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# Preparation of high $T_c$ Tl-Ba-Ca-Cu-O thin films by pulsed laser evaporation and $Tl_2O_3$ vapor processing

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Tl-Ba-Ca-Cu-O superconducting thin films with zero-resistance temperatures up to 115 K have been prepared using a  $Tl_2O_3$  vapor process on Ba-Ca-Cu-O precursor thin films. The Ba-Ca-Cu-O thin films were made by laser deposition on Y-stabilized  $ZrO_2$  substrates. This technique minimizes problems caused by the toxicity of  $Tl_2O_3$ , and its subsequent decomposition to the volatile and toxic  $Tl_2O$  upon heating. Therefore, it may have practical application in the fabrication of high  $T_c$  Tl-Ba-Ca-Cu-O superconducting thin-film devices.

With the advantages of ease of formation, the highest temperature (120 K) Tl-Ba-Ca-Cu-O superconductors may be the first superconductors for practical commercial applications at liquid-nitrogen temperatures. However, the high toxicity of the thallium compounds commonly used in superconductor preparation has introduced safety concerns in the fabrication of Tl-based superconductors. In order to alleviate this problem, we have developed a  $Tl_2O_3$  vapor process<sup>1</sup> which consists of two steps: (a) preparation of Ba-Ca-Cu-O precursors by pulsed laser evaporation,<sup>2</sup> and (b)  $Tl_2O_3$  vapor processing of the precursors. Vapor processing has produced high quality Tl-Ba-Ca-Cu-O superconductors in bulk, thick wire, and thick-film form.<sup>1</sup> In this letter we report that we have successfully used these techniques for fabricating Tl-Ba-Ca-Cu-O superconducting thin films with zero-resistance temperatures up to 115 K, which is much higher than that previously reported by Qiu and Shih<sup>3</sup> using a similar processing method.

A Ba-Ca-Cu oxide target with a given nominal composition was prepared using the method described in Ref. 1. The oxide film was then deposited by laser deposition onto an Y-stabilized  $ZrO_2$  substrate at 20 °C using a frequency-doubled Nd-YAG laser operating at 523 nm and 10 Hz,<sup>2</sup> forming a Ba-Ca-Cu-O thin film with a thickness of 2–3  $\mu m$ . This precursor thin film was subjected to a  $Tl_2O_3$  vapor process similar to that described in Ref. 1. Briefly, a platinum boat containing a small amount of  $Tl_2O_3$  (typically 0.1–0.2 g) was placed in a quartz boat. The Ba-Ca-Cu-O precursor thin film was then put above the platinum boat. The quartz boat with the contents was put into a tube furnace, which had been heated to 900 °C and was heated for about 3 min in flowing oxygen followed by furnace cooling.

The as-deposited film was a dull black color and an x-ray diffraction scan of the film did not exhibit any peaks other than that of the substrate, indicating that the precursor film was amorphous or extremely fine grained. After  $Tl_2O_3$  vapor processing, a superconducting thin film was formed. Films deposited from a  $Ba_2Ca_2Cu_3O_7$  target will be designated by a Tl-223 prefix while films deposited from a

$Ba_2Ca_3Cu_3O_8$  target will be designated by a Tl-233 prefix. Figure 1 shows the temperature dependencies of resistance for a  $Tl_2O_3$  vapor-processed Tl-223 film and a  $Tl_2O_3$  vapor-processed Tl-233 film. Their zero-resistance temperatures are 115 and 104 K, respectively.

The superconducting behavior of vapor-processed thin films depends strongly on processing conditions. The resistance of film Tl-223B as shown in Fig. 2 reached zero only at 80 K since it was heated at too high a temperature (about 920 °C) for 3 min. The film Tl-233B did not show a transition above liquid-nitrogen temperature as seen in Fig. 2. This film was heated at too low a temperature (850 °C) and for too short a time (2 min). After reheating at 900 °C for 3 min, this film reached zero resistance at 104 K, as also seen in Fig. 2. This zero-resistance temperature is identical to film Tl-233A, which underwent a single thallination step.

An x-ray diffraction scan of sample Tl-223A is shown in Fig. 3. The scan shows that the film is multiphase with a *c*-axis orientation. The dominant phase is the  $Tl_2Ba_2Ca_1Cu_2O_8$  with the indexed (001) peaks corresponding to a lattice parameter of  $c = 29.2 \text{ \AA}$ .<sup>4</sup> The  $Tl_1Ba_2Ca_1Cu_2O_7$  and  $Tl_1Ba_2Ca_2Cu_3O_6$  phases are also

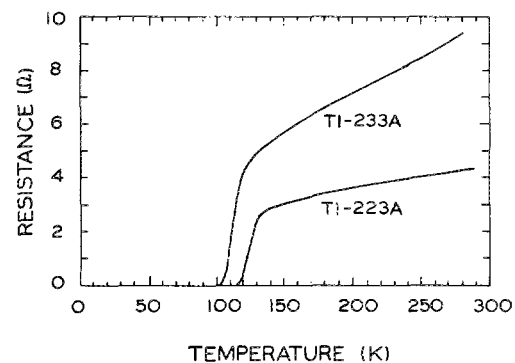


FIG. 1. Temperature dependences of resistance for a  $Tl_2O_3$  vapor processed  $Ba_2Ca_3Cu_3O_8$  thin film (Tl-223A) and a  $Tl_2O_3$  vapor-processed  $Ba_2Ca_2Cu_3O_7$  thin film (Tl-233A).

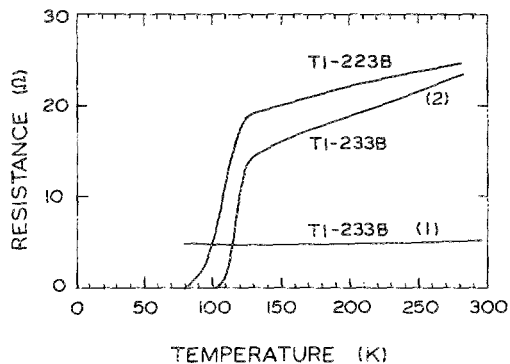


FIG. 2. Film TI-223B was processed at too high a temperature (920 °C) and exhibits a substantially lower zero-resistance temperature than film TI-223A. Curve (1) for film TI-223B resulted when the film was processed at too low a temperature and for too short a time. Curve (2) shows  $R$  vs  $T$  for the same film after a second thermal cycle under the appropriate conditions.

present, with lattice parameters of  $c = 12.7 \text{ \AA}$  and  $c = 15.8 \text{ \AA}$ , respectively.<sup>5,6</sup> The two unidentified peaks may represent insulating phases. It should be pointed out that the intensity of the substrate peak is quite low. This may be due to a substrate-film interaction. The x-ray diffraction scans of the other films also exhibited multiphase characteristics with  $c$ -axis orientation.

Mechanical stylus scans of the films showed that they are not uniform in thickness, and have a high degree of surface roughness. The surface roughness was confirmed by the scanning electron micrograph of film TI-223A shown in Fig. 4, where the grain size is seen to be on the order of 5–10  $\mu\text{m}$ . This micrograph also shows the plate-like structure of the crystal grains, which is a common feature of  $c$ -axis oriented grains.<sup>2</sup> However, needle-like structures are also clearly imbedded throughout the film. These structures may be associated with the unidentified x-ray diffraction peaks seen in Fig. 3.

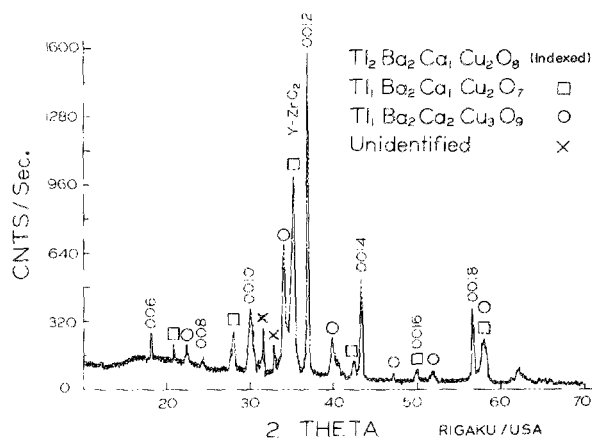


FIG. 3. X-ray diffraction scan of film TI-223A. The 2212 phase peaks are indexed, while the 1212 and 1223 phase peaks are also identified. All these peaks indicate  $c$ -axis orientation. There are also two unidentified peaks in the scan.

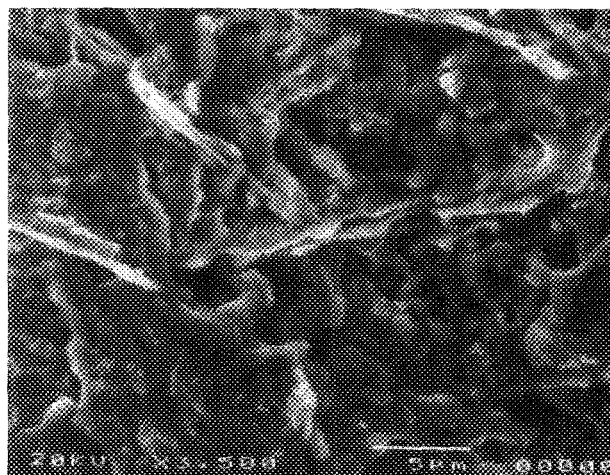


FIG. 4. SEM micrograph of film TI-223B showing plate-like structure of the crystal grains and a grain size of 5–10  $\mu\text{m}$ . Also present are needle-like structures imbedded in the plates.

The transport  $J_c$  at 77 K was estimated for film TI-223B, where the temperature dependence of the resistance of this film is shown in Fig. 2. The  $J_c$  of this film was less than 100  $\text{A}/\text{cm}^2$  in zero magnetic field, and decreased by an order of magnitude when the magnetic field was increased to 1.2 T. The nonuniform film thickness and film porosity may account for the low  $J_c$ . It is also possible that nonsuperconducting phases exist in the grain boundaries which may be limiting  $J_c$ . We believe  $J_c$  can be substantially increased by densifying the precursor film and adjusting its stoichiometry.

A major advantage of the  $\text{Ti}_2\text{O}_3$  vapor process is that this process uses toxic  $\text{Ti}_2\text{O}_3$  only in the final step, and thus potential contamination with Ti is greatly decreased during processing. In particular, the thin-film vacuum deposition system is never contaminated by Ti. Since the  $\text{Ti}_2\text{O}_3$  vapor process can be carried out in suitable closed containers, we believe that this technique should be useful in practical fabrication of Ti-based superconducting thin films and devices.

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