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An He(何安)1, Cun Xue(薛存), Youhe Zhou(周又和)
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Fabrication of $Tl_2Ba_2CaCu_2O_8$ superconducting films without thallium pellets*

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A new improved two-step method in fabricating $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) thin films is presented in this paper. In the first process of dc magnetron sputtering, the thallium content in the precursor film is largely increased by adjusting the ratio of thallium in the sputtering targets. After the second annealing process in the absence of additional thallium pellets or powder source, high-quality Tl-2212 thin films can be obtained. The proper content of thallium in the precursor film provides a relatively stable atmosphere to guarantee the growth of Tl-2212 film. This method avoids the repeated production of the thallium pellets in the post-annealing process, the repeatability and controllability of the experiment are greatly improved. X-ray diffraction (XRD) scans show that all of the sharp peaks of the sample films can be assigned to the $(00l)$ peaks of Tl-2212 phase. The highest superconducting critical temperature (T_c) of the films is 105 K and the critical current density (J_c) can achieve 1.93 MA/cm^2 in zero magnetic field at 77 K for a 600 nm film.

Keywords: Tl-2212 superconducting films, post-annealing, critical temperature, critical current density

PACS: 74.78.–w **DOI:** 10.1088/1674-1056/27/5/057403

1. Introduction

Owing to their high critical temperature, high critical current density and low microwave surface resistance, thallium-based high temperature superconducting (HTS) thin films are popularly used in microelectronic applications.[1–3] While, for the toxicity and volatility nature of Tl_2O_3, the investigation on Tl-based superconducting is not very deep, and the complicated fabrication of Tl-based superconducting thin films limits their development.

Many reports on the preparation of Tl-based HTS films, such as $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) films, have been presented in the past several decades. Unlike the fabrication of $YB_2C_3O_{7-x}$ films,[4–7] most of Tl-based films were fabricated by a two-step process due to the high volatility of thallium at high temperature. In the first step, it usually involves the deposition of an amorphous precursor film (with or without thallium) by a variety of methods, such as sputtering,[8,9] pulsed-laser deposition,[10–12] or chemical vapor deposition.[13,14] And in the second step, the superconducting thallium phase thin films will be formed in the presence of thallium oxide vapor at high temperature.[15,16] For the volatile nature of thallium oxide at the annealing temperature, the vapor pressure of thallous oxide over condensed thallium oxides rises rapidly, the loss of thallium is inevitable. Due to the difference of annealing conditions, it is difficult to guarantee the balance of thallium vapor–solid equilibrium in the growth of thallium phase films.[17] Keeping the balance of thallium oxide is the key to the synthesis of the Tl-based superconducting films.[18]

Many groups have suggested methods to solve this problem. Using thallium pellet or powder to provide thallium oxide vapor in the annealing step is a popularly used method. Siegal and co-workers deposited Tl-free precursor oxide films on $LaAlO_3$ substrates, and the precursor films were annealed with the thallium pellets in pure O_2. The Tl-2212 films exhibited superconducting critical temperature $T_c > 95$ K and the critical current densities $J_c > 10$ MA/cm^2 in zero field at 5 K.[19] In our group's previous work, high quality Tl-2212 films have been obtained on $LaAlO_3$ substrates by annealing the Tl–Ba–Ca–Cu metal precursor together with the thallium pellet in the second step. The T_c values of the Tl-2212 films were above 105 K, and the J_c of the films were measured to be around 3–5 MA/cm^2 in zero field at 77 K.[20] The thallium pellets used in the experiments above, which provide the thallium oxide pressure in the second step, can only work for a few times at high annealing temperature and need to be replaced continuously. Besides, the consumption of Tl_2O_3 is large in the growth of these thallium pellets, the Tl_2O_3 powder used in the process of making the pellets is far more than the content of thallium in the Tl-2212 films, and the preparation of the thallium pellets is complicated too. Furthermore, these thallium pellets dominate the growth of the Tl-2212 films, each annealing process is

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not exactly the same because of the repeated use of the pellets, the optimized experimental condition is difficult to achieve.

To simplify the formation process and improve the efficiency of the experiment, we present an improved post-annealing process for the fabrication of Tl-2212 films. By adjusting the composition of Tl_2O_3 in the precursor films and the annealing conditions, the new process can maintain the vapor–solid equilibrium. Therefore, high quality pure phase Tl-2212 films can be obtained in the absence of thallium pellets.

2. Experimental details

Tl-2212 superconducting thin films were fabricated on (10 mm×10 mm) $LaAlO_3$ (00l) substrates by a two-step process: deposition of amorphous Tl–Ba–Ca–Cu–O precursor films, then converting the precursor films into the Tl-2212 phase by annealing. The Tl–Ba–Ca–Cu–O precursor films were deposited on $LaAlO_3$ (00l) substrates by dc magnetron sputtering from a pair of facing $Tl_2Ba_2CaCu_2O_8$ superconducting targets at room temperature. The superconducting targets were prepared by solid-state reaction of stoichiometric amounts of CaO, BaO_2, CuO and Tl_2O_3 powders with an initial cation ratio of 2.5–2.8 Tl: 2 Ba: 1.2 Ca: 2 Cu. The substrate was placed parallel to the symmetrical centerline of the two facing targets. Sputtering was carried out in a mixture of 80% argon and 20% oxygen gases with a total pressure of about 2.0 Pa. The deposition rate was about 5 nm/min and the thickness of the film was approximately 0.3–0.6 μm.

The precursor films were sealed in a sapphire crystal crucible for the second processing step. The sapphire crystal crucible was delicately designed, the crucible included a base and a cover. According to the size of the substrate, a 1 cm^3 closed space was designed on the base. The contact surface between the base and the cover was smooth. The whole assembly was then placed into a furnace for the annealing process in flowing oxygen. In the conventional annealing process, the Tl-2212 phase is formed at 800–860 °C in flowing oxygen[21] or at 720–760 °C in argon.[22] Therefore, the temperature range of 730–830 °C for 90–240 min was chosen to be applied for annealing in this method.

3. Results and discussion

For the relatively closed cavity in this special sapphire crystal crucible, with the increment of the proportion of Tl in the precursor films, the post annealing conditions would be similar to that of the process with additional thallium pellets. After a series of experiments about annealing the precursors with different thallium contents, by using this specially designed crucible, the best results were obtained with the precursor films from a $Tl_{2.7}Ba_2Ca_{1.2}Cu_2O_x$ sputtering target.

The structural characterizations of the films were performed by x-ray diffraction (XRD) scans on a Rigaku DMAX-2500 x-ray diffractometer with Cu $K\alpha$ radiation. Siegal and co-workers demonstrated that the Tl-2212 phase is a stable superconducting phase with annealing temperatures around 775 °C. When the annealing temperature is below 750 °C, single Tl-layer phases, such as $TlBa_2CaCu_2O_7$ (Tl-1212), will be formed. And with the annealing temperatures rising to above 780 °C, the $TlBa_2Ca_2Cu_3O_9$ (Tl-1223) phase will appear.[18] Our experimental results are consistent with these reports on the crystalline properties. The annealing temperature and annealing time dominate the growth of Tl-2212 films in this new treating process.

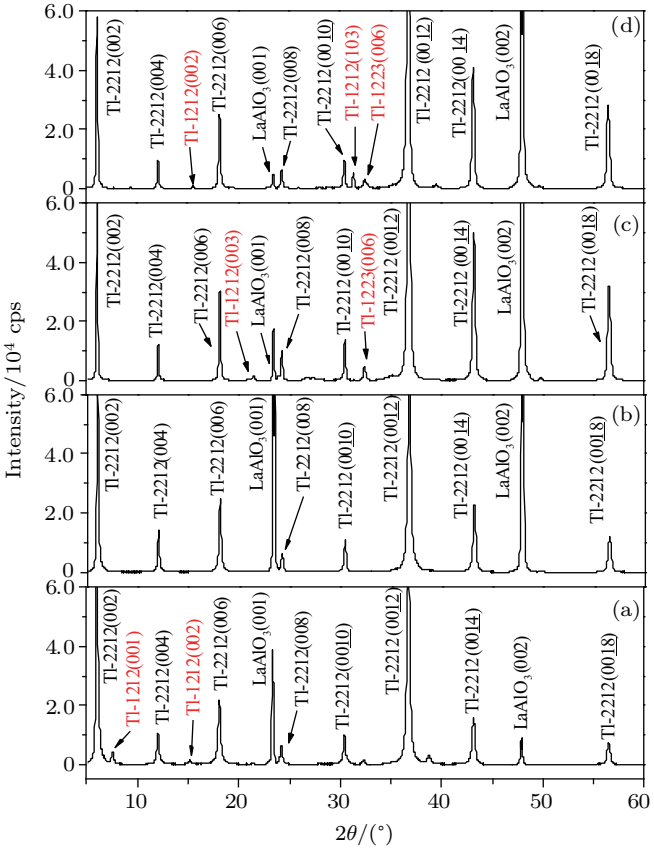


Fig. 1. (color online) XRD patterns of Tl-2212 films prepared with different annealing conditions: (a) at 750 °C for 120 min, (b) at 770 °C for 120 min, (c) at 790 °C for 120 min, (d) at 770 °C for 240 min.

Figures 1(a)–1(d) illustrate the XRD θ–2θ patterns of 0.6-μm-thick films annealed at different annealing temperatures and processing time. Figure 1(a) shows the sample annealed at 750 °C for 120 min, the sample is dominated by the Tl-2212 phase and most of the sharp peaks can be assigned to the (00l) peaks of the Tl-2212 phase. The Tl-1212 phase appears at the same time, but the intensity of the Tl-1212 phase peaks is weak. The result shows that the films are entirely oriented with their c-axis perpendicular to the plane of the substrate surface. With the annealing temperature rising to 770 °C in Fig. 1(b), all the peaks of the Tl-1212 phase disappear completely, pure Tl-2212 phase is obtained. In Fig. 1(c), when the

annealing process is set at 790 °C for 120 min, all the main (00l) peaks of the Tl-2212 phase are similar to those of the sample shown in Fig. 1(b), but the mixed Tl-1212 and Tl-1223 phases can be found clearly, 790 °C is a bit high for this annealing process. Figure 1(d) shows the result of the sample obtained at 770 °C for more than 120 min. The Tl-1212 and Tl-1223 phases appear on the diffraction plots when the annealing time is extended to 240 min. A longer annealing time will reduce the purity of Tl-2212 phase crystal structure.

Compared with the four diffraction plots shown above, the main peaks of all the samples are Tl-2212 phase diffraction peaks. It is suggested that we can fabricate the Tl-2212 phase films at a relative wide temperature range in this new process, but the purity of the film is sensitive to the variation of annealing temperature and annealing time.

The rocking curve of the (0012) peak of the Tl-2212 thin films annealed at 770 °C for 120 min is also measured and shown in Fig. 2. The full width at half maximum (FWHM) of the (0012) peak of the Tl-2212 phase is about 0.24°. The result indicates that the films annealed at 770 °C for 120 min possess a good crystalline structure.

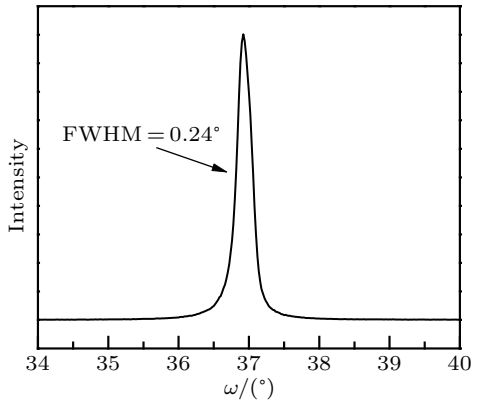


Fig. 2. Rocking curve of the (0012) peak of the Tl-2212 thin films.

The surfaces of the Tl-2212 films prepared by the new method were uniform and mirror-like. The morphologies of the Tl-2212 films were obtained by scanning electron microscopy (SEM). Figures 3(a)–3(d) show the SEM images of the films annealed under different conditions: (a) at 750 °C for 120 min, (b) at 760 °C for 120 min, (c) at 760 °C for 180 min, (d) at 810 °C for 120 min. The surface morphology of the sample film is smooth in Fig. 3(a). For the film annealed at a higher temperature 760 °C, a coarser morphology emerges on the surface of the film as seen in Fig. 3(b). When the annealing time is extended to 180 min at 760 °C, it has small influence on the sample surface, the film in Fig. 3(c) exhibits a smooth surface morphology with a flat plate-like terrace feature, which is similar to that in Fig. 3(b). With the annealing temperature raised to above 800 °C, the out of flatness is clearly observed on the surface shown in Fig. 3(d). At the temperature above 800 °C, high volatility of thallium will lead to many pits and holes on the surface of the film.

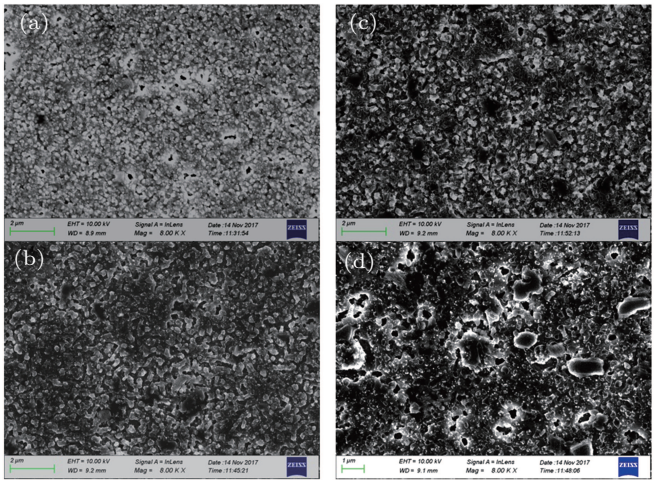


Fig. 3. (color online) SEM micrographs of Tl-2212 films annealed under different conditions: (a) at 750 °C for 120 min, (b) at 760 °C for 120 min, (c) at 760 °C for 180 min, (d) at 810 °C for 120 min.

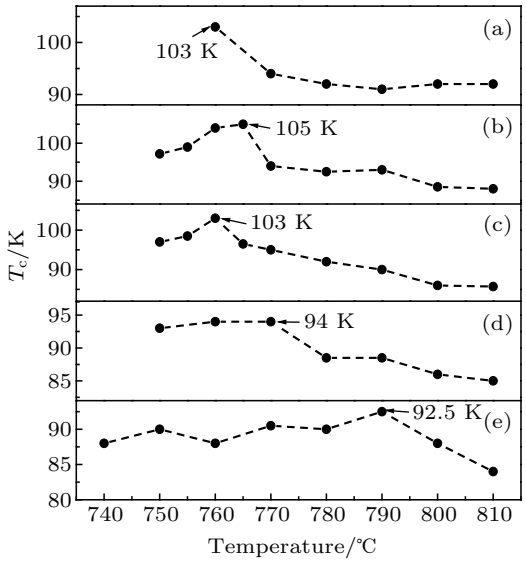


Fig. 4. Superconducting critical temperatures of Tl-2212 films annealed for (a) 90 min, (b) 110 min, (c) 120 min, (d) 150 min, (e) 180 min.

The superconducting critical temperatures were measured by the non-contact inductance method.[23] Figure 4 shows the critical temperatures T_c of the Tl-2212 films annealed under different annealing conditions. In Fig. 4(a), the samples annealed for 90 min below 760 °C have no superconductivity, and the highest T_c of the films annealed for 90 min is 103 K at 760 °C. The T_cs are below 95 K for the films with the annealing temperature ranging from 770 °C to 810 °C. In Fig. 4(b), the samples annealed for 110 min below 750 °C are not superconducting. The T_c increases slowly with the annealing temperature increasing from 750 °C to 760 °C, and the highest T_c of 105 K is observed at 765 °C, then the T_c falls dramatically to 94 K at 770 °C. The T_cs of the samples annealed at 770–810 °C are around 90 K. The T_c tendency of the films

annealed for 120 min shown in Fig. 4(c) is similar to that of the samples annealed for 110 min, and the highest T_c of the sample film annealed for 120 min is 103 K. From Fig. 4(d), the T_cs of the samples annealed for 150 min climb slowly with the annealing temperature increasing from 750 °C to 770 °C. The highest T_c of 94 K is obtained at 770 °C. In Fig. 4(e), the T_cs of the samples annealed for 180 min are around 90 K, and the highest T_c is only 92.5 K at 790 °C. When the annealing temperature is between 760 °C and 765 °C, and the annealing time is between 90 min and 120 min, the T_cs of the samples are usually higher than 100 K, the highest T_c is 105 K.

Transport critical current densities J_c of the Tl-2212 films were measured by using a four-point-probe technique at 77 K and zero applied magnetic field. Firstly, the Tl-2212 films were patterned into a micro bridge by photolithography and wet chemical etching using diluted hydrochloric acid, the bridge is 550 μm long and 20 μm in width. A voltage criterion of 10 μV was used for the determination of J_c. Figure 5(a) illustrates the critical current densities of the Tl-2212 films annealed at different temperatures for 120 min. The J_cs of the samples annealed at 750–765 °C increase slowly, and the highest J_c is 1.6 MA/cm^2 obtained at 765 °C. As the annealing temperature increases from 765 °C to 800 °C, J_c gradually decreases to 0.52 MA/cm^2. Figure 5(b) shows a group of J_cs of the Tl-2212 films annealed at 760 °C with different post-annealing time. With the annealing time increasing, the highest J_c of a sample annealed for 110 min can achieve 1.93 MA/cm^2 in our experiment. It drops to 0.775 MA/cm^2 for the film annealed for 150 min. The Tl-2212 films annealed at the temperature of 760–770 °C for 90–120 min will lead to the best T_c and J_c.

The variability in T_c and J_c correlates with the crystallization process, and it is consistent with the results analyzed from the XRD figures. When the annealing temperature is below 750 °C, it cannot meet the requirement of the lowest thermal energy growth, the sample films are usually not superconducting. With the appearance of mixed phases, the impurity phase will also affect the purity of the film and reduce the superconductivity of the film. In the traditional method with thallium sources, the additional thallium pellet can provide thallium oxide vapor balance continuously for a long time. While in this method, the content of thallium in the precursor films is fewer compared to the pellet, the balance of thallium vapor–solid equilibrium can only be maintained in a short period at around 760–770 °C. A higher annealing temperature or a longer annealing time will reduce the superconducting properties of the Tl-2212 film. Without the protection of the balance of thallium oxide, both T_c and J_c will drop quickly when the annealing condition is not optimal.

Compared to the traditional process in fabricating Tl-2212 thin films, the annealing temperature in oxygen[21] is reduced by 40–60 °C. The annealing temperature is similar to that of the conventional process in argon,[22] while the post-annealing time is reduced to 90–120 min.

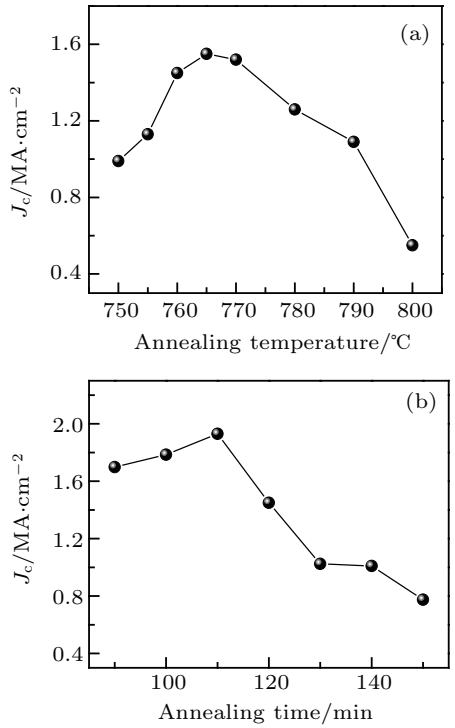


Fig. 5. (a) J_c versus annealing temperature. (b) J_c versus annealing time.

Based on the discussion above, this new method has two advantages. One is reducing the cost of fabrication. This method significantly reduces the use of Tl_2O_3. By adjusting the content of thallium in the precursor films and the selection of the appropriate size of the crucible, high quality Tl-2212 films are successfully obtained. The other is improving the repeatability and efficiency of the experiment. This new method avoids the uncontrollable conditions and the experimental condition is basically consistent, the repeatability and manipulability of the experiment are greatly improved. In addition, compared to 6 hours of annealing in the traditional process,[22] the post-annealing time is reduced to 90–120 min, the efficiency of the experiment is improved.

Although the best J_c obtained in this new method is lower than that from the conventional ways, a better J_c result will be reached through the further experiments. If the manufacturing process of the thallium films is continuously simplified and optimized, more high-quality thallium films, such as $TlBa_2Ca_2Cu_3O_9$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$, will be popularly studied and widely used in applications.

4. Conclusion

Tl-2212 films were fabricated by dc magnetron sputtering and post-annealing without the thallium pellet in flowing

oxygen. This new method uses less Tl_2O_3 than the conventional two-step method and avoids the repeated fabrication of thallium pellets, it effectively improves the efficiency, controllability and repeatability of the experiment. The XRD patterns of θ–2θ scans proved that the thin films could obtained pure Tl-2212 phase only. And the films were strongly textured with the c axis perpendicular to the substrate surfaces and epitaxially grown on $LaAlO_3$ (001). The best T_c of the films is 105 K and the J_c is close to 2 MA/cm^2 at 77 K zero field.

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