Growth of $TlBa_2Ca_2Cu_3O_9$ Epitaxial Thin Films by Two-Step Method in Argon *

Jian Xing(邢建)[1], Li-Tian Wang(王荔田)[1], Xiao-Xin Gao(高晓欣)[1], Xue-Lian Liang(梁雪连)[1], Kai-Yong He(何楷泳)[1], Ting Xue(薛婷)[1], Sheng-Hui Zhao(赵生辉)[1], Jin-Li Zhang(张金利)[1], Ming He(何明)[1,2], Xin-Jie Zhao(赵新杰)[1,3], Shao-Lin Yan(阎少林)[1], Pei Wang(王培)[4], Lu Ji(季鲁)[1,3]**

[1]*College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350*
[2]*Tianjin Key Laboratory of Optoelectronic Sensor and Sensing Network Technology, Tianjin 300350*
[3]*Key Laboratory of Photoelectronic Thin Film Devices and Technology of Tianjin, Tianjin 300350*
[4]*Beijing Institute of Radio Measurement, Beijing 100854*

(Received 3 January 2019)

$TlBa_2Ca_2Cu_3O_9$ (Tl-1223) films have promising applications due to their high critical temperature and strong magnetic flux pinning. Nevertheless, the preparation of pure phase Tl-1223 film is still a challenge. We successfully fabricate Tl-1223 thin films on $LaAlO_3$ (001) substrates using dc magnetic sputtering and a post annealing two-step method in argon atmosphere. The crystallization temperature of Tl-1223 films in argon is reduced by 100°C compared to that in oxygen. This greatly reduces the volatilization of Tl and improves the surface morphology of films. The lower annealing temperature can effectively improve the repeatability of the Tl-1223 film preparation. In addition, pure Tl-1223 phase can be obtained in a broad temperature zone, from 790°C to 830°C. In our study, the films show homogenous and dense surface morphology using the presented method. The best critical temperature of Tl-1223 films is characterized to be 110 K, and the critical current J_c (77 K, 0 T) is up to 2.13×10^6 A/cm^2.

PACS: 74.78.−w DOI: 10.1088/0256-307X/36/5/057401

In Tl-based high temperature superconductor (HTS) films, $TlBa_2Ca_2Cu_3O_9$ (Tl-1223) has a superior flux-pinning property than those of thallium-based superconductors with double Tl–O layers, which is believed for the strong coupling of single Tl–O layer.[1,2] This property allows Tl-1223 films to work in strong magnetic fields, thus following $YBa_2Cu_3O_{7-\delta}$ (YBCO),[3,4] it is the next candidate to work in power applications. Comparing with YBCO,[5] Tl-1223 films have a higher critical temperature T_c,[6] which significantly reduces the demand for refrigeration in the fields of engineering applications. All these potential benefits motivate us to fabricate reproducible high quality Tl-1223 films.

A major challenge in fabrication of Tl-1223 films is controlling the purity of the Tl-1223 phase. Particularly, using the traditional two-step method, a coexistent $TlBa_2CaCu_2O_7$ (Tl-1212) or $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) phase often emerges in Tl-1223 films, which degrades the Tl-1223 film properties.[7,8]

To overcome the above challenge, many strategies have been proposed to improve the purity of Tl-1223. For example, by partial substitution of Tl atoms with Bi or Pb and replacing most Ba atoms with Sr, the ratio of the Tl-1212 or Tl-2212 phase in entire Tl-1223 phase crystal can be reduced.[9−11] Taking advantage of this method, the films with the 1223 structure and high T_c above 110 K have been fabricated successfully,[12] but the preparation process becomes rather complicated and brings critical feasibility issues of practical implementation. Therefore, it is still necessary to seek an effective and reproducible method for the preparation of pure Tl-1223 phase films.

In our previous works,[13] by adjusting the Tl ratio in sputtering targets, $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223) phase could be firstly formed, then it could be converted into the Tl-1223 phase in the further annealing process with selected Tl-based pellets. A key advantage of this method is that Tl-1212 and Tl-2212 phases are suppressed in the preparation of Tl-1223 films. However, the preparation process in oxygen requires a high annealing temperature of around 900℃. At this temperature, the volatilization of Tl_2O_3 makes the Tl atmosphere difficult to control, meanwhile the reliability and repeatability of experiments is poor. Considering the active volatilization of Tl-oxides, a lower annealing temperature will be more suitable for the preparation of Tl-1223 films.

During the annealing process, Tl_2O_3 vaporizes according to the equilibrium[14]

$$Tl_2O_3(c) \xleftrightarrow{k_1} Tl_2O(g) + O_2(g), \tag{1}$$

where k_1 is equilibrium constant for reaction (1) and given by

$$k_1 = P(Tl_2O)P(O_2). \tag{2}$$

*Supported by the National Natural Science Foundation of China under Grant No 51002081, the Fundamental Research Funds for the Central Universities of China, and the Research Program of Application Foundation and Advanced Technology of Tianjin under Grant No 15JCQNJC01300.

**Corresponding author. Email: luji@nankai.edu.cn

© 2019 Chinese Physical Society and IOP Publishing Ltd

Hence, the decomposition of Tl_2O_3 to Tl_2O and O_2 can be promoted by reducing the oxygen partial pressure, and a suitable $P(Tl_2O)$ for the growth of Tl-based films can be obtained at a lower temperature.

In this Letter, growth of Tl-1223 film is investigated in argon atmosphere. The result demonstrates that Tl-1223 films can be successfully obtained in the temperature range 790℃–830℃. Compared with the temperature of around 900℃ in oxygen, this work has an effective reduction in temperature. The experimental result meets the above theory insights successfully. In addition, this annealing temperature improves the experimental repeatability greatly.

In our experiment, the Tl–Ba–Ca–Cu–O precursor films were deposited on $LaAlO_3$ (001) substrates by dc magnetron sputtering from a pair of facing $Tl_{1.1}Ba_2Ca_2Cu_3O_8$ superconducting targets. The 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 Tl:Ba:Ca:Cu=1.1:2:2:3. The sputtering was carried out under 80% argon and 20% oxygen at a pressure of 50 mTorr. During the sputtering process, the substrates were kept at ambient temperature. The combined deposition rate was about 11 nm/min and the thickness of the film was in the range 0.6–1 μm.

An *ex situ* post-annealing treatment was used to convert the amorphous precursor films into the Tl-1223 superconducting film. The precursor films, together with an accompanying TlBaCaCuO pellet, were sealed in an Al_2O_3 crucible. The pellet provided an appropriate Tl vapor atmosphere and replenished the lost Tl cations in precursor films during the Tl vapor annealing process. The composition of the accompany pellets played a key role in the two-step method. In this annealing process for Tl-1223 films, the pellets were prepared similarly to the sputtering targets, with an initial cation ratio of Tl:Ba:Ca:Cu = (0.8–1.1):2:2:3. The whole assembly was then placed in a furnace for the post annealing process. After being pumped for vacuum, the furnace was filled with 1 atm pure argon below 250℃, and then raised to 790–830℃ with a temperature rising rate at about 12℃/min. The annealing time was in the range of 2—6 h depending on different annealing temperatures.

The crystal structures of the Tl-1223 on $LaAlO_3$ (001) substrates were characterized by x-ray diffraction (XRD) θ–2θ scans, ω scans and phi scans on a Philips X'Pert diffractometer with Cu K_α radiation. The surface morphologies of these films were observed by scanning electron microscopy (SEM). The critical temperature T_c of samples was measured using a non-destructive inductance technique. The transport critical current densities (J_c) of the Tl-1223 films were measured using a standard four-probe technique. Before the measurements, a micro-bridge with 20 μm width and 200 μm length should be patterned on Tl-1223 films by photolithography and wet chemical etching, and a voltage criterion of 1 μV across the bridge was used for determining the critical current I_c.

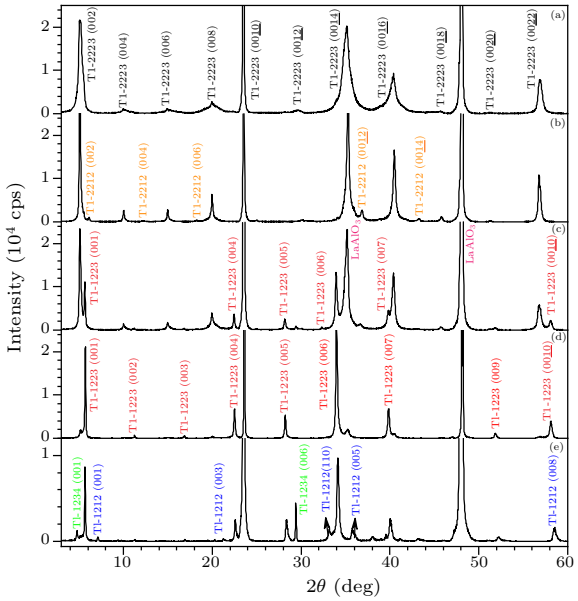

Fig. 1. XRD θ–2θ spectra of the film samples with different Tl ratios in accompany pellets: (a) $Tl_{1.1}Ba_2Ca_2Cu_3O_x$, 800℃ for 2 h, (b) $Tl_{1.1}Ba_2Ca_2Cu_3O_x$, 800℃ for 4 h, (c) $Tl_{1.0}Ba_2Ca_2Cu_3O_x$, 800℃ for 4 h, (d) $Tl_{0.9}Ba_2Ca_2Cu_3O_x$, 800℃ for 4 h, and (e) $Tl_{0.8}Ba_2Ca_2Cu_3O_x$, 800℃ for 4 h.

In general, the crystallization temperature of Tl-based films relies on the oxygen pressure in the annealing environment. A higher oxygen pressure yields a higher annealing temperature.[14,15] With the replacement of pure argon to oxygen, the annealing temperature is reduced, which was confirmed in the growth of Tl-2212 films as well.[16] Based on the crystallization temperature of Tl-2212 phase in argon, the annealing temperature for Tl-1223 films was firstly set at 800℃ in argon. The crystalline structure and phase purity of sample films were analyzed using XRD. Figure 1(a) depicts the XRD θ–2θ spectra of a Tl-1223 film formed in argon at 800℃ for 2 h with an accompanying Tl pellet at a cation ratio of Tl:Ba:Ca:Cu=1.1:2:2:3. Interestingly, the result shows a pure Tl-2223 phase on the spectra, and all the peaks are aligned with the *c*-axis substrate.

According to the result of Fig. 1(a), with the same pellets, we prolonged the annealing time to 4 h. Consequently, the diffraction peaks become narrow and sharp, and a small amount Tl-2212 phase appears (Fig. 1(b)). Comparing Figs. 1(a) and 1(b), we find that the crystallization of Tl-2223 phase has been improved with the prolongation of annealing time, but no Tl-1223 phase appears in the film. It was noted that the two samples were not superconducting, even though pure Tl-2223 phase was obtained.

Aselage *et al.*[17–20] proposed that higher $P(Tl_2O)$ causes double Tl–O layers to form easily in the growth of Tl-based films. The appearance of Tl-2223 phase should be attributed to the small abundant Tl cations from accompanying pellets under these post annealing conditions. Thus, the cation ratio of Tl was reduced in the accompanying pellets. Figure 1(c) shows the spectra of films prepared in the same annealing temperature and time with that of the sample in Fig. 1(b), but the accompanying pellets were formed with a cation ratio of Tl:Ba:Ca:Cu = 1:2:2:3. By adjusting the Tl ratio in pellets, Tl-1223 phase diffraction peaks appear. Although the Tl-2223 phase is still dominant in this spectra, the intensity of peaks is reduced, which can be attributed to the conversion from Tl-2223 phase to Tl-1223 phase. The result indicates that the reduction of Tl cation ratio in Tl accompany pellets does help the formation of the Tl-1223 structure.

Following this idea, Tl cation ratio is continually reduced in accompanying pellets. Figure 1(d) shows the films formed in 800℃ for 4 h in argon with pellets at Tl:Ba:Ca:Cu = 0.9:2:2:3. According to XRD analysis results, with the decrement of the ratio of Tl cation to accompanying pellets, the Tl-2223 diffraction intensity of peaks is significantly reduced, and the intensity of Tl-1223 diffraction peaks is increased accordingly. All main diffraction peaks are Tl-1223 (001) peaks, indicating that the Tl-1223 film grows along the *c*-axis of the substrate. As shown in Fig. 2, the full width at half maximum (FWHM) of the Tl-1223 (003) reflection peak is only 0.58°, which shows that the film possesses a good crystalline structure.

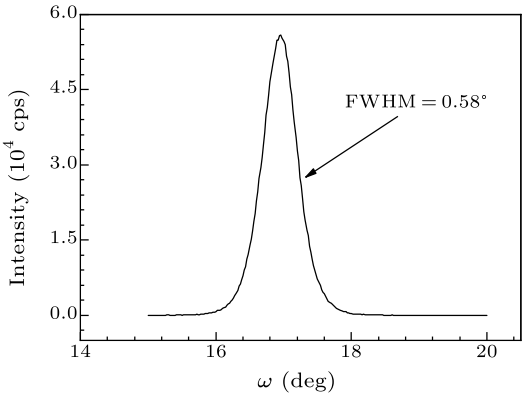

Fig. 2. Rocking curve of the (003) peak of the Tl-1223 thin film.

To explore the effect of Tl content on the growth of Tl-1223 films, Tl ratio in accompanying pellets was further reduced in the annealing process. The spectra of the precursor film formed at 800℃ for 4 h in argon with the target ratio of Tl:Ba:Ca:Cu = 0.8:2:2:3 are shown in Fig. 1(e). Tl-2223 phase peaks almost disappear due to the low ratio of Tl, but more single Tl–O layer undesired phases, e.g., Tl-1212 and $TlBa_2Ca_3Cu_4O_{11}$ (Tl-1234) phases can be found clearly in this spectrum. This is attributed to the conversion of Tl-1223 phase to Tl-1234 or Tl-1212 phase.

During the post annealing process, the solid-vapor equilibria existing above the thallium oxide source and precursor film dominates the fabrication of thin films of the Tl-based HTS phases, and the equilibria is mainly controlled by the accompanying pellets. By adjusting the Tl ratio in pellets, we obtained a suitable thallium oxide atmosphere for the growth of Tl-1223 phase in argon. Next, the influence of annealing temperature on Tl-1223 films was further studied.

From the above experimental results, the cation ratio of the accompanying pellets was set at Tl:Ba:Ca:Cu = 0.9:2:2:3 to guarantee the purity of the Tl-1223 phase. With this selected Tl ratio in pellets, the 0.6-μm thick Tl-1223 films could be obtained after the post annealing process carried out in argon at temperatures from 790℃ to 830℃ for 2–6 h. The annealing time varies with the annealing temperature to ensure that the precursor film obtains proper energy to crystallize.

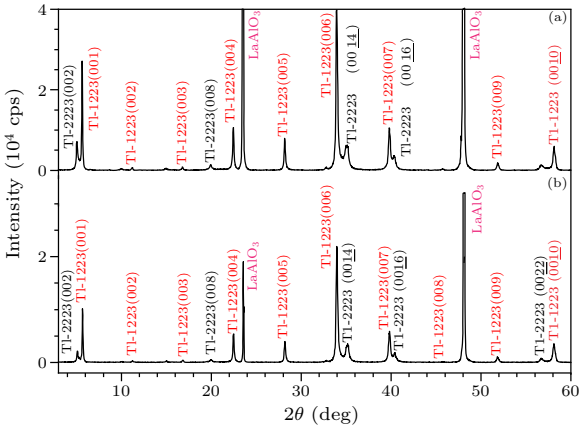

Fig. 3. XRD θ–2θ spectra of the film samples annealing under different conditions: (a) 790℃ for 6 h, and (b) 830℃ for 2 h.

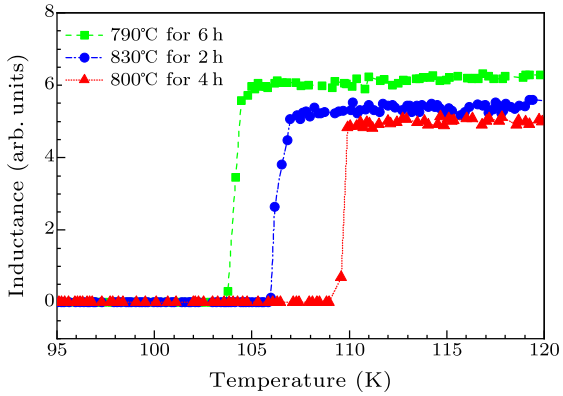

Fig. 4. Temperature dependence of inductance on Tl-1223 films.

Figure 3 shows the XRD patterns of films formed at 790℃ for 6 h and 830℃ for 2 h, respectively. In

Figs. 3(a) and 3(b), although there are still small peaks of Tl-2223 phase, Tl-1223 phase dominates in these two samples. It is indicated that the c-axis oriented Tl-1223 film can form in this broad temperature range 790–830℃.

Using the non-contact inductance method,[21] T_c values of films fabricated in this broad temperature range were measured to be above 105 K. In addition, the samples annealed at temperatures ranging from 800℃ to 820℃ have T_c of 110 K. Figure 4 shows the T_c values of samples annealed under various conditions. The variance in T_c may be attributed to the different oxygen contents in samples.[22]

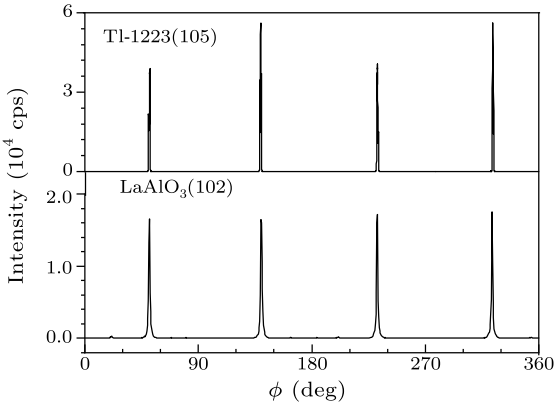

Fig. 5. Rotational phi scans: Tl-1223 (105) reflection and $LaAlO_3$ (102) reflection.

To investigate the crystallization of the films, we measured rotational phi scans for Tl-1223 films on LaAlO3 substrates. As depicted in Fig. 5, a typical phi scan of a 0.6-μm-thick film with the T_c value of 110 K (see in Fig. 1(d)) shows a fourfold symmetry. The overlap of Tl-1223(105) and $LaAlO_3$ (102) peaks in this figure indicates Tl-1223[001]//$LaAlO_3$[001], implying the occurrence of cube-on-cube epitaxy. The clean spectrum between peaks also indicates the lack of misoriented grains. The FWHM of the Tl-1223 peak is 1.1°, which is comparable to 0.89° of $LaAlO_3$ substrates, suggesting that the crystallization of the film is good.

The XRD measurements confirm the purity of the Tl-1223 phase in this procedure. From XRD θ–2θ scans and rotational ϕ scans, it proves that the films are strongly textured with the c-axis perpendicular to the substrate's surface. Compared with the Tl-1223 film prepared in oxygen at around 900℃, the Tl-1223 film can be formed in argon at a lower annealing temperature around 800℃ with a broadened annealing temperature zone. These advantages effectively raise the reproducibility of experiments and improve the surface morphology of films.

The surface morphologies of different samples formed in argon from 790℃ to 830℃ were also observed and compared, as shown in Figs. 6. In Figs. 6(a)–6(c), these samples were formed at 800℃ for 2 h, 810℃ for 2 h and 830℃ for 80 min. As shown in Fig. 6(a), the surface of this film is rough, and many uneven size particles distribute randomly. In Fig. 6(b), there are still some small particles on the film surface, while the evenness of surface morphology is much better than that in Fig. 6(a). Dense and layered platelike structures are also observed in this picture. In Fig. 6(c), the film exhibits a dense and smooth surface morphology with almost no particles. Comparing Figs. 6(a), 6(b) and 6(c), we can see that a higher annealing temperature enhances the energy of crystallization, which increases the size of the crystalline grains.

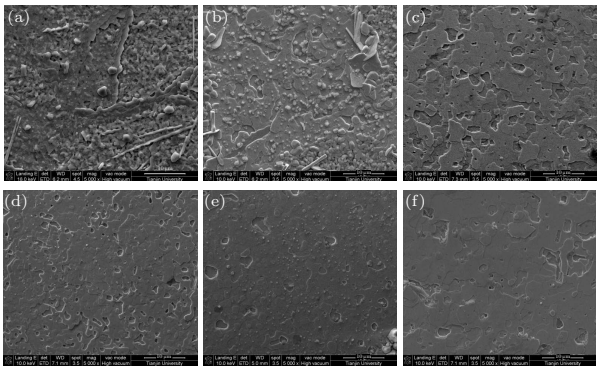

Fig. 6. SEM images of samples annealing at different temperatures and times: (a) 800℃ for 2 h, (b) 810℃ for 2 h, (c) 830℃ for 1 h and 20 min, (d) 800℃ for 4 h, (e) 810℃ for 3 h, and (f) 830℃ for 2 h.

Figures 6(d)–6(f) present the film samples prepared at 800℃ for 4 h, 810℃ for 3 h and 830℃ for 2 h, respectively. As shown by these three similar graphs, the morphologies of these films exhibit the typical features of a post-annealed HTS film, flat terraces, smooth and compact. It is illustrated that Tl-1223 films grow well at around 800℃ to 830℃. The comparison between Figs. 6(e) and 6(f) shows that high temperature can shorten the annealing time. Comparing Figs. 6(c) and 6(f), similar morphology of those two samples indicates that the scope of annealing time is also extended in the preparation process.

Figure 7 shows the magnetic dependence of J_c of the films formed at 800℃ for 4 h and 3 h. Interestingly, the T_c values of these films could reach 110 K, while the performances of J_c were very different. The curve with a red dot shows the magnetic dependence of J_c of the film formed at 800℃ for 4 h. The value of J_c (77 K, 0 T) for this film is 2.13×10^6 A/cm^2. When the dc field increases to 800 G, J_c of this sample falls to 7.5×10^5 A/cm^2. At 5000 G, J_c of this film still remains 1.3×10^5 A/cm^2, which is only less than 6% of this film in a self magnetic field. It could be reinforced that the Tl-1223 film has a better J_c performance in magnetic field. The curve with blue triangles shows the J_c performance of the film obtained at 800℃ for

3 h. In self magnetic field, this film has a J_c value of 1.2×10^6 A/cm^2. At 800 G, J_c of this sample still can be kept in 3.8×10^5 A/cm^2. However, the J_c value falls far more rapidly to 1.5×10^2 A/cm^2, while the magnetic field reaches 4000 G. Comparing the XRD spectra of these two samples, we find that shorter annealing time makes the conversion from Tl-2223 phase into Tl-1223 phase insufficient, and the intensity of Tl-2223 phase was comparable to that of Tl-1223 phase. Taken together the result with the J_c performance, it seems that Tl-2223 phase in Tl-1223 films destroys the integrity of the film structure, and the appearance of weak connections between Tl-2223 phase and Tl-1223 phase reduces the J_c performance of the Tl-1223 film.

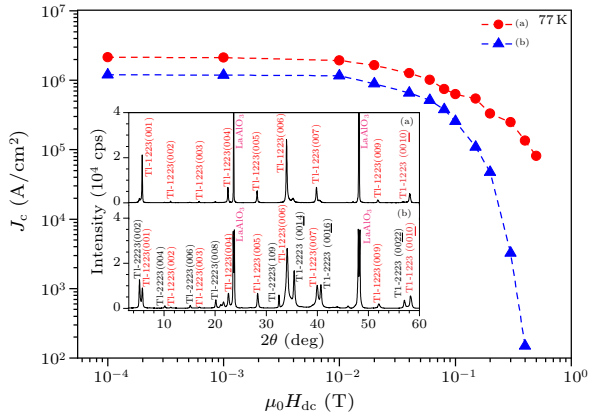

Fig. 7. Magnetic dependence of J_c on Tl-1223 phase films: (a) 800℃ for 4 h, Tl-1223 phase, (b) 800℃ for 3 h, Tl-1223 phase and Tl-2223 phase.

The prospect of adjusting the ratio of accompanying pellets, the composition of precursor films and annealing condition to improve the quality of Tl-1223 films deserves future explorations.

In conclusion, Tl-1223 films have been successfully grown on $LaAlO_3$ (001) substrates in argon with a high repeatability. Firstly, the temperature of preparation is greatly reduced. Secondly, compared with the Tl-1223 films prepared in oxygen annealing process, the temperature range (around 10℃) is broadened to 40℃. Thirdly, these annealing temperatures improve the quality of the surface morphology of film samples, yielding enhanced J_c values. Using this method, high quality Tl-1223 films with the T_c of 110 K are obtained, and the J_c values of films could reach 2.13×10^6 A/cm^2 at 77 K for zero field.

References

[1] Kim D H, Orey K E, Kampwirth R T et al 1991 *Physica C* **177** 431
[2] Vinokur V M, Kes P H and Koshelev A E 1990 *Physica C* **168** 29
[3] Kim S I, Kametani F, Chen Z et al 2007 *Appl. Phys. Lett.* **90** 252502
[4] Wang T, Karino H, Michitsuji K et al 2014 *IEEE Trans. Appl. Supercond.* **24** 1
[5] Wu M K, Ashburn J R, Torng C J et al 1987 *Phys. Rev. Lett.* **58** 908
[6] Liu R S, Zheng D N, Loram J W et al 1992 *Appl. Phys. Lett.* **60** 1019
[7] Tkaczyk J E, DeLuca J A, Karas P L et al 1992 *Appl. Phys. Lett.* **61** 610
[8] Juang J Y, Horng J H, Chen S P et al 1995 *Appl. Phys. Lett.* **66** 885
[9] Awad R, Al-Zein A, Roumie M et al 2013 *J. Mater. Sci. Technol.* **29** 1079
[10] Ren Z F, Wang C A and Wang J H 1994 *Appl. Phys. Lett.* **65** 237
[11] Auinger M, Gritzner G, Bertr C et al 2007 *Supercond. Sci. Technol.* **20** 704
[12] Heiml O and Gritzner G 2002 *Supercond. Sci. Technol.* **15** 956
[13] Gao X X, Xie W, Wang Z et al 2014 *J. Supercond. Novel Magn.* **27** 1665
[14] Cubicciotti D and Keneshea F J 1967 *J. Phys. Chem.* **71** 808
[15] Ahn B T, Lee W Y and Beyers R 1992 *Appl. Phys. Lett.* **60** 2150
[16] Yan S L, Fang L, Song Q X et al 1993 *Appl. Phys. Lett.* **63** 1845
[17] Aselage T L, Venturini E L and van Deusen S B 1994 *J. Appl. Phys.* **75** 1023
[18] Aselage T L, Voigt J A and Keefer K D 1990 *J. Am. Cerom. Soc.* **73** 3345
[19] Aselage T L, Venturini E L, van Deusen S B et al 1992 *Physica C* **203** 25
[20] Aselage T L, Venturini E L, Voigt J A et al 1996 *J. Mater. Res.* **11** 1635
[21] Doss J D, Cooke D W, Mccabe C W et al 1988 *Rev. Sci. Instrum.* **59** 659
[22] Li Y J, Xiong G C, Gan Z Z et al 1993 *Acta Phys. Sin. (Overseas Edn)* **2** 211