In-situ Fabrication of Tl-Based Superconducting Thin Films by Two-zone RF-sputtering

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Abstract— **Attempts to fabricate Tl-based superconducting thin films in-situ were made using a two-zone off-axis rf-sputtering method. The effects of Tl_2O partial pressure on the phase formation and growth of various Tl-based superconducting phases were first investigated by an *ex-situ* two zone postannealing scheme to simulate the depsoition environment of subsequent *in-situ* process. The conditions obtained were then used as guidelines for *in-situ* processes. The rf-sputtering system used for *in-situ* deposition is equipped with heating facilities capable of controlling the temperatures of the substrates and the Tl_2O_3 source separately. Preliminary results indicate that, by varying the substrate temperature and the partial pressure of Tl_2O in a similar manner, Tl-based superconducting phases can be obtained *in-situ* with properties comparable to those obtained by two-step annealing processes.**

I. Introduction

Due to the complexity of the chemistry and high volatility of the thallium oxides (primarily Tl_2O and Tl_2O_3) involved in the synthesis process[1], [2], obtaining single-phase Tl-based superconducting thin films, especially *in-situ,* has been one of the most challenging issues in this field. Early attempts by Face and Nestlerode [3] produced phase pure $TlBa_2CaCu_2O_{7\pm x}$(Tl-1212) films on $LaAlO_3$and $NdGaO_3$by magnetron sputtering from a $Ba_2CaCu_2O_x$ target in the presence of thermally evaporated Tl_2O vapor. However, because of the low substrate temperature used (490-650 °C), the films required further post-deposition annealing at 800 °C to obtain a T_c of 97 K. On the other hand, Betz et al. [4], by combining laser ablation from a target of $Ba_2Ca_2Cu_3O_x$ with subsequent thermal evaporation of Tl_2O, produced Tl-BaCaCuO films with $T_c^{R=0}\approx$110 K. However, the films evidently consist of multiple phases, as revealed by X-ray diffraction. Recently, by laser ablating a thallium-free target in the presence of Tl_2O vapor, $TlBa_2Ca_2Cu_3O_{9\pm x}$(Tl-1223) films with T_c up to 100 K were successfully made on $LaAlO_3$(100) in an *in-situ* manner by Reschauer et al. [5]. Although the results shown in [5] are indeed stimulating, it is noted that in such a process the Tl_2O vapor is present in a rather open environment which is very different from the conditions used in usual two-step postannealing processes. Consequently, understanding how, in a similar open environment, the P_{Tl_2O} would affect the formation and growth of various Tl-based superconducting phases should be beneficial for optimizing the *in-situ* processing conditions.

In this study, we first investigate the effects of P_{Tl_2O} on the phase formation and growth of various Tl-based superconducting thin films using an *ex-situ* two-zone postannealing scheme to imitate the growth conditions of [5]. By varying P_{Tl_2O}, P_{O_2}, annealing temperature and time, we conclude that it might be necessary to lower both P_{Tl_2O} and P_{O_2} in order to further improve the stabilty and properties of Tl-based films in an open environment. This assertion, though is quite consistent with that suggested by Aselage et al. [6], is somewhat different from many of previous conjectures. In that, in order to avoid the loss of Tl-contained constituents, excessive supply of Tl_2O has been considered to be a crucial factor for obtaining high-quality Tl-based superconductors. The results obtained were then further used for designing the two-zone rf-sputtering system for making Tl-based films *in-situ.*

II. Experimental

As mentioned above, in order to delineate the effects of P_{Tl_2O} and P_{O_2} on the formation and growth of Tl-based superconducting phases, the films used in this study were prepared by two different methods. In the first method, amorphous precursor films were obtained by single target dc-sputtering from a calcined bulk disk with a nominal $Tl_2Ba_2Ca_2Cu_3O_{10\pm\delta}$ (Tl-2223) composition and then followed by postannealing. However, instead of sealing the precursor films with sintered Tl-2223 bulk pellets [7], in the present study only Tl_2O_3 powder was used as source of Tl_2O in an open two-zone scheme. The resultant P_{Tl_2O} was estimated by referring to the phase diagrams reported in [1] and [2] according to the particular annealing temperature (T_A) and P_{O_2} used. The phases existing in the resultant films and their surface morphologies were then identified and investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The superconducting properties were characterized by measuring the transport T_c and J_c of the films by a standard four-probe method.

A three-gun rf-sputtering system equiped with two separated heating facilities, as depicted schematically in

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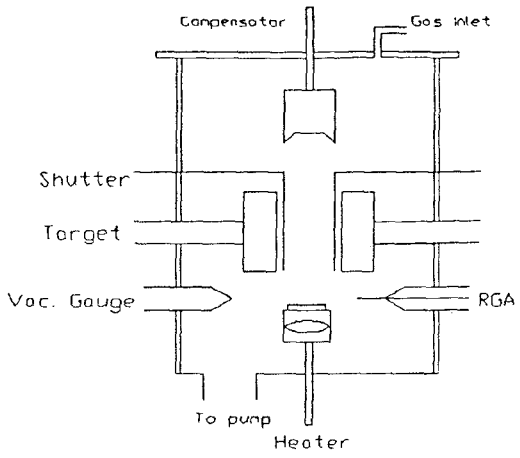

Fig. 1. Schematic diagram of the two-zone rf-sputtering system.

Fig.1, was used to prepare films *in-situ*. Each sputtering gun was operated with a total power of 50 W producing a total sputtering rate of about 500 Å/hr. The sputtering gas used was a mixture of argon and oxygen with $Ar:O_2$=4:1 and a total pressure of 0.2 Torr. The system was designed such that, during deposition, a stream of Tl_2O vapor decomposing from solid Tl_2O_3 powder heated resistively at temperatures of 650-800°C flows onto the substrate due to the differential pressure established by continous pumping. The substrate temperature is maintained within the range of 800-910 °C *via* thermal contact provided by high-temperature silver epoxy to a silicon wafer which can effectively absorb heat delivered by a halogen lamp situated at the center of a hemispherical reflective plane. With this particular setup, the substrate temperature can be controlled to within ±1°C.

III. Results and Discussion

A. Ex-situ postannealing on dc-sputtered Tl-based films

The effects of P_{Tl_2O} and P_{O_2}on the formation and stability conditions of Tl-based superconducting phases have been investigated extensively previously [2], [6], [8]. Although it has been pointed out that it is advantageous to lower the P_{O_2} to obtain Tl-2223 at lower T_A[8], other studies have indicated that, at fixed P_{O_2}, lowering the P_{Tl_2O}, in some cases, can result in significant improvement on the stability and superconducting properties of the Tl-based superconducting phases [6]. However, since in a single zone annealing scheme the magnitudes of P_{Tl_2O} and P_{O_2} are inevitably correlated through the reaction: $2Tl_2O_x(c) \rightleftharpoons 2Tl_2O(g) + (x\text{-}1)O_2(g)$, the roles played by the two vapor species are not independent and require further clarification. In this section, we first report on the results obtained from systematic studies aimed at this question.

Using Tl_2O_3 powder as the source of Tl_2O vapor, four different postannealing schemes were performed to study the effects of P_{Tl_2O} and P_{O_2} on the formation of Tl-based superconducting phases. In the first process, Tl_2O_3 powder was placed in an alumina crucible. The crucible was then covered with an alumina plate onto which the precursor film was attached such that the film surface faces the Tl_2O_3 powder separated by a distance of about 2 cm. The whole assembly was then wrapped with gold foil and annealed at 900 °C, which was the temperature used to grow Tl-1223 phase by enclosing films with bulk pellets in quartz tube [7]. Although, at 900 °C the expected P_{Tl_2O} and P_{O_2}as decomposed from Tl_2O_3[1] as well as the T_A used are about the same as that of [6], most area of the precursor film appeared to be evaporated, leaving only some scattered spots with $T_c \approx$98 K. This indicates that in the present quasi-open system the reactions between Tl_2O and the precursor films and hence the growth kinetics may be very different from that which prevailed in a sealed system.

TABLE I
Two-zone Annealing at P_{O_2}=1 atm, T_A=900°C

Sample	T_S(°C)	Time (min)	T_{c0}(K)	Major Phase
II-A	700-760	30-120	No	film transparent
II-A	700-760	30-120	No	film transparent
II-B	800	30	80	2201+2212
II-C	830	25-30	95-100	2212+2223
II-D	840	28	100	2212+2223
II-E	850	30	80	2212+2223
II-F	865	3.5	102	2212+2223
II-G	865	20	No	film transparent

In the second process, the P_{O_2} was fixed at 1 atm by a continuously flowing oxygen through the furnace tube . Since at P_{O_2} =1 atm, the optimum annealing temperature for the formation of the Tl-2223 phase is T_A =890~900 °C [8], we fixed T_A =895 °C and varied the Tl_2O_3 source temperature (T_S). As shown in Table I, depending on the annealing time and T_S, the resultant films can have a wide variety of properties. In the range of T_S used here, the corresponding P_{Tl_2O} is somewhere between 0.01-0.1 atm[1]. The extremely narrow growth window for the superconducting phases is believed to arise from the high T_A and P_{O_2} used[1]. As revealed from the SEM picture (Fig. 2), the microstructure of the resultant films evidently displays signature of melting.

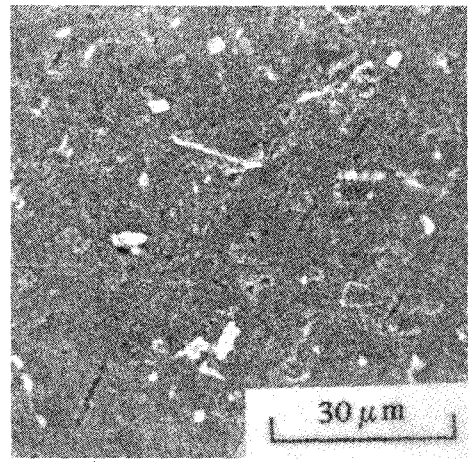

Fig. 2. Grain morphology of films obtained by the second *ex-situ* process.

As a consequence, in the third process, we have replaced oxygen with 1 atm of pure argon and lowered T_A to 850 °C. In the same range of T_S, where the corresponding P_{Tl_2O} was estimated to be around 0.1 atm[1], surprisingly, all the precursor films turned transparent for annealing time of 20-600 minutes. This implies that, though the superconducting phase can form at lower temperature with reduced P_{O_2}[8], some residual oxygen partial pressure over film surface may still be needed to control the vapor-film reaction for phase formations.

In the fourth *ex-situ* process, the flowing gas was changed to a mixture of Ar+O_2 (P_{Ar}: P_{O_2}= 10:1) with a total pressure of 1 atm. By fixing T_A at 825 °C, T_S between 800-810 °C, all of the precursor films became superconducting after 35 minutes of annealing. The films consist mostly of Tl-2212 phase with small amount of Tl-2223 phase and have T'_{c0}s in the range of 98-101 K. However, since T_A is much lower in this case, the film microstructure (as revealed by SEM in Fig. 3) is quite different from that shown in Fig. 2. As can be seen from Fig. 3, distinct orthogonal rod-like structure, whichis identified to be mostly c-axis oriented Tl-1223 is evident. Figure 4 compares the typical temperature dependent critical current densities, J_c(T), of the two types of films. With nearly identical T'_cs (see the inset of Fig. 4), it is clear that, due to the microstructure differences resulting from different T'_As, the transport J_c at 77 K can differ by over an order of magnitude.

The above *ex-situ* annealing studies performed in an open environment similar to previous *in-situ* processes [3]-[5], suggest that, while lowering P_{O_2} can be advantageous for the Tl-based superconducting phases to form at lower temperatures, a minimal amount of oxygen appears to be necessary for controlling P_{Tl_2O} and hence the reaction kinetics. We have used these results as guidelines in designing our two-zone rf-sputtering system for *in-situ* growth of Tl-based superconductors. As a consequence, in the third process, we have replaced oxygen with 1 atm of pure argon and lowered T_A to 850 °C. In the same range of T_S, where the corresponding P_{Tl_2O} was estimated to be around 0.1 atm[1], surprisingly, all the precursor films turned transparent for annealing time of 20-600 minutes. This implies that, though the superconducting phase can form at lower temperature with reduced P_{O_2}[8], some residual oxygen partial pressure over film surface may still be needed to control the vapor-film reaction for phase formations.

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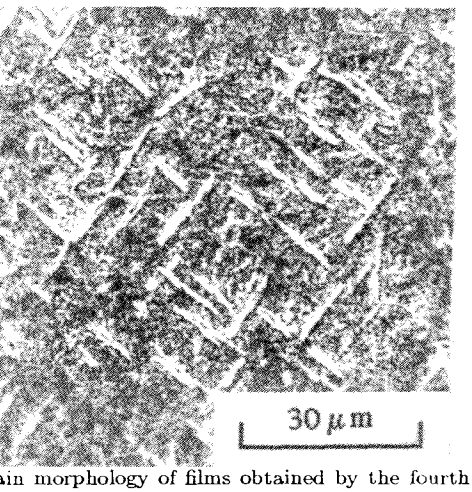

Fig. 3. Grain morphology of films obtained by the fourth *ex-situ* process.

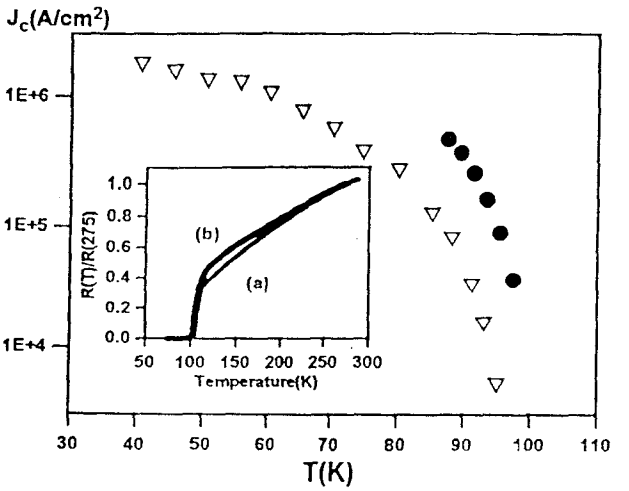

Fig. 4. The J_c(T) of films obtained by the second process (•) and by the fourth process (▽), respectively. The inset shows the R(T) of the two corresponding films where curve (a) is for the films prepared by the second process and (b) is for the other.

B. *In-situ fabrication of Tl-1223 films by two-zone rf-sputtering*

The setup of the two-zone rf-sputtering system and deposition conditions used in this study were shown and described in Fig. 1 and in the EXPERIMENTAL section, respectively. It is noted that with a total pressure of 0.2

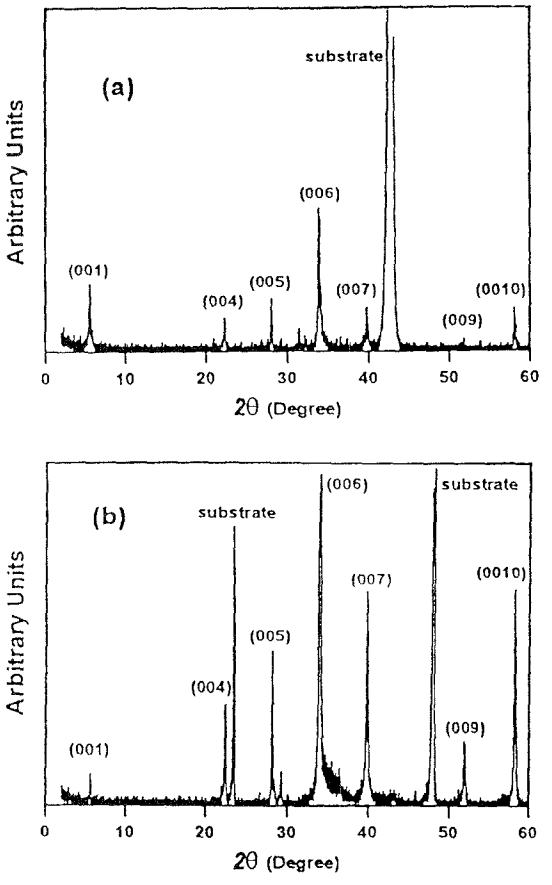

Fig. 5. The XRD results for Tl-12223 films prepared by *in-situ* rf-sputtering on (a) MgO and (b) $LaAlO_3$.

Torr the corresponding P_{O_2} over the substrate should be on the order of 0.05 atm. Figure 5 shows the XRD results for two films deposited on $LaAlO_3(100)$ and MgO(100) substrates, respectively. The substrate temperature, as measured beneath the silicon wafer used for holding the substrate, was about 880 °C, which is higher than that in our fourth *ex-situ* process. However, we are unable to quantify the value of T_S precisely. From the input power of the heater, it was estimated to be in the range of 700 °C. As is evident from the XRD results, the films thus obtained consist mostly of Tl-1223 and Tl-2223 phases. This is consistent with the general consensus that Tl-1223 and Tl-2223 are stable phases at higher temperature[2],[6]. Moreover, by comparing the two films, it appears that MgO is more favorable for obtaining single phase films at lower temperatures which is also consistent with our previous observation in making single phase Tl-2223 films[9].

Figure 6 shows the transport R(T) curves of the two films shown in Fig. 5. As can be seen from the results, not only are the T_c's (102 K and 104 K for films on $LaAlO_3$ and MgO, respectively) lower than expected for pure Tl-1223 or Tl-2223, but also the normal state resistiviies deviates from the usual linear behavior significantly. We believe that this probably is due to inhomogeneities in both film microstructures and stoichiometries. Further refinements on the control of process parameters to achieve our primary goal of fabricating single-phase Tl-based superconducting films with better morphologies are currently under investigation.

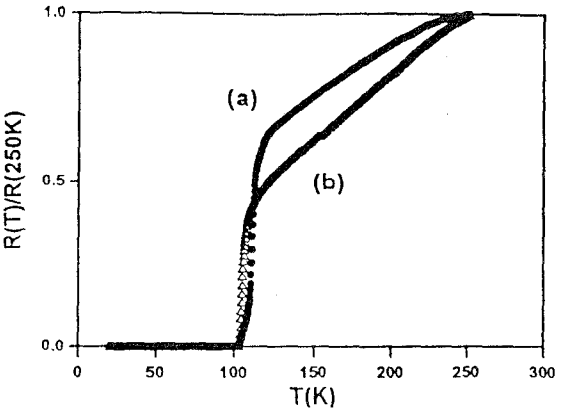

Fig. 6. The R(T) of films on (a) MgO and (b) LAO.

IV. Summary

We have reported preliminary results on the *in-situ* fabrication of Tl-1223 films by a two-zone rf-sputtering method based on information obtained from a series of studies of *ex-situ* processes performed in an open two-zone environment. The results indicate that, in the relatively open scheme, maintaining a small but certain amount of oxygen partial pressure is necessary for obtaining stable Tl-based superconducting phases in both *in-situ* and *ex-situ* processes.

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