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*Title:* SUPERCONDUCTING $Tl_2BA_2CACU_2O_8$ THIN FILMS PREPARED BY POST-ANNEALING IN A FLOW-THROUGH MULTIPLE-ZONE FURACE

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# Superconducting $Tl_2Ba_2CaCu_2O_8$ Thin Films Prepared by Post-Annealing in a Flow-Through Multiple-Zone Furnace

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***Abstract*--$Tl_2Ba_2CaCu_2O_8$ thin films were prepared for the first time by use of a multiple-zone flow-through thallination process. Thallous oxide was volatilized from condensed thallium oxide in a low temperature source zone and convectively transported to a higher temperature thallination zone in which initially amorphous $Ba_2CaCu_2O_5$ precursor films were located. By careful control of the source temperature, film temperature, flow rate, anneal time, and rates of heat up and cool down, smooth $Tl_2Ba_2CaCu_2O_8$ thin films were prepared on (100) $LaAlO_3$ with the following properties: inductive $T_c$ of 107.6 K and 80% transition width of 1.3 K, transport $J_c$ at 75 K of 1.3 X $10^5$ A/cm$^2$, and $R_s$ at 10 GHz and 80 K of 1.3 m$\Omega$. The scalability of the process to large area film processing was demonstrated by the preparation of $Tl_2Ba_2CaCu_2O_8$ thin films on $LaAlO_3$ three-inch diameter wafers.**

## I. Introduction

Several of the TlBaCaCuO superconducting phases possess critical transition temperatures $T_c$ well in excess of the boiling point of liquid nitrogen [1]. Of these phases, $Tl_2Ba_2CaCu_2O_8$ (2212-TlBaCaCuO), with a $T_c$ up to 110 K reported for powders [2], has found the greatest use to date for thin film microwave applications due to the relative ease with which it can be fabricated into thin films with good electrical properties and acceptable surface morphology [3], [4].

A variety of thallination processes have been used to prepare TlBaCaCuO superconducting thin films. Most work has concentrated on thallinations carried out in the presence of thallium oxide-containing buffer powders (usually one of the superconducting phases) within either sealed gold pouches [5], [6] or closed, but unsealed, platinum or alumina crucibles [3], [7] - [9]. While 2212-TlBaCaCuO thin films have been made on substrates as large as 3 inches in diameter with such processes [10], further scale up is anticipated to be difficult.

DeLuca et al. [11] demonstrated the first successful use of a closed tube, stagnant gas two-temperature zone thallination process, in which the thallium oxide source zone was kept at a lower temperature than the film. Such a two-temperature zone process has the major advantages over the buffer powder processes of allowing for the use of condensed thallium oxide as the source of gaseous $Tl_2O$ and for the independent control of the $Tl_2O$ partial pressure throughout the entire process.

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The use of a two-temperature zone process with a flowing - rather than a stagnant - gas atmosphere is anticipated to have several advantages over the stagnant gas process because of the greater control of the thallination step afforded by the more rapid convective versus diffusive transport of thallous oxide from the source zone to the thallination zone [12]. An earlier attempt at such a process yielded mixed-phase TlBaCaCuO films reportedly due to the transport of the Ba, Ca, and Cu atoms away from the substrate [7].

In this work, we describe the first successful preparation of thallium-containing TlBaCaCuO thin films in a flow-through multiple-zone thallination process. Results are presented predominantly for 2212-TlBaCaCuO, but $TlBa_2CaCu_2O_7$ (1212-TlBaCaCuO) thin films were also successfully prepared, and we anticipate that the process will prove to be adaptable to the preparation of a wide variety of other thallium-containing phases.

## II. Experiment

### A. Materials

Thallic oxide ($Tl_2O_3$) powder (Aldrich, 99.99% purity) was used as the sole source of volatile thallous oxide ($Tl_2O$), and all experiments were carried out with 10% $O_2$/Ar as the carrier gas. All films were prepared on (100) $LaAlO_3$ substrates polished on both sides, and substrate size varied from 5 mm square to 3 inch diameter.

$Ba_2CaCu_2O_5$ precursor films of thickness about 500 nm were deposited by off-axis rf magnetron sputtering [3]. The precursor films were amorphous as determined by x-ray diffraction. Both scanning electron microscopy and optical microscopy showed them to be smooth and featureless.

### B. Apparatus

The experimental system is shown in Fig. 1. The reactor vessel consisted of a 3.5 inch diameter alumina reactor tube located inside a furnace with three independent temperature-control zones. Alumina-sheathed thermocouples monitored the temperatures of the high temperature zone containing the film and the low temperature zone containing the thallium oxide source powder. The temperature profile was controlled to provide for a uniform temperature of ±2°C over the area the substrates were placed. Gold foil flow restrictors were used to minimize the axial diffusive transport of $Tl_2O$ upstream, downstream, and between zones [13].

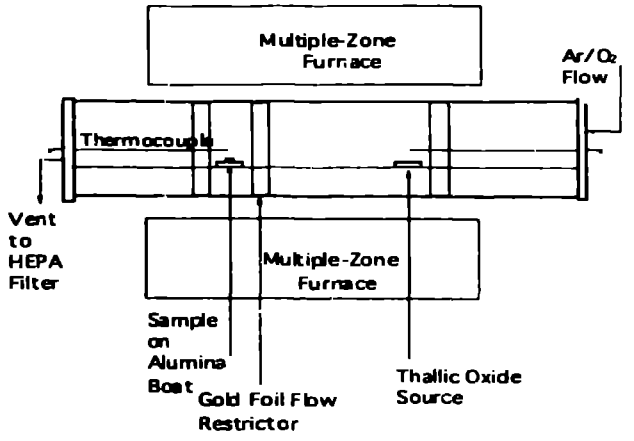


Fig. 1. Apparatus for producing 2212-TlBaCaCuO superconducting films.

The flow-through thallination process was carried out at ambient pressure (0.8 atm in Los Alamos). The $O_2$/Ar carrier gas was passed through a column of ascarite (sodium hydroxide-coated silica) and drierite ($CaSO_4$) to further remove $CO_2$ and residual water prior to entering the reactor. After passing through the reactor, the gas entered a region of low temperature where condensation of thallium oxide took place. The gas was then passed through a high efficiency particulate (HEPA) filter to trap any residual thallium oxide particulates transported out of the condensation zone before being exhausted to a vent.

Prior to the start of each run, the gas flow was established and the tube was flushed with the 10% $O_2$/Ar gas mixture. The process flow rate was set and the three zones of the furnace were then independently controlled to produce the desired temperature-time profile for the source and thallination zones. Following cooldown to room temperature, the films were removed for analysis. The entire run - from heatup to cooldown - lasted about 8 hours.

### C. *Characterization Techniques*

Uptake of thallium oxide was measured with x-ray fluorescence (XRF) using the relative integrated peak intensities (uncorrected) for Tl Lα and Cu Kα peaks. X-ray diffraction (XRD) θ-2θ scans recorded with Cu Kα radiation determined the primary and secondary phases in the films. In addition, XRD rocking curves using the (00,12) 2212-TlBaCaCuO reflection were used to measure the degree of c-axis alignment with the substrate. Film morphology and roughness were studied by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). Critical current density $J_c$ was measured by a four-point method at 77 K.

Surface resistance was measured at 27.5 GHz by the HTS-sapphire dielectric resonator method using films prepared on 12 mm square substrates [14]. Surface resistance was calculated from the measured Q-value and S parameters at low power. For purposes of comparison, the results are reported at 10 GHz using the commonly accepted scaling law that surface resistance is proportional to the square of the frequency, which has been shown previously to hold for 2212-TlBaCaCuO thin films [10].

## III. Results

### A. *Phase Formation*

The following process variables were first investigated to scope out the range of conditions leading to 2212-TlBaCaCuO thin films: thallium oxide source temperature, film temperature, flow rate, time at maximum temperature and cooldown rate. It was found that smooth 2212-TlBaCaCuO thin films could be produced at a film temperature of 785 °C, which is higher than the lowest thallination temperature of 720 °C previously reported [15] but much lower than the temperature of 850 °C commonly used for buffer powder crucible thallination processes [3], [6], [9], and more extensive experiments were carried out at this temperature.

The following results were obtained at a constant film temperature of 785 °C, constant flow rate, and variable source temperature. Under such conditions, the source temperature determines the partial pressure of thallous oxide delivered to the thallination zone. If the gas stream is saturated with thallous oxide in the source zone, the partial pressure of $Tl_2O$ can be determined from thermodynamic data available in the literature [13]. Since we did not ascertain that the gas stream was saturated in the present study, we present results qualitatively in terms of increasing source temperature instead of quantitatively in terms of $Tl_2O$ partial pressure.

At the lowest source temperatures studied, c-axis oriented 1212-TlBaCaCuO thin films were produced. The uncorrected integrated Tl/Cu XRF peak ratio for these films was 1.0 ± 0.1. The inductive $T_c$ was 82 ± 2 K and the 80% transition width was less than 2 K.

As the source temperature was increased, first mixed phase 1212-TlBaCaCuO/2212-TlBaCaCuO and then predominantly single phase 2212-TlBaCaCuO thin films were formed. For those 2212-TlBaCaCuO thin films containing the lowest concentrations of secondary phases, the Tl/Cu XRF peak ratio was 1.4 ± 0.2. The $T_c$ onset for predominantly 2212-TlBaCaCuO thin films varied considerably as source temperature was varied, ranging from 94 K to 107.6 K. Transition widths varied from 0.5 K for films with higher $T_c$s to as high as 15 K for films with lower $T_c$s. However, when source temperature was held constant the 2212-TlBaCaCuO thin film properties were fairly reproducible, with typical $T_c$ values ranging between 103 K and 106 K and transition widths less than 2.5 K.

At the highest source temperatures, thallium-rich phases dominated the x-ray diffraction patterns. Tl/Cu XRF peak ratios ranged from 2.0 to as high as 3.7. All films with Tl/Cu XRF peak ratios greater than 2.5 were non-superconducting.

These results are in qualitative agreement with the thermodynamic results measured on powders by Aselage et al. at 840 °C [16] and comparable oxygen partial pressure with one exception. In the earlier study, 1212-TlBaCaCuO was not observed as a thermodynamically stable phase under any condition of thallous oxide partial pressure. Instead 2212-TlBaCaCuO was observed to transform directly into thallium-free phases, including $BaCuO_2$ and CaO at low thallous oxide

partial pressures. In this study, nearly single phase 1212-TlBaCaCuO thin films with intense XRD (00ℓ) reflections and $T_c$ comparable to bulk 1212 TlBaCaCuO were readily formed. The results raise the question of whether 1212-TlBaCaCuO forms in reduced oxygen partial pressure as a thermodynamically stable phase or only as a metastable phase.

### *B. Film Characterization*

The primary goal of the present investigation was to produce smooth 2212-TlBaCaCuO thin films with good electrical properties. Results are presented in this section for the best films produced to date. All results are reported for films produced on 5 mm to 12 mm square $LaAlO_3$ substrates under identical conditions at 785 °C.

An XRD θ-2θ pattern for a 2212-TlBaCaCuO thin film on (100) $LaAlO_3$ is shown in Fig. 2. The pattern is dominated by the (00ℓ) reflections of 2212-TlBaCaCuO and the reflections from the $LaAlO_3$ substrate.

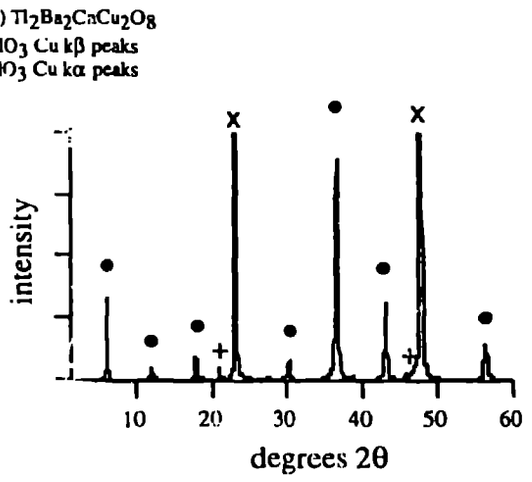


Fig. 2. XRD pattern for 2212-TlBaCaCuO superconducting thin film.

XRD rocking curve analysis (Fig. 3) taken over the (00,12) reflection at 2θ=36.632° yielded a peak with a full width at half maximum value of 1.11°. This value is somewhat higher than that of 0.68° previously reported for crucible-annealed 2212-TlBaCaCuO thin films on $LaAlO_3$ at 850 °C [3], and the difference may be due to the much lower thallination temperature in the present study.

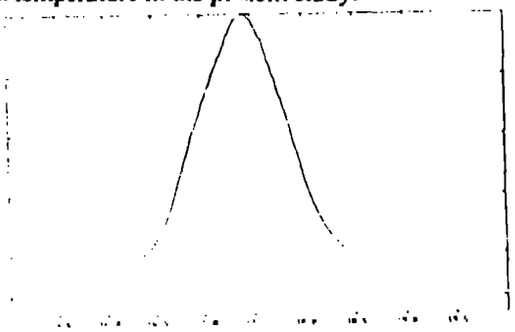

Fig. 3. Rocking curve for the (00,12) reflection of a 2212-TlBaCaCuO superconducting thin film

The ac inductive measurement of $T_c$ (Fig. 4) yielded an inductive $T_c$ onset of 107.6 K and an 80% transition width of 1.3 K, comparable to the highest $T_c$ reported for 2212-TlBaCaCuO thin films [3], [15].

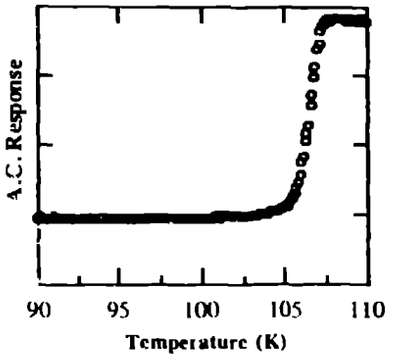


Fig. 4. The ac response versus temperature (K) for a 2212-TlBaCaCuO thin film. $T_c$=107.6 K and $\Delta T_c$=1.3 K for 80% of the transition.

The best $J_c$ value measured in this study was 1.3 X $10^5$ A/cm$^2$ at 77 K. This value compares to the highest reported $J_c$ value for 2212-TlBaCaCuO films of 2.0 X $10^6$ A/cm$^2$ at 77 K [17].

The surface resistance was measured for a film with a $T_c$ onset of 106 K, yielding an $R_s$ value at 80 K and 10 GHz of 1.3 mΩ. This value compares to the lowest reported value at 80 K for 2212-TlBaCaCuO thin films of 145 ± 15 μΩ [10].

The higher $R_s$ and lower $J_c$ for the present films compared to the best values previously reported was expected since the flow-through multiple-zone thallination process has not yet been optimized. Nevertheless, these early results clearly demonstrate the viability of the process for producing films with good electrical properties.

The SEM micrograph of the 2212-TlBaCaCuO thin film prepared in the multiple-zone furnace (Fig. 5.) taken at 5 kV indicates that the film surface was smooth and the grains were approximately 400 nm in size. The thin films made by this process have smaller grain sizes and were smoother than buffer powder crucible-annealed films thallinated at higher temperatures [17].


Fig. 5. An SEM micrograph of the surface of a 2212-TlBaCaCuO thin film taken at 5 kV

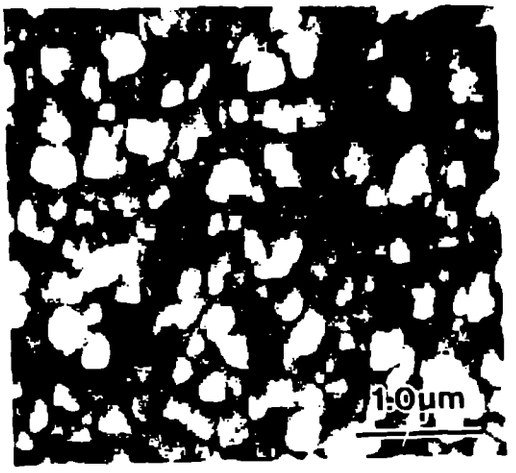


Fig. 6. An AFM image of a 2212-TlBaCaCuO thin film. Root mean square roughness (RMS) = 27.5 nm.

The AFM image of the 2212-TlBaCaCuO thin film (Fig. 6) illustrates the roughness of the film. The surface of this film was covered with particles approximately 130 nm in diameter and had a root mean square (RMS) roughness of 27.5 nm indicating that the film was relatively smooth.

### *C. Scale Up*

Scale up of the process was demonstrated by thallination of several precursor films prepared on 2 inch X 1 inch rectangular and 3 inch diameter $LaAlO_3$ wafers. Using similar conditions to those yielding the results described above for films prepared on smaller substrates, 2212-TlBaCaCuO thin films on 2 inch X 1 inch rectangular wafers with an inductive $T_c$ of 101 K were readily prepared. Further work on optimizing the scale up process is in progress.

## IV. Conclusions

The flow-through multiple-zone thallination process has been demonstrated for the fabrication of smooth 2212-TlBaCaCuO thin films on (100) $LaAlO_3$. The $T_c$ of the films of 107.6 K is comparable to the highest $T_c$ previously reported for thin films of this phase. While the $J_c$ at 77 K of 1.3 X $10^5$ A/cm$^2$ and $R_s$ of 1.3 mΩ at 10 GHz and 80 K are somewhat degraded compared to the best values previously reported, we anticipate that further process optimization will eventually yield films with comparable properties. Initial results indicate that scale up of the new process is relatively straightforward, and fabrication of films on three-inch diameter wafers has been demonstrated. Anticipated advantages of this process over other thallination processes include enhanced run-to-run and areal uniformity, decreased processing time, and the potential for its scale up to very large wafer areas or even multiple wafer processing.

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