Fabrication and Properties of DC–Sputtered Tl–1223 Superconducting Thin Films

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***Abstract*— A multi-step deposition and post annealing scheme has been developed for preparing nearly single phase, c-axis oriented $TlBa_2Ca_2Cu_3O_9$ (Tl-1223) superconducting thin films by dc-sputtering. The effects of the compensates used during post annealing on final phase formation suggest the crucial role played by thermodynamic conditions and further validates the viability of the present process scheme. In particular, films obtained by the present process have shown, for the first time in this system, a critical current density (Jc) above 10^6 A/cm^2 at 77 K with a zero- resistance transition temperature (Tco) above 110 K. The results are attributed to the improvement of film morphology, specifically a decreased density of weak-links.**

I. INTRODUCTION

Recently, due to the stronger interlayer Josephson coupling between the superconductive CuO_2 layers expected [1] and its high Tc, the Tl-1223 phase has been of great interest both from the theoretical and practical points of views [2-9]. Transport measurements on Tl-1223 films, however, have not only suffered from low Jc values (Jc(77 K, 0 T)$\approx 10^5$ A/cm^2) but also from difficulties in obtaining pure Tl-1223 films [4-9]. The reasons are primarily as follows. All of the Tl-based superconductors are inherently difficult to fabricate *in–situ*, especially in thin film form, because of the high volatility of thallium oxides. As a result, standard processes for preparing the Tl-based superconducting thin films usually involve deposition of a precursor film, which normally is amorphous and may or may not contain Tl, followed by very strict post- annealing scheme at high temperatures (800-900 ° C) [4-9]. The high temperatures and solid state interdiffusion involved in the post-annealing processes generally result in granular films with rough surfaces and, hence, degraded superconducting properties. Thus, methods of obtaining weak-link free,single phase Tl-1223 films are clearly in order.

In this paper, results showing encouraging progress of fabricating Tl-1223 thin films are repoted. With the experiences acquired from fabricating Tl-2223 superconducting thin films using a dc-sputtering + post annealing scheme [10], we have been able to locate the annealing temperature and time windows necessary for obtaining pure Tl-1223 superconducting thin films with much improved transport properties. Currently, films with Tco $\approx$ 110 K and Jc (77 K) $> 10^6$ A/cm^2 have been obtained.

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II. EXPERIMENTAL

Precursor films with nominal composition Tl:Ba:Ca:Cu = 1:2:2:3 were deposited on single crystal $LaAlO_3(100)$ substrates by dc-sputtering from a single target of similar stoichiometry. The target was fabricated by a solid-state reaction-sintering process. Proper amounts of Tl_2O_3, $BaCO_3$, CaO, and CuO powders were mixed, ground thoroughly, pressed into 1" disk, and sintered at 875 ° C for a prolonged period of time, typically ranging from 6-12 hours. The resultant product, as revealed by X-ray diffraction analysis, is a multi-phased material consists of the Tl-1223 phase and other unreacted residuals. It is important that the target be conductive for sputtering to occur. The sputtering gas was a mixture of high purity Ar and O_2 with a nominal molar ratio of 80 % Ar and 20% O_2. The total pressure was kept at around 0.2 Torr through the entire sputtering process. The dc power supply was operated at a typical voltage of 0.6 kV with a current of about 1.2-1.3 A, corresponding to an output power of about 700 Watts. A target to substrate distance of about 8 mm coupled with the above power supply conditions, produced a discharge current of $\approx$ 38 mA. Typically, with a sputtering time of 90 minutes, the films are about 0.6-0.7 μm thick.

Since the films were all deposited at low temperatures (the substrate temperature was estimated to be around 130 ° C), the as-deposited films were all amorphous and nonsuperconductive. Consequently, they can only serve as precursors and a proper post- annealing scheme must be performed to obtain superconductivity. Our post annealing process involves two main steps; namely the preparation of the bulk compensates and the final annealing of the precursor films with compensates. In order to investigate the effects of thermodynamic conditions on the phases formed from the precursor films, both Tl-2223 and Tl-1223 bulk materials were used as the annealing compensates.

To prepare the Tl-1223 bulk compensates, the bulk Tl-2223 materials were first prepared by sintering the calcined mixture of Tl_2O_3, $BaCO_3$, CaO, and CuO powders (with molar ratio of Tl:Ba:Ca:Cu = 2:2:2:3) at 850 ° C for several hours. The sintering temperature was then ramped to 875 ° C with a rate of $\approx$ 3 ° C/min and held for 2-3 hours prior to furnace-cooling in the oxygen-flow environment.

As is evident from Fig. 1(a), the resultant phase was nearly 100 % Tl-2223. The obtained Tl-2223 material was then put into a quartz tube sealed with pure oxygen of about 60 Torr. The whole assembly was then annealed at 875 ° C for about 70 minutes to extract Tl directly from the Tl-2223 phase. As illustrated in Fig. 1(b), the resultant products obtained consists mostly of Tl-1223 and some $BaCuO_2$. The fact that this procedure can convert the Tl-2223 phase into Tl-1223 phase is very interesting by itself. Whether it is caused by a direct evaporation of one of the Tl-O layers originally existent in the Tl-2223 structure or by Tl evaporation-induced structure reorganization [2] is not clear. Nevertheless, it is believed that this probably is one of the most effective ways for preparing bulk Tl-1223 phase at present. Direct sintering, as we have practiced for preparing the sputtering target, usually results in multiphase products.

Either the Tl-2223 or Tl-1223 pellets were then wrapped with the as-deposited precursor films in a gold foil. The assembly was again sealed in a quartz tube with 760 Torr of pure oxygen and then annealed at 910 ° C for about 30 minutes. The samples were quenched or furnace-cooled to about 600 ° C then quenched in air.

For Jc(T) measurements, films were patterned into 20 μm wide, 200 μm long bridges by photolithographic and etching processes. A dc four-probe method with an 1 μV/cm criterion was employed to determine Jc.

III. RESULTS AND DISCUSSION

Fig. 2 shows the resulting films obtained by using the Tl-2223 (Fig. 2(a)) and Tl-1223 (Fig. 2(b)) as the annealing compensate, respectively. As is evident from the results, it is clear that, despite of the same starting precursor films and annealing conditions practiced, the final phases obtained are very different. Since one would expect that the primary effects of using different compensating materials is to change the thermodynamics parameters such as the partial pressures of oxygen and Tl-contained constituents, the results are suggestive that with appropriate conditions used the desired phase, at least in thin film form, can be obtained directly. This is in contrast to the notion of sequential phase evolution proposed by Sugise and Ihara [2] to account for the phase formation of bulk materials. Where the phase formation sequence Tl-2212==>Tl-2223==>Tl-1223 ==>Tl-1234 due to the evaporation of Tl and reorganization of CuO_2 layers is believed to be prevailing. As will become clear in the following, this also has important implications to the design of a viable process for obtaining the desired Tl-1223 films with much improved film morphology and properties.

To further test that the phase formation in these films is indeed governed primarily by annealing thermodynamics and growth kinetics, films with various thickness were prepared and subjected to the same annealing conditions

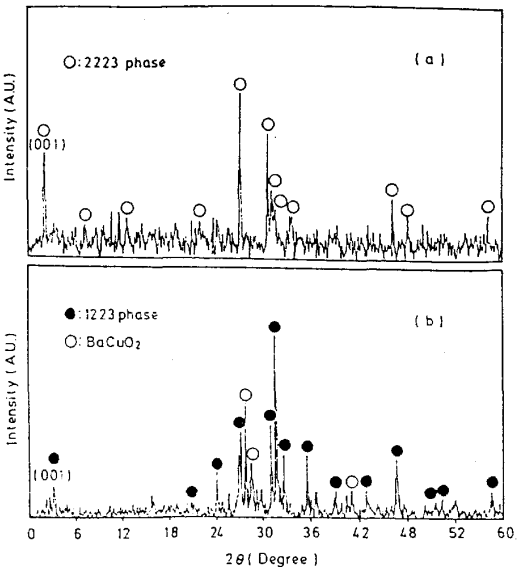

Fig. 1. The XRD results of the bulk materials used as compensates during subsequent post annealing. (a) Tl-2223 and (b) Tl-1223 with minor Tl-1212 phases.

described above. As shown in Fig. 3, the resistive transitions R(T) have demonstrated a progressive improvement with decreasing film thickness. Since, except for the trace amount of Tl-1212 phase, there was no other phase observed in the XRD analysis, the results are considered to be purely

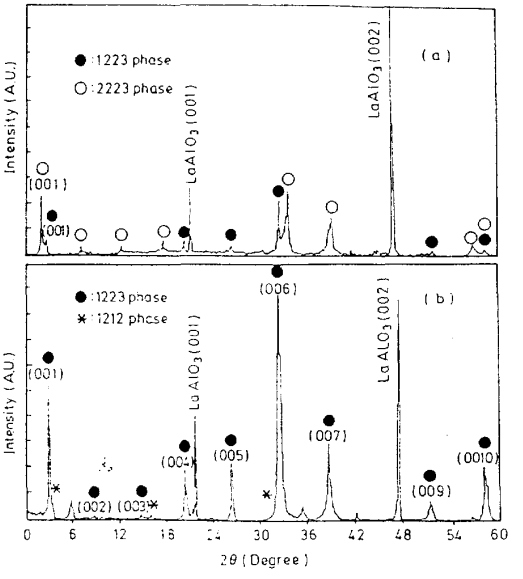

Fig. 2. The XRD results of films obtained by using pellets of (a) Tl-2223 and (b) Tl-1223 as annealing compensates, showing the effects of thermodynamic conditions on phase formation.

kinetics dependent. Indeed, as revealed by optical microscopy (not shown here), the untransformed amorphous regions have greatly reduced, within the same annealing period, with decreasing film thickness. It is noted that, although apparent improvement can be realized by reducing the film thickness, this is impractical for most device applications. As a result, alternative means have to be considered.

Toward this end, we have tried to extend the grain growth duration by conducting a multi-step post annealing procedure with replenished compensates to promote a more complete grain coalescence under similar growth environment [11]. The results have not only demonstrated that the multi- connected plate-like film morphology [8-9] commonly encountered in films with only one step annealing can be significantly improved, but that the transport Jc (77 K) has, for the first time in Tl-1223 system, been raised to exceed 10^6 A/cm^2, as shown in Fig. 4. We note that though the voids, left over after grain coalescence, can be significantly reduced both in numbers and size *(see below)*, they are, however, very difficult to remove completely. This may become a serious impediment when microwave applications are to be considered.

As a result, an alternative process scheme based on the same notion has been practiced. It is anticipated that the outcome would further demonstrate the crucial roles played by thermodynamics and growth kinetics in phase formation. Equally important it may point out a way of fabricating films with improved properties, especially for cases where *ex–situ* processes are unavoidable. Unlike the multi-step annealing used previously, we have re-deposited a second precursor layer on top of the film subjected to the first step annealing. This approach not only takes advantage of reduced film thicknesses for in improved phase formation (as demonstrated in Fig. 3) but also utilizes the Tl-1223 phase that already exists in the bottom layer as a nucleation agent for the top layer. Fig. 5 shows the R(T) result of a film having a total thickness of about 0.6 μm (i.e. with a total deposition time of 90 minutes). As is evident

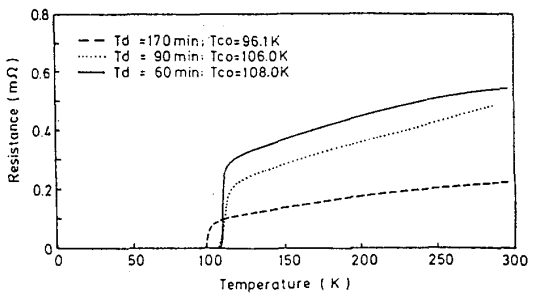

Fig. 3. The R(T) results showing the effects of film thickness on phase formation. The corresponding film thicknesses are 1.4 μm, 0.6 μm, and 0.4 μm for deposition time of 170 min., 90 min., and 60 min, respectively.

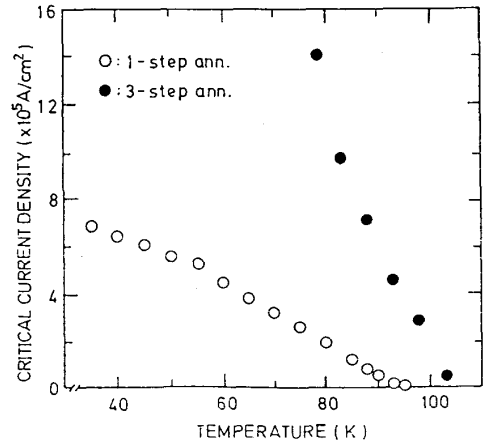

Fig. 4. The Jc(T) results (replotted from [11]) for films subjected to 1-step and 3-step annealing, showing the improvement in film properties by prolonged treatment.

from the results (for comparison the 60 minute result of Fig. 3 is replotted in Fig. 5), not only has the transport Tc been enhanced to over 110 K, but also the extrapolated zero-temperature residual resistance has been reduced to nearly zero. The results unassailably indicate the validity of the notion anticipated in the mechanism of film formation and, more importantly, the viability of the process scheme designed on that basis.

To further demonstrate that the film surface morphology can also be improved by the present process, results for one-step annealing, three-step annealing, and re-deposited films are illustrated in Fig. 6(a), 6(b), and 6(c), respectively. As can be seen in Fig. 6, the multi-connected plate-like features have clearly been improved by prolonged processing. In addition, the voids left over after grain coalescence even for films subjected to three annealing steps (Fig. 6(b)) are absent in the re-deposited films. Although, from Fig. 6(c), it appears that the grain morphology is still somewhat granular, further improvement is expected with the optimization of process parameters. Methods such as

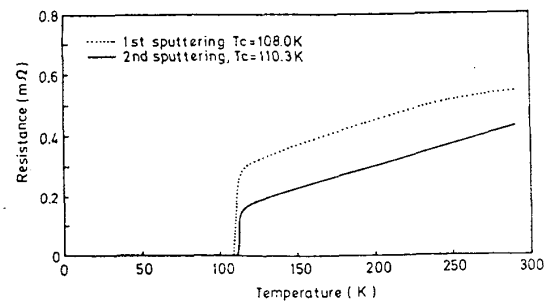

Fig. 5. The R(T) results of single layer and re-deposited double layered films.

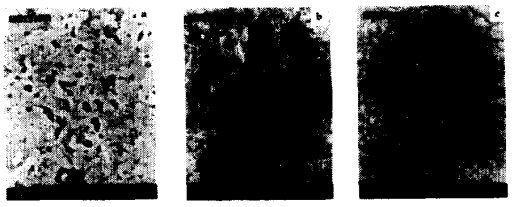

Fig. 6. Surface morphology revealed by SEM for (a) single layer + 1-step annealing, (b) single layer + 3-step annealing, and (c) two-layer with 1-step annealing each, respectively. Notice the progressive elimination of the multi-connected plate-like feature of the grains.

combining re-deposition with multi-stage annealing are currently in pursuit.

IV. SUMMARY

In summary, we have demonstrated a viable technique for preparing single phase, c-axis oriented $TlBa_2Ca_2Cu_3O_9$ superconducting thin films. Films with Tco above 110 K and Jc(77 K) > 10^6 A/cm^2 have been obtained by combining re-deposition with a multi-step post-annealing scheme. The results suggest that the mechanism of the formation of Tl-1223 phase may be dominated by the nucleation and growth kinetics of the desired phase. As a result, the morphology and properties of the films can be improved by prolonged treatment.

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