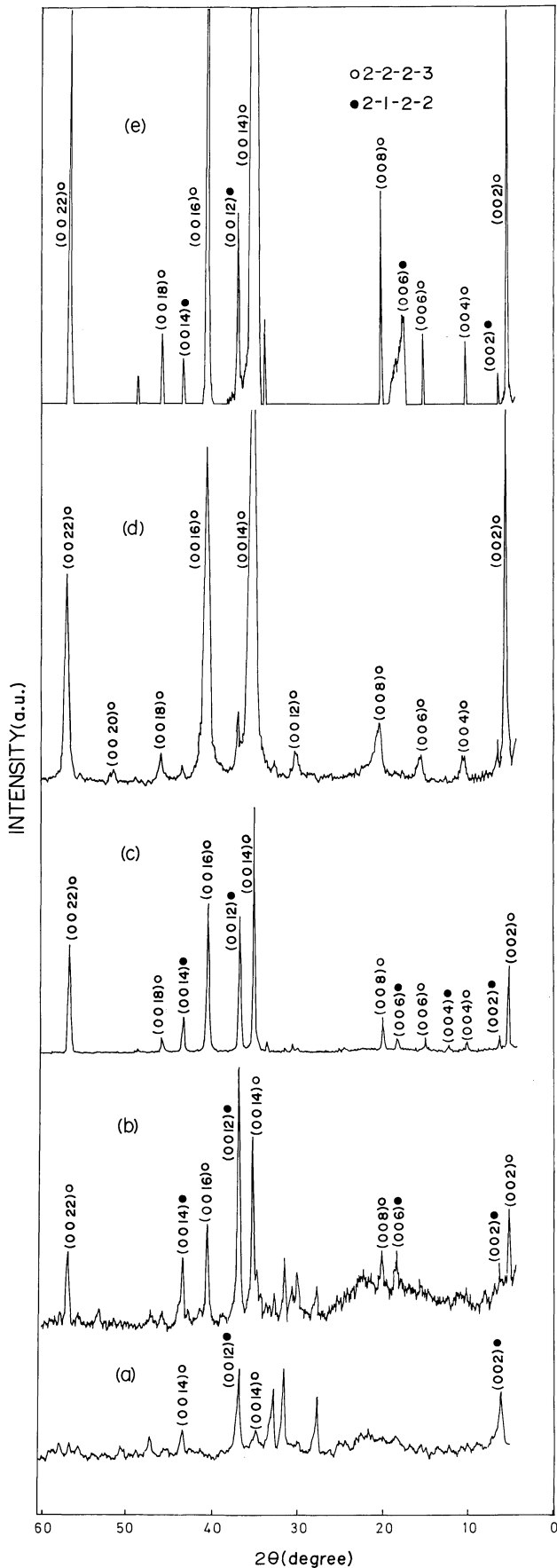


Fig. 3. X-ray diffraction patterns of Tl-Ca-Ba-Cu-O thin films for samples A-E, correspond to (a)-(e), respectively.

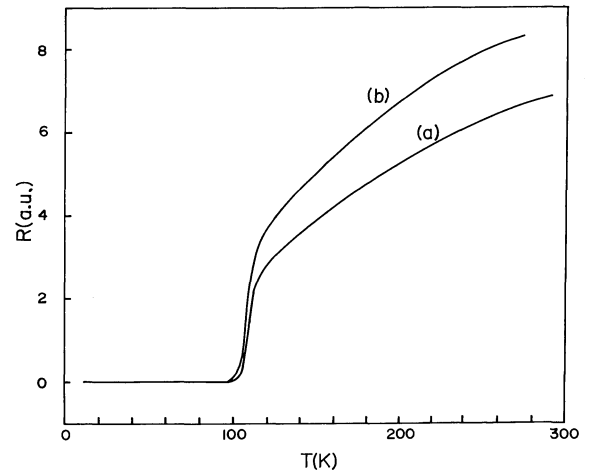


Fig. 4. Temperature-dependent resistivity of the selected sample measured when (a) freshly annealed (b) one month later.

Heat treatment at 900°C transformed the majority of the 2-1-2-2 phase into the 2-2-2-3 structure. However, overheating to 910°C made the 2-1-2-2 peaks increase again. These results provide an explanation for the variation of T_{co} . The lattice constant calculated from the pattern of sample D is $c \approx 35.6 \text{ \AA}$. The T_{co} 's obtained from the series are lower than those of the pellet samples,³⁾ and this may indicate that the intergrain connections of the superconducting crystals on the films need further improvement. The X-ray diffraction patterns of the films which were sputtered with substrates at $350\text{--}650^{\circ}\text{C}$ were also made after a postannealing at 880°C . We observed some 2-1-2-2 peaks along with many unidentified peaks in the patterns.

It is worth noting that the film which possessed a T_{co} of 97 K had been immersed in a supersonic bath of n-butyl acetate for ~ 2 min in order to remove the silver paint. It was then washed by acetone and running water, and exposed to air for one month. The temperature-dependent resistivity showed little modification as a result of these treatments (see Fig. 4).

In summary, we have made Tl-Ca-Ba-Cu-O thin films by using dc sputtering with a single target of a nominal composition of $Tl_2Ca_2Ba_2Cu_3O_x$. The superconducting properties of the films are found to be very sensitive to the annealing condition. Postannealing at $900^{\circ}\text{C} \times 3$ min with the same target materials in gold foil enables the films to form the 2-2-2-3 structure with $T_{\text{co}} \sim 95$ K which possess good stability in various environments. The X-ray diffraction patterns and the SEM photographs show that the films are preferentially c-axis oriented perpendicular to the YSZ substrates. These results illustrate a reliable method used to prepare superconducting thin films of predictable structures by dc sputtering from a target of the same composition.

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References

- 1) M. Maeda, Y. Tanaka, M. Fukutomi and T. Asano: *Jpn. J. Appl. Phys.* **27** (1988) L209.
- 2) Z. Z. Sheng and A. M. Hermann: *Nature* **332** (1988) 138.
- 3) S. S. P. Parkin, V. Y. Lee, E. M. Engler, A. I. Nazzal, T. C. Huang, G. Gorman, R. Savor and R. Beyers: *Phys. Rev. Lett.* **60** (1988) 2539.
- 4) R. M. Hazen, L. W. Finger, R. J. Angel, C. P. Prewitt, N. L. Ross and C. G. Hadidiacos: *Phys. Rev. Lett.* **60** (1988) 1657.
- 5) E. Takayama-Muromachi, Y. Uchida, Y. Matsui, M. Onoda and K. Kato: *Jpn. J. Appl. Phys.* **27** (1988) L556.
- 6) A. Maeda, T. Yabe, H. Ikuta, Y. Nakayama, T. Wada, S. Okuda, T. Itoh, M. Izumi, K. Uchinokura, S. Uchida and S. Tanaka: *Jpn. J. Appl. Phys.* **27** (1988) L661.
- 7) D. S. Ginley, J. F. Kwak, R. P. Hellmer, R. J. Baughman, E. L. Venturini and B. Morosin: *Appl. Phys. Lett.* **53** (1988) 406.
- 8) I. Shih and C. X. Qui: *Appl. Phys. Lett.* **53** (1988) 523.
- 9) 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.
- 10) Y. Ichikawa, H. Adachi, K. Setsune, S. Hatta, K. Hirochi and K. Wasa: *Appl. Phys. Lett.* **53** (1988) 919.