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Preparation and Properties of $Tl_2Ba_2CaCu_2O_8$ Thin Films

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An *ex situ* process has been developed to produce thin superconducting $Tl_2Ba_2CaCu_2O_8$ films. The properties of films grown on different substrates using different annealing regimes were studied. Critical temperatures of 103–107 K were measured on films prepared in a broad range of annealing temperatures on $SrTiO_3$, $LaAlO_3$, and Y-ZrO_2 substrates. A critical current density, J_c, of 2×10^6 A/cm^2 at 77 K was measured on $LaAlO_3$. Film morphology was studied by SEM, AFM, and STM.

KEY WORDS: Tl cuprates; thin films; *ex-situ* thin film processing.

1. INTRODUCTION

In the area of Tl cuprate superconducting thin films much interest is directed toward, e.g., $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) and $Tl_2Ba_2CaCu_2O_8$ (Tl-2212). The former compound has a maximum T_c of about 125 K. Tl-2212 is characterized by greater ease of preparation while the optimum T_c is slightly lower compared to Tl-2223. Typical values of some important parameters for Tl-2212 and Tl-2223 films include T_c of about 107 and 115 K, respectively, critical current density J_c at 77 K of 5–10×10^5 A/cm^2, and microwave surface resistance R_s of 0.5 mΩ at 77 K and 10 GHz [1,2]. Thus, the thallium cuprate thin films offer several advantages compared to $YBa_2Cu_3O_x$ (YBCO) thin films, including higher critical temperature, low surface resistance, and low $1/f$ noise [3]. Epitaxial superconducting Tl cuprate thin films and a low noise Tl cuprate SQUID were reported already in 1989 [4]. Nevertheless, progress has been slow compared to the YBCO system because of the difficulty in preparing pure and homogeneous films with good superconducting properties and by a lack of reproducibility of the process. In this paper we report on a simple and reliable method for the preparation of superconducting $Tl_2Ba_2CaCu_2O_8$ thin films.

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2. EXPERIMENTAL

The preparation of superconducting Tl-2212 films was carried out in two consecutive steps:

(i) Tl-free precursor films with nominal composition Ba:Ca:Cu = 2:1:2 were deposited on different 5×5 mm^2 substrates by pulsed laser deposition. The beam of a KrF eximer laser ($\lambda = 248$ nm) was focused on a rotating oxide target with the elemental composition $Ba_2CaCu_2O_x$. The beam energy density was 1–1.5 J/cm^2 in a spot of 1×3 mm^2. The substrates were kept at room temperature, and the films were amorphous after deposition.

(ii) Formation of the superconducting film by annealing the precursor film from 30 min to several hours at 835–895°C in Tl_2O vapor generated by ceramic Tl-2212:

$$Tl_2Ba_2CaCu_2O_8 \rightleftharpoons Tl_{2-x}Ba_2CaCu_2O_{8-3x/2} + x/2\, Tl_2O(g) + x/2\, O_2(g)$$

Ex-situ processes for preparing thallium cuprate thin films usually employ Tl_2O sources that are more thallium-rich than the ideal film stoichiometry (see,

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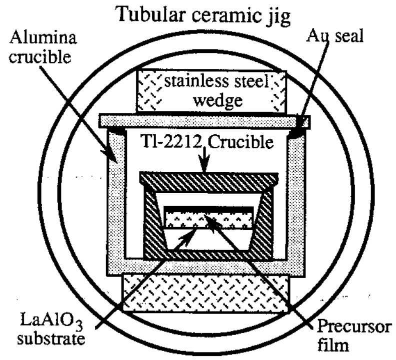

Fig. 1. Schematic cross-section of the experimental set-up used in the annealing of precursor films. The gold seal is put under compression during annealing using the stainless steel wedges.

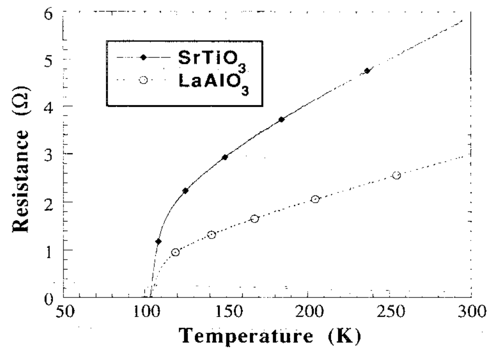

Fig. 2. Resistance vs. temperature for films grown on (001) $LaAlO_3$ and $SrTiO_3$. Annealing time = 30 min. Annealing temperature = 895°C.

for example, [5]). The extra thallium oxide is added to compensate for thallium losses from the system or because the thallium source has a lower temperature than the film. We present a method that involves the annealing of the film under near-equilibrium conditions, avoiding the difficulties of controlling vapor phase transport of Tl_2O. Figure 1 shows a schematic view of the experimental set-up. The Tl-free precursor film is annealed inside a crucible made from ceramic Tl-2212 with a lid of the same material. The Tl-2212 crucible is in turn enclosed in a gold-sealed alumina crucible. With this method, the precursor film is exposed to a vapor pressure of thallium oxide corresponding to the equilibrium value over pure Tl-2212. Thallium losses from the film are thus avoided, and the thallium content of the film can be kept at the optimum value.

The loss of thallium from the crucible was monitored by weighing the closed alumina crucible before and after each annealing. In a typical run, less than 2 mg of thallium oxide was lost during annealing. The thallium oxide loss mainly occurred from the outer surface of the Tl-2212 crucible and consequently did not affect the film. Due to the minimal thallium loss and to the small amount of thallium absorbed by the film, the same Tl-2212 crucible could be used repeatedly with no change of film characteristics.

The films were deposited on (001) $LaAlO_3$, $SrTiO_3$, and Y-ZrO_2 single crystal substrates. The effect of annealing temperature in the range 835–895°C was studied using T_c measurement (standard four-probe resistive measurements), θ–2θ X-ray diffractometry, scanning electron microscopy (SEM), atomic force microscopy (AFM), and scanning tunneling microscopy (STM). The in-plane orientation was studied using Φ-scan X-ray diffractometry.

3. RESULTS AND DISCUSSION

The films on Y-stabilized ZrO_2, $SrTiO_3$, and $LaAlO_3$ all showed similar transitions to the superconducting state; see Fig. 2 for films on $SrTiO_3$ and $LaAlO_3$. Films deposited on different substrate materials, but otherwise under identical deposition conditions, exhibited different surface morphologies. A comparison between films deposited at 855°C on (001) $LaAlO_3$ and (001) Y-ZrO_2 substrates is shown in Fig. 3. The films on $LaAlO_3$ were in general smoother on a local scale with relatively large flat regions. This was confirmed by STM and AFM which showed that the films on $LaAlO_3$ were locally atomically smooth; an AFM picture is shown in Fig. 4. Using the Φ-scan technique, the films grown on $SrTiO_3$ and $LaAlO_3$ were shown to be epitaxial (see Fig. 5 for a Φ-scan of Tl-2212 on $LaAlO_3$). Double-side-coated films were prepared on $LaAlO_3$ substrates, the two sides exhibiting identical properties.

The annealing temperature affected phase purity, T_c, surface resistance, as well as the surface morphology. The optimal annealing temperature was found to be 875°C, giving a T_c of 107 K for films on $LaAlO_3$. Films treated at 835°C were insulating, while treatments at temperatures above 875°C caused T_c to decrease by 1–2 K (see Fig. 6).

Films treated with thallium oxide vapor in the appropriate temperature range and during a sufficient time were single phase c-axis oriented Tl-2212, no crystalline impurities being detected by X-ray diffraction. However, T_c as well as phase purity were affected by the annealing time, longer annealing times being necessary in the lower part of the temperature range. Annealing at 845°C initially produced films with Tl-1212 as the dominating phase and with Tl-2212 and small amounts of Tl-2201 also present, all three

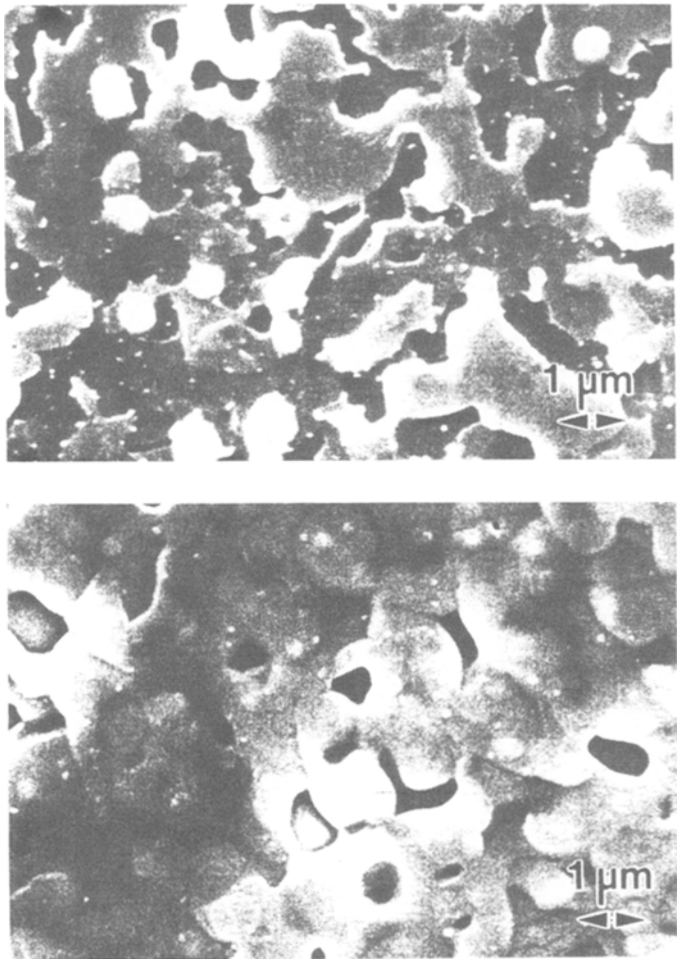

Fig. 3. SEM microphotographs showing the surface morphology of $Tl_2Ba_2CaCu_2O_8$ films on Y-ZrO_2 (below) and $LaAlO_3$ (above). The films were annealed at 855°C for 30 min.

compounds being perfectly *c*-axis oriented; see Fig 7a. Re-annealing the film for 3 hours at the same temperature converted the film to Tl-2212 (with traces of Tl-1212); see Fig 7b. The formation of Tl-1212 after short annealing times at relatively low temperature shows that the film has not yet reached its equilibrium composition with respect to Tl. The prolonged exposure of the film to Tl_2O vapor at high temperature apparently converts the single TlO-layer Tl-1212 into its double-layer counterpart. It is suggested that the formation of double-layer thallium cuprate thin films by *ex-situ* methods may in general be preceded by the formation of the corresponding single-layer compounds. The formation of Tl-2201 and its subsequent disappearance after prolonged Tl_2O annealing indicates the presence of a compound on the surface that contains calcium and copper and that is able to react with Tl-2201 to form Tl-2212.

The measured T_c values of our films were typical of bulk Tl-2212, as synthesized. It has been reported that treatment in argon atmosphere at 300–400°C may increase the T_c of bulk Tl-2212 to about 112 K [6]. Annealing in Ar at 300°C for 15 hours caused the T_c of the film to drop to 90 K from its starting value of 104 K (Fig. 8). Re-annealing this film at 855°C for 30 min resulted in an increase of T_c to 105 K. Tl losses as well as changes in oxygen concentration may be responsible for the observed behavior. At this point we cannot resolve this question, and further studies are needed. The observed reversibility of the annealing process may have important implications for Tl-2212 films since it allows the modification of film properties in a controlled way.

To measure the critical current densities, microbridges with width 4–8 μm and length 50 μm were patterned by two different methods. In the first method the precursor film was deposited through a lift-off mask of photoresist and thallium-annealed afterwards. In the second method the film was patterned *after* annealing using a photoresist mask and Ar ion beam etching. The first method was simple, avoiding Tl processing, but resulted in microbridges

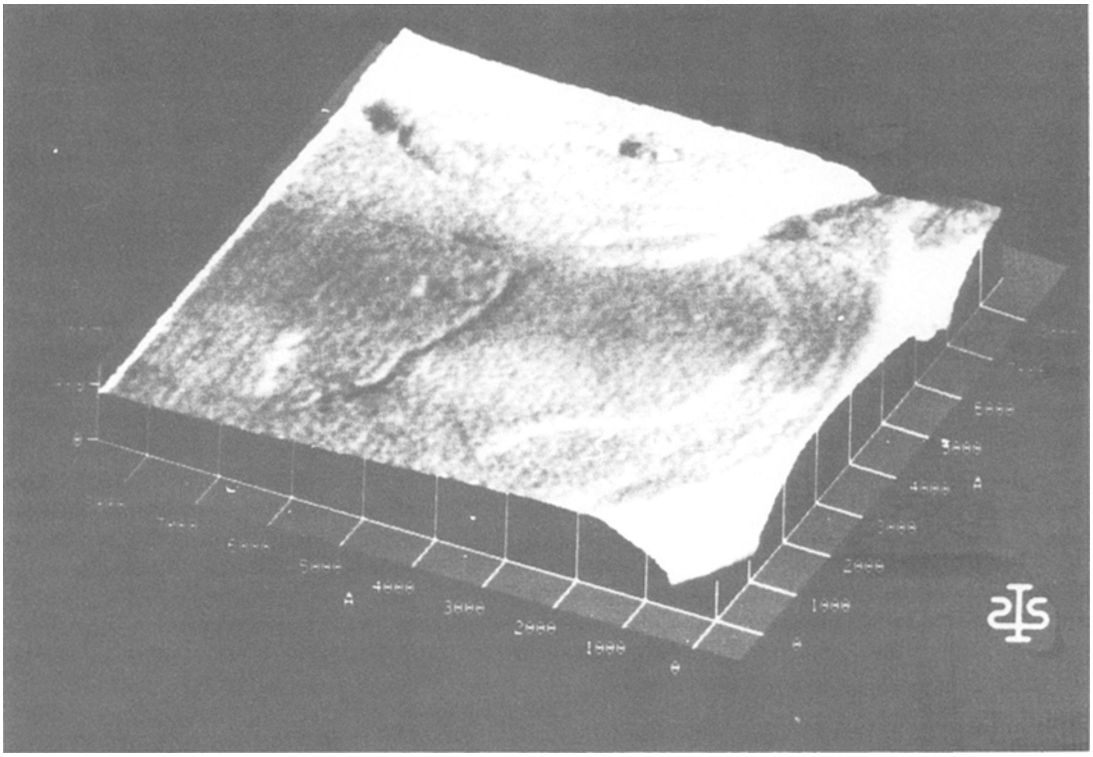

Fig. 4. An AFM image of the surface morphology of a Tl-2212 film on a $LaAlO_3$ substrate. Note the terrace-like structure with step height corresponding to one to several unit cells.

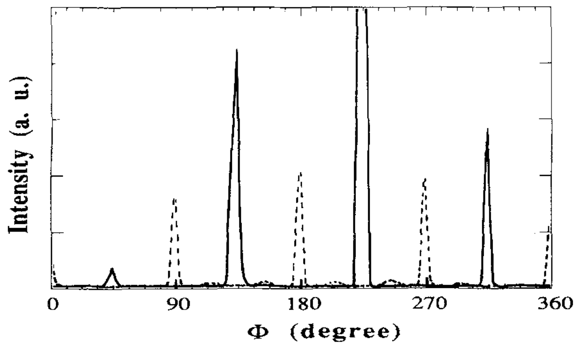

Fig. 5. Φ-scans of 300 nm thick $Tl_2Ba_2CaCu_2O_8$ film on $LaAlO_3$ substrate treated at 875°C for 6 min. The Tl-2212 (1, 1, 18) family of peaks (dotted line) ($2\theta = 66.8°$), indicating the [110] direction in Tl-2212, is shifted by 45° in relation to the pseudo-cubic (1, 0, 2) peaks of the $LaAlO_3$ substrate (full line) ($2\theta = 54.1°$), indicating cube-on-cube epitaxy. Intensity differences are due to mounting inaccuracy.

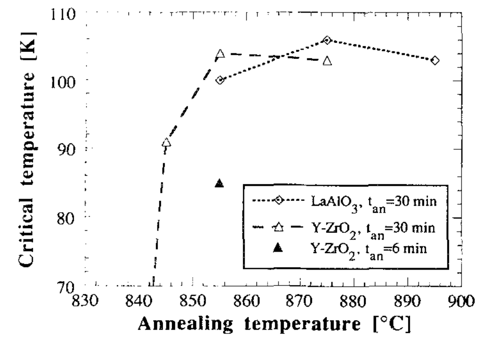

Fig. 6. T_c as a function of annealing temperature for films grown on $LaAlO_3$ and $Y\text{-}ZrO_2$.

with needle-like outgrowths at the edges. The measured T_c's of 80–90 K and J_c's of 10^3–10^4 A/cm^2 were very low, and we relate this to residues of photoresist on the substrate. For films annealed in the temperature interval 855–895°C, the microbridges patterned by the second method showed a decrease of 3–5 K in T_c compared to the unpatterned film, while the critical current densities were 2×10^6 A/cm^2 at 77 K. At the high end of the temperature range, holes developed in the films, which in turn increased the proportion of defect bridges.

The microwave surface resistance was measured at 21.5 GHz by the parallel-plate resonator method and was found to be 1.5 mΩ at 4.2 K. Films on double-side-coated substrates exhibited identical surface resistance.

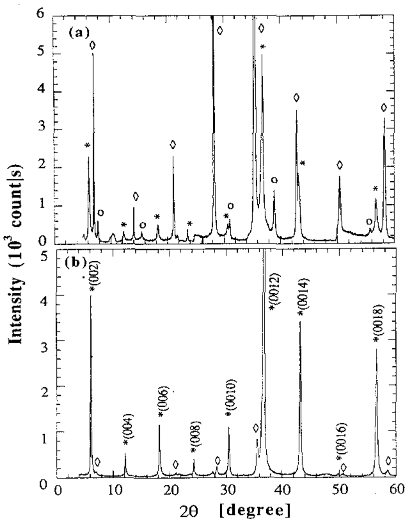

Fig. 7. XRD θ–2θ scan of 240 nm thick Tl-2212 film on $LaAlO_3$ substrate annealed at 855°C for (a) 30 min and (b) another 3 h. (001) peaks are identified by (*) for 2212 phase, (◇) for 1212 phase, and (○) for 2201 phase. The substrate peaks have been subtracted.

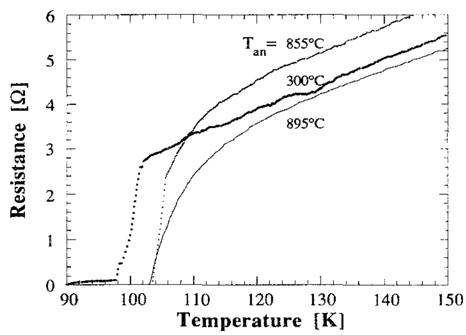

Fig. 8. Resistance vs. temperature for Tl-2212 film on $LaAlO_3$ after different annealing procedures. Note the reversible behavior of T_c of the film after annealing at 855°C for 30 min.

4. CONCLUSIONS

An annealing procedure is presented that allows *ex-situ* double-side-coated epitaxial Tl-2212 films to be prepared routinely on (001) $SrTiO_3$, $Y\text{-}ZrO_2$, and $LaAlO_3$ substrates. The films on $LaAlO_3$ were epitaxial and locally smooth on an atomic scale. T_c ranged from 103 to 107 K depending on annealing time and temperature (835–895°C), J_c reaching 2×10^6 A/cm^2 at 77 K for films on $LaAlO_3$. Short annealing times at low temperature resulted in the formation of single-layer Tl-1212 that was converted to Tl-2212 by prolonged annealing at the same temperature. It is suggested that the formation of single-layer Tl cuprates may generally precede the formation of the corresponding double-layer compounds. High annealing temperature (895°C) resulted in films containing holes down to the substrate. Argon annealing of Tl-2212 films at 300°C resulted in a deterioration of the superconducting properties. Re-annealing in Tl_2O vapor at high temperature led to a recovery of T_c.

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