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DEVELOPMENT OF SUPERCONDUCTING THIN FILMS WITH A CRITICAL TEMPERATURE GREATER THAN 110K

Corporation for Studies and Analysis

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CSA provided superconducting thin films consisting of $Tl_2Ca_1Ba_2Cu_2O_x$ on $LaAlO_3$. Films were generated using the pulsed laser deposition (PLD) method. The company achieved a zero resistance temperature of 115°K and a critical current density of 10^5 A/cm^2 at 77°K.

Relationships between the deposition process, the as-deposited film, annealing conditions, and the annealed film were investigated. Twenty thallium-based high temperature superconducting films on microwave compatible substrates were delivered under provisions of this contract.

** microwave compatible substrates, critical current densities, zero resistance temperatures.

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1.0 Summary

This final report is submitted by the Corporation for Studies and Analysis (CSA) as CRDL 101 of Contract No. F19628-89-C-0090. The contract effort, entitled *Development of Superconducting Thin Films with a Critical Temperature Greater than 110°K,* is sponsored by the Electronics Systems Division, Hanscom AFB, MA, under the technical direction of Dr. Michael J. Suscavage. This report covers work performed from 31 March 1989 to 3 October 1990.

1.1 Project Goals and Summary of Results

The main thrust of CSA's work was to produce films via pulsed laser deposition (PLD), with a T_c in excess of 110°K and a J_c at 77°K in excess of 10^6 A/cm^2, on microwave compatible substrates if possible. Toward this end we have achieved the following results:

1. Deposition and growth of superconducting films on $LaAlO_3$, a microwave compatible substrate.
2. Growth of near epitaxial $Tl_2Ca_1Ba_2Cu_2O_x$ with a zero resistance temperature of 101°K and critical current density in excess of 10^5 A/cm^2 at 77°K.
3. Growth of $Tl_{2-x}Ca_2Ba_2Cu_3O_x$ films with a zero resistance temperature of 115°K and a critical current density of 10^5 A/cm^2 at 77°K.
4. Growth of $Tl_1Ca_2Ba_2Cu_3O_x$ films with a zero resistance temperature of 103°K and a critical current density of 10^5 A/cm^2 at 77°K.
5. Development of high yield process technology for thallium-based superconducting thin films.

1.2 Summary of Technical Approach

The previously listed results were achieved by developing an understanding of the relationships between the deposition process, the as-deposited film, annealing conditions, and the annealed film. This was accomplished in a systematic manner by first producing a dense, homogeneous stoichiometric as-deposited film, and then optimizing the annealing conditions to yield the desired final film. The remainder of this report will explicitly discuss all aspects of the deposition and subsequent processing of thallium-based high temperature superconducting films.

2.0 Film Deposition and Processing

2.1 Pulsed Laser Deposition — System Overview

Briefly, PLD entails making a high intensity laser pulse incident on a target, where the laser pulse vaporizes the near surface of the target. The vapor is then condensed onto a substrate surface, producing a thin film of the target material. The physical mechanisms involved in target vaporization can range from simple melting to photochemical bond breaking, where this is a strong function of the laser wavelength and target. This technique offers several advantages over most conventional thin film deposition techniques. First, a wide range of ambient gases and gas pressures can be employed during deposition, where deposition can occur in an ultra high vacuum or with gas pressures as high as hundreds of mTorr of virtually any gas. Second, stoichiometric films can deposited from a single, compound target. This allows relatively simple systems to deposit complex materials. Also, multilayer materials can be easily deposited by changing targets between laser pulses.

A schematic diagram of the PLD system is seen in Figure 1. *(NOTE: For ease of reference, all figures are located in Section 5 of this report.)* Briefly, it consists of an excimer laser and deposition chamber. The output of the excimer laser is apertured to promote beam uniformity, focused and passed through a window in the chamber, and made incident on the target. The chamber consists of a six-inch I.D. cross-pumped from below by an oil diffusion pump, backed by an oxygen service mechanical pump, to a base pressure of 5×10^{-5} Torr. The target is mounted on a stainless steel rod and rotated at 10 RPM to prevent target trenching. The substrate is mounted directly opposite the target on a temperature-controlled heater block capable of operating at 700°C in one atmosphere of oxygen. The heater unit is connected to a quick access door to allow rapid substrate changing. This method requires approximately 20 minutes to load a new substrate and evacuate the chamber to a suitable base pressure. There is one gas inlet port for oxygen.

2.2 Deposition Studies

This section discusses the effect of substrate temperature, wavelength, target chemistry, and oxygen background pressure on the film properties. We begin with an overview of processing conditions. These include deposition parameters and target fabrication procedures. This overview is followed by a discussion of the results obtained using a frequency doubled Nd:YAG laser operating at 532 nm and an excimer laser operating at 248 nm.

2.2.1 *Overview of Processing Conditions*

Typical deposition conditions are: substrate temperature 200 to 600°C, deposition time of 30 minutes, laser pulse rate of 4 Hz, laser pulse width of 10 nsec, background pressure of 10^{-5} torr, or 170 mTorr oxygen, and an energy density of 0.5 to 2.0

J/cm^2. The as-deposited films, between 0.5 and 1 micron thick, were not superconducting, and a post annealing step was required. The annealing procedure was similar to that used by Lee, et al.[1]

The laser beam spot size was determined by placing a glass slide coated with liquid graphite in front of the target and exposing it to a few laser pulses. Dividing the size of the spot into the energy of the pulse (as measured by a calorimetric power meter) yields the energy density. The main source of error associated with this technique arises from spatial non-uniformities in the laser beam. We estimate the total error to be on the order of 25 percent in determining the absolute energy density. However, this method does allow reproducible conditions to be easily and accurately established. We estimate the error involved in reproducing a given set of conditions to be on the order of 5 percent.

The composite Tl-Ca-Ba-Cu-O target was made by grinding together a mixture of Tl_2O_3, CaO, BaO, and CuO with a metal cation ratio of 2:2:2:3. Three grams of the ground mixture was pressed into a cylindrical target, which was then re-ground and pressed again to increase its density to approximately 75 percent of the theoretical value. The target was wrapped in a gold foil and placed in a closed-end quartz furnace tube, where the tube entrance was partially sealed. The temperature was ramped to 600°C in approximately 20 minutes and then held for 2 hours, whereupon the furnace fell switched off and allowed to cool. The target was removed when the temperature was below 50°C. Scanning electron micrographs of the target before and after sintering indicate that the heat treatment has virtually no effect on the target morphology, where the target consists of small, roughly spherically shaped particles on the order of 5 microns in size. An X-ray diffraction scan taken after sintering shows only peaks corresponding to the individual oxides. Based on these results, we conclude that the target is a mixture of the individual starting oxides. Also, the target experienced very little weight loss during sintering (less than 2 percent). This could be accounted for by some loss of thallium and/or water vapor which could be driven of the hygroscopic target components. In any event, the weight loss is minimal, leading to the conclusion that the overall target stoichiometry is nominally that of the starting material.

The compound superconducting target was made from a 1:3:1:3 mixture of the above oxides, following the procedure outlined by Parkin, et al.[2] A target was cleaved in air where the cleaved surface was analyzed by RBS with a He+ energy of 6.0 MeV. The metal cation stoichiometry was found to be $Tl_{0.75}Ca_{3.08}Ba_{0.90}Cu_{3.10}$. A powder X-ray diffraction scan of the processed material indicated the presence of 2:2:2:3 phase material, a relatively small amount of 2:1:2:2 material, and a variety of non-superconducting phases.

2.2.2 Nd:YAG Laser Deposition

Current research on the pulsed laser deposition of Y-Ba-Cu-O indicates that an elevated substrate temperature can enhance film properties.[3-6] This is believed to result from the fact that the elevated temperature enhances crystal orientation and growth during deposition. In view of this, the first set of experiments involved a systematic variation of the sub-

strate temperature while holding other parameters constant. Initially the energy fluence was held constant at 1.2 J/cm^2 (532 nm), the pulse rate was held at 4 Hz, the deposition was performed at a base pressure of 10^{-5} torr, all substrates were (100) MgO, and the substrate temperature during deposition was varied between 200°C and 600°C. Rutherford Back Scattering (RBS) was performed on these films with a He+ energy of 2.5 MeV and, as seen in Figure 2, the only significant difference in as-deposited stoichiometry as a function of substrate temperature occurs in the thallium concentration. Also, X-ray diffraction scans of these films indicated that they were either amorphous or had an extremely fine grained structure.

A duplicate set of films on the order of a few thousand angstroms thick were deposited. Upon annealing, they exhibited zero resistance temperatures between 105°K and 110°K. An X-ray diffraction scan is shown in Figure 3a and a typical resistance vs temperature curve is shown in Figure 3b. The film is single phase 2:2:2:3 with c-axis orientation. Under the given conditions of laser wavelength, fluence, and base pressure, these results indicate that an elevated substrate temperature does not substantially affect the ultimate film properties.

At first glance, these results were rather surprising, since it was expected that an elevated temperature would enhance chemical reactions between the various components and promote crystal growth. Closer examination of the as-deposited films reveals that they are extremely rough; in fact, they appear to consist of small "chunks" of material as seen in the SEM micrograph (Figure 4).

It was felt that the particulate nature of the film might require solid phase reactions to occur. Reactions of this type generally require higher temperatures than those used here. In view of this, we varied the energy fluence in an attempt to produce a more homogeneous film. While the remaining deposition conditions were kept at the standard values used previously, four different fluences were used: 0.2 J/cm^2, 0.5 J/cm^2, 1.0 J/cm^2, and 2.0 J/cm^2. Virtually *no* deposition occurred at 0.2 J/cm^2, even after 45 minutes. Each of the films produced at the other fluences had essentially the same surface morphology. Energy dispersive X-ray analysis (EDA) was performed on these films. It should be pointed out that, while oxygen is probably present in the film, it could not be detected by EDA. Results are shown in Figure 5. The barium, calcium, and copper concentrations are nearly stoichiometric, although a trend was clearly observed toward a more stoichiometric film as the fluence was decreased. These results indicate that laser fluence has little effect on the as-deposited film properties, provided it is above the deposition threshold.

The EDA analysis is in general agreement with the RBS results, except for the fact that EDA shows considerably more thallium than RBS does. This is probably due to the fact that the films prepared for RBS were extremely thin, on the order of 200 angstroms. Films this thin may very well be thallium-deficient, since thallium is volatile. However, the films used for EDA analysis were at least 5,000 angstroms thick, where EDA provides an average composition over a significant depth into the film. The near surface of the thicker film may be thallium-deficient, but

EDA is not sensitive to this. However, it is apparent that the average thallium content of an as-deposited film at least 0.5 microns thick is nearly stoichiometric, at least for a substrate temperature of 200°C.

Results from energy dispersive X-ray analysis of a large area (approximately 250 microns in diameter) and several small points (approximately 5 microns in diameter), are shown in Figure 6. The large area composition, normalized to Ca = 2.0, is $Tl_{1.7}Ca_2Ba_{2.2}Cu_{3.2}$, which is close to the starting target. However, the small area results show that, on a microscopic scale, the film consists of localized non-stoichiometric regions. The structure of this film is similar to that of the target, which is stoichiometric on a bulk scale but consists of a mixture of individual oxides.

This result explains the lack of effect of substrate temperature on the as-deposited films, and provides some insight into the mechanisms of pulsed laser deposition under the conditions used here. Briefly, since it is known that solid Tl-Ca-Ba-Cu-O mixtures do not react to form compounds below 850°C,[7] and since the maximum substrate temperature was only 600°C, it is not reasonable to expect any reaction to occur. Also, since thallium and its oxides are volatile at these temperatures, it is reasonable to expect the thallium concentration to decrease as the substrate temperature increases, especially in films as thin as those analyzed by RBS.

We feel these overall results indicate that this particular combination of composite target and laser parameters resulted in a *physical* transport of the target material to the substrate, as opposed to a vapor phase transport. While physical transport may help maintain the film stoichiometry, since the target material is being directly transported to the substrate, films of this type generally have poorer electrical properties than dense, homogeneous films.[8] We believe this is the primary reason that these films have critical current densities on the order of 10^4 A/cm^2.[9] This result is in agreement with recent work involving the Y-Ba-Cu-O system, where longer wavelength radiation yielded films with lower critical currents.[8]

This work raises a key question: *do the observed results arise from the pulsed laser deposition process, the composite target, or both?*

In order to address this issue, films have been deposited under the standard set of conditions (532 nm, 1.2 J/cm^2, substrate temperature = 200°C, background pressure 10^{-5} torr, (100) MgO substrate) from a Tl-Ca-Ba-Cu-O compound superconducting thallium target fabricated as described previously.

Mechanical stylus traces of this film and a typical film deposited from the composite target are shown in Figure 7. As can been seen, the film deposited from the compound target is markedly different than the films deposited from the composite target. It is much smoother and contains relatively few large particles. Energy dispersive X-ray analysis of this film shows that the smooth portion of the film is a homogeneous mixture of the elements, while the particles are primarily calcium. This result tends to indicate that these deposition conditions, combined with a compound target, produce a predominantly vapor phase transport of the target material to the substrate, as opposed to the physical transport observed with the

composite target. As seen in Figure 7, the deposition rate from the compound target is a factor of three less than the deposition rate from the composite target. Since less material is being removed from the compound target than from the composite target per pulse, the energy density deposited into the compound target is significantly greater than that deposited into the composite target. This may account for greater fragmentation of the compound target and vapor phase transport. Also, the fragments initially produced from the compound target may more efficiently absorb the 532 nm radiation than those produced from the composite target, leading to greater fracturing of the compound target fragments and a smoother film.[8] This work indicates that the physical nature of the target strongly influences the properties of the as-deposited film under the deposition conditions used here.

The stoichiometry of the as-deposited film from the compound target, as determined by EDA, is $Tl_{1.39}Ca_2Ba_{1.04}Cu_{2.12}O_x$. Upon annealing, this film did not superconduct. In fact, it exhibited *semiconducting* properties. This illustrates some of the problems that arise when a using a compound superconducting thallium-based target. While a bulk superconducting target can be fabricated, and the predominant superconducting phase identified, the overall stoichiometry differs substantially from the superconducting phase.[2] Therefore, films deposited from this material, even under conditions of complete vaporization, may exhibit a composition inappropriate for formation of a superconducting thin film.

In summary, as-deposited films fabricated from a *composite* target under the conditions stated above are similar to the target. That is, the films are non-homogeneous mixtures of the elements of the superconducting compound. We believe that this stems from the fact that the pulsed laser deposition process produces physical transport of the target to the substrate. For a fixed laser wavelength of 532 nm, this appears to result from the composite nature of the target. The films produced to date are superconducting after annealing in a thallium/oxygen atmosphere at 870°C.

In contrast, films fabricated from a *compound* superconducting target are smooth and homogeneous. We believe this results from the fact that vapor phase transport is the dominant deposition mechanism under conditions used here. However, the stoichiometry of the as-deposited film was such that it could not be made superconducting.

2.2.3 Excimer Laser Deposition

In order to improve film properties, the deposition process should rely on vapor phase transport rather than solid phase transport. Under vapor phase transport conditions chemical reactions can occur at moderate temperatures and the films are considerably denser. Therefore, smooth, well-connected films should result. In view of the current work involving wavelength effects,[8] we feel that shorter wavelength laser radiation will lead to vapor phase transport and deposition of a homogeneous film.

We have fabricated films using an excimer laser operating at 248 nm, 4 Hz, with a 10 nsec pulse width, and focused to an energy density of 0.5 J/cm^2. A com-

posite target, (100) MgO substrate heated to 200°C and background pressure of less than 10^{-5} torr are the remaining deposition conditions. Briefly, then, we have used the same conditions that previously produced superconducting films after annealing, except that the wavelength is more than a factor of two shorter.

A SEM micrograph of the as-deposited film is shown in Figure 8. This film is essentially featureless, with the exception of a few scattered particles. This is in direct contrast to the film deposited at 532 nm (see Figure 4). Also, the deposition rates at the different wavelengths are approximately equal; therefore, the difference in film morphology cannot be attributed to a higher energy density being deposited into the target at 248 nm.

It should also be pointed out that, unlike the previous work performed on the Y-Ba-Cu-O system, the pulse width at each wavelength is nearly identical.[9] Therefore, the observed effect is not related to an intensity difference in the pulses, but is strictly a function of the difference in wavelength. More than likely, the shorter wavelength is producing different species upon initial absorption by the target and interacting more strongly with these species after they leave the target surface. This has been observed through optical emission studies of laser-produced plasmas as a function of wavelength, where shorter wavelengths are known to produce hotter plasmas.[10]

Figure 9 shows the energy dispersive X-ray analysis of a film deposited at a fluence of 0.5 J/cm^2, laser rep rate of 4 Hz, and a substrate temperature of 200°C in vacuum. The EDA was performed over a large film area and four randomly located 5-micron by 5-micron spots. As seen, the film is *extremely* homogeneous, in direct contrast to the films deposited at 532 nm. However, the as-deposited stoichiometry, normalized to calcium = 2, is $Tl_{1.2}Ca_2Ba_{3.2}Cu_{3.0}$, which is dramatically different from the target stoichiometry and from that obtained for a film produced under identical conditions at 532 nm.

A similar result has also been observed for the PLD of Y-Ba-Cu-O from a composite Y_2O_3-BaF_2-CuO target at 308 nm, where composition of the target was adjusted to yield a stoichiometric film.[11] Rather than work from an off-stoichiometric target, we investigated the as-deposited film composition as a function of fluence and oxygen background pressure. Figure 10a graphs the film composition, normalized to calcium = 2, of a film deposited at a fluence of 1.5 J/cm^2 in vacuum, with all deposition conditions as described previously. Under these conditions, the film composition is $Tl_{1.5}Ca_2Ba_{2.3}Cu_{2.75}$, which is much closer to the target stoichiometry. The effect of oxygen background pressure on the as-deposited film composition at 0.5 J/cm^2 and 1.5 J/cm^2 is seen Figures 10b and 10c, respectively. The composition at 0.5 J/cm^2 in vacuum is repeated in Figure 10d for completeness.

Clearly, the addition of oxygen has a dramatic effect on the film stoichiometry at both laser fluences. At 0.5 J/cm^2, the barium and copper are reduced from a relative concentration of 3 to less than 2.25, while the thallium content in the film is slightly increased. At a fluence of 1.5 J/cm^2, the barium and copper relative concentrations remain almost con-

stant, but the thallium content is increased from 1.5 to 2.7. The higher fluence combined with the presence of oxygen in the chamber during deposition has improved the as-deposited film stoichiometry.

Recall that the thallium concentration dropped to virtually zero at a substrate temperature of 600°C, at 532 nm with a background pressure of 1 x 10^{-5} Torr. However, since the as-deposited films produced a 248 nm are smooth and homogeneous, deposition is occurring in an oxygen background pressure, and thallium-based thin films annealed in flowing oxygen at temperatures up to 750°C show little thallium loss,[12] the as-deposited film stoichiometry as a function of substrate temperature was investigated at a wavelength of 248 nm. Film composition as a function of substrate temperature at a fluence of 1.5 J/cm^2 and an oxygen background pressure during deposition of 170 mTorr was determined by EDA. The thallium concentration dropped dramatically with increasing substrate temperature and was virtually zero at 600°C, which is identical to its behavior at 532 nm in a vacuum. At substrate temperatures below 500°C the films were smooth, homogeneous, and amorphous. However, at 600°C, the as-deposited films exhibited a granular structure (refer to the SEM micrograph of Figure 11). An X-ray diffraction scan of the film deposited at 600°C exhibits peaks corresponding to CaO and BaO, as well as several unidentified peaks. We feel these results indicate that a constant supply of thallium during film growth is necessary in order to produce an in-situ thallium-based superconducting thin film, and that a substrate temperature in excess of 600°C is necessary in order to form the thallium superconducting compounds.

Films deposited at a fluence of 1.5 J/cm^2, a substrate temperature of 200°C in an oxygen background pressure of 170 mTorr, were annealed using the method discussed previously. These films were selected because their as-deposited stoichiometry was the most appropriate for formation of the 2:2:2:3 phase. An X-ray diffraction scan of an annealed film is virtually identical to the one presented previously in Figure 3. The resistance vs temperature curve of a typical film is seen in Figure 12. The transition begins at 112°K and is complete at 107°K, which is considerably narrower than the transition width of the films deposited at 532 nm. The critical current density for these films as measured by the standard four point probe method at 77°K in zero field is 5 x 10^4 A/cm^2, a factor of 5 improvement over films deposited at 532 nm.

2.2.4 *Summary — Wavelength, Target Chemistry, Substrate Temperature, and Oxygen Pressure*

As-deposited films fabricated at 532 nm are similar to the composite target. That is, they are a non-homogeneous mixture of the elemental components of the material. The microstructure and morphology of the films are independent of the substrate temperature and energy fluence at this wavelength, although the thallium content drops to zero at a substrate temperature of 600°C. We feel that this is because solid phase transport is the dominant deposition mechanism under these conditions. In direct contrast, films deposited from a bulk superconducting target at 532 nm are considerably smoother. Clearly, the dominant mechanism in this case is vapor phase transport. However, composition of the films

deposited from the compound target was not suitable for formation of a superconducting film. This is a direct result of the fact that the superconducting target was fabricated from an off-stoichiometric starting mixture. While this process yields a single superconducting phase, the overall composition of the target remains off-stoichiometry. This composition is transferred to the film, which cannot be made superconducting.

Films fabricated at 248 nm are essentially featureless, and are a homogeneous mixture of the individual material components. We feel this results from the fact that the shorter wavelength radiation promotes vapor phase transport of the target material to the substrate. The stoichiometry of films deposited from a composite target is a function of the laser fluence at 248 nm and oxygen background pressure. X-ray diffraction scans of the annealed films produced under these conditions are identical to those produced previously. However, the resistance vs temperature curve exhibits a sharper transition, and the critical current density of these films is a factor of 5 greater than those produced at 532 nm. We believe improvement in film properties is a result of vapor phase transport of the target material to the substrate, which produces a denser as-deposited film.

In view of these results, CSA will exclusively use the excimer laser operating at 248 nm, and an oxygen background pressure of 170 mTorr.

2.2.5 Substrate Studies

All previously described deposition studies were performed using (100) oriented MgO as the substrate. While this material has a relatively low dielectric constant of 9.65, its loss tangent is unacceptably large (91 x 10^{-4} at 1 MHz). Also, while good quality films have been grown on this substrate, the lattice mismatch between it and the higher order thallium phases is greater than 10 percent. This mismatch may limit the overall film quality, since epitaxial growth of thallium-based films is impossible with this great a mismatch.

In view of this, microwave properties of a variety of substrates have been evaluated. This led to the conclusion that the psuedo-perovskite crystalline compounds have good microwave properties and a lattice structure appropriate for deposition of thallium-based films. In particular, $LaAlO_3$, with its dielectric constant of 16, loss tangent of 5 x 10^{-4} at 10 GHz, and unit cell dimension of 3.79 angstroms at room temperature, is an excellent substrate.[13] The good microwave properties are complemented by the fact that its unit cell dimension provides a lattice mismatch of less than 2 percent to both the 2-1-2-2 and 2-2-2-3 thallium-based material, where each of these phases is tetragonal with a and b lattice parameters of 3.85 angstroms.[14]

For these reasons, CSA deposited thallium-based films on $LaAlO_3$. Deposition conditions were: fluence = 1.5 J/cm^2, substrate temperature = 200°C, oxygen pressure = 170 mTorr, and a composite target. These conditions have been shown to yield high quality as-deposited films on MgO. We anticipated that the change of substrate would have no effect on the as-deposited film, unless a severe chemical interaction occurred between the film and substrate. However, this did not occur and the as-deposited films are virtually identical to those on MgO. Films deposited on

$LaAlO_3$ were annealed in an identical manner to those deposited on MgO. An X-ray diffraction scan of a typical film on $LaAlO_3$ is shown in Figure 13. This film contains both the 2-1-2-2 and 2-2-2-3 phases, where films deposited on MgO and annealed under these conditions were virtually single-phase 2-2-2-3. A SEM micrograph of this film (Figure 14) shows the needle-like 2-1-2-2 structure and the sheet-like 2-2-2-3 structure. The resistance vs temperature curve of this film (Figure 15) is similar to the ones for MgO films; however, the critical current density at 77°K is near 10^5 A/cm^2.

It is not clear whether this represents a higher quality material, or whether it indicates that mixed phase films may exhibit higher critical current densities than single phase films.

Clearly, good quality thallium-based films can be deposited on (100) $LaAlO_3$. However, the film properties can be improved. This can be accomplished by improving the as-deposited film and optimizing the annealing conditions for films deposited on $LaAlO_3$.

2.2.6 Deposition from Bulk, Single Phase Stoichiometric Targets

CSA has shown that for a laser wavelength of 532 nm, the as-deposited film properties improve when a bulk compound target, rather than a composite target, is used. However, the overall bulk target composition was off-stoichiometry, leading to films that did not become superconducting after annealing. Recently, methods have been developed that yield bulk, single phase stoichiometric superconducting targets from initially stoichiometric mixtures.[15] This technique entails preparing a Tl-2, Ca-2, Ba-2, Cu-3, O-x pellet in much the same manner as previously described. The pellet can be prepared from individual oxides or from a commercially available calcium cuprate, barium cuprate mixture with a metal cation ratio of $Ca_2Ba_2Cu_3$. The pellet is placed in an alumina tube with one closed end, while the other end is sealed with a MACOR (machinable glass) plug. The entire tube is then wrapped in silver foil, sealing the end of the tube with the plug. This is inserted into an oven preheated to 900°C, in flowing oxygen. The pellet is processed for 5.5 hours at 900°C and slowly cooled to room temperature, also in flowing oxygen. We have found that pellets prepared from the commercially available cuprate yielded denser targets than those prepared from individual oxides. Therefore, we used this mix exclusively in our target preparation.

This process yields a final bulk target with an overall composition of $Tl_{1.6}Ca_2Ba_2Cu_3O_x$. An X-ray diffraction scan of a typical target is seen in Figure 16, which shows peaks corresponding to the 2-2-2-3 superconducting phase. The resistance vs temperature curve of this target (Figure 17) shows that a zero resistance temperature of 122°K was obtained.

We also estimate the density of this target to be on the order of 75 percent of the theoretical value, which is similar to the composite targets used previously. Figure 18a is a SEM micrograph of a film deposited from a bulk target at a fluence of 0.75 J/cm^2, 170 mTorr of oxygen background pressure, a substrate temperature of 200°C on (100) oriented $LaAlO_3$. Figure 18b is a high magnification SEM micrograph of the same film. As can be seen, the film is extremely

dense and smooth. This should be compared with Figure 18c, which is a high magnification SEM micrograph of a film deposited from a composite target under the same conditions. Upon close examination the film deposited from the composite contains a substantial amount of microscopically small particulates, while the film deposited from the bulk target is homogeneous and dense. Energy dispersive X-ray analysis indicates that the film compositions are within a few percent of one another. Based on our previous results, the denser film should posses superior electrical properties.

2.3 Annealing

At this point in the research, it was felt that the annealing procedure needed improvement. While high quality films were being produced, sealing the film into a quartz crucible was both time consuming and costly. Also, although the gold foil used to wrap the target and film was reusable, it did have a finite lifetime and was expensive to replace. Based on our work with alumina and MACOR in bulk target preparation, CSA felt these materials could easily tolerate the conditions encountered in film annealing, and would have very long lifetimes. Also, since these materials are reasonably inexpensive, and, in the case of MACOR, machinable, fabrication of a film and target holder was easily achievable.

A boat was machined from MACOR, as seen in Figure 19a. The boat allows the sample to rest on a bulk thallium pedestal, while a bulk thallium target is suspended a fixed distance above the sample surface. The boat is inserted into a closed end alumina tube. The open of the tube could either be sealed with a MACOR, or left open. In either case, the alumina tube is wrapped in silver foil and both ends of the tube are enclosed by the foil. The wrapped alumina tube containing the MACOR boat is inserted into the furnace for film annealing.

This arrangement uses relatively inexpensive materials with long lifetimes, and allows efficient sample changing. Most importantly, the MACOR boat allows highly reproducible annealing conditions to be maintained. However, since the sample and thallium source are no longer vacuum sealed in the boat, thallium is able to escape from the alumina tube during annealing. This requires that the furnace be vacuum-tight and the thallium vapors be properly condensed and handled. In view of this CSA used a vacuum-sealed Inconel furnace tube with gas input on one side and a thallium condensing system on the output side. A schematic of the furnace is shown in Figure 19b.

Another difference in the annealing conditions is the fact that the total gas pressure over the sample will remain constant throughout the annealing process, whereas in the sealed tube the pressure increased as the temperature increased. In view of these differences in the new process, new annealing conditions will have to be developed.

2.3.1 Thallium Source

All samples processed previously were annealed with a composite oxide target as a thallium source. Our initial work in the new annealing system also utilized this type of source. A wide range of processing conditions was investigated, but in general the annealed films were of extremely poor quality. Energy

dispersive X-ray analysis showed the annealed films to have little or no thallium. Either the source is not providing an adequate thallium over pressure, or it is losing all its thallium since it is not vacuum sealed in a confined volume. During a typical annealing run, the target would lose less than 0.1 percent of its total weight. Since the target consists of approximately 40 percent thallium by weight, it is clear that loss of thallium from the source is not the problem.

Before annealing, the target is a composite oxide, where the electrical resistance of the target as measured by an ohmmeter across the surface of the target is a few ohms. This results from the fact that CuO is a conducting oxide. After one annealing run, the resistance across the surface is extremely large. However, if the surface layer is removed, the bulk of the target is conducting. While we are not sure of the chemical composition or chemical bonding of the surface layer, we believe that this layer is either thallium deficient, or that it prohibits vaporization of thallium from the bulk of the target. In either case, the composite target is an inadequate source of thallium in the current annealing system.

In view of this result we used a bulk, superconducting target as the thallium source during annealing. During a typical annealing the resistance of the target would change very little, while a typical weight loss would be on the order of 0.3 percent. The films exhibited room temperature conductivity, and X-ray diffraction scans showed only higher order superconducting phases.

2.3.2 Investigation of Process Parameters

Once this initial success was achieved, a variety of annealing conditions was explored to optimize the process. Process temperature and the presence of oxygen during annealing are the major parameters in determining phase formation and overall film quality. Briefly, the process sequence we developed is as follows:

1. Insert alumina tube containing MACOR holder, film, and target into furnace tube and start oxygen flow.
2. Ramp furnace to 870°C in one hour, as determined by external thermocouple.
3. Hold at 870°C for 15 minutes.
4. Ramp to 700°C at a cooling rate of 1.5°C/min.
5. Hold at 700°C for one hour.
6. Ramp to 100°C at a cooling rate of 2°C/min.
7. Turn oxygen flow off at 100°C.
8. Let cool to room temperature.

This process yields dense films that completely cover the substrate, and exhibit intense X-ray diffraction peaks. An example is shown in Figure 20a. In general, lower precessing temperatures do produce different phases, but perhaps more importantly, the X-ray signals are not nearly a intense, indicating that the fraction of the film converted into superconducting phases is not as high. This is seen in Figure 20b, an X-ray diffraction scan of a film processed at 850°C.

Process time does not dramatically alter the phase formation. However, if the film is processed for too long a period of time, pits form in the film surface. In our work, we found that the presence of oxygen during the annealing had a dramatic effect on the overall properties. In our initial experiments, oxygen

was only flowed during the ramp down to 700°C, the hold at 700°C, and ramp down to 100°C. While good phase formation occurred, an optical micrograph of the film (Figure 21), clearly shows that the film has pulled away from the edges of the substrate.

Figure 22 is an optical micrograph of similar film processed with oxygen flowing the entire process. As can be seen, the film appears dense and uniform to the edge of the substrate.

There may be several possible explanations for this result. First, the flowing oxygen may reduce the process temperature of the film. This was investigated by inserting a thermocouple into the wall of the alumina tube and measuring the alumina tube's temperature during annealing – with and without oxygen flow. There was no detectable change in the alumina tube temperature, indicating that the oxygen flow did not alter the process temperature.

A second possibility is that high concentrations of oxygen raise the melting temperature of the thallium-based material to the point where melting does not occur at 870°C, and the film continues to cover the entire substrate. In the absence of oxygen, the film undergoes at least a partial melt at 870°C. As a result, it "balls up" or pulls away from the edge of the substrate. This result has been observed by others, although at this time direct proof of film melting or non-melting has not been obtained.[12] Clearly, more work needs to be done in this area.

3.0 Film Patterning and Electrical Contact Formation

In order to produce thin film structures that can be used to measure critical current density, reliable patterning techniques must be developed. CSA used standard photolithographic techniques based on both positive and negative photoresist to fabricate simple four-point probe structures. As-deposited thallium-based films are easily etched in a pH balanced ethlyenediaminetetraacetic acid (EDTA)/water solution.[16] This etchant does not appear to affect the photoresist, and when thickened by the addition of glycerol, it can produce patterns with a high aspect ratio. A typical EDTA patterned film is seen in Figure 23. CSA also used a 0.5 percent HCl solution to pattern annealed films, where we achieved similar results. However, this solution etches isotropically, with a resultant loss in pattern definition.

In order to measure the critical current density of the films, reproducible, low resistance electrical contact to the film must be made. We sputtered silver contact pads through a shadow mask, and using standard four-point probe geometry, measured the contact resistance. The contact resistance of the as-deposited silver films is on the order of 10^{-3} ohm-cm^2. This value is adequate for low current resistance vs temperature measurements, but not for critical current density measurements. Upon annealing at 600°C in flowing oxygen for 10 minutes, the contact resistivity drops to below 10^{-6} ohm-cm^2, with no detectable degradation in the film properties.

4.0 Summary

The Corporation for Studies and Analysis (CSA) has fabricated thallium based films on $LaAlO_3$, a microwave compatible substrate. The films have zero resistance temperatures between 103 and 115°K, depending on the phase present in the film. The critical current density of the films is at least 1×10^5 A/cm^2, at 77°K. These results were achieved by developing an understanding of the pulsed laser deposition and annealing processes. Our work pointed out areas where development was needed. Specifically, bulk, single phase stoichiometric targets dramatically improved the as-deposited, and subsequently the annealed, film properties. In concert with development of bulk target processing was an improvement in the annealing process. This was based on utilizing machinable, long life ceramics. The ceramics were machined into boats which permitted highly reproducible annealing conditions to be maintained.

5.0 Illustrations

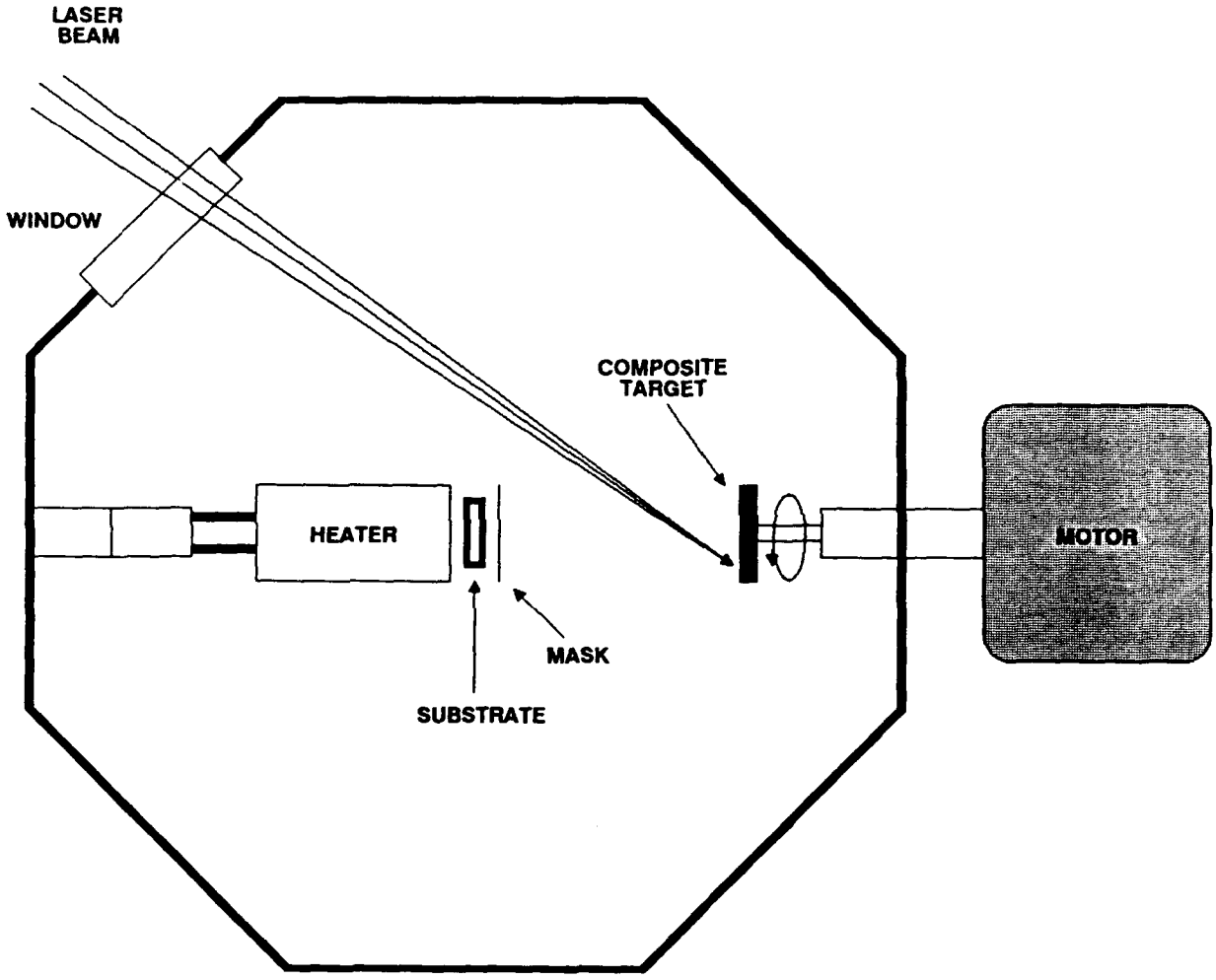


Figure 1. Schematic Diagram of PLD System

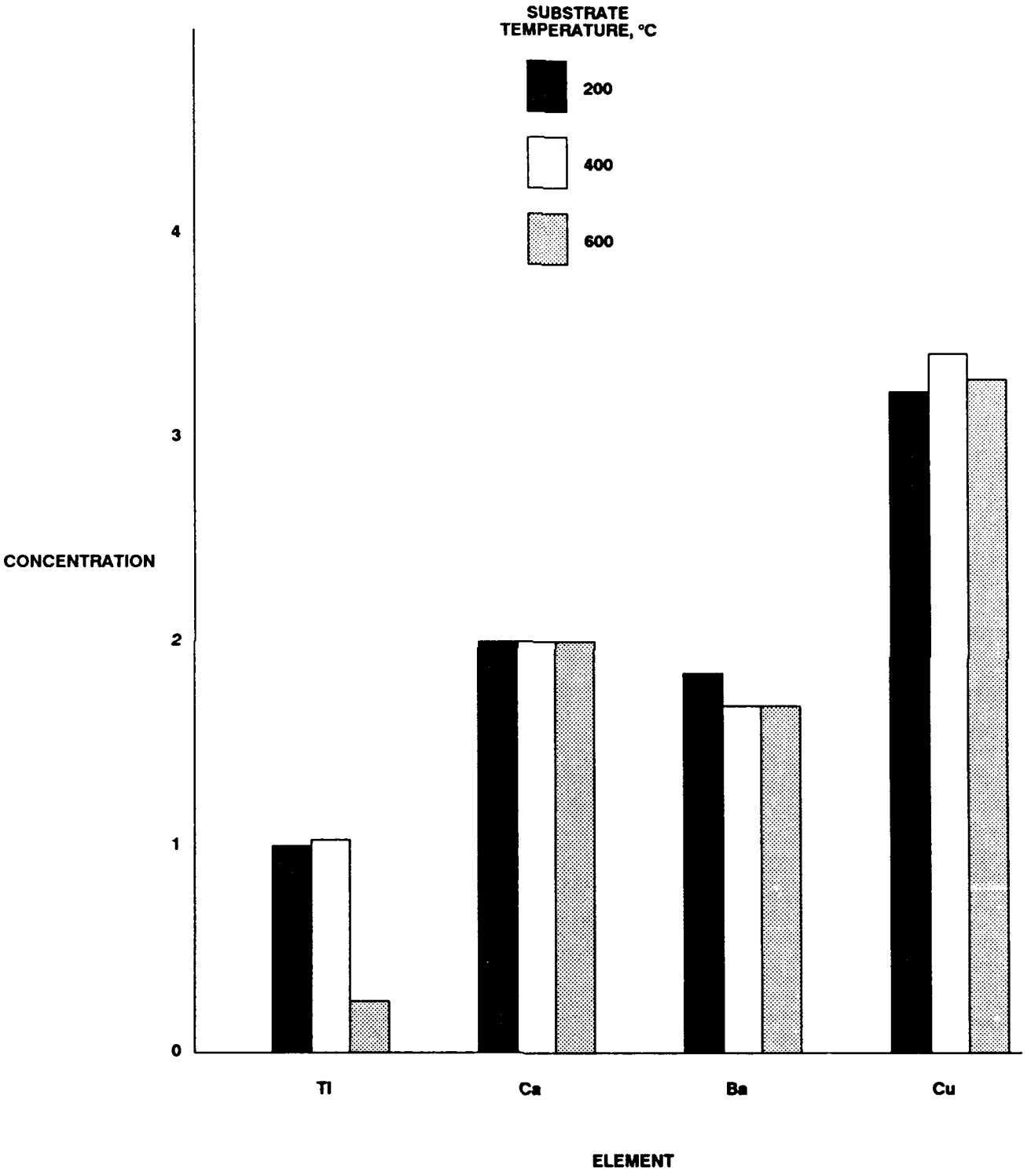


Figure 2. Composition of As-Deposited Films as a Function of Substrate Temperature as Determined by RBS Analysis

The films were deposited by PLD using a Nd:YAG laser operating at 532 nm, with a fluence of 1.2 J/cm^2 and 10 nsec pulsed width.

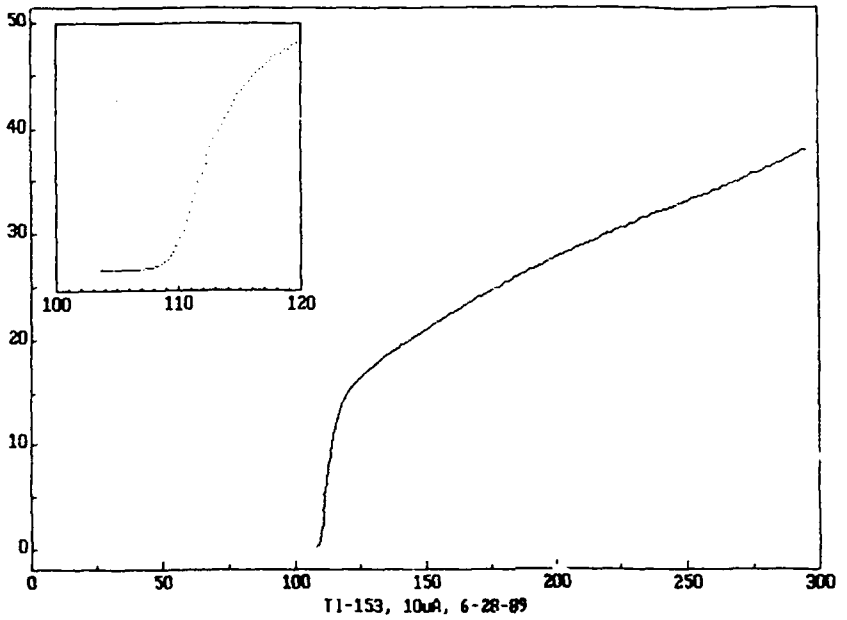


Figure 3a. Typical R vs T Curve for Tl-Ba-Ca-Cu-O Film Annealed at 870°C for 10 Minutes

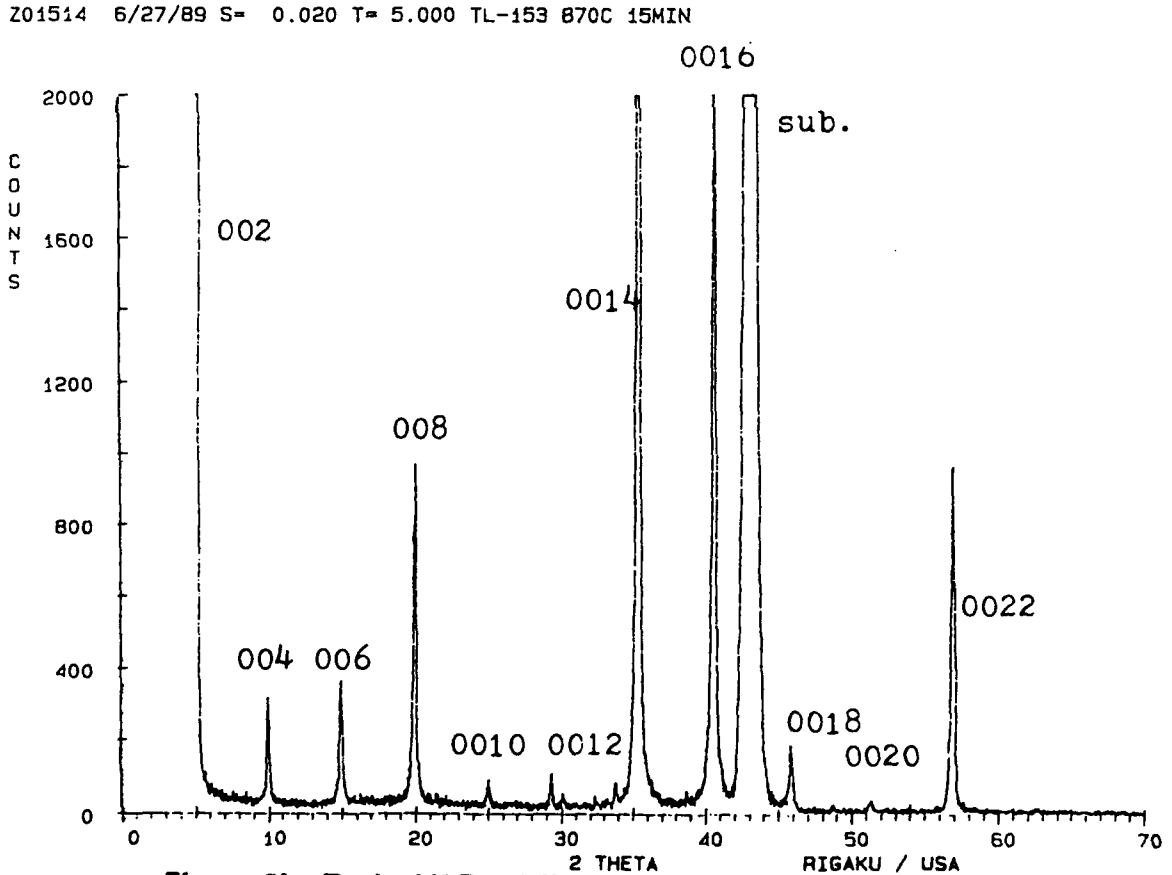


Figure 3b. Typical X-Ray Diffraction Pattern for Annealed Film

NOTE: All lines are substrate are 2:2:2:3 c-axis oriented lines. Also, all x-ray lines are present.

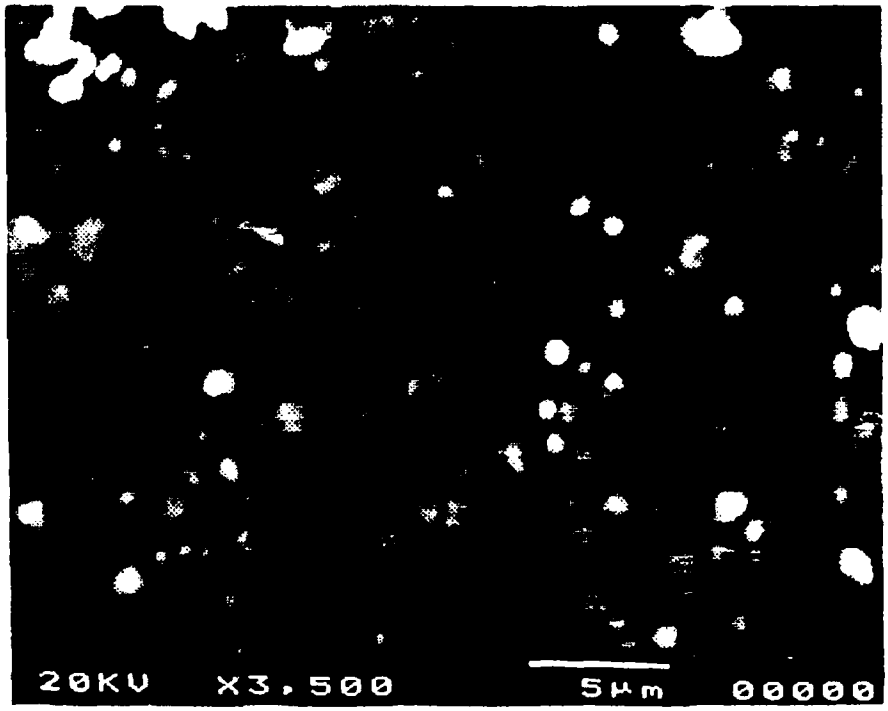


Figure 4. SEM Micrograph of Typical As-Deposited Tl-Ba-Ca-Cu-O Film

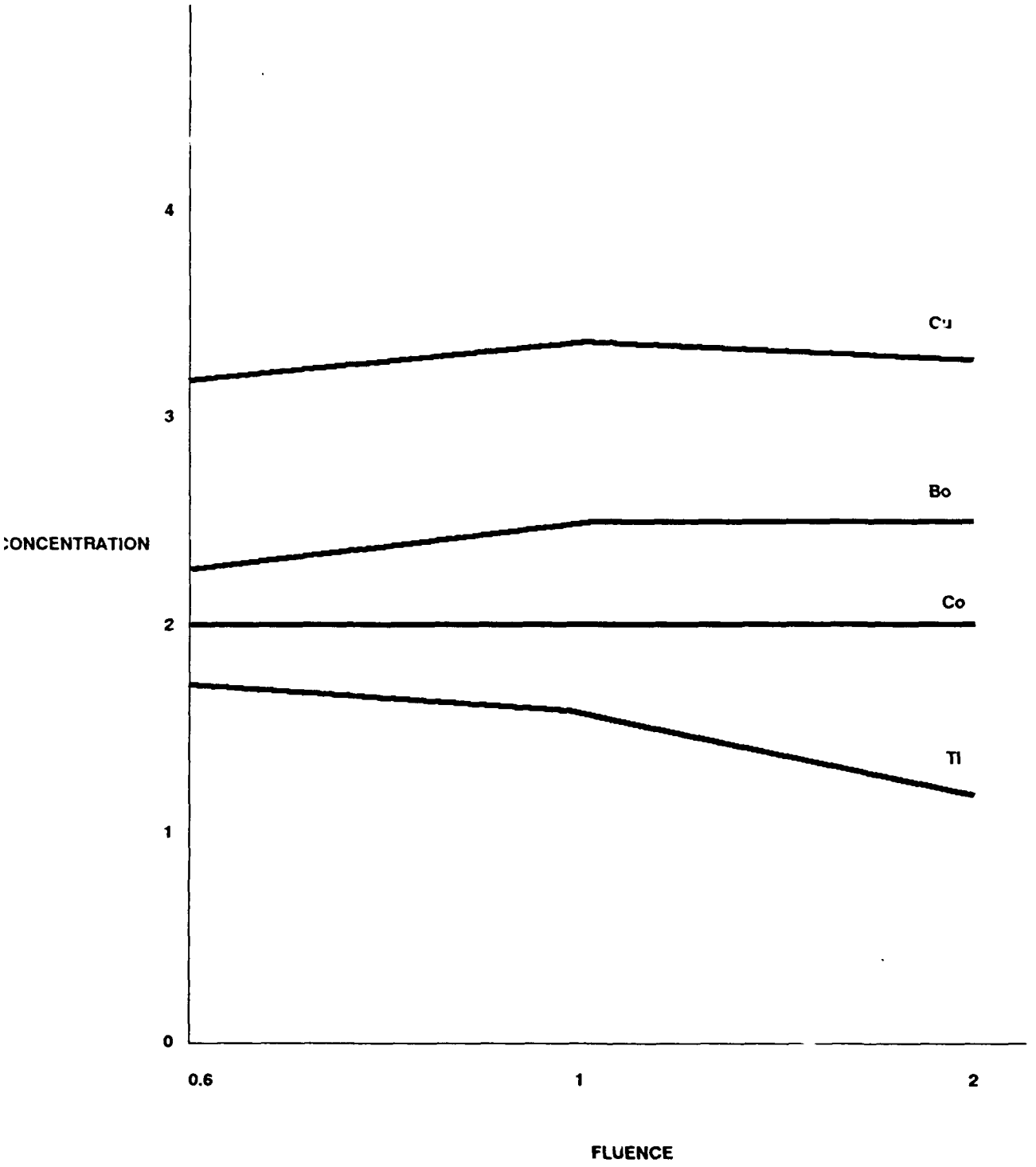


Figure 5. Graph of the Composition of As-Deposited Films as a Function of Laser Energy Fluence as Determined by EDS Analysis

The films were deposited by a Nd:YAG laser operating at 532 nm, a substrate temperature of 200°C, and a background pressure of $5x10^{-5}$ Torr

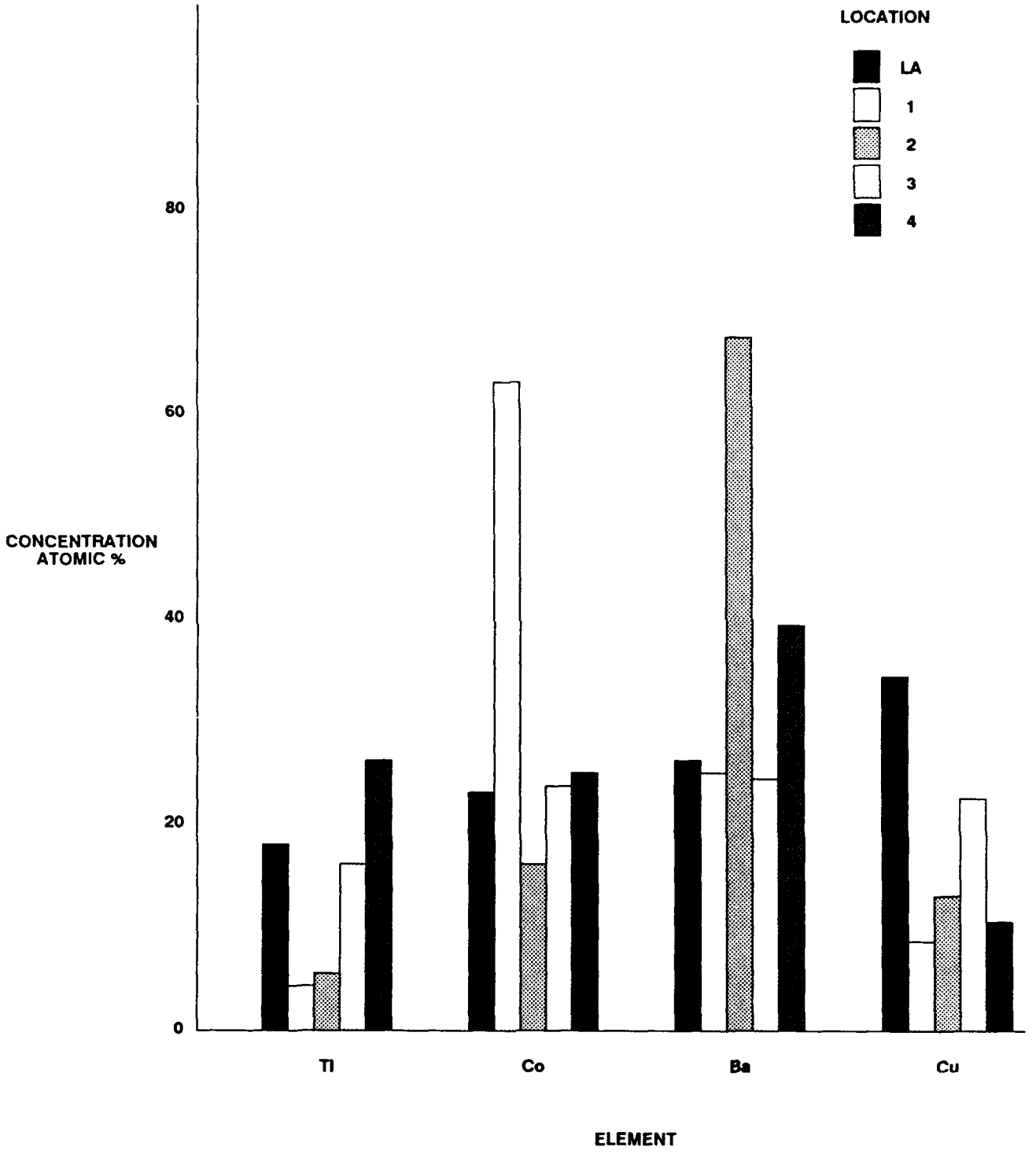


Figure 6. Concentration, in Atomic Percent, of Thallium, Calcium, Barium, and Copper for a Film Deposited at 532 nm Over a Large Area (LA) and Four Randomly Located Small Points

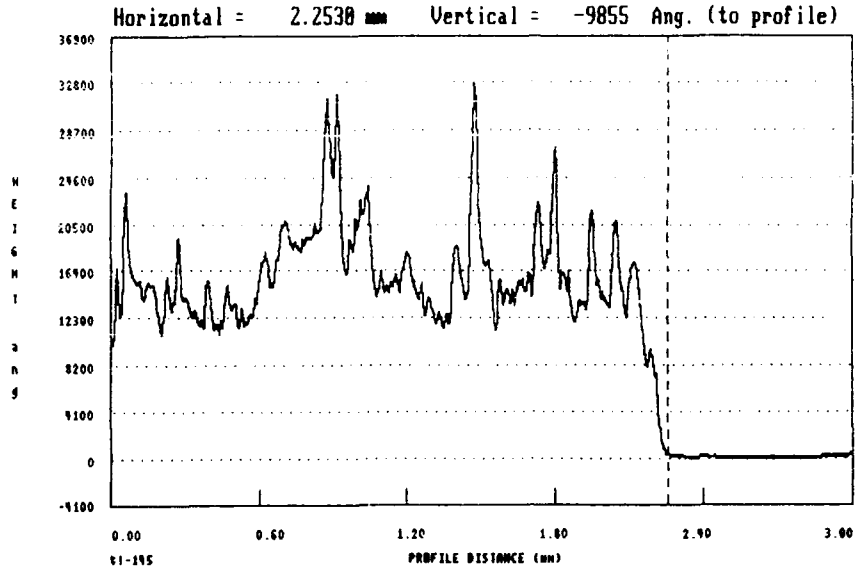


Figure 7a. Tl-145, From 2-2-2-3 Composite Tl Target, F= 1.2 J/cm^2, t = 20 min

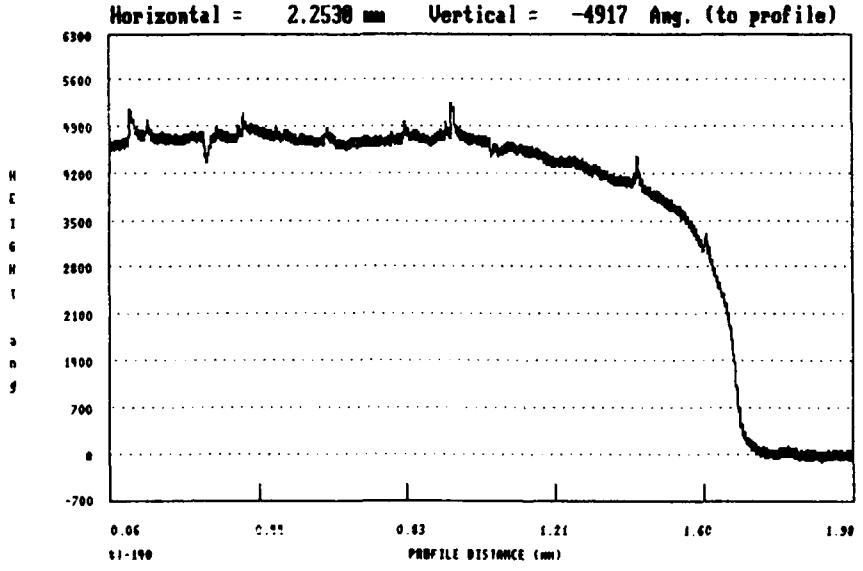


Figure 7b. Tl-140, From Compound Tl Target, F = 1.2 J/cm^2, t = 15 min

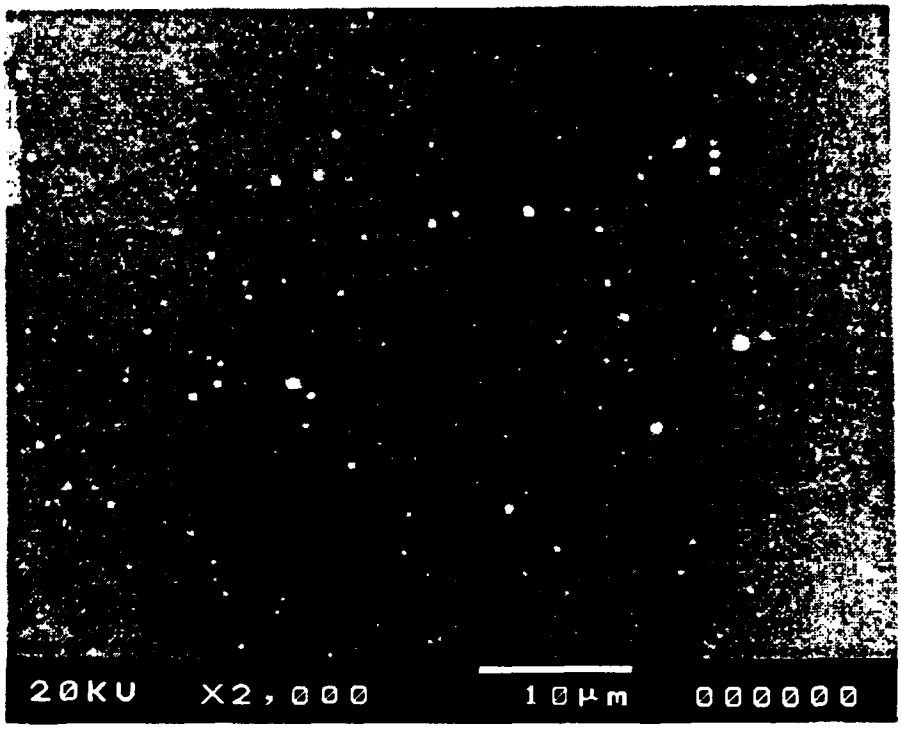


Figure 8. As-Deposited Tl-Ca-Ba-Cu-O Film at 248 nm

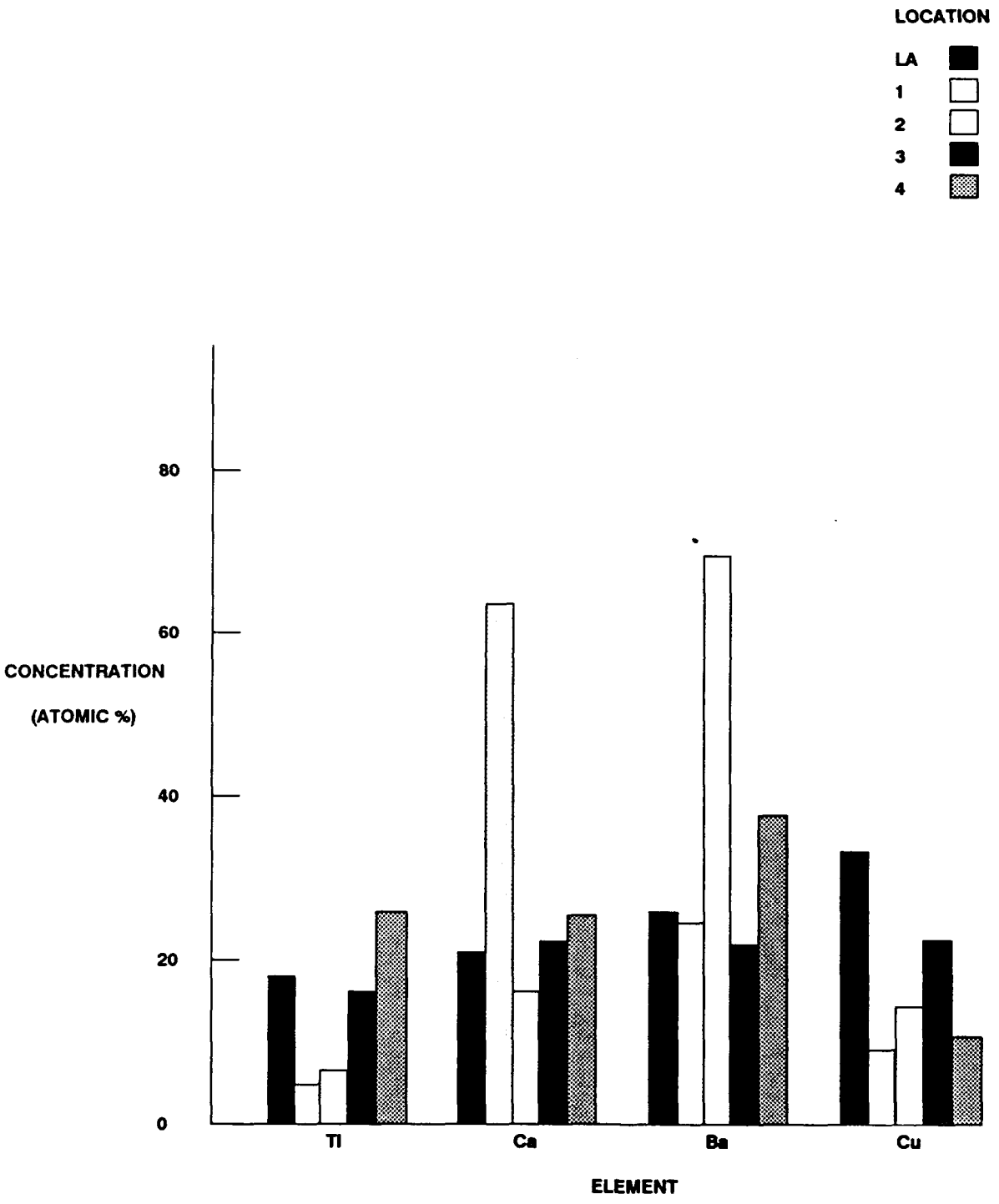


Figure 9. Graph of Concentration, in Atomic Percent, of Thallium, Calcium, Barium and Copper for a Film Deposited at 532 nm over a Large Area (L.A.) and Four Randomly Located Small Points

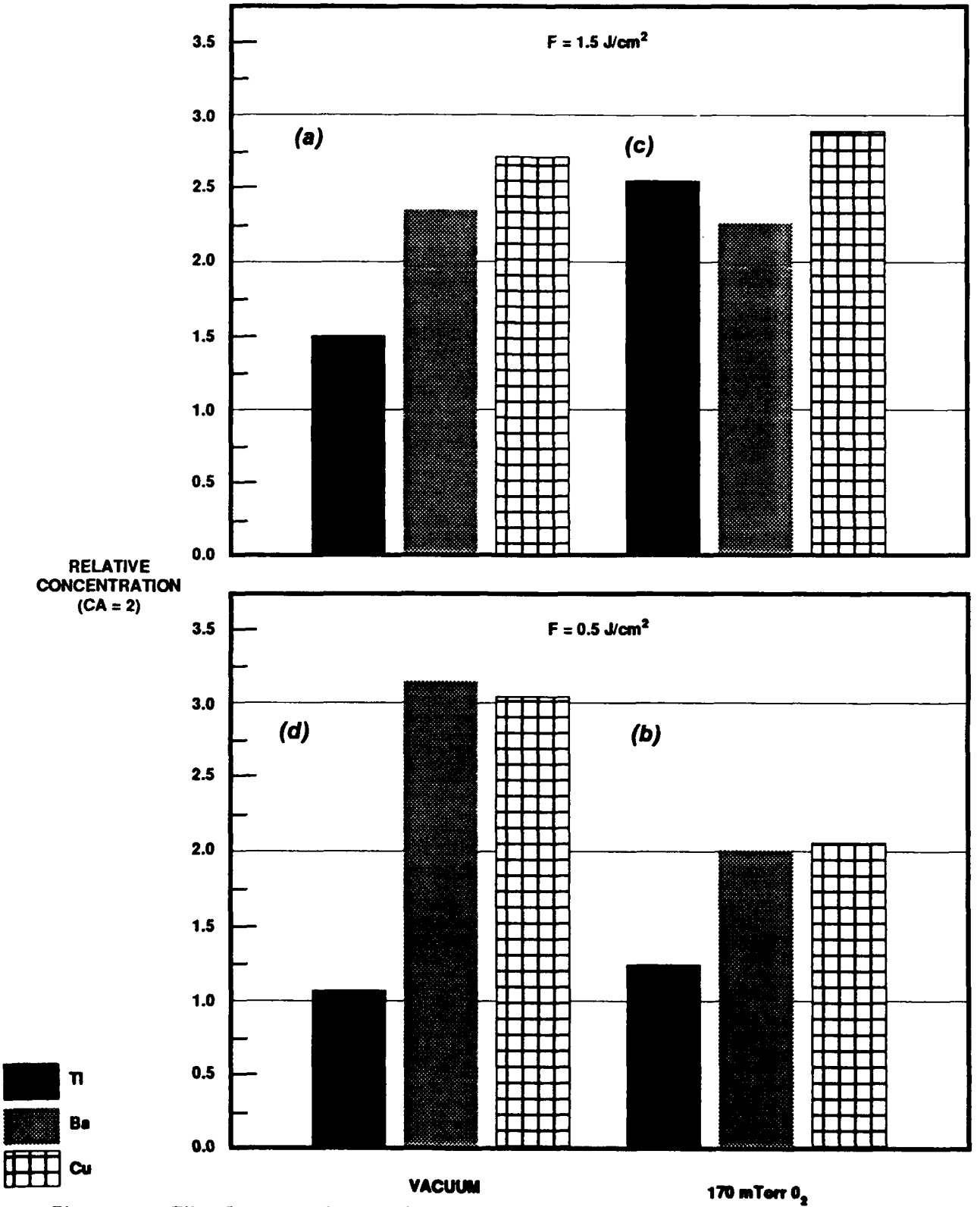


Figure 10. Film Composition of Fluence (F) and Oxygen Background Pressure (BP), Normalized to CA = 2

(a) F = 1.5 J/cm2, BP = 0; (a) F = 0.5 J/cm², BP = 170 mTorr; (c) F = 1.5 J/cm², BP = 170 mTorr; (d) F = 0.5 J/cm², BP = 0;

Figure 11. SEM Micrograph of an As-Deposited Film at Substrate Temperature of 600°C, Fluence of 1.5 J/cm^2 in an Oxygen Background Pressure of 170 mTorr

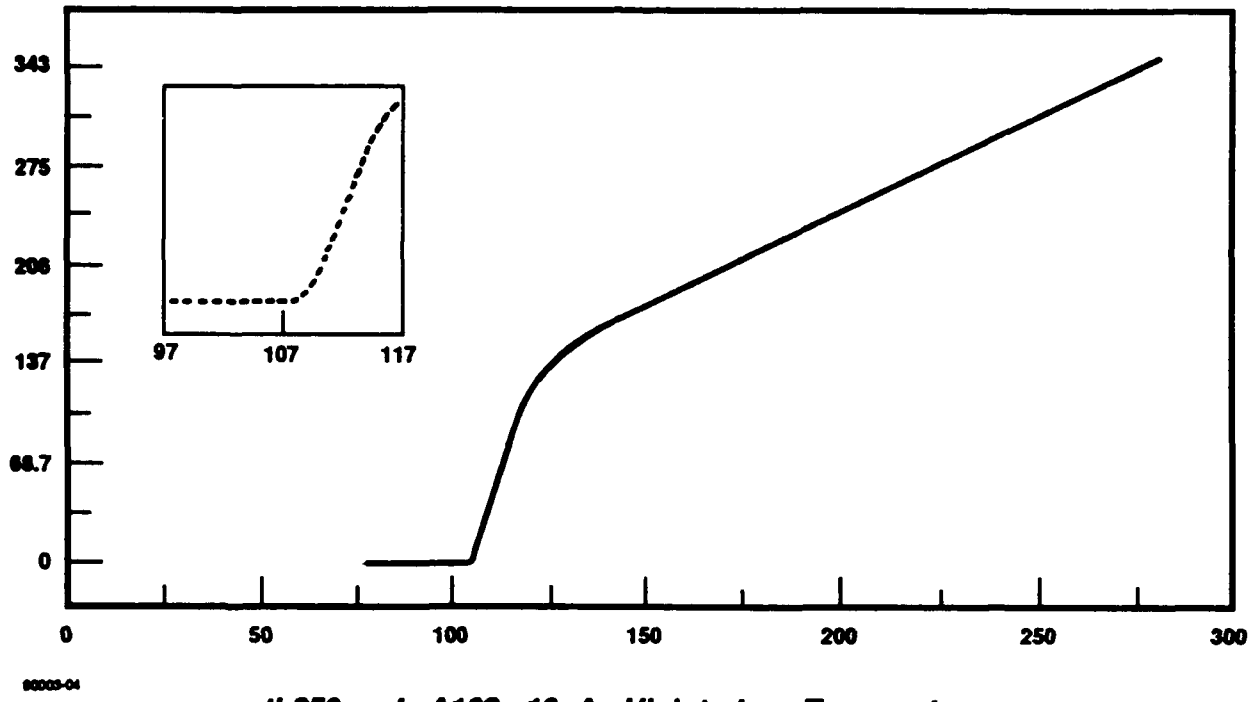
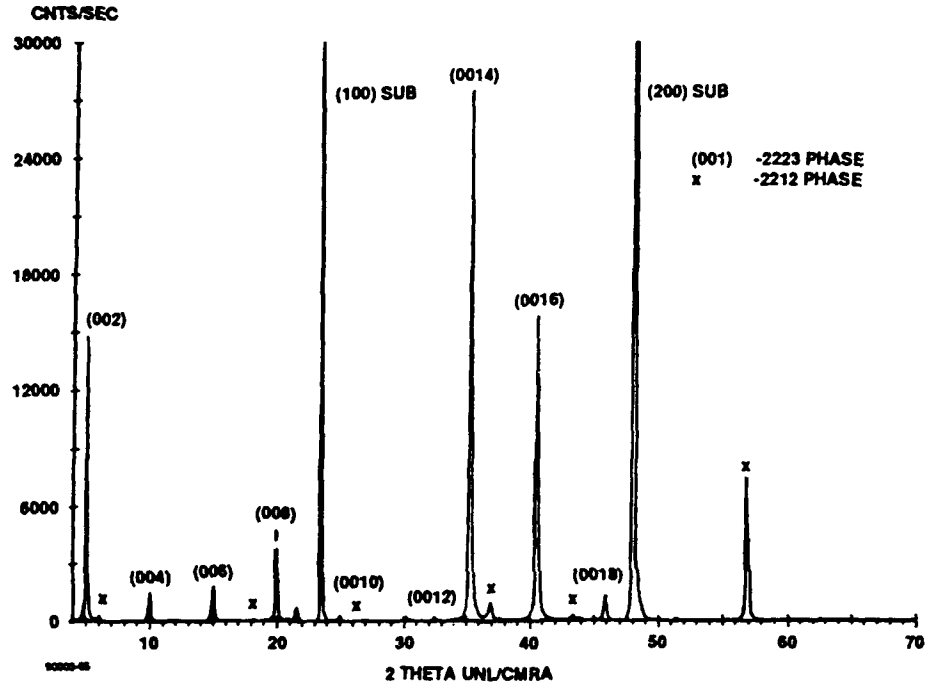


Figure 12. Resistance vs Temperature Curve of an Annealed Film on (100) Oriented $LaAlO_3$



Z02380 3/28/90 S= 0.020 T= 2.000 TL-257 on $LaAlO_3$

Figure 13. X-Ray Diffraction Scan of an Annealed Film on (100) Oriented LaAlO3 Showing the 2-2-1-2 and 2-2-2-3 Phases

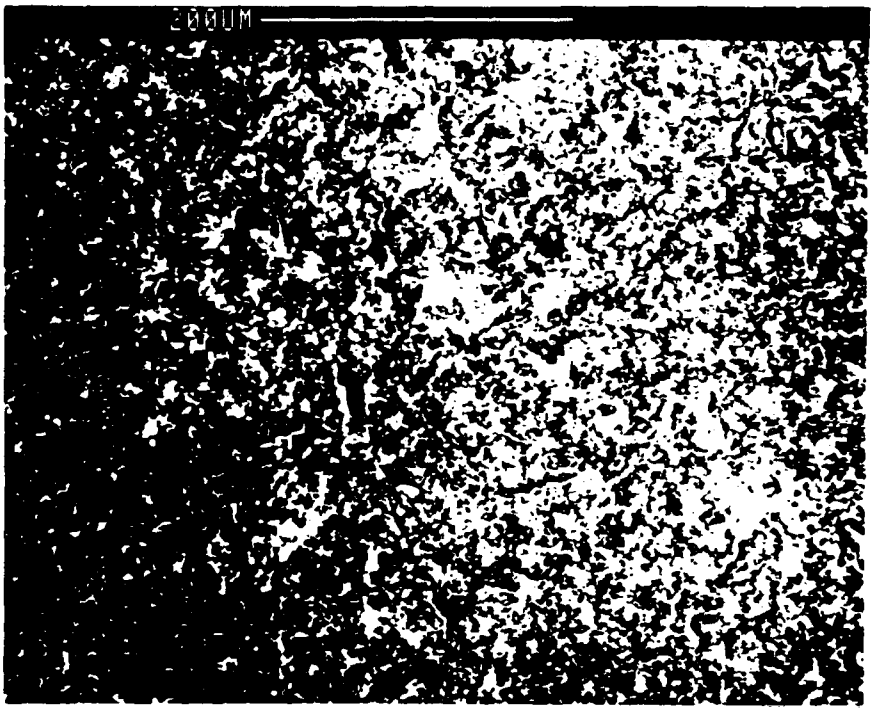


Figure 14. SEM Micrograph of an Annealed Film

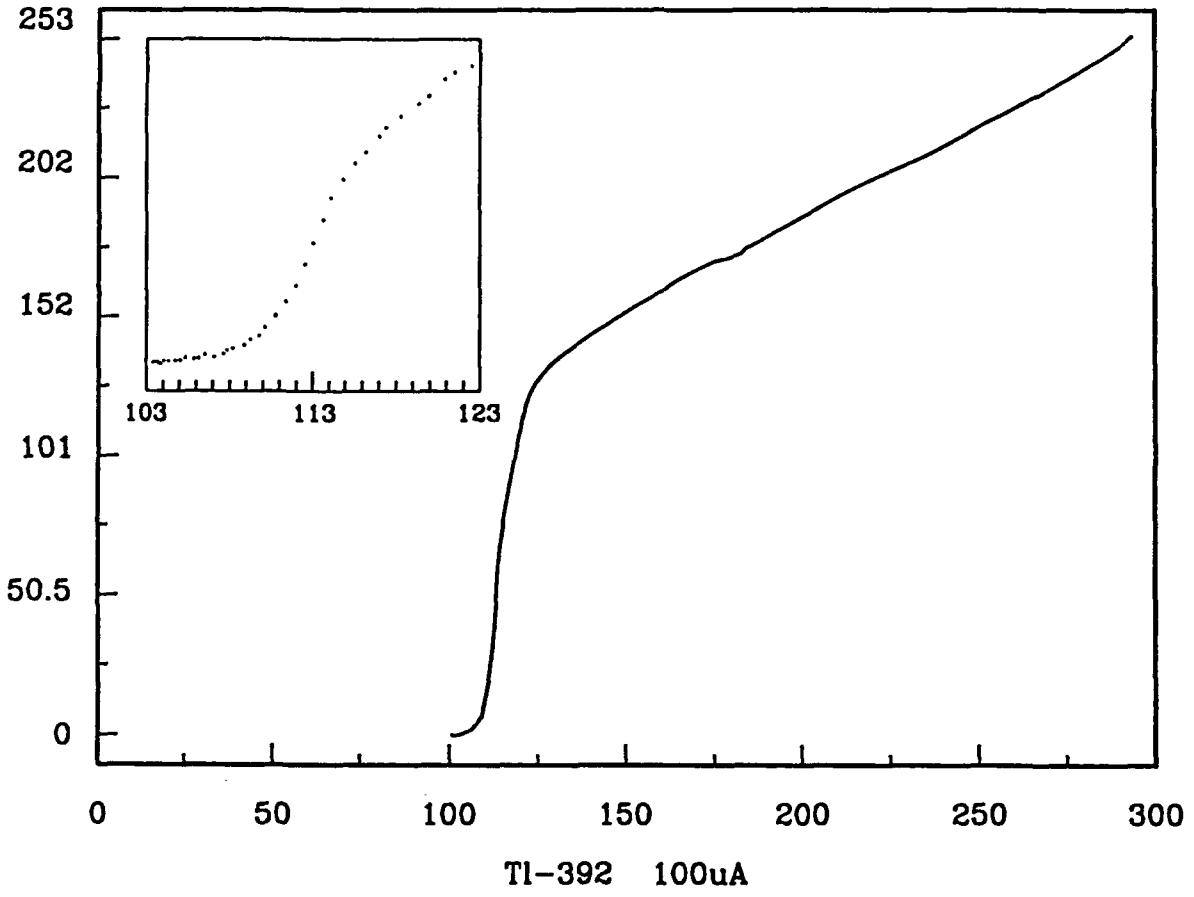


Figure 15. Resistance vs Temperature Curve of Film Seen in Figure 14

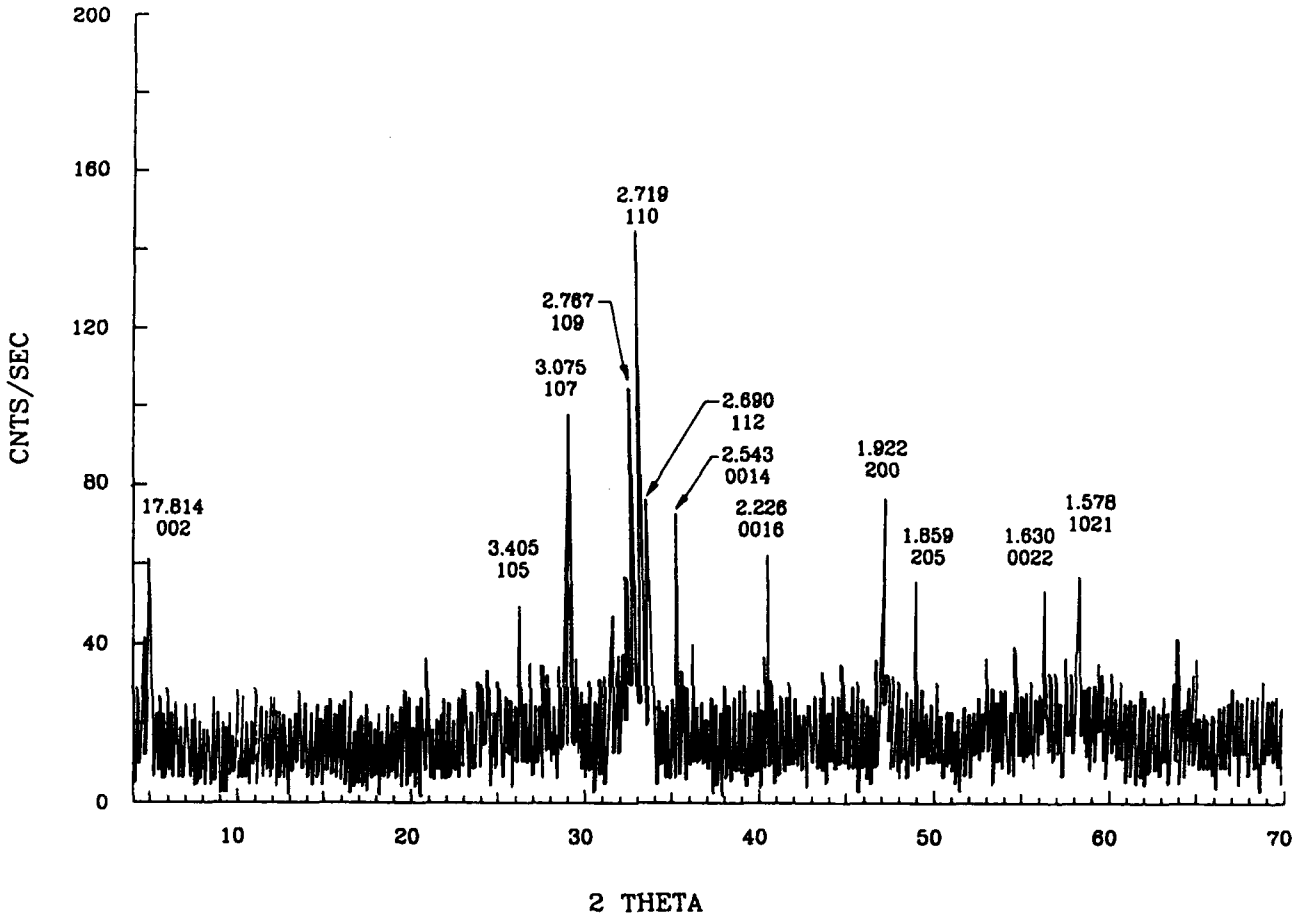


Figure 16. X-Ray Diffraction Scan of Powdered Bulk Superconducting Target

Note all lines are from $Tl_2Ca_2Ba_2Cu_3O_x$ phase.

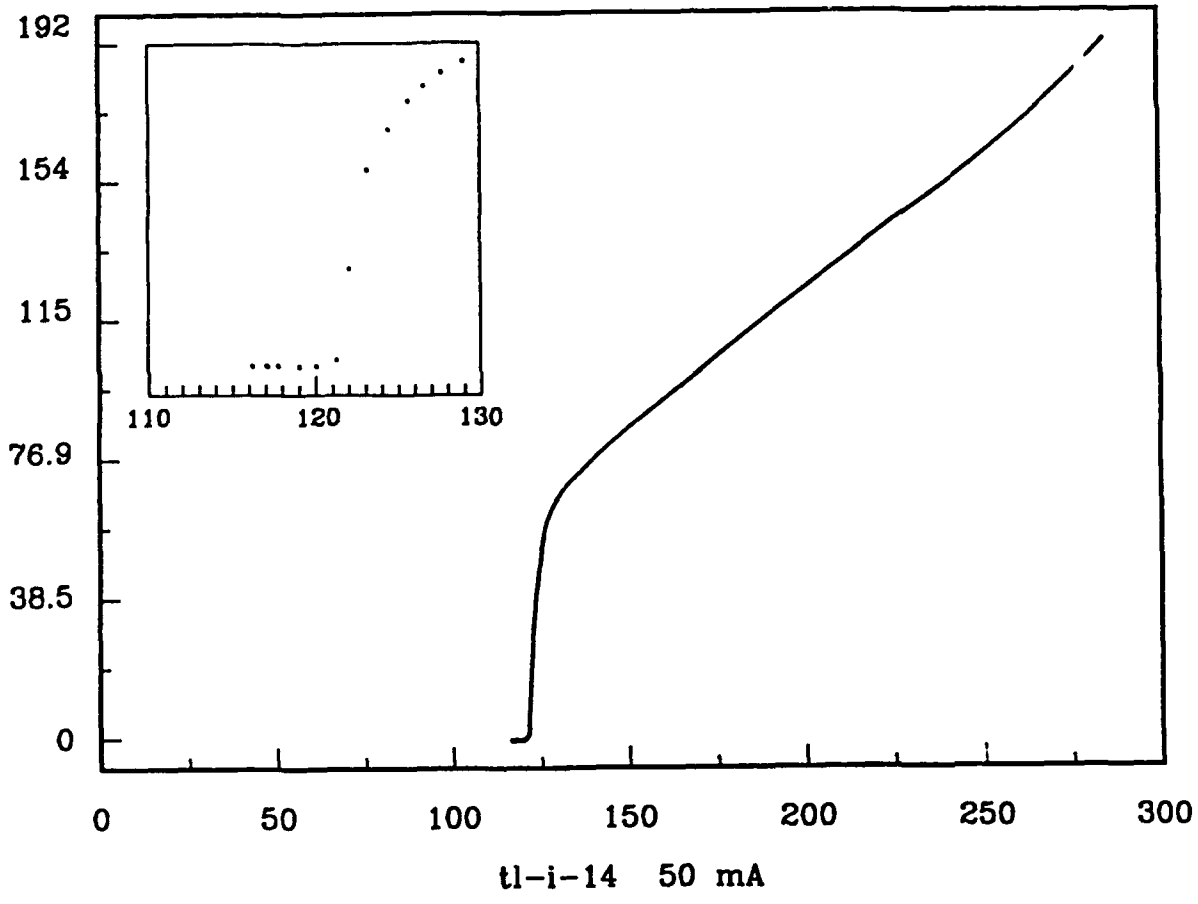


Figure 17. Resistance vs Temperature Curve of a Bulk Superconducting Target With Zero Resistance Temperature of 122°K

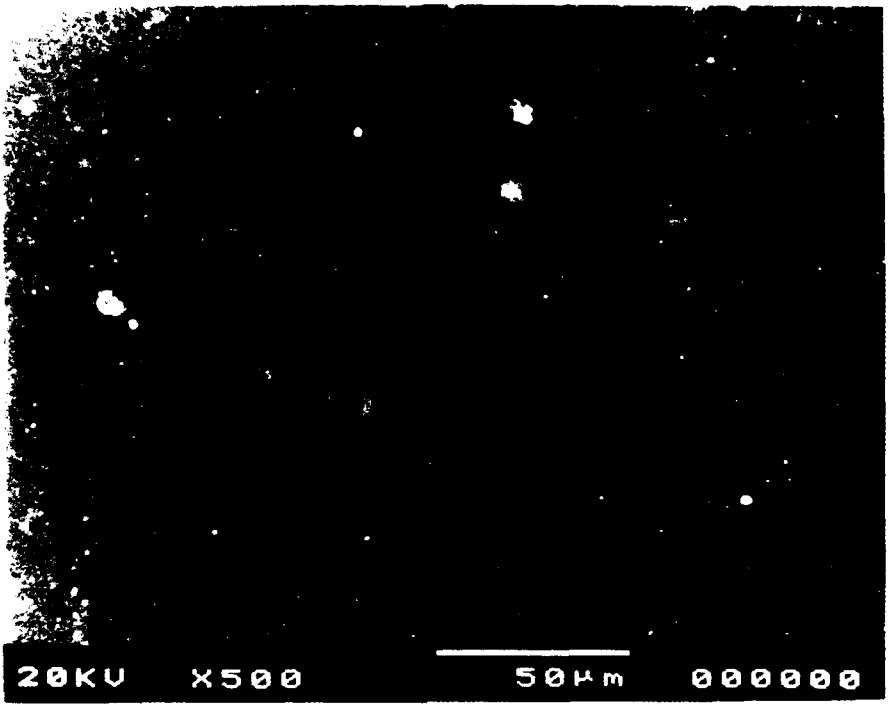


Figure 18a. SEM Micrograph of a Film Deposited from a Compound Target

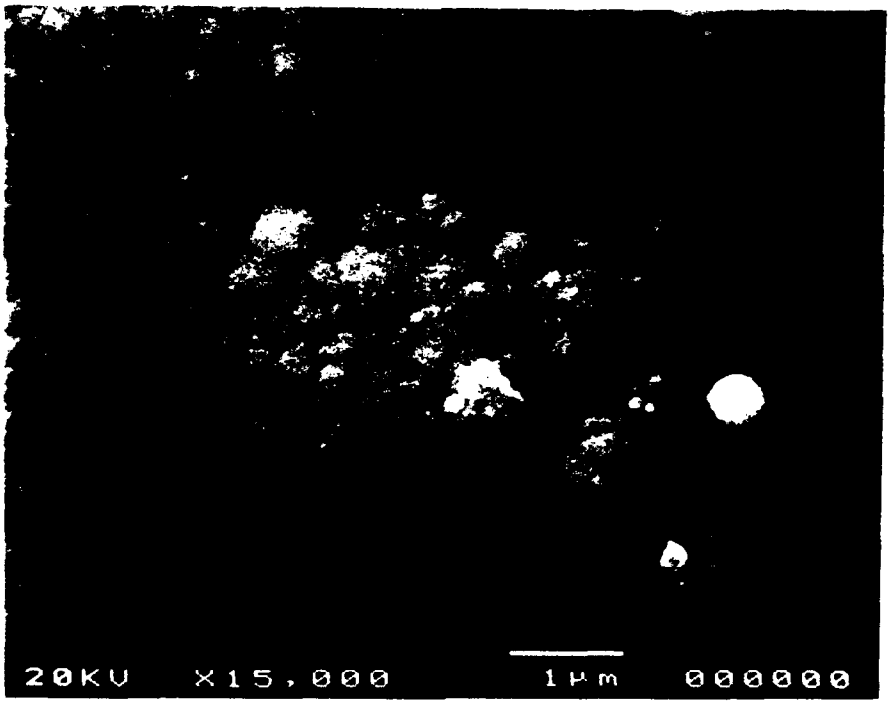


Figure 18b. Close Up of Smooth Background Seen in Figure 18a

Note Microscopic Roughness Of The Surface

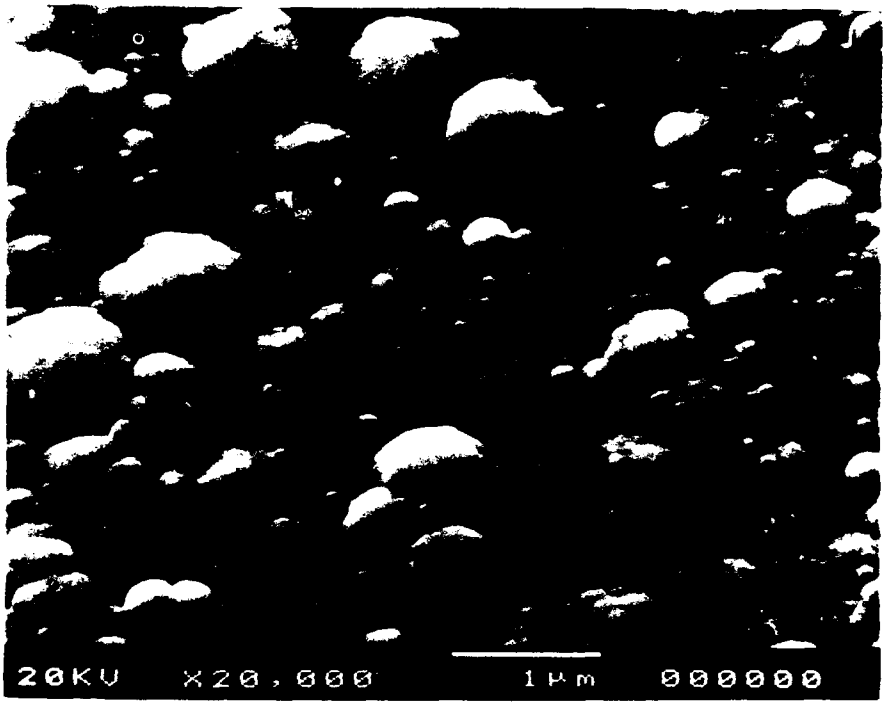


Figure 18c. SEM Micrograph of a Film Deposited From a Composite Target of the Same Magnification Seen in Figure 18b

Note The Film Consists Of Larger Particulates than The Film Seen In Figure 18a

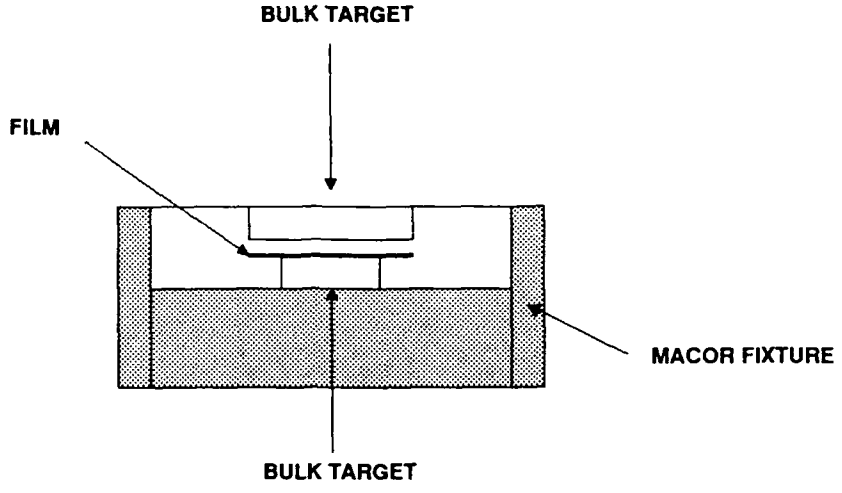


Figure 19a. Cross Section of the MACOR Fixture Used to Support the Film and Annealing Targets

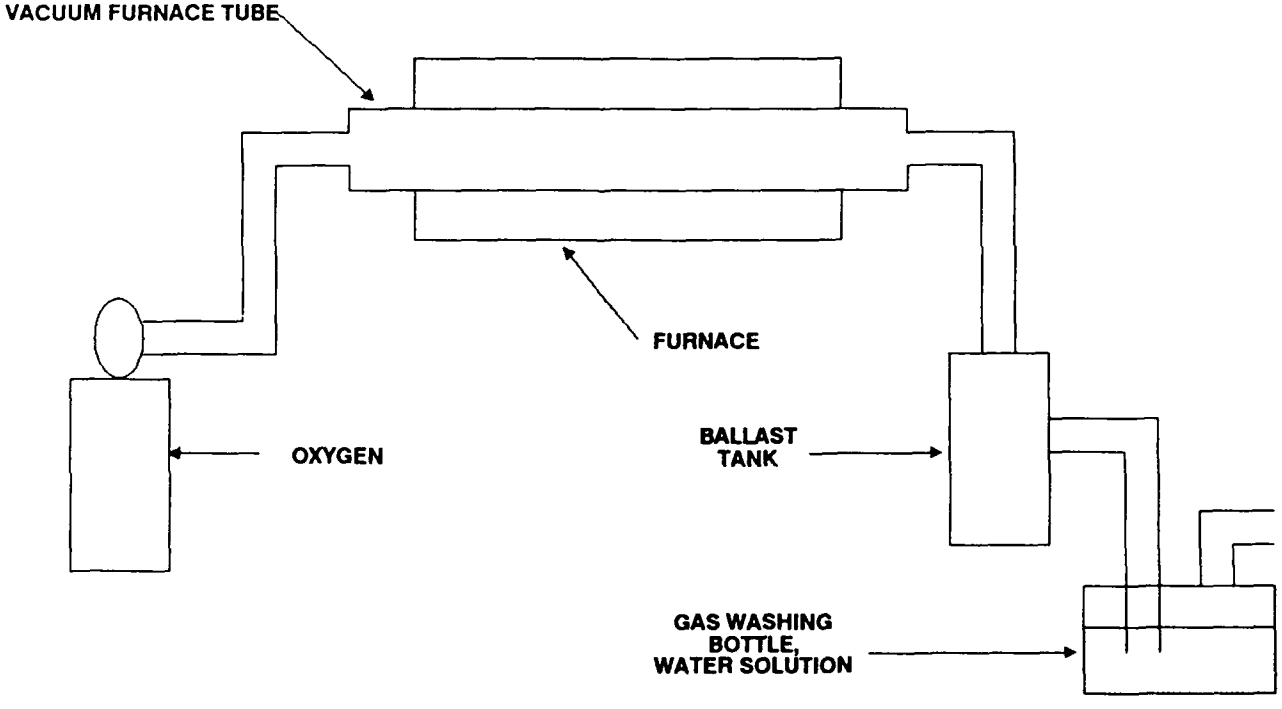


Figure 19b. Schematic Diagram of Furnace Annealing System

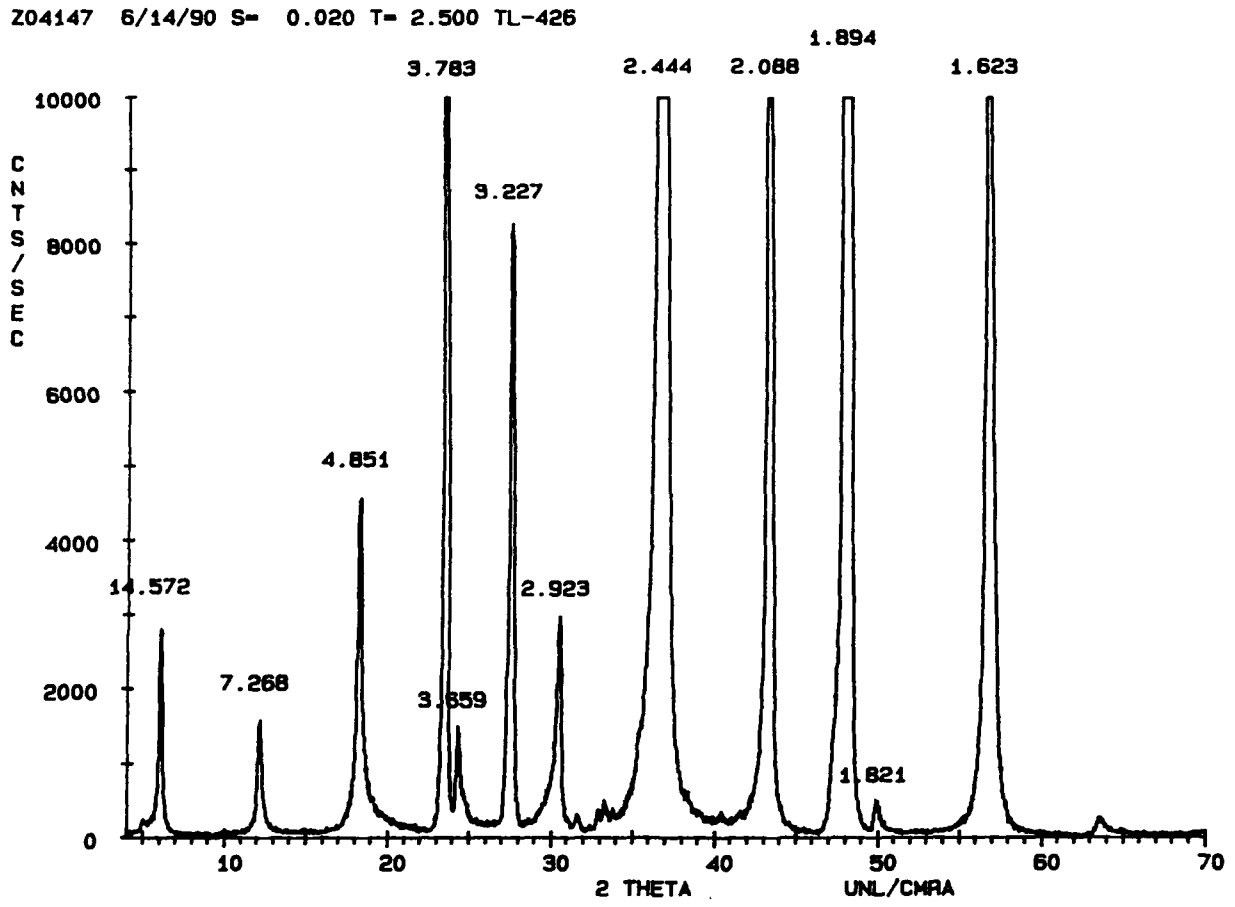


Figure 20a. X-Ray Diffraction Scan of a Film Annealed at 870°C

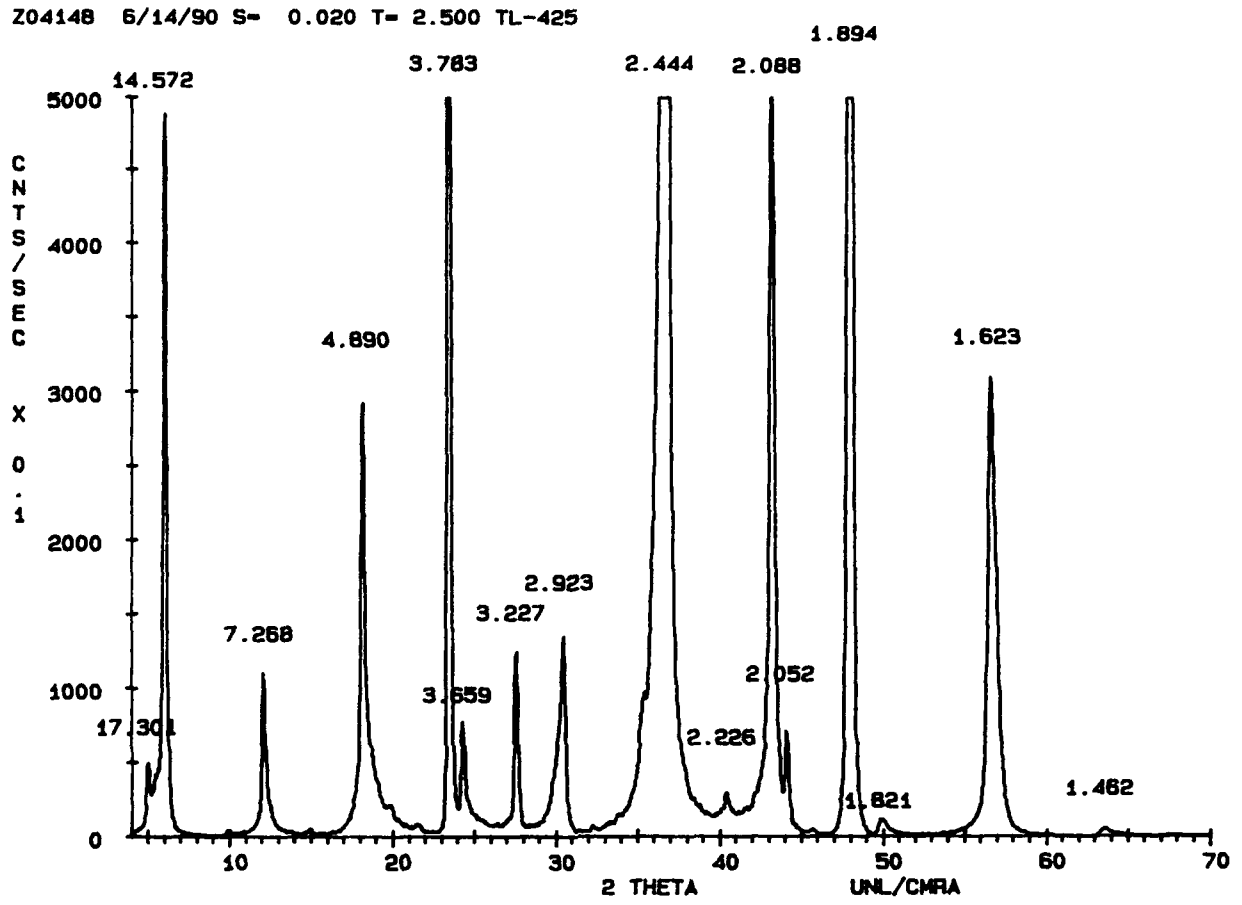


Figure 20b. Scan of a Film Processed at 850°C

Both films exhibit good phase formation, but the 870°C film has more intense peaks.

Figure 21. Optical Micrograph of Film Processed Without Oxygen During Ramp-Up and High Temperature Hold Cycle

Note the Film Degradation Near Edge of the Substrate

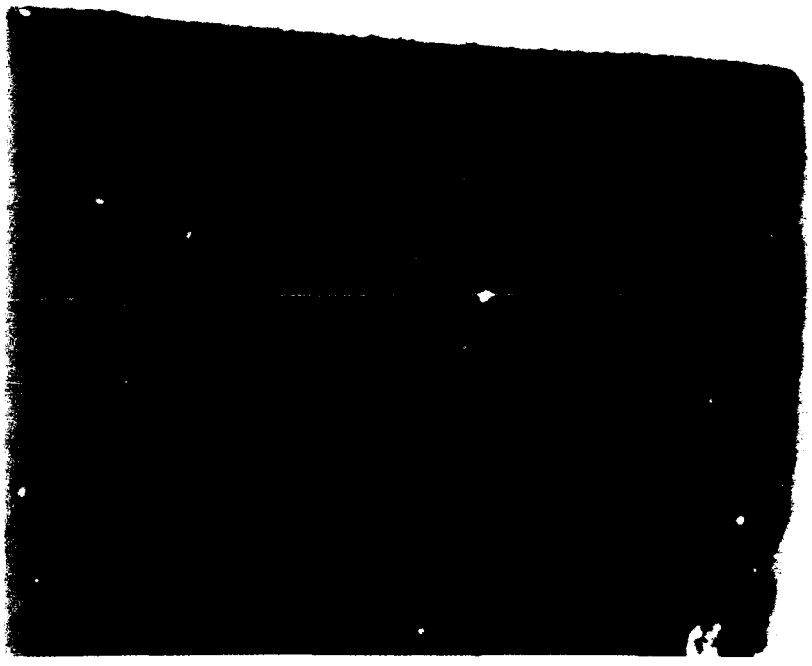


Figure 22. Optical Micrograph of a Film Annealed Under the Same Conditions as the Film in Figure 21, Except that Oxygen was Flowed During the Entire Process

Note the Good Morphology that is Maintained to the Edge of the Substrate

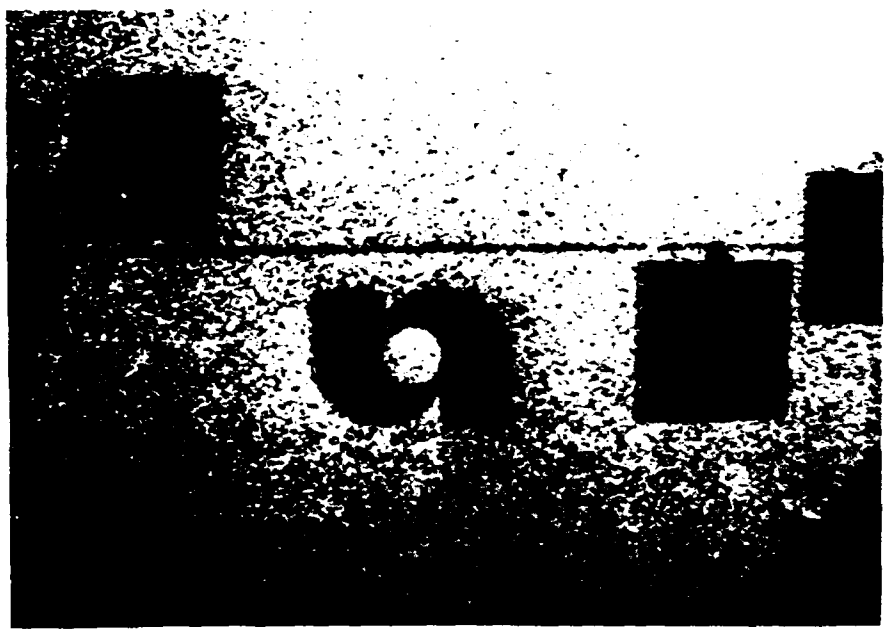


Figure 23. SEM Micrograph of an EDTA Patterned Film

6.0 References

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