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MOCVD SYNTHESIS OF THALLIUM SUPERCONDUCTOR MATERIALS

FINAL TECHNICAL REPORT
JULY 31, 1990

Contract Period: July 25, 1989 to Feb. 28, 1990 Cp
Contract No: N00014-89-C-0111
ARPA Order No: 6912

Prepared for: OFFICE OF NAVAL RESEARCH
Code 9E20
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ONR/Code 1131F
TELECON 8/14/90 VG

Section I
REPORT SUMMARY

Superconducting films of $Tl_2Ba_2Ca_1Cu_2O_x$ were produced on Al_2O_3 and $LaAlO_3$ substrates via a two step process. Initially, an oxide precursor containing barium, calcium, and copper was deposited by either MOCVD or a chemical deposition process. Subsequently, thallium was added to the precursor by vapor transport from a solid source in order to form the superconducting phase. The chemical, physical, and superconducting properties of the resultant films were characterized. The quality of the films obtained from the two types of precursors appears to be equivalent. Highly c-axis oriented films of the 2212 phase were prepared on both substrate types. The best films exhibited a zero resistance T_c of 98 K and critical currents of nearly 10^4 A/cm^2.

The results demonstrated in this report are among the best obtained anywhere for a two-step process in which thallium is added to a non-thallium containing precursor. They are indicative of remarkable progress in a relatively short period of time. Although the values we have reported do not represent the best values reported to date for thin film thallium HTSC materials, the chemical deposition technology developed as an ancillary method for producing precursor films not only yielded excellent reproducibility but is a scalable technology that could be economically applied to a number of applications including large-area coatings for interconnects, cavities, shielding, and conductors.

MOCVD offers a great deal of potential for the in-situ deposition of high-quality Tl-HTSC films. As this preliminary study of the tri-component deposition process has demonstrated, difficulties pertaining to the stability and reproducibility of both the barium and calcium sources need to be resolved. However, direct deposition of the four-component oxides offers the best possibility of preparing fully superconducting films, as grown, with a quality comparable to the highest-quality YBCO films produced by this method. Funding for the extension of this program, along with support for the development of dedicated equipment, should be continued.

Section II
STATUS / ACCOMPLISHMENTS

A. PROGRAM OBJECTIVES

The objective of this study was to develop metal-organic chemical vapor deposition (MOCVD) process technology for the preparation of thallium-containing HTSC films. Initially formulated as a six-month study, this program focused on the deposition of a three-component calcium-barium-copper-oxide precursor film and subsequent thallium addition. Subsequently, with appropriate funding, we had hoped to extend the current work leading to the development of an in-situ process for production of thallium HTSC films. The objective of the first phase of the study was to initiate development of an MOCVD process for producing thallium HTSC films by: (1) preparing a tri-component oxide precursor film containing barium, calcium, and copper; (2) addition of thallium to the precursor film; and (3) demonstration of a set of target film properties including a zero-resistance critical temperature, T_c, of 100 K and a critical current value, J_c, of 10,000 Amps/cm^2.

The current research program consists of three parts: (1) development of the MOCVD process for the preparation of tricomponent oxide precursor films; (2) addition of thallium and conversion to the superconducting phase; and (3) characterization of the chemical and superconducting properties of the samples. The appropriate characterization of both the precursor and thallium-containing films will be discussed in the pertinent sections.

B. MOCVD SYNTHESIS PROCESS DEVELOPMENT

MOCVD is an extremely useful and versatile technique that has been successfully employed in the growth of many complex materials such as III/V compounds, optoelectronic materials, and magnetic bubble memory material. Advantages of the method include the ability to cover large surface area with a high degree of uniformity and reproducibility. Recently, excellent results on the in-situ preparation of fully oxygenated YBCO films have been reported by several groups. Zhao *et. al.* (Appl. Phys. Lett. **56** , 2342-2344) described the growth of fully oxygenated YBCO films at substrate temperatures as low as 570°C using a PE-MOCVD technique using plasma-activated nitrous oxide as the reactant gas. Yamane and co-workers (Appl. Phys. Lett. **53**, 1548-1550) utilized more conventional MOCVD technology and substrate temperatures in excess of 800°C to prepare high-quality YBCO films.

Two variations of the MOCVD technique, without plasma activation, have been commonly employed for the synthesis of YBCO HTSC thin films. The atmospheric pressure method employs volatile fluorinated metal chelate compound such as the hexafluoro-2,4-pentanedione (hfacac) complexes. The decomposition of the fluorinated ligand leaves a residual amount of fluoride ion that must be removed by treating the samples with water vapor and oxygen at elevated temperatures. The low-pressure (vacuum) process utilizes the tetramethyl-heptanedionate (tmhd) metal source materials. For the YBCO compound, a further oxygenation step is required in order to overcome the negative effects of the vacuum on the oxygen content of the material, unless a source of activated oxygen is present during the deposition of the YBCO film.

The system that we have utilized for these experiments, combines the advantages of both of the previous methods. By operating in a reduced pressure oxygen/argon atmosphere, it is possible to utilize the less volatile metal tetramethyl-heptanedionate source materials and still obtain a fully oxygenated product. A diagram of the EMCORE Series 5000 MOCVD reactor as it is normally configured for deposition of YBCO films is shown in Fig. B-1. In this work, the initial step was to modify the system in order to replace the yttrium source with a calcium source for the deposition of the tricomponent oxide precursor films.

The system incorporated a resistance-heated, high-speed (0-2000 rpm) rotating disk in a vertical cylindrical cold wall growth chamber. The internal components of the reactor were chosen for their resistance to high-temperature oxidation. The 5-in.-diameter wafer carrier was configured to allow simultaneous growth on multiple substrates.

SYSTEM 5000 DIAGRAM

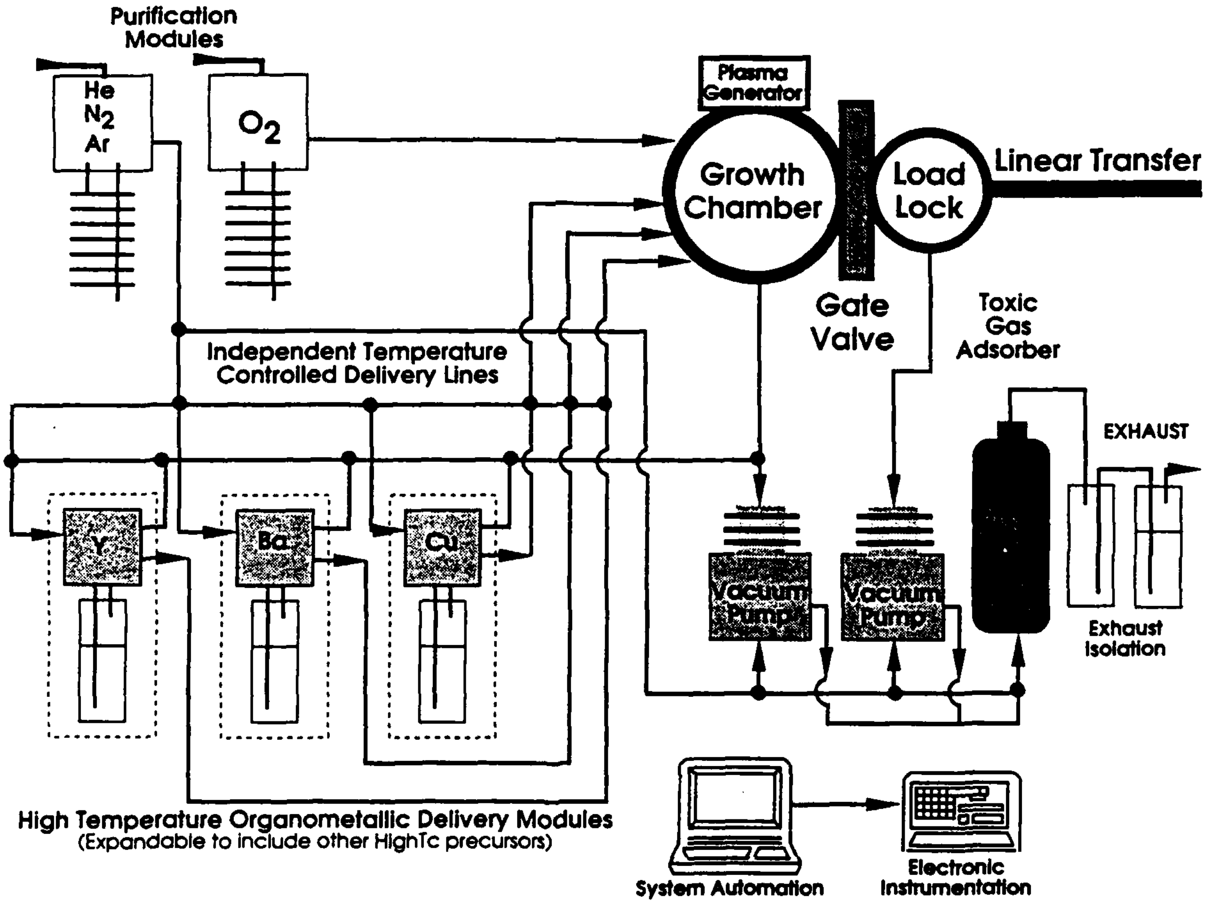


Figure B-1 EMCORE MOCVD Reactor

The three precursors were transported, by N_2 carrier gas to individual dividing flow manifolds (injectors) mounted 120° apart. The separate injector arrangement for each source was chosen to minimize the possibility of gas phase reactions and to give additional degrees of freedom or optimizing compositional uniformity. The precursors were uniformly injected through small holes on the injector tubes at a speed of about 200 m/min. The high velocity injection of precursors significantly reduced prereactions. Thus resulting in a significant improvement in deposition efficiency. The vapor sources (bubblers) were configured for vent/run operation, which allows for pressure-balanced operation.

Among the conceivable volatile metalorganic precursors for HTSC MOCVD, metals- diketonates are attractive since they are easily synthesized, purified, and handled in air. The b-diketonate complexes $Ca(tmhd)_2$, $Ba(tmhd)_2$, and $Cu(tmhd)_2$ were used as calcium, barium, and copper precursors, respectively. The bubblers for the copper and calcium sources were specially designed to yield a constant mass transport rate since the precursors are solid at these temperatures. $Ba(tmhd)_2$ is the only known nonfluorocarbon-based β diketonate complex, which has a significant volatility. However, $Ba(tmhd)_2$ partially decomposed during the evaporation process, which caused its vapor phase concentration to drop as a function of time at a constant source temperature. An apparatus for adding vapors of the tetramethyl-heptanedionate ligand to the carrier gas was developed to stabilize the evaporation rate of $Ba(tmhd)_2$ so that its vapor pressure remained constant. All transport lines and valves were maintained about 10°C above the bubbler temperature to avoid precursor condensation and decomposition in the gas transport system.

Deposition was carried out at a system pressure of 10 Torr and substrate temperature of 500°C-600°C with a rotation speed of 1100 rpm. The film deposition rate was controlled at 0.5-1μ/h, and the films were up to 1.0-μ thick. After deposition, the films were slowly cooled to 100°C under 1 atm of oxygen.

Deposition temperatures were measured by a thermocouple that directly contacted the substrate and were frequently checked by a pyrometer. Energy-dispersive X-ray spectroscopy (EDX) and electron probe microanalysis were utilized to determine the composition of the films. The proportions of Ca, Ba, and Cu were adjusted to match the measured composition of known standard samples. Scanning electron microscopy (SEM) was used to examine film morphology.

As reported previously, the initial CaO growth runs were conducted using 2-in.-diameter silicon wafers. Six MOCVD growth runs of CaO were performed. Each run took from 0.6 to 3.0 h and contained from 1 to 3 wafers. The substrate temperatures were varied from 600°C to 700°C, and the Ca(tmhd)$_2$ source temperatures ranged from 180°C to 245°C. White shiny CaO films were formed in-situ on the silicon wafers. Uniform coatings were deposited over a 1-in.^{2} area of 0.7-μ thickness. The thickness deviation over the entire 2-in.^{2} diameter wafer was +/- 0.1 μ.

From 11/9/89 to 11/16/89 and 1/21/90 to 2/9/90, 17 runs were performed. Oxides of Ba, Ca, and Cu were deposited on 2-in. sapphire wafers. Energy dispersive X-ray spectroscopy indicates that the three elements were present in the films. The as-deposited films looked dark brown.

However, the uniformity over 2-in. wafers was not good. Significant efforts were then focused on improvements of the uniformity across 2-in. wafers. Systematic adjustment of the position and angles of the three injector tubes for Ba, Ca, and Cu did not result in significant improvement. The main cause of the non-uniformity was identified as the aerodynamic interference among the gas flows from three sources. We then combined Cu and Ba injector tubes to form a single tube so that the number of injector tubes were reduced to two. The uniformity of Ba and Cu, which were premixed and injected through a single tube was greatly improved over 2-in. wafers. Evidently, Ca should also be combined with the Ba and Cu injector tube prior to entering the deposition chamber to improve Ca uniformity across the 2-in. wafer. However, due to the cost and time limitation, such effort was left to the Phase II program. Since the uniformity over 1 cm^2 substrates was very good, we then focused on growth of 1 cm^2 substrates in order to achieve the required stoichiometry.

Twenty-seven growth runs were performed to achieve the desired composition and desired thickness. The growth temperature was varied from 500C to 700°C. Ten runs were grown for over 3 h to reach the thickness of about 1 μm with composition close to 223 or 212 (Ba/Ca/Cu). The wafer carrier used for those runs was specifically designed for simultaneous growth of six 1 cm^2 samples and was fully loaded with Al_2O_3 and $LaAlO_3$ substrates. In addition, the new wafer carriers are platinum-coated to reduce possible contaminations.

A summary of the EDAX results obtained on the precursor films is shown in Table 1. Samples from the later runs were used to prepare superconducting films.

TABLE I
SUMMARY OF EDAX RESULTS

Sample	Spot 1			Spot 2			Spot 3			Comments
	Ba	Ca	Cu	Ba	Ca	Cu	Ba	Ca	Cu	
EMC 29	2.0	1.4	12.2	2.0	1.5	12.0	2.0	1.5	12.0	Al_2O_3
EMC 30	2.0	1.1	6.6	2.0	1.1	6.6	2.0	1.1	6.8	Al_2O_3
EMC 31	2.0	0.7	7.2	2.0	0.7	7.2	2.0	0.7	7.2	Al_2O_3
EMC 32	2.0	1.0	4.5	2.0	0.9	4.5	2.0	0.9	4.4	Al_2O_3
EMC 35	0.2	1.9	3.0	0.2	1.9	3.0	0.2	2.0	3.0	Al_2O_3
EMC 36	0.5	1.6	3.0	0.5	1.5	3.0	0.5	1.4	3.0	Al_2O_3
EMC 37	0.7	3.9	3.0	0.7	3.5	3.0	0.8	3.7	3.0	Al_2O_3
EMC 38	2.0	2.3	2.9	2.0	2.2	3.0	2.0	2.1	2.9	Al_2O_3
EMC 39A	1.4	2.4	3.0	1.4	2.3	3.0	1.5	2.2	3.0	Al_2O_3
EMC 39B	1.5	2.3	3.0	1.5	2.4	3.0	1.4	2.2	3.0	Al_2O_3
EMC 39C	1.5	2.4	3.0	1.4	2.2	3.0	1.4	2.4	3.0	Al_2O_3
EMC 40	0.2	1.3	3.0	0.1	1.3	3.0	0.2	1.2	3.0	Al_2O_3
EMC 42	12.4	1.3	3.0	17.5	1.3	3.0	13.0	1.4	3.0	Al_2O_3
EMC 43	2.0	2.9	2.0	2.0	2.8	2.0	2.0	2.8	2.0	Al_2O_3
EMC 44	2.0	1.6	0.5	2.0	1.6	0.5	2.0	1.5	3.1	Al_2O_3
EMC 45	2.0	1.6	3.1	2.0	1.5	2.9	2.0	1.5	3.1	Al_2O_3
EMC 46	--	--	--	2.0	1.5	2.9	2.0	1.5	3.1	Al_2O_3
EMC 47	2.0	2.0	3.7	2.0	2.0	3.8	2.0	2.0	3.8	$LaAlO_3$
EMC 48	2.0	2.2	3.4	2.0	2.7	4.0	2.0	2.7	4.0	Al_2O_3
EMC 49	2.0	2.5	3.1	2.0	2.5	3.2	2.0	2.5	3.0	$LaAlO_3$
EMC 50	2.0	2.4	3.5	2.0	2.5	3.6	--	--	--	$LaAlO_3$
EMC 51	2.0	3.4	4.2	3.2	4.2	2.0	2.0	3.2	4.2	Al_2O_3
EMC 52A	2.0	1.7	2.2	2.0	1.7	2.1	2.0	1.7	2.0	$LaAlO_3$
EMC 52B	2.0	1.8	2.3	2.0	1.7	2.3	2.0	1.8	2.3	Al_2O_3
EMC 53A	2.0	1.5	2.0	2.0	1.5	2.0	2.0	1.5	2.0	$LaAlO_3$
EMC 53B	2.0	1.5	2.0	2.0	1.5	2.0	2.0	1.6	2.0	$LaAlO_3$
EMC 53D	2.0	1.6	2.2	2.0	1.6	2.1	2.0	1.6	2.1	Al_2O_3
EMC 54A	2.0	1.9	2.4	2.0	1.9	2.3	--	--	--	$LaAlO_3$
EMC 54B	2.0	1.8	2.5	2.0	1.9	2.4	--	--	--	Al_2O_3
EMC 55	2.0	1.5	2.4	2.0	1.6	2.4	2.0	1.5	2.4	Al_2O_3

C. POST-SYNTHESIS ANNEALING

The thallium annealing furnace was assembled from a single zone tube furnace with a modified quartz tube as shown in Fig. C-1. The end caps of the 2-in.-diameter quartz tube were modified for oxygen gas entry and exit and for accommodation of a quartz push rod. With the push rod, it was possible to rapidly move the sample into and out of the hot zone while minimizing release of the thallium vapor. The out-flowing gases were scrubbed with a 1.0 N NaOH solution, which was changed after approximately every 25 runs. Extensive air-sampling testing indicated that no thallium vapors were released to the air during the normal experimental procedure. The samples were contained in a quartz capsule 3 in. in length and 1.5 in. in diameter. The capsule provided a semi-stagnant zone to contain the thallium vapors in the vicinity of the samples while providing access to the oxygen atmosphere. In addition, the capsule provided a large reproducible thermal mass to facilitate reproducible heat transfer when several samples were fired simultaneously. An enlarged view of the capsule assembly is shown in Fig. C-2.

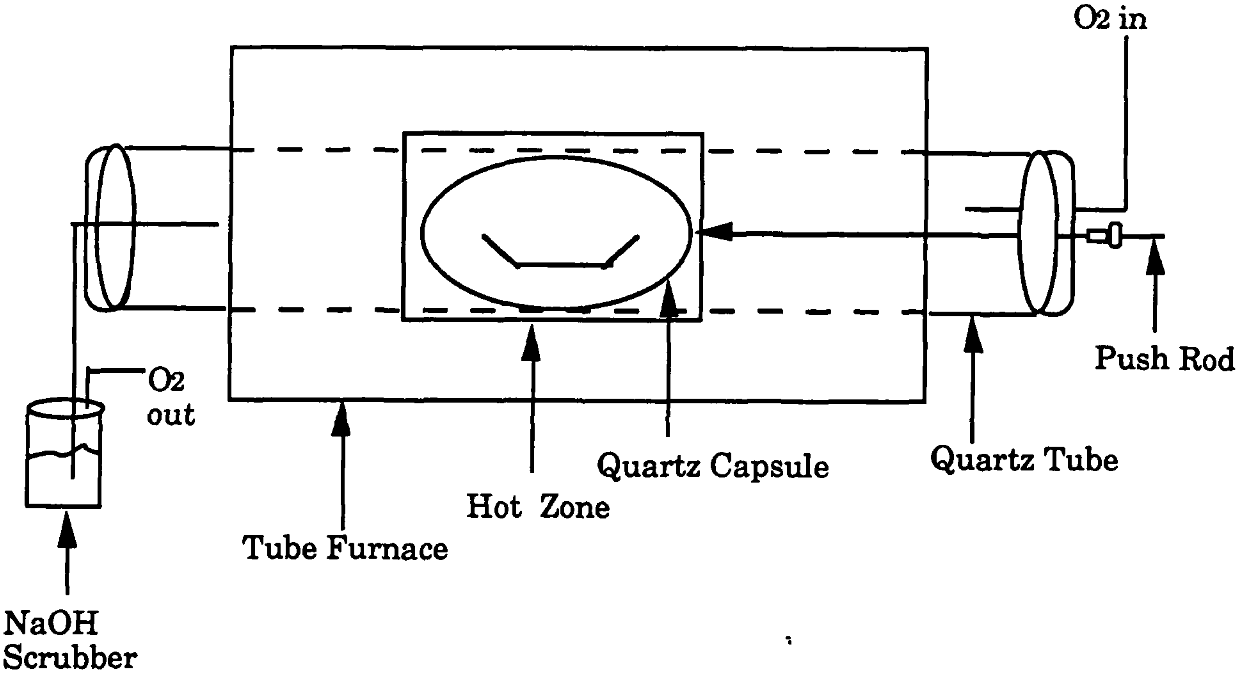


Figure C-1 Diagram of thallium annealing furnace assembly.

Thallium Incorporation Methods

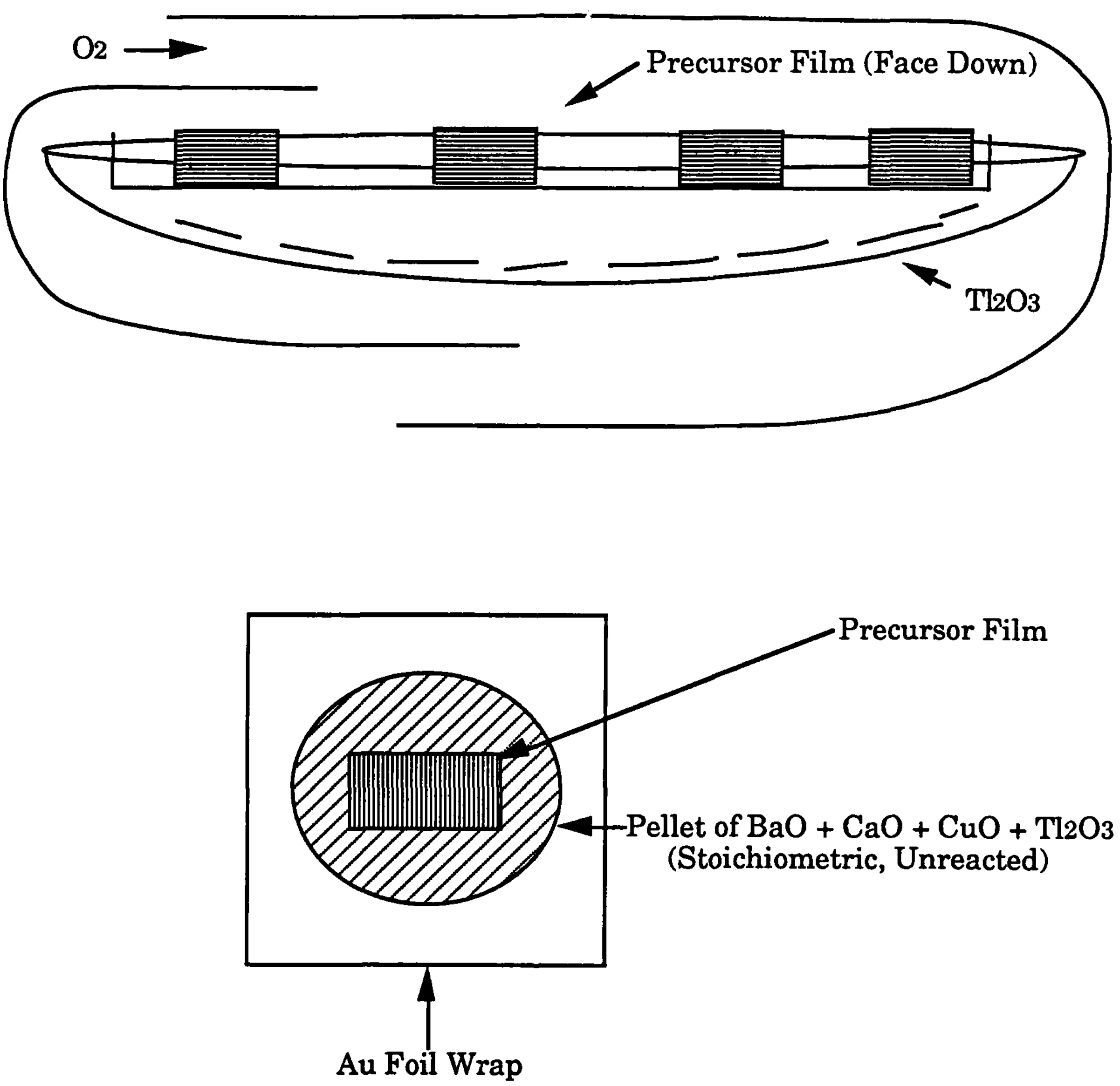


Figure C-2 Thallium incorporated methods.

Two different thallium incorporation methods were employed. In the first method, thin film samples were placed oxide-side-down resting on the grooved edges of either quartz or alumina boats. A bed of 0.25 g of Tl_2O_3 or 1.0 g of Tl-HTSC powder was placed on the bottom of the boat. Alternatively, the precursor film was placed oxide-side-down atop a pellet composed of either a stoichiometric reactant mixture of the Tl-HTSC component oxides, a blended mixture of Ba and Cu cuprates and thallium oxides, or reacted Tl-HTSC. The pellet sandwich was wrapped in gold foil. Both of the arrangements were then loaded into the quartz capsule and inserted into the cold end of the furnace tube.

Detailed temperature profiling studies indicated that the furnace required three hours at temperature in order to attain maximum reproducibility from run to run. This is due to the fact that small tube furnaces tend to overshoot the temperature settings during rapid heat-up with the complication of localized hot spots. In the thallium system, four different compounds have been shown to be stable within a 25° temperature range. Therefore, careful reproducible temperature control is necessary. The quartz tube was thoroughly flushed with oxygen, flowing at 1-5 cfm, for 1 h prior to the introduction of the quartz capsule into the hot zone. Studies with a thermocouple inserted into the capsule assembly indicated that 6 min. were required for the internal temperature of the capsule to stabilize to a delta value of ± 0.1°C in the range of 800°C-900°C. If the furnace temperature was at equilibrium, then there was no tendency for the internal temperature to exceed the target value. Processing times were varied from 3 to 60 mins. The majority of the tests were conducted with 6 to 10-min firing times. Superconducting films were obtained in the temperature window of 865°C-880°C using 6 to 10-min. firing times.

Bulk material was used during the thallium addition step as the source of thallium in the vapor phase. The use of thallium oxide alone did not provide satisfactory results. Later studies utilized compacted pellets consisting of blended, unreacted component oxides (or peroxides) in either the 2223 or 2212 stoichiometric mixture, fully reacted 2212 bulk material, or mixtures of Ba and Cu cuprates and thallium oxide. The best results were consistently obtained using the unreacted pellets.

In order to facilitate the development of the thallium addition step while the MOCVD process for the tricomponent oxide was being optimized, precursor films obtained via a chemical deposition process developed at Sarnoff were utilized. A flow diagram for the chemical deposition process is depicted in Fig. C-3.

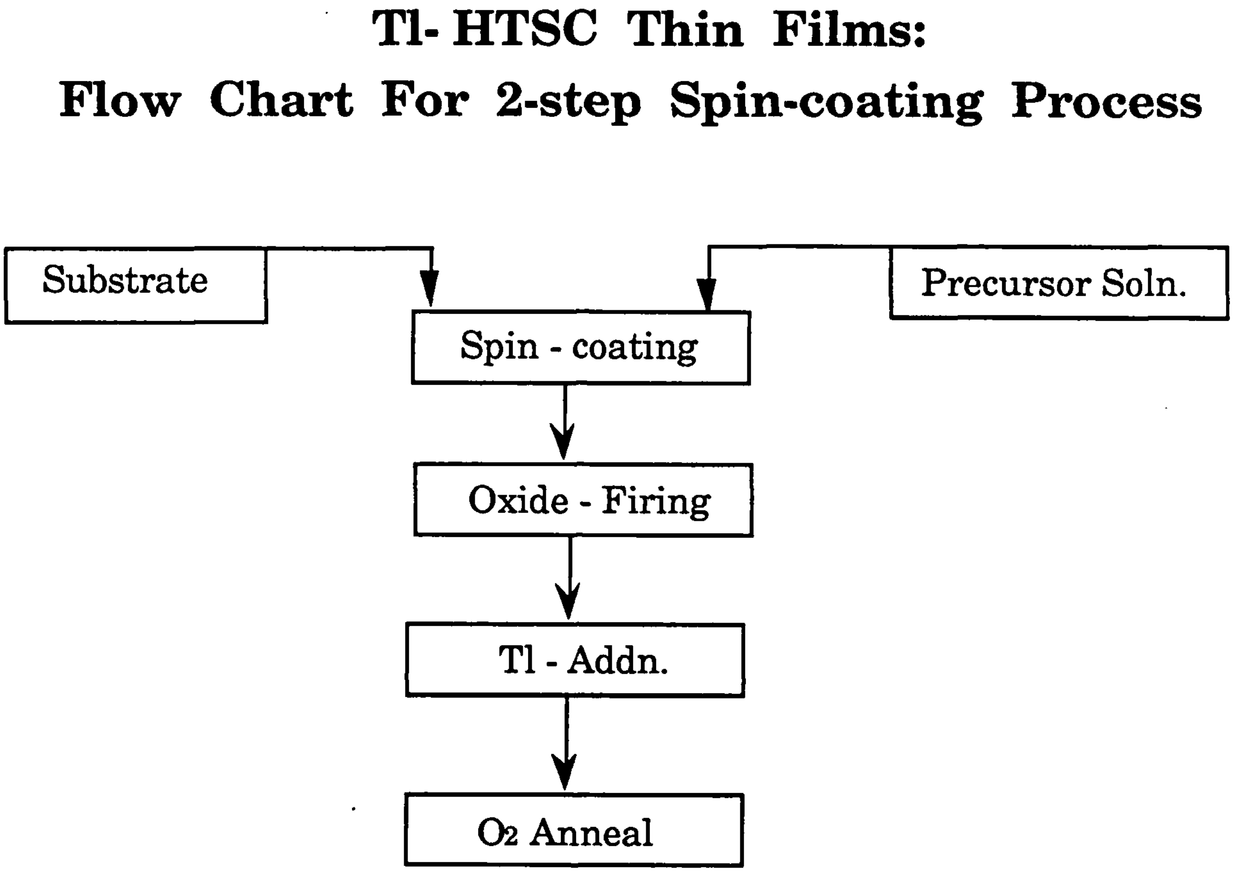


Figure C-3 Process diagram.

Organometallic complexes of barium, calcium, and copper were dissolved in $CHCl_3$ to provide a total metals concentration of approximately 0.875 M in the solution. This concentration gave an excellent viscosity for spin-coating onto a variety of substrates including $LaAlO_3$ (100), Al_2O_3 $(1\underline{1}02)$, and MgO (100). Fifteen coats of the organometallic solution resulted in a 1-μ-thick coating of the tricomponent oxide after a carefully controlled thermal decomposition. The metals ratios were formulated to provide either 212 Ba/Ca/Cu or 223 compositions using weights of reagents calculated for the individual organometallics based on TGA data. Some compositional differences between the organometallic and oxide films were noted. In general, the loss of both barium and copper are observed for films deposited on sapphire. Copper is lost from the films due to evaporation of copper oxide. Barium is lost to the substrate due to the formation of barium aluminate at the interface. On lanthanum aluminate substrates, only the copper changes appreciably. Combined metal loss may be on the order of 15%. In addition to the changes in the overall composition, there are also nonuniformities created by segregation of individual elements into discrete phases such as barium cuprate and calcium cuprate. Despite these difficulties, smooth and shiny precursor films were produced which demonstrated excellent adherence to all three substrates and proved quite suitable for further studies on thallium incorporation.

Using the thallium incorporation procedure described above, over 110 samples were prepared during the contract period. The entirety of the early work employed the chemically deposited precursor films, due to the unavailability of MOCVD precursors with the correct stoichiometry. Although as much as 50% 2223 phase (by XRD) was observed in some of the higher temperature firings, several factors caused us to optimize our process for the lower T_c 2212 phase. The film quality defined by appearance, adhesion, and physical characteristics were superior for the 2212 films. In addition, it appeared that it would be difficult to simultaneously and reproducibly generate sufficiently high levels of barium and calcium in the MOCVD reactor while simultaneously maintaining control over the composition. The formation of the 2212 phase occurs over a much broader compositional range.

1. X-ray Diffraction Analysis of Films

C-axis oriented, phase pure 2212 films were prepared on $LaAlO_3$ (100) substrates as evidenced by the XRD spectrum shown in Fig. C-4. Similar results were obtained for the Tl-HTSC films derived from MOCVD prepared tri-component oxide precursor films. However, due to deviations of the film composition from the theoretical stochiometry, an additional line due to the 100% intensity peak of CaO is observed in the XRD spectrum shown in Fig. C-5. The formation of highly oriented films of the 2212 Tl-HTSC phase on (1102) Al_2O_3 substrates has also been demonstrated, as shown in Fig. C-6. The degree of orientation is not as high on the sapphire substrate as observed for films deposited on lanthanum aluminate substrate. Diffraction intensity corresponding to the (107) line at 32° two theta is observed in the XRD spectrum. In addition

BC C-0330-D Tl-Ba-Ca-Cu-O film / LaAlO3 2.50

2-Theta	Range	Step	h k l	Xr/Flt	kV	ma	Entrance	Exit
4.00	61.00	.020	1 0 0	Cu/ Ni	30	30	1.00:1.00	1.00: .150

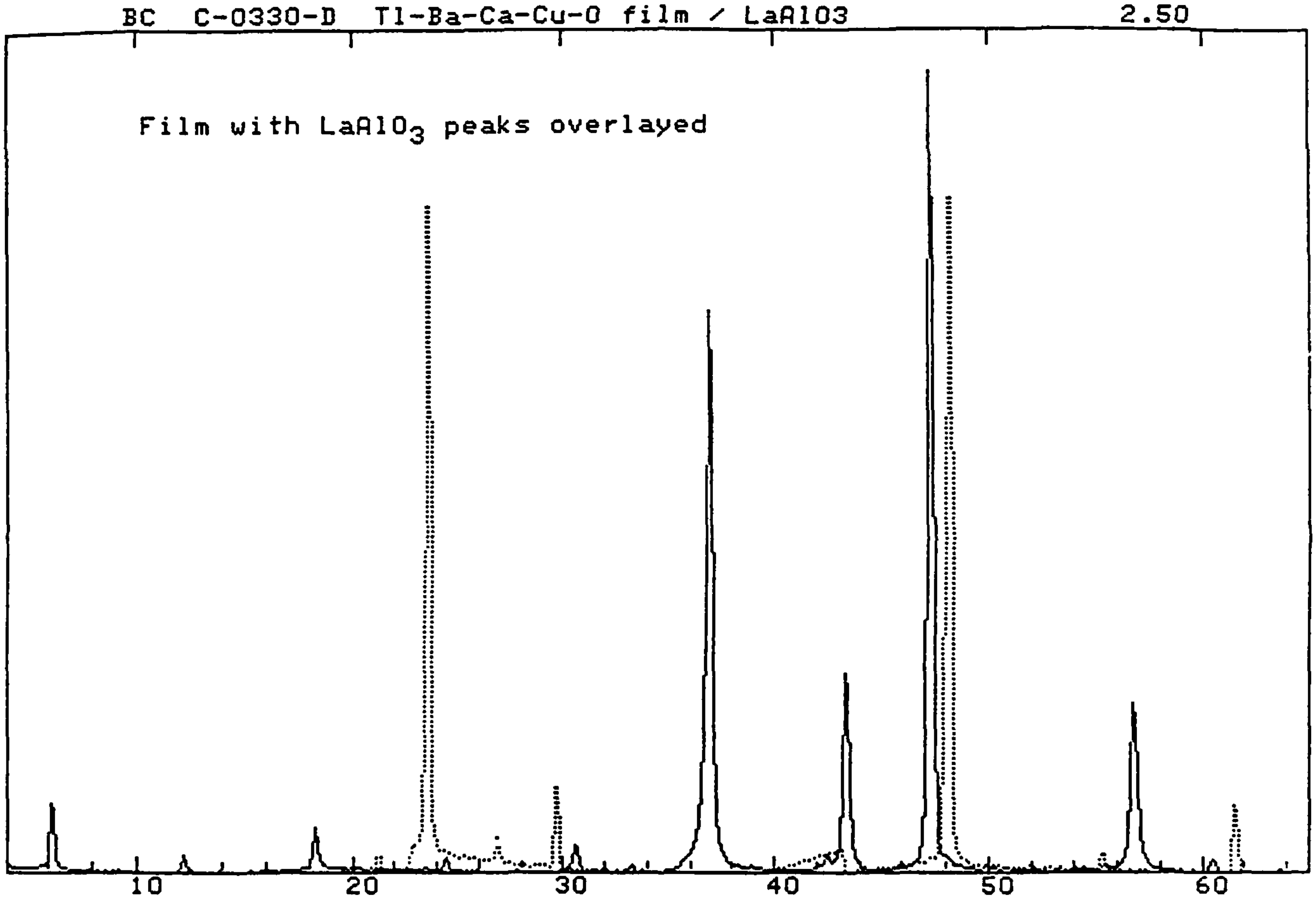


Figure C-4 XRD spectrum of 2212 Tl-HTSC film on LaAlO$_3$ (100) substrate.

EMC 53 Tl2 Ba2 Ca Cu2 O8 film on LaAlO3

2-Theta	Range	Step	h k l	Xr/Flt	kV	ma	Entrance	Exit
5.00	60.00	.020	1 0 0	Cu/ Ni	30	30	1.00:1.00	1.00: .150

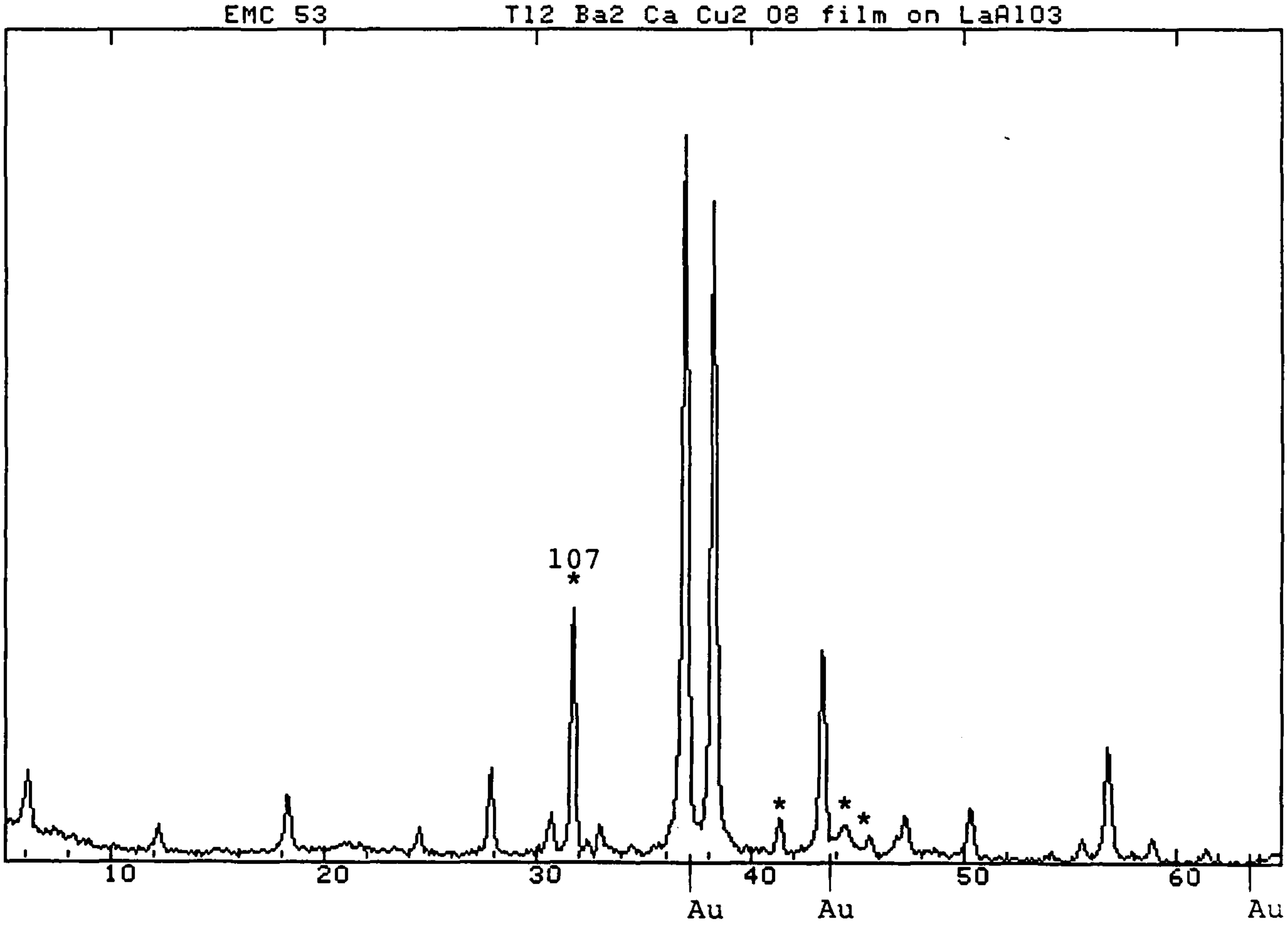


Figure C-5 XRD spectrum of 2212 phase on $LaAlO_3$ from MOCVD precursor.

BC C-0323-A Tl-Ba-Ca-Cu-O film / Al2O3 2.0

2-Theta	Range	Step	h k l	Xr/Flt	kV	ma	Entrance	Exit
4.00	61.00	.020	1 0 0	Cu/ Ni	30	30	1.00:1.00	1.00: .150

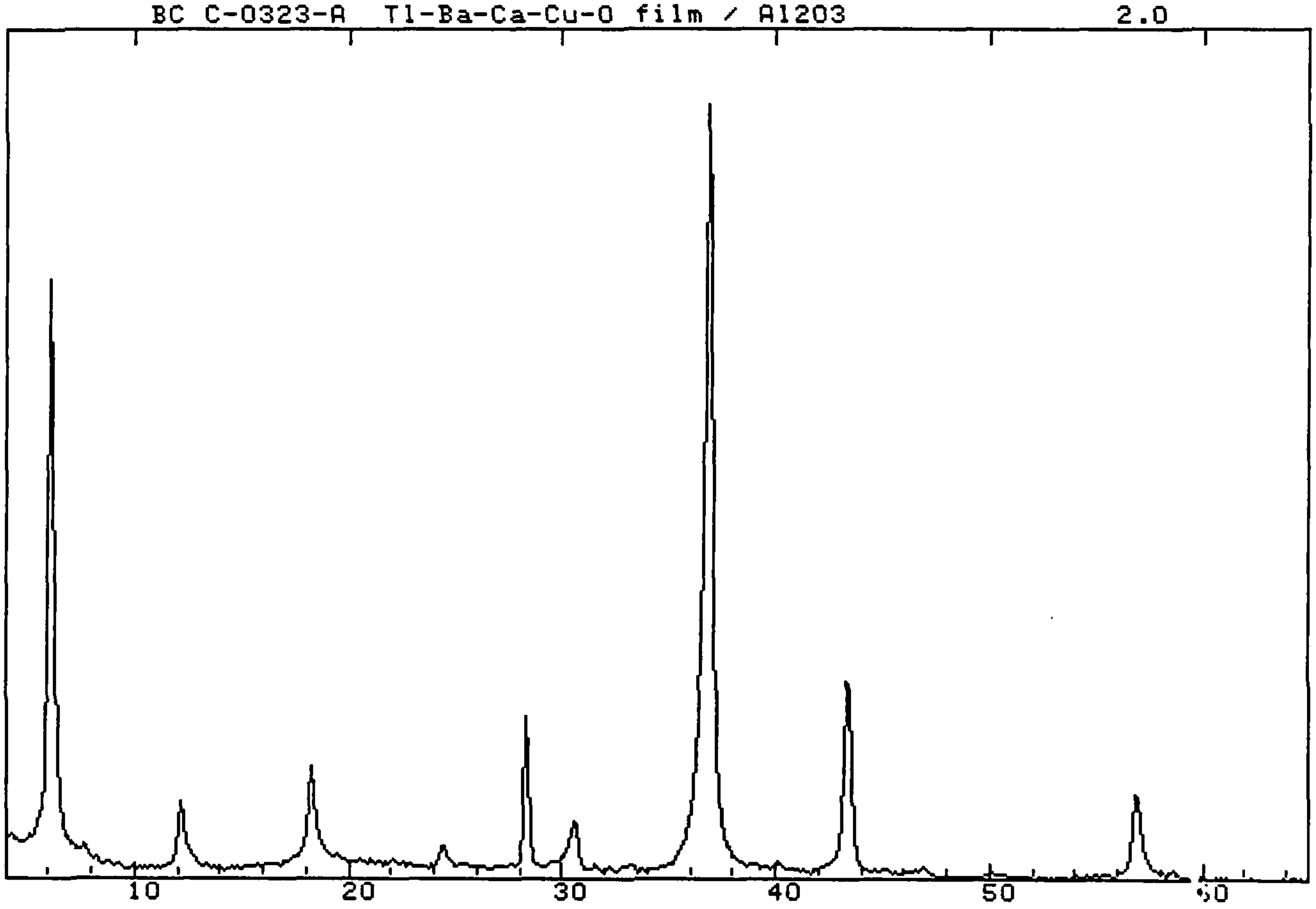


Figure C-6 XRD spectrum of 2212 Tl-HTSC on $(1\bar{1}02)$ sapphire substrate.

peaks corresponding to the two strongest intensity lines in the $BaAl_2O_4$ pattern are evident.

The degree of c-axis orientation of the film is only a qualitative measure. The in-plane orientation of the individual grains of the film is important due to the highly anisotropic nature of the high-temperature cuprate superconducting compounds. As the number of high-angle grain boundaries (i.e, misorientation of the grains within the a-b plane) increases, the ability of the film to carry high currents diminishes. One of the methods used to assess the degree of in-plane orientation of thin films is the X-ray rocking curve measurement. For nearly epitaxial films on single crystal substrates, peak widths on the order of 0.2 to 0.3 degrees are obtained. The results obtained for two superconducting thallium films, one on Al_2O_3 $(1\bar{1}02)$ and the other on $LaAlO_3$ (100), are shown in Fig. C-7.

BC C-0420-C Tl-Ba-Ca-Cu-O film / Al2O3 RkCv @ 36.850

2-Theta	Range	Step	h k l	Xr/Flt	kV	ma	Entrance	Exit
18.00	40.00	.020	1 0 0	Cu/ Ni	35	35	.30: .30	.10: .018

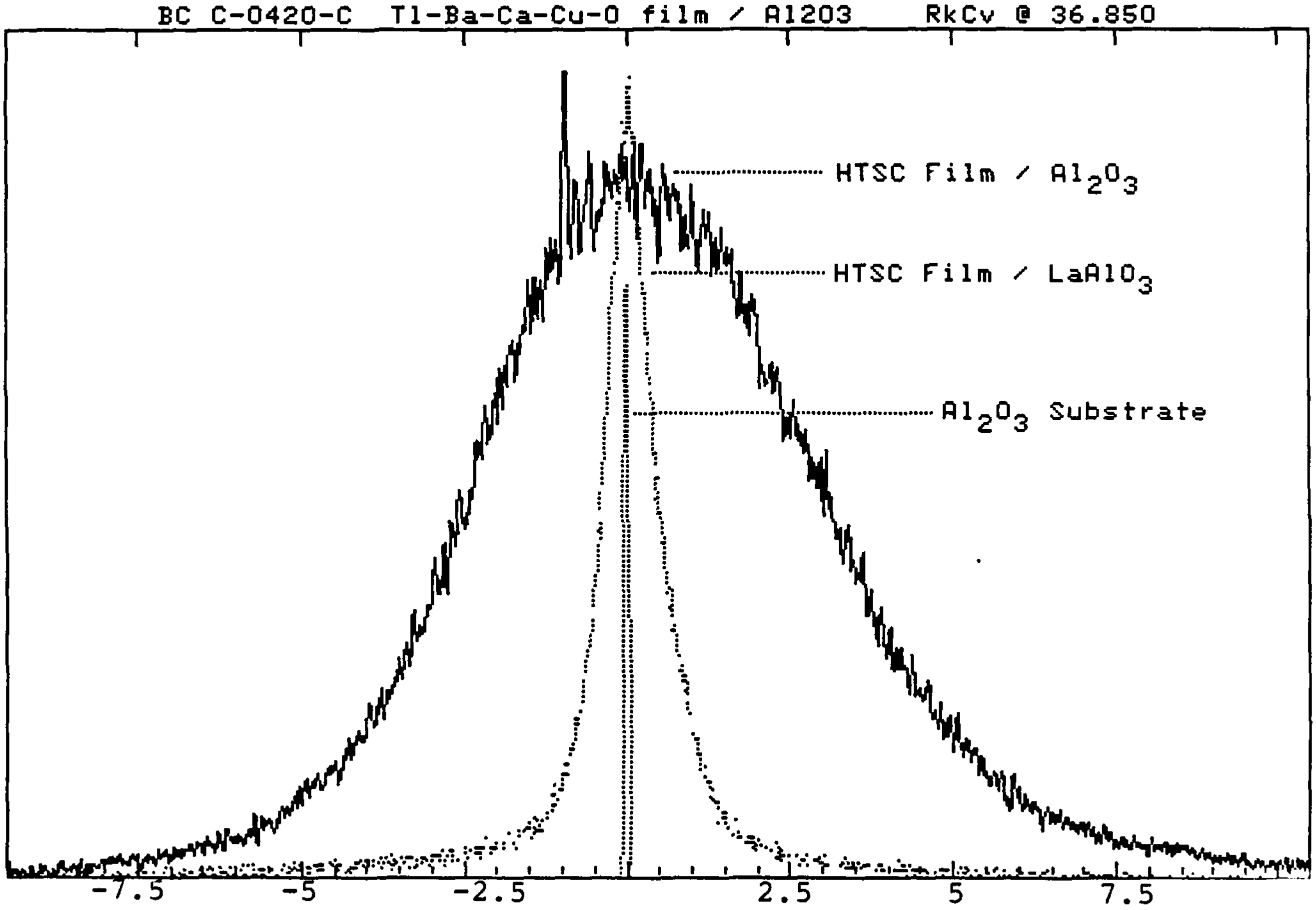


Figure C-7 X-ray rocking curve measurement for Tl-2212 films on $LaAlO_3$ and Al_2O_3.

The breadth of the 38.5° peak in the 2212 pattern, calculated by finding the width of a rectangle with the same height and area as the peak, was a slightly greater than 1° on $LaAlO_3$ and over 6° on Al_2O_3. The larger value obtained on sapphire is a reflection of the larger degree of mismatch between the substrate and the film. The large rocking curve width of the peaks on $LaAlO_3$, compared to the theoretical value pf 0.2° for an epitaxial film on a single crystal substrate may be due in part to the twinning of the substrate which occurs during processing. Fig. C-8 graphically illustrates the point by showing the splitting of a substrate reflection peak overlayed with a reflection from the Tl-HTSC film. The splitting of the reflection indicates that the diffracted intensity originates from a number of very slightly misaligned crystallites within the substrate. Twinning of the substrate is visibly evident after processing and remains a serious problem associated with the use of $LaAlO_3$ substrates.

BC C-0430-C Tl-Ba-Ca-Cu-O film / LaAlO3 RkCv @ 36.850

2-Theta	Range	Step	h k l	Xr/Flt	kV	ma	Entrance	Exit
33.85	6.00	.004	1 0 0	Cu/ Ni	30	30	.30: .30	.10: .018

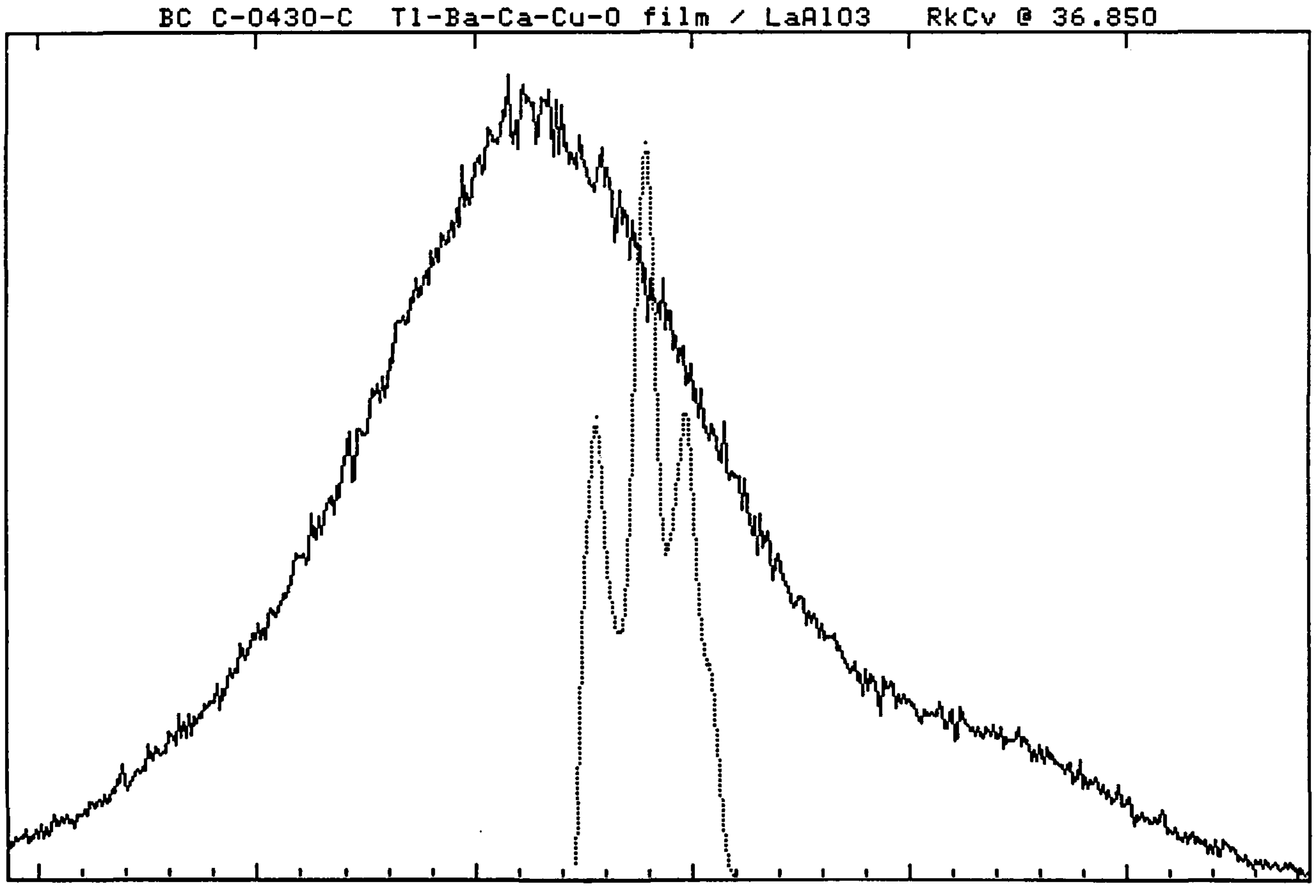


Figure C-8 Splitting of La AlO_3 diffraction peaks.

2. Compositional Analysis and Morphology of Films

The compositional uniformity of both the precursor films and the films obtained after thallium addition was characterized via electron microprobe analysis and EDAX. In general, the precursor films produced by both MOCVD and Chemical deposition were quite uniform. The MOCVD precursors occasionally exhibited slight gradients in composition across the film; however, in the optimized deposition process these deviations tended to be less than 5% of the elemental composition. EDAX data for MOCVD films before and after thallium addition, obtained using a 50 μ by 50μ raster area, are shown in Table C-1 along with the calculated mole ratios normalized to Ba = 2.00. The composition of the precursors ranges from approximately 2/1.5/2 for Ba/Ca/Cu to 2/2/4. The individual variations within the films are slight. In contrast, a higher degree of variation is observed in the films after thallium addition. Deviations of up to 2 at% are observed in different areas of the same sample.

TABLE C-1

COMPARISON OF COMPOSITION BEFORE AND AFTER Tl ADDITION
(Spot 2 is in the center, Spots 1 and 3 are near edges)

	After Thallium Addition				Precursor		
	At %				At %		
	Ca	Ba	Cu	Tl	Ca	Ba	Cu
EMC-S3- Spot 1	17.75	25.98	23.91	21.82	25.64	35.02	33.85
Spot 2	16.37	26.93	25.32	20.79	25.95	35.10	33.95
Spot 3	16.49	27.21	25.02	21.68	25.58	34.96	34.38
(Mole Ratio)	(~1.21)	(2.00)	(1.84)	(1.59)	(1.46)	(2.00)	(1.97)
EMC-S2A-Spot 1	18.09	24.13	22.99	20.30	26.34	31.84	34.24
Spot 2	17.63	24.56	23.75	20.73	26.64	32.18	33.68
Spot 3	16.81	24.66	23.54	21.01	27.00	32.65	33.31
(Mole Ratio)	(~1.36)	(2.00)	(1.91)	(1.70)	(1.70)	(2.00)	(2.10)
EMC-47F-Spot 1	15.59	15.01	18.69	12.32	23.77	23.97	44.94
Al_2O_3 Spot 2	14.80	14.04	26.55	13.18	23.67	23.14	44.05
Spot 3	15.15	13.36	26.21	11.47	23.58	23.78	44.93
(Mole Ratio)	(~2.26)	(2.00)	(3.92)	(1.72)	(1.98)	(2.00)	(3.78)

Although the average compositions of the films suggest the presence of the 2212 and 2223 phases, only the 2212 is observed by XRD. An explanation for this is suggested by the examination of electron microprobe data obtained on three superconducting films and shown in Table C-2. Data were obtained using either a 1 μ or 20 μ spot size. Certain small areas of the film seem to be enriched in particular elements relative to the bulk of the film. In general, the pattern of enrichment corresponds to known compounds within the Tl-Ba-Ca-Cu-O phase field. Occasionally, the larger 20 μ spots exhibit large deviations in composition. For the most part, the data for the precursor film shown in Table C-3 are much more uniform, while that data for a non-superconducting film exhibits an extreme degree of variation. We therefore conclude that these differences are due to segregation effects which occur during the thallium incorporation step, which is almost certainly due to the presence of liquid phases during processing. The assertion is consistent with the observations that the best films are obtained using short processing times. The morphology of both the precursor films and the thallium-added films has been characterized by scanning electron microscopy. SEM photographs of Ba-Ca-Cu-O films deposited by either MOCVD or chemical deposition are shown in Fig. C-9. Both films consist of extremely fine grained (micron or smaller feature size) uniform structures. The MOCVD precursors are somewhat smoother and more uniform than those prepared by chemical deposition. The bright features on the surface of the MOCVD prepared precursor film are precipitates of excess copper oxide, similar to those observed on the surfaces of YBCO films grown by MOCVD.

Addition of thallium to the precursor film leads to a change in volume as the superconducting phase is formed. The cross-sectional views of a chemically deposited oxide precursor film, before and after thallium addition, are shown in Fig. C-10. Approximately a 40% reduction in the film thickness is observed. In addition, the porosity (holes and channels) observed in the precursor are absent in the film after thallium addition.

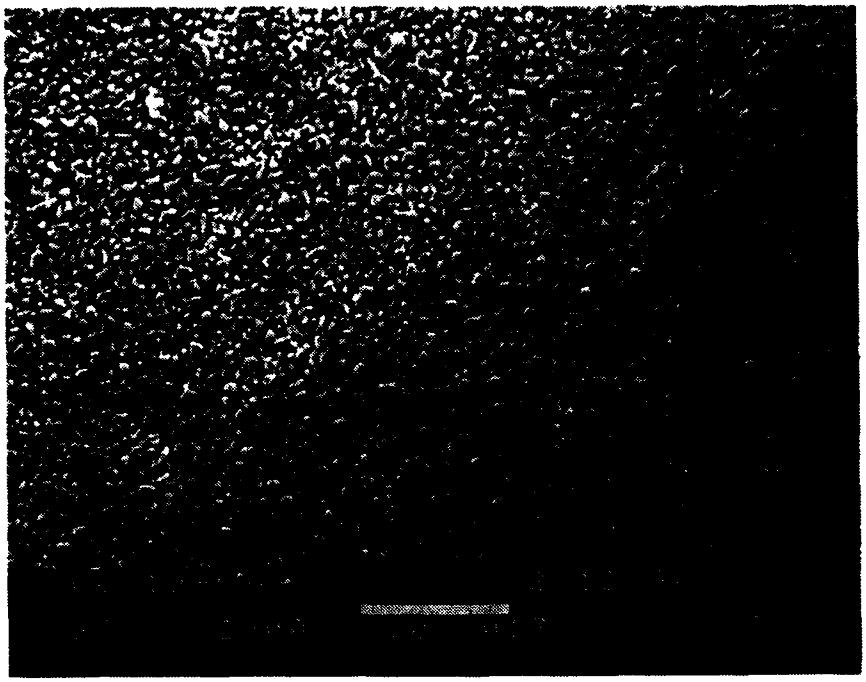
The surface structures of three Tl-HTSC films prepared by the two-step process utilizing MOCVD precursors are shown in Figs. C-11, 12, and 13. Common features include smooth overlapping platelets ranging in size up to roughly 5 μ in diameter along with an interpenetrated network of long, rectangular grains. The overall appearance of the films is highly reproducible and strongly dependent on processing conditions. The three films shown were all processed at 870°C for 6 mins.

TABLE C-2
ELECTRONIC MICROPROBE DATA FOR TL-HTSC SAMPLES

SAMPLE	AREA	SPOT SIZE, microns	SPOT NO.	TL	BA	CA	CU	
C0227-A	AREA A	1	1	3.6	2.0	2.9	3.1	
		1	2	3.3	2.0	2.6	2.8	
		1	3	4.8	2.0	4.6	2.5	
		1	4	4.7	2.0	3.7	2.4	
	AREA B	1	1	16.6	2.0	16.6	4.0	Ca2Tl2O5??
		1	2	4.7	2.0	5.3	5.8	
		1	3	6.1	2.0	4.9	2.5	
		1	4	4.0	2.0	3.4	1.6	
		1	5	18.4	2.0	18.7	3.4	Ca2Tl2O5??
	AVERAGE	20	1	7.1	2.0	6.2	4.6	
		20	2	6.9	2.0	16.0	29.9	CaCu2O3??
		20	3	4.7	2.0	3.7	2.9	
		20	4	3.3	2.0	2.4	2.4	
C0227-B	AREA A	1	1	2.1	2.0	5.2	2.7	
		1	2	1.9	2.0	4.3	2.6	
		1	3	2.1	2.0	2.0	3.4	
		1	4	2.1	2.0	4.6	3.5	
	AREA B	1	1	3.6	2.0	11.3	19.6	CaCu2O3??
		1	2	2.3	2.0	2.1	3.0	
		1	3	2.8	2.0	5.7	7.9	
	AVERAGE	20	1	2.2	2.0	5.7	6.6	
		20	2	1.4	2.0	4.1	1.4	
		20	3	2.6	2.0	2.6	4.5	
C0227-C	AREA A	1	1	2.2	2.0	3.4	2.8	
		1	2	3.0	2.0	9.1	12.5	???/
		1	3	2.5	2.0	7.1	7.3	
		1	4	2.1	2.0	2.7	3.1	
	AREA B	1	1	2.2	2.0	2.8	2.5	
		1	2	2.2	2.0	3.8	4.7	
		1	3	2.1	2.0	5.4	2.5	
		1	4	2.2	2.0	3.6	2.9	
	AVERAGE	20	1	2.1	2.0	5.5	4.3	
		20	2	2.1	2.0	5.1	4.2	
		20	3	2.1	2.0	4.1	2.9	
		20	4	2.0	2.0	5.8	4.4	
		20	5	2.0	2.0	4.9	3.8	
		20	6	2.1	2.0	4.8	3.8	
		20	7	2.0	2.0	5.1	3.8	
		20	8	2.3	2.0	5.5	4.8	
		20	9	2.1	2.0	4.7	3.3	
		20	10	2.1	2.0	4.6	3.1	

TABLE C-3
ELECTRON MICROPROBE DATA FOR TL-HTSC SAMPLES

SAMPLE	AREA	SPOT SIZE, microns	SPOT NO.	TL	BA	CA	CU
C0323-C (PRECURSOR)	AVERAGE	20	1	- - -	2.0	3.1	2.5
		20	2	- - -	2.0	3.2	2.9
		20	3	- - -	2.0	3.3	3.1
		20	4	- - -	2.0	3.2	3.1
		20	5	- - -	2.0	3.1	3.1
		20	6	- - -	2.0	2.7	3.0
		20	7	- - -	2.0	3.2	3.1
		20	8	- - -	2.0	3.1	2.8
		20	9	- - -	2.0	3.2	3.2
		20	10	- - -	2.0	3.2	2.9
C1026-3 (not SC FILM)	Area A	1	1	5.0	2.0	27.9	36.9
		1	2	0.6	2.0	0.4	0.8
		1	3	1.5	2.0	0.8	1.7
		1	4	17.9	2.0	89.4	125.0
	Area B	1	1	2.4	2.0	21.0	679.9
		1	2	12.1	2.0	16.3	713.9



Good precursor Ba-Ca-Cu-O -19

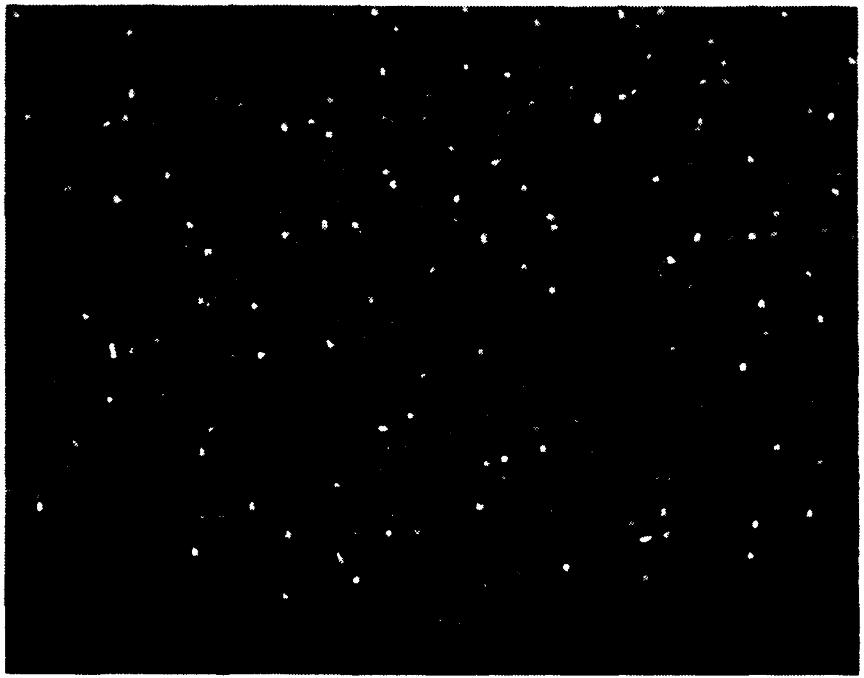


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Figure C-9 SEM Photographs of Ba-Ca-Cu-O precursors produced by MOCVD (EMC-26) and Chemical Deposition (C-0119-N).

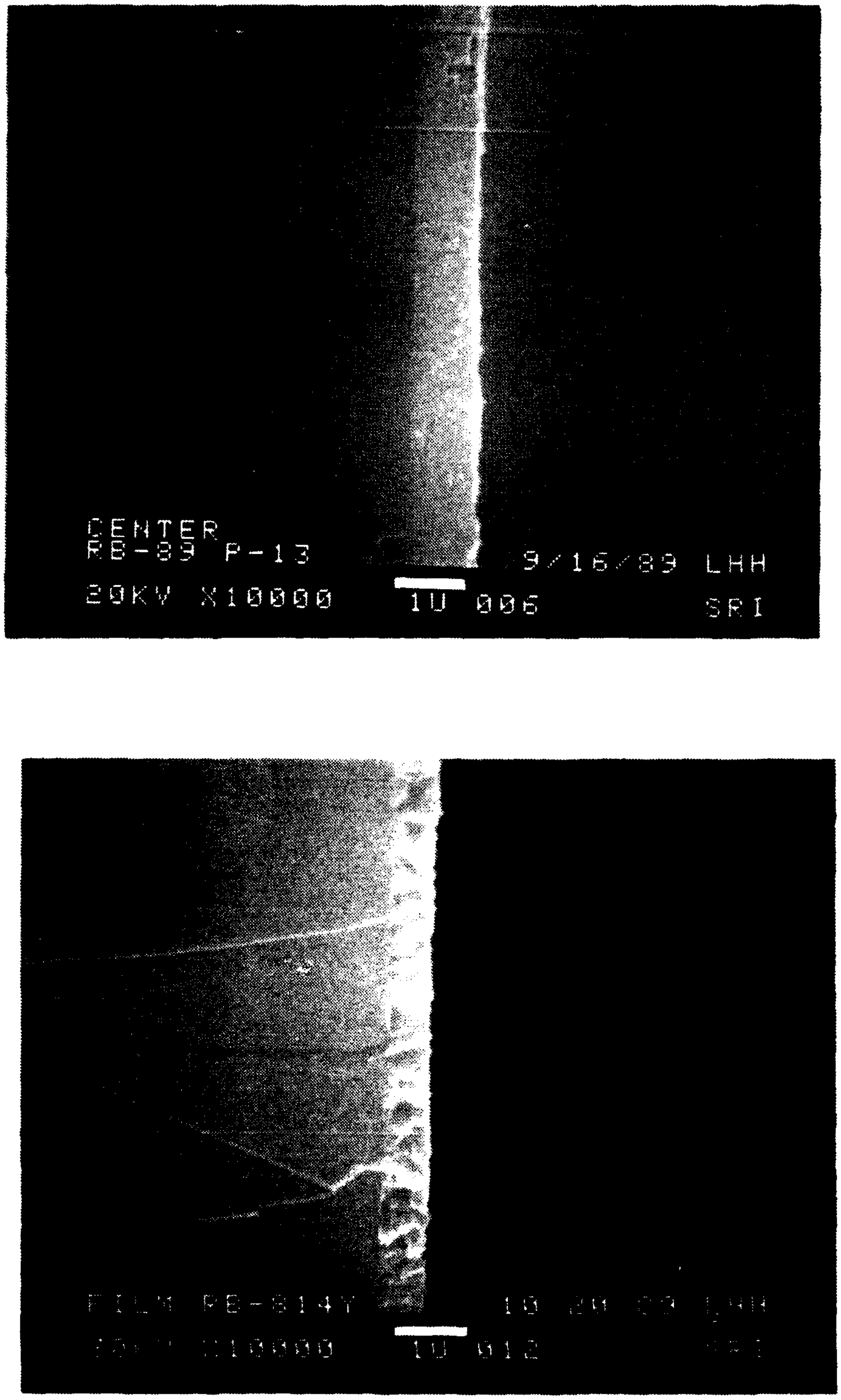

Figure C-10 SEM photographs of cross-section of chemically deposited precursor films before (RB-89) and after (RB-814Y) thallium addition.

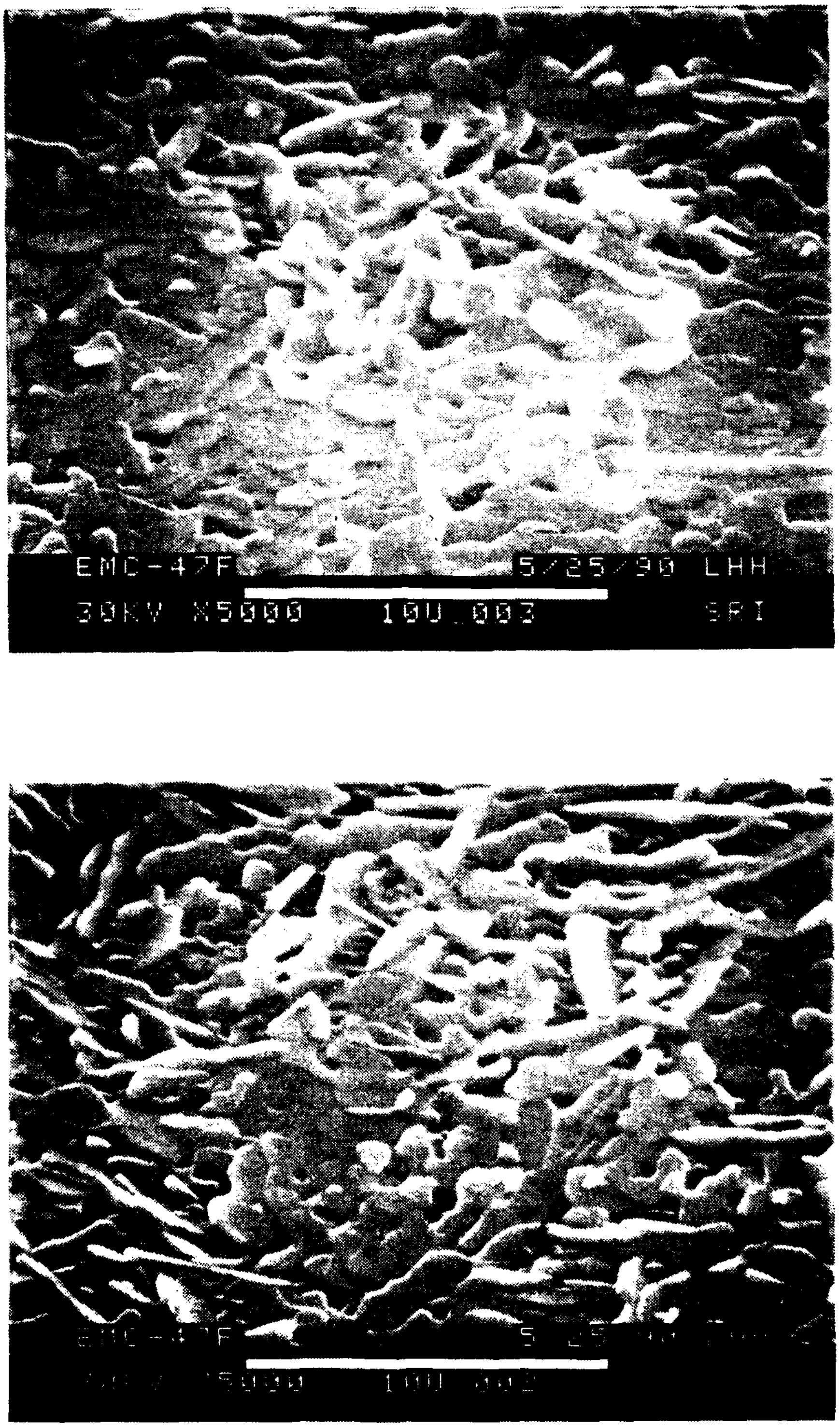

Figure C-11 SEM photographs of 2212 Tl-HTSC films.

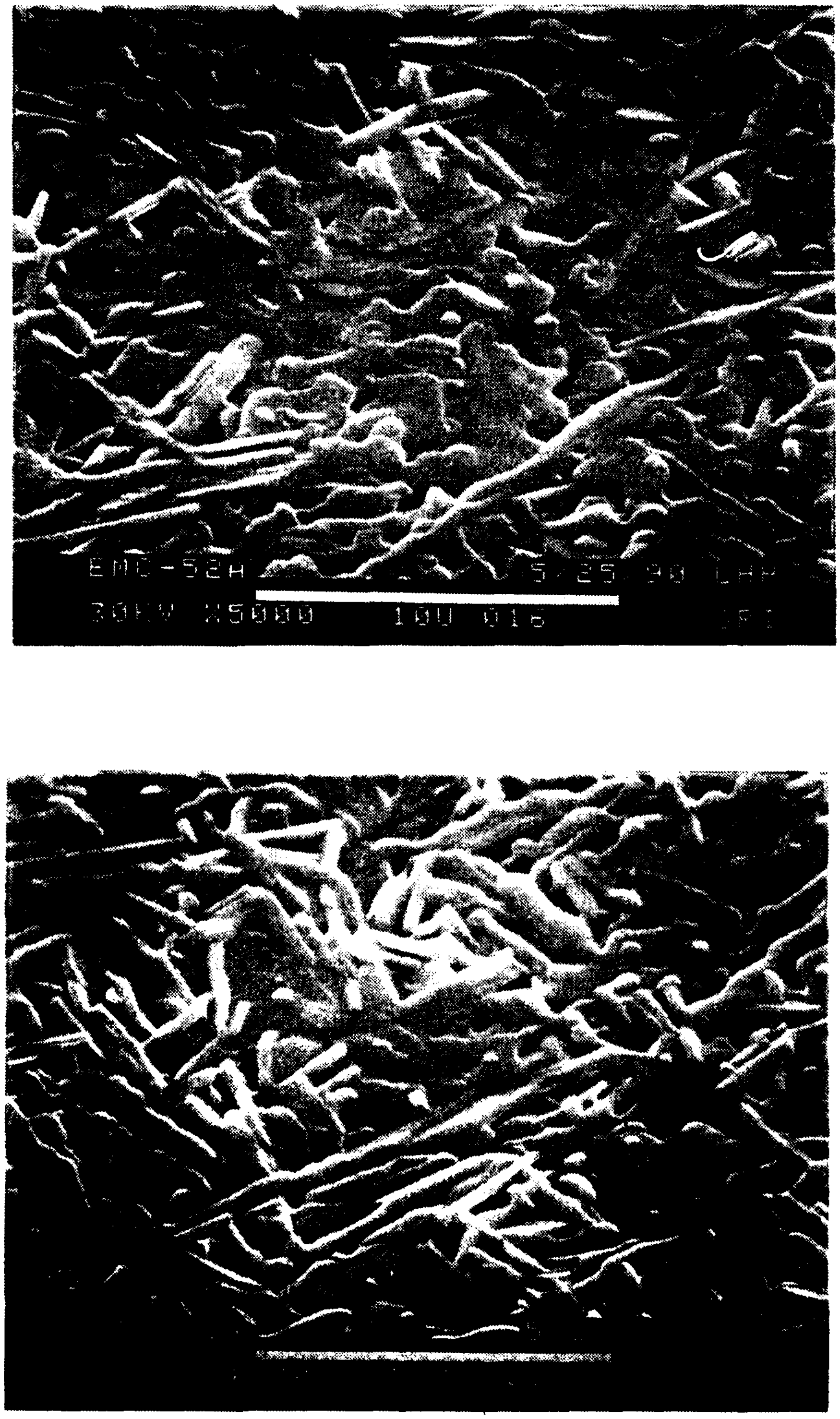

Figure C-12 SEM photographs of 2212 Tl-HTSC films.

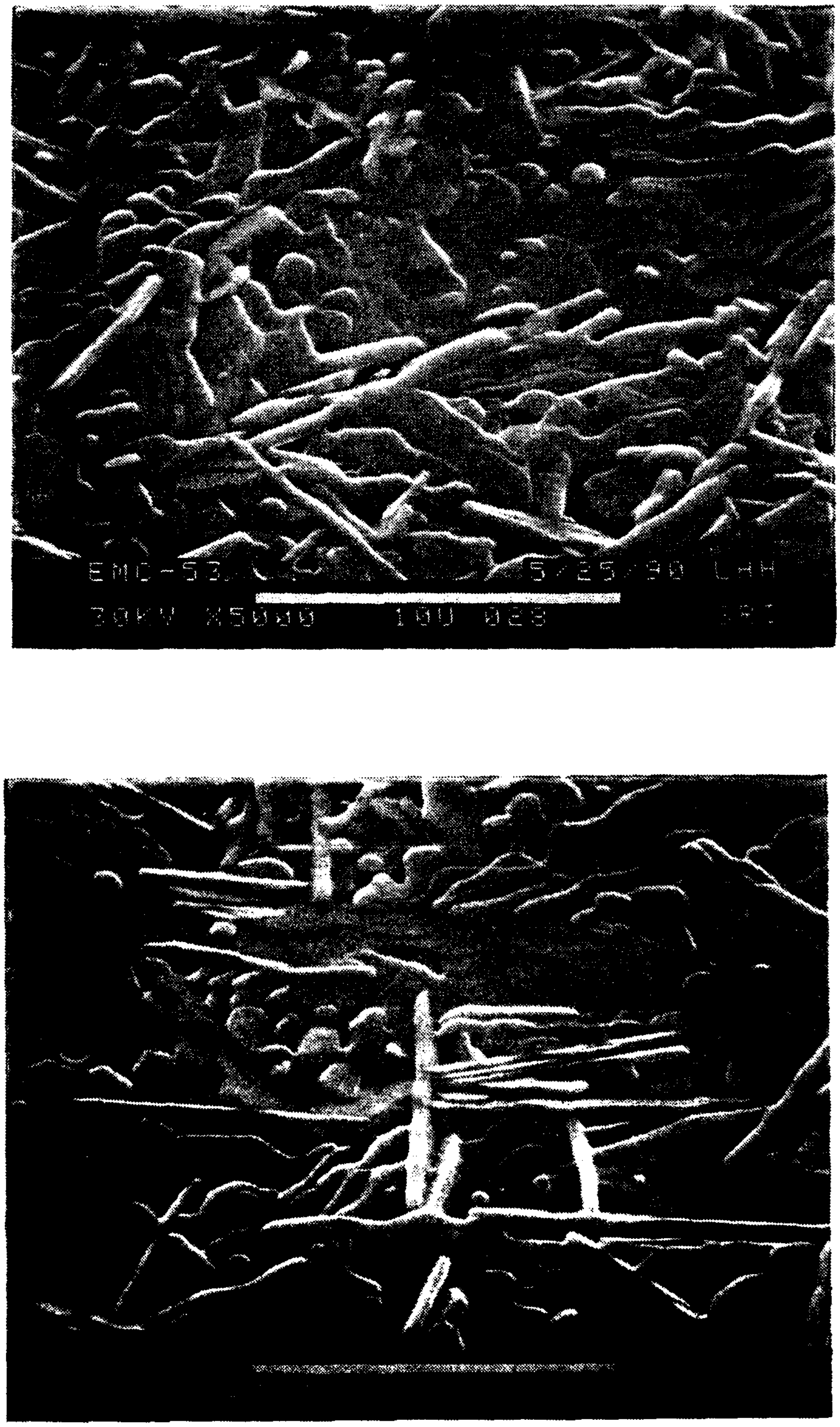

Figure C-13 SEM photographs of 2212 Tl-HTSC films.

3. Characterization of Superconducting Properties

Measurement of the mutual inductance of the samples as a function of temperature was performed using a dedicated low-temperature cryostat and thin-film ac-susceptometer system specifically designed for this purpose. Details of the system and the measurement technique have been reported elsewhere (J.R. Matey, in Proceedings of Thin Film Superconductors '88, Plenum Press). This is a non-contact, non-destructive method useful for the routine screening of superconducting samples.

In order to characterize the resistance of the samples as a function of temperature and to determine their critical currents, gold contacts were applied to the films by thermal evaporation. The thickness of the evaporated gold was about 3000 A and the contacts were arranged in a pattern of bars with 1 mm spacing. Leads for the current and voltage measurements were attached to the contacts using silver paint. Four-point critical current measurements were performed using a Keithley II programmable current source in the range 1-150 mA. The voltage was measured using a Keithley 181 nanovoltmeter. For the critical current measurements, the sample was immersed in liquid nitrogen. The temperature of the sample was monitored by means of a thermocouple in contact with the sample using Apiezon N grease. The thickness of the samples were determined by etching off a corner of the film with HCl solution and profiling the step using a DEKTAK II recorder.

The resistivity and ac susceptibility curves for two samples are shown in Figs. C-14 and 15. In Fig. C-14, the Tl-2212 film deposited on a $LaAlO_3$ substrate exhibits a zero resistance transition at 98 K. The susceptibility transition goes to zero at approximately 85 K. This film was prepared by thallium addition to an MOCVD precursor for 6 mins. at 870°C using a 2212 stoichiometry bulk source. Figure C-15 illustrates similar results obtained for a Tl-2212 film deposited on a sapphire substrate by the two-step process using a chemically deposited precursor. To date, the best films on sapphire have been prepared from the chemically deposited precursor films. The zero resistance temperature for this film is 95 K.

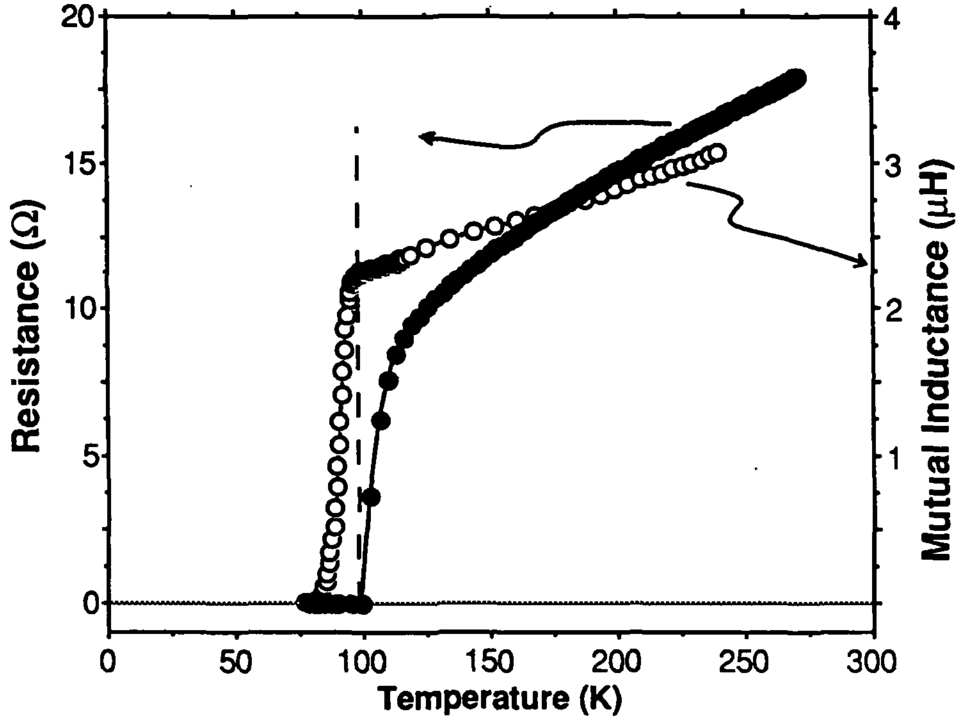

Figure C-14 Resistivity and AC susceptibility curves for Tl-2212 film on $LaAlO_3$ substrates.

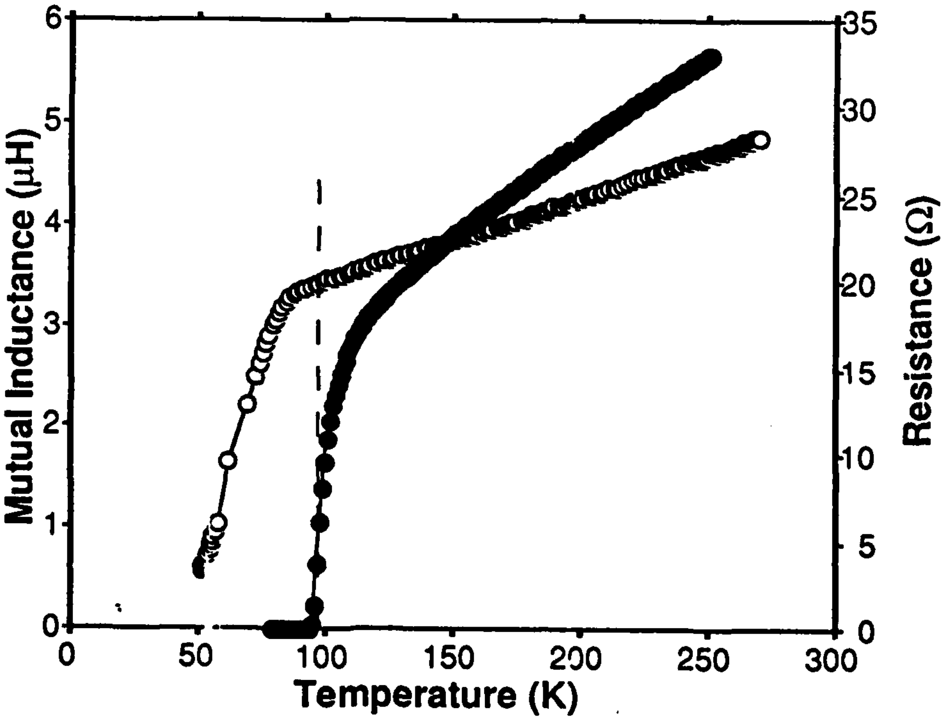

Figure C-15 Resistivity and AC susceptibility curves for Tl-2212 film on Al2O3 substrate.

The effects of oxygen annealing post treatments of the superconducting properties of the films were briefly examined. Annealing times of 1-4 hours at temperatures ranging from 400-600°C were employed. The film, placed face-down on a pellet of 2212 composition which had been previously used for the thallium addition step, was wrapped in gold foil and placed in a furnace tube under flowing oxygen. The results from one test are shown in Fig. C-16 for a Tl-2212 film on $LaAlO_3$. After annealing for four hours at 500°C, the onset of the ac susceptibility transition was actually shifted to lower temperature; however, the overall width of the transition was decreased and the susceptibility transition went to zero at a higher temperature than before annealing. Similar results have been obtained several times. The compositions, by EDAX, and x-ray diffraction spectra of the films were not significantly altered by the annealing process.

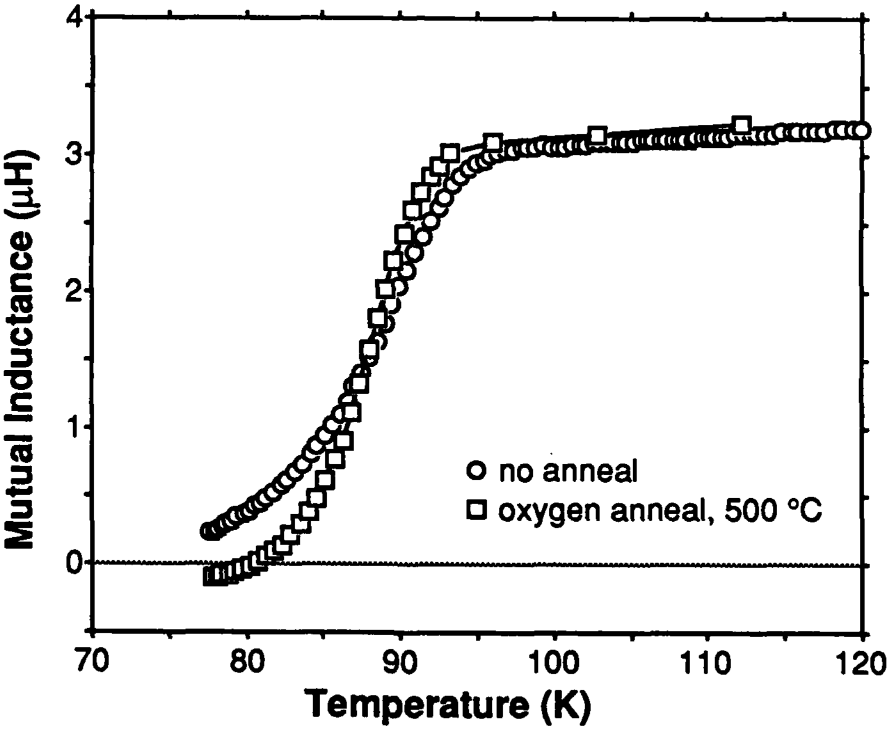

Figure C-16 Effect of O_2 anneal treatment on AC susceptibility transition.

The voltage versus current plot for a Tl-2212 film on LaAlO3 is shown in Fig. C-17. Using a thickness value of 0.5 microns, the critical current was calculated to be 0.8 x 10^4 A/cm^2.

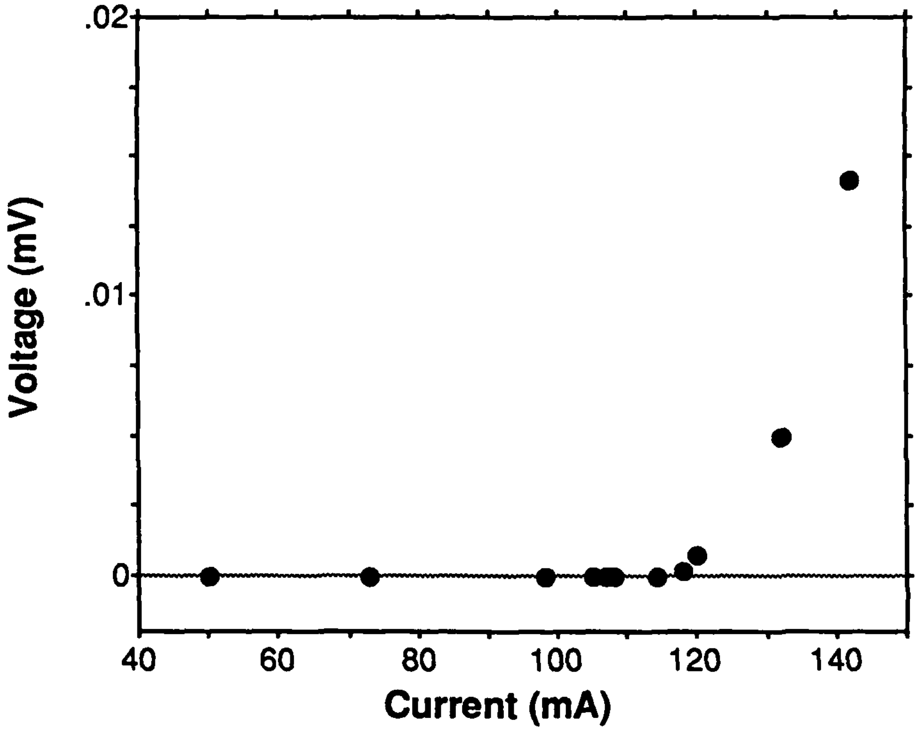

Figure C-17 Voltage versus current plot for Tl-2212 film on LaAlO3 substrate.

Section III

CHANGE IN KEY PERSONNEL

No change in key personnel.

Section IV

SUMMARY OF INFORMATION FROM SPECIAL EVENTS

J. Ladd attended the Conference on the Science and Technology of Thin-Film Superconductors which was held from April 30 to May 4,1990 in Denver, Colorado. The conference was organized by the U.S. DOE and the Solar Energy Research Institute. Over 185 attendees, including 55 scientists representing 18 foreign countries, participated in vigorous and open discussions on the state-of-the-art in this rapidly moving field.

In general, the Japanese programs are continuing to advance rapidly with particular emphasis on three terminal and Josephson junction device development. Preferred deposition methods include sputtering, MBE, and MOCVD. In many cases, the desire to prove a device concept has led to the fabrication of prototypes, which are workable, albeit at very low temperatures. The types of device structures appear to be modeled directly after conventional designs for low temperature materials without significant modification. Their materials preparation may be lagging slightly compared with the best thin-film results of American and European groups. However, many Japanese resources seem to be deployed to study the more practical aspects of device construction such as contacts, interfaces, insulators, dielectrics, etc.

European efforts that were described at the conference focused on materials preparation (laser ablation, sputtering, and MBE), detailed characterization of materials (TEM, electrical, and magnetic) and theory. The quality, particularly of the German YBCO materials, was quite good.

Soviet and Eastern Block efforts reported at the conference were dominated by materials work with some high quality theoretical studies also being done. They presented the only paper which dealt with thermodynamics in any detail. No results were presented on any of the alternate HTSC materials.

Several groups from the United States reported on the preparation of very-high-quality YBCO films. The best results were reported by the Bellcore/Rutgers group for laser ablated YBCO films on LaAlO3 substrates. Clarke (Berkeley) described the fabrication of YBCO-SrTiO3-YBCO crossovers and multi-turn YBCO input coils. The superconducting films were deposited by an in-situ laser ablation process. Both structures were superconducting at 77 K. No failures in the crossover structures due to shorting have been observed in several hundred samples produced.

Koch and co-workers at IBM reported the fabrication of Tl-HTSC SQUIDS which exhibited 1/f noise comparable to commercial low temperature devices. These were used together with a patterned YBCO input coil in a sandwich structure to make a magnetometer that functioned at 77 K.

Ginley and others at Sandia described the production of several types of Tl-HTSC devices from films deposited by their thermal e-beam evaporation/oxidation process. Both negative and positive photoresist and a Br_2/i-PrOH etch process have been used to pattern the films. Contacts were applied by either sputtering or evaporation. Annealing was found to reduce the contact resistivities. Prototype devices fabricated include SQUIDS, meander lines, cross bridges, and flux flow transistors. The latter device utilizes a characteristic of the thallium system, relatively easy flux flow behavior, in a novel way and can be combined to form NOR gates with switching times less than 1 nsec. Additional devices that have been made include oscillators, phase modulators, comb generators, and mixers.

Section V
PROBLEMS ENCOUNTERED

During the course of the work on the MOCVD deposition process several problems were encountered. The most serious of these dealt with the (lack of) stability of the starting materials. Both the barium and calcium sources tend to thermally decompose at the temperatures required to obtain adequate deposition rates. In addition, the decomposition problem appears to be aggravated by the presence of water vapor in the gas streams. Although a system was devised to condition the in-flowing gases by passing them through a bubbler filled with the tmhd ligand prior to the barium source, this may not be an adequate permanent solution. An additional difficulty was due to the fact that different lots of the same starting material, from the same vendor, exhibited different thermal stability and volatility characteristics. Additional work on the development of improved source materials would be highly desirable.

In the thallium addition portion of the process, the technician operating the annealing furnace used to incorporate the thallium into the experimental samples reported being nauseous on the same day that she operated this equipment. This part of the experimentation was suspended as a precaution and a detailed safety study of the annealing furnace and the procedure for incorporating the thallium was begun. The study included air sampling measurements that took a significant amount of time to arrange and process. The results of the study confirmed the safety of the furnace and procedures being used. No thallium was detected in the gases exiting the scrubber on the furnace exhaust. Additional studies are required in order to obtain highly reproducible and controllable vapor pressures of thallium in the reaction system.

In general, a one step process for the production of Tl-HTSC films will ultimately be the most favorable. The best films reported in the literature to date have been prepared by incorporating thallium during the initial deposition process and subsequently converting the film to the superconducting phase. The four component MOCVD deposition process appears to be workable and is the logical and proposed extension of the current effort.

Section VI
GOVERNMENT ACTION REQUIRED

Support work on phase diagram of Tl-Ba-Ca-Cu-O system especially with regards to effects of over-pressure of Tl and O during processing (i.e. conversion to S.C. phase).

Support future development of 4-component MOCVD deposition process.

Support development of improved stability and reproducibility of source materials, especially for Ba and Ca.

Quantitate the environmental and health/safety risks of thallium as incorporated in this chemical system. Develop set of standards or recommendations for working with these materials. This action will facilitate research activity in the field.

Support continued efforts on the deposition of Tl-Ba-Ca-Cu-O materials onto sapphire, because of the compatibility of this substrate with a variety of end applications, particularly new applications in the optoelectronic area. Continue efforts to reduce maximum temperature during deposition process.