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# Sputter Deposition and Thallination of TI-Ba-Ca-Cu-O Superconducting Thin Films

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## Abstract

Thallination techniques used for the fabrication of sputter-deposited  $Tl_2Ba_2CaCu_2O_x$  and  $Tl_2Ba_2Ca_2Cu_3O_x$  superconducting thin films were investigated. Differences in elemental composition of precursor Ba-Ca-Cu-O sputtering targets were found to yield different superconducting phases. Thallination conditions which yielded transition temperatures as high as 122 K for samples annealed in air are described. Finally, reactive ion etching of films using a mixture of chlorine and argon gases is discussed.

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## Introduction

The TI-Ba-Ca-Cu-O superconducting system has received considerable attention due to the inherent high temperature transition,  $T_c$ , and critical current density  $J_c$  of some of its phases. The  $Tl_2Ba_2Ca_2Cu_3O_{10}$  (2223) phase compound has the highest  $T_c$  ( $R=0$ ) at 127 K (Sheng and Hermann, 1988; Sheng et al., 1988). Superconducting TI-Ba-Ca-Cu-O thin films can be fabricated by sputtering, laser ablation or evaporation of Ba-Ca-Cu-O from a single target followed by a complicated high-temperature annealing sequence in an excess TI-vapor pressure ambient (Qui and Shih, 1988; Sheng et al., 1988; Shah et al., 1990). Interest in this material is high because the potential commercial applications of TI-Ba-Ca-Cu-O thin films in passive and active electronic devices are enormous (Superconducting Technologies, Inc., private communication).

The properties of TI-Ba-Ca-Cu-O superconducting thin films are greatly influenced by the elemental composition of the precursor Ba-Ca-Cu-O target and the post-deposition thallination conditions of the Ba-Ca-Cu-O precursor films. It has been shown that their  $T_c$  values are primarily determined by the number of copper layers involved in the perovskite slabs (Martin et al., 1990). Under optimum conditions, the  $T_c$ s for (2212) phase films are around 100 K with a  $J_c$  of greater than  $10^5$  A/cm<sup>2</sup> and, for (2223) phase films, are around 122 K with  $J_c$  of about  $5 \times 10^4$  A/cm<sup>2</sup> on <100>-oriented magnesium oxide (MgO) substrates.

In addition to the fabrication of high-quality films, it is important to develop appropriate microfabrication techniques and junction fabrication technology to realize high-

$T_c$  electronic devices. The patterning of thin superconducting films has been demonstrated using.

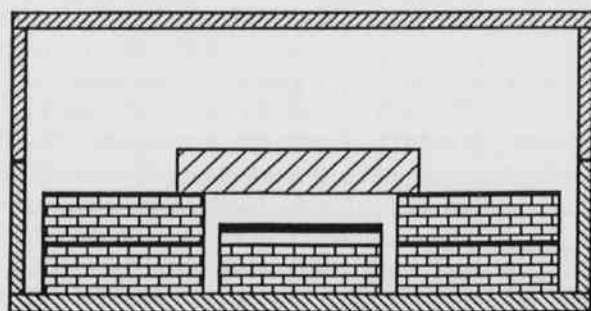
In this paper, a two-step fabrication technique for the fabrication of high  $T_c$  (2212) phase and (2223) phase superconducting films is reported. The etching of precursor films using reactive ion etching (RIE) with a chlorine and argon plasma is discussed.

## Materials and Methods

Ba-Ca-Cu-O precursor films were RF magnetron sputtered onto polished <100>-oriented MgO substrates in a modified Perkin-Elmer PE 2400 sputtering system using either  $Ba_2Ca_2Cu_3O_x$  or  $Ba_2Ca_{2.3}Cu_3O_x$  targets. All sputter depositions were performed in an argon atmosphere at room temperature. The chamber pressure during deposition was maintained constant at 10 mT. The target-substrate separation was constant at 10 cm. The best precursor films were obtained when the substrates were placed directly beneath the target. The RF power densities were optimized for the  $Ba_2Ca_2Cu_3O_x$  and  $Ba_2Ca_{2.3}Cu_3O_x$  targets. Deposition times were varied to obtain film thicknesses of 4500 to 8000 Å. Film thicknesses and deposition rates were determined using a Sloan Dektak surface profilometer.

Post-deposition thallination of the precursor films was accomplished by placing the films in platinum-coated alumina boats along with  $Tl_{1.7}Ba_2Ca_2Cu_3O_x$  (TI1.7) pellets. The pellets were formed using a mechanical press at a pressure of 10000 kg., from a stoichiometric mixture of  $Tl_2O_3$ , BaO, CuO, and CaO.

The precursor films of the first sample group were deposited using a  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  target. The films were then annealed at  $815^\circ\text{C}$  for 10 hours in an air ambient using the T11.7 pellets without any physical contact between the films and pellets as shown in Fig. 1. The second sample group was obtained by annealing precursor films, deposited using a  $\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_x$  target, for 20 hours in air ambient at  $810^\circ\text{C}$  and then reducing the temperature at  $500^\circ\text{C}$  at a rate of  $1^\circ\text{C}/\text{min}$ . The thallination pellet and the physical arrangement of the pellet and the samples, were the same as for the first sample group.



- → MgO SUBSTRATE
- → PRECURSOR FILM
- ▨ → UNANNEALED PELLETS
- ▩ → ANNEALED PELLETS

Fig. 1. Thallination configuration

Transition temperatures for the samples were obtained from plots of resistance ( $R$ ) versus temperature ( $T$ ) performed using a standard four-point contact method. Epotek H20E silver paste was used to attach four leads to the sample film (Ginley et al., 1988; Subramaniam et al., 1990). The four leads were soldered to a module that fits into a cryogenic cooler capable of lowering the temperature at 19K. The thermostat, lock-in amplifier, and cryostat were all under the control of a personal computer.

$J_c$  measurements were also performed using a simple four point contact arrangement (Lin et al., 1991). The sample was enclosed in a glass capsule and submerged in a tank of liquid nitrogen. The current through the sample was increased until the voltage across the sample became non-zero.  $T_c$  and  $J_c$  measurements were also performed using an inductive method. Inductively-Coupled Plasma (ICP) spectroscopy was used to study the composition of

the sputtering targets as a function of sputtering time by scraping off the altered layer of the target material.

Reactive ion etching was used to define  $120\ \mu\text{m}$  lines and  $200\ \mu\text{m}$  concentric ring structures in  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  films deposited on  $\langle 100 \rangle$ -oriented silicon substrates. Hunt's HPR-204 positive photoresist was used for masking. Conventional microelectronic fabrication techniques were used to deposit, define, develop and remove the photoresist. The reactive ion etching was performed using a mixture of  $\text{Cl}_2$  (25%) and Ar for 45 minutes at a power density of  $1\ \text{W}/\text{cm}^2$ . Following the etching step, the photoresist was removed and a Dektak surface profilometer was used to examine the etch profiles.

## Results and Discussion

The best precursor films obtained using the  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  and  $\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_x$  targets were sputter-deposited using RF power densities of  $1.1\ \text{W}/\text{cm}^2$  and  $1.65\ \text{W}/\text{cm}^2$ , respectively. The surface roughness of the precursor films was typically  $40\ \text{\AA}$ . However, it was observed that surface roughness increases as RF sputtering power increases.

Fig. 2, showing a  $T_c$  value of approximately 119 K, is a resistance versus temperature plot of a typical sample from group one. EDS analysis of films produced using the  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  precursor target indicates that the films are predominantly of the (2212) phase. For these samples, the  $T_c$  is quite high, but the  $J_c$  value is low. Room temperature resistance of the film was measured to be about 30 ohms. This can be explained in terms of oxygen non-stoichiometry in the superconducting thin film which results due to thallination of the film in air ambient. Martin et al. (1990) have shown that, in bulk thallium cuprates,  $T_c$  is essentially governed by the oxygen non-stoichiometry. Furthermore, the conductivity of cuprate superconductors is primarily due to the cuprate planes so that as oxygen non-stoichiometry increases, the conductivity falls proportionately. The  $J_c$  results for this sample group is only about  $5 \times 10^3\ \text{A}/\text{cm}^2$ , suggesting that these films are oxygen deficient.

ICP spectroscopy analysis of the target after several depositions revealed that the composition had changed to  $\text{Ba}_{0.5}\text{Ca}_2\text{Cu}_{1.4}\text{O}_y$  from an original composition of  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . This indicates that calcium, unlike barium and copper, was not being depleted from the target even after many sputtering runs. This means that elemental components of the target were being consumed non-stoichiometrically because of preferential and selective sputtering (Betz and Wehner, 1983). Hence, pure (2223) phase films could not be obtained using the  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  target. Consequently, the calcium content in the second target was increased in order to be able to sputter (2223) phase precursor films.

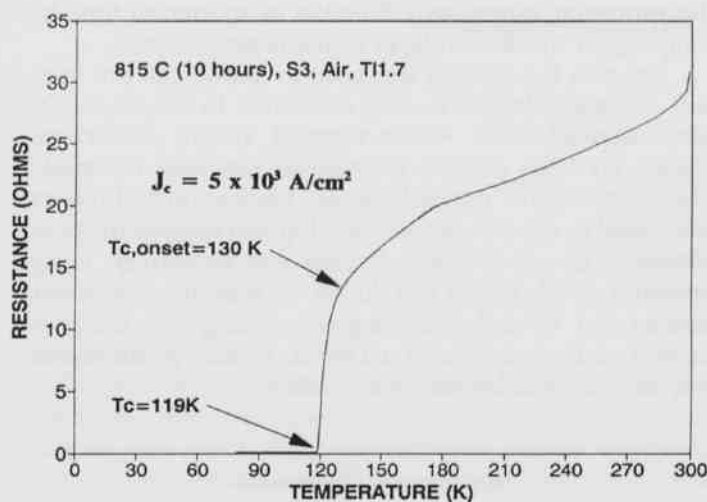


Fig. 2.  $T_c$  measurement plot of a typical sample from group one using four-point transport method.

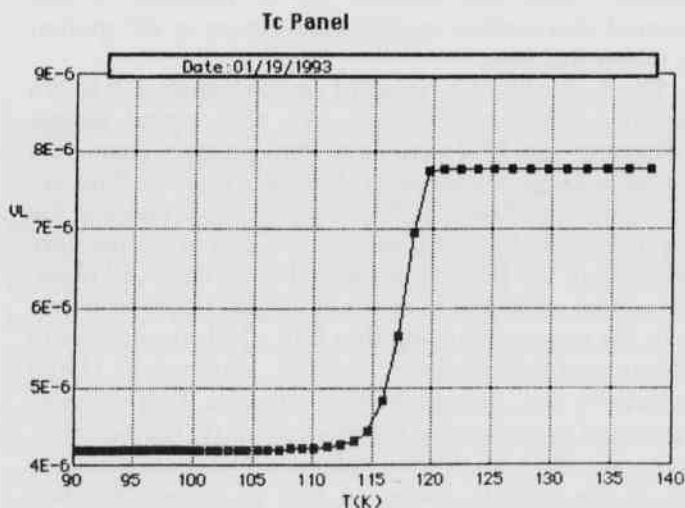


Fig. 3.  $T_c$  measurement plot of a typical sample from group two using inductive method.

Superconducting samples from group two typically yielded  $T_c$  values of 122 K and  $J_c$  values of  $5 \times 10^4$  A/cm<sup>2</sup> as determined using the inductance measurement method (Fig. 3). The films were shiny black and extremely uniform with a density only slightly less than values previously reported for some of the best (2223) phase films. X-ray diffraction pattern for these films clearly show highly pure (2223) phase without any noticeable low  $T_c$  phase impurity spikes. The films are highly oriented with the C-axis normal to the substrate, consistent with the fact that longer

annealing times are conducive to the creation of (2223) phase films.

Reactive ion etching of the precursor films using a  $Cl_2$  and Ar plasma is anisotropic as evident from the sharp sidewalls of both the 120  $\mu$ m lines and 200  $\mu$ m concentric ring structures shown in Fig. 4. It is believed that activated chlorine species react with barium, calcium and copper in the precursor films to form their respected chloride species and that the etching is primarily accomplished by argon sputtering. The patterns etched in the precursor films can be tallinated to yield superconducting films.

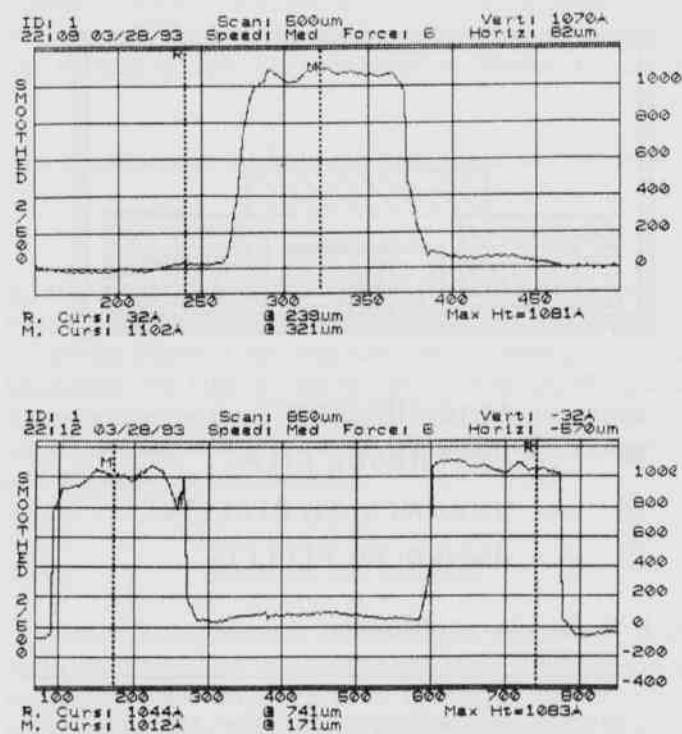


Fig. 4. Etch profiles for 120  $\mu$ m line and 200  $\mu$ m concentric ring structure.

### Summary and Conclusions

A transition temperature of 119 K was achieved for (2212) phase films thallinated in an air ambient using a non-contact arrangement of the precursor film and thallium containing pellets. A low critical current density for this sample is attributable to oxygen deficiency. By enriching the sputtering target with calcium and optimizing the tallination conditions, pure (2223) phase superconducting films were readily fabricated. The (2223) phase films typi-

cally have a  $T_c$  of about 122 K and a  $J_c$  of about  $5 \times 10^4$  A/cm<sup>2</sup>. It was also shown that reactive ion etching using a mixture of Cl<sub>2</sub> and Ar gases can be effectively used to pattern to precursor films.

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