Influences of Thalliation on the Morphology and Critical Temperature of $Tl_2Ba_2CaCu_2O_8$ Thin Films *

LEI Chong(雷冲)[1,2], ZHAO Xin-Jie(赵新杰)[1], WANG Tian-Sheng(王天生)[1,2], PENG Wei(彭纬)[1], YU Hong-Chun(虞红春)[1], CHEN Ying-Fei(陈莺飞)[1], TIAN Yong-Jun(田永君)[2], LI Lin(李林)[1]

[1] *National Laboratory of Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing 100080*
[2] *Department of Material Science and Chemical Engineering, Yanshan University, Qinhuandao 066004*

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$Tl_2Ba_2CaCu_2O_x$ (Tl-2212) thin films were prepared by the two-step technique. A precursor film was first prepared by the pulsed laser deposition method, and then experienced the incorporation of thalliation in a one-step or two-step annealing process. The experimental results show that the two-step annealing process produces dense and smooth films, and that the one-step annealing process produces a high critical temperature film of 101K, but the transition width is wide. Precursor films with homogeneous $Ba_2Ca_{1.3}Cu_{2.1}O_x$ composition are essential for producing high-quality Tl-2212 films.

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Since the discovery of high-temperature superconductors with a critical temperature (T_{C0}) higher than 77 K, a worldwide interest has arisen in applications of superconducting materials for passive microwave devices. Amongst the high-temperature cupric superconductors, the $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) film of the Tl-system is a very promising material because it shows a critical temperature (T_{C0} ~110 K) much higher than that of $YBa_2Cu_3O_{7-\delta}$ (T_{C0} ~92 K) which is usually employed for passive microwave components. It also shows a much lower microwave surface resistance $R_S \sim 130\mu\Omega$ (77 K, 10 GHz).[1-4] However, due to the toxicity and volatility of Tl_2O,[5] the thin film of Tl-2212 cannot be prepared in an ordinary laboratory. It must be prepared in a fume cupboard with a specially designed furnace[6] and the laboratory should be well ventilated to protect against contamination. So, there are not many groups in the world who can prepare Tl-system thin films.

In this Letter, we report on the influences of thalliation on the morphology and T_{C0} of the Tl-2212 thin films. The Tl-2212 films were grown on (001) $LaAlO_3$ substrates and prepared by the two-step technique. In the first step, an amorphous Tl-free BaCaCuO precursor film with a thickness of ~1.4 μm was deposited by the pulsed laser deposition (PLD) method. The film was deposited under the conditions of energy density 2 J/cm^2, repetition rate 5 Hz and partial oxygen pressure 30 Pa. The target used was a sintered $Ba_2CaCu_2O_x$ ceramic disc, and the target–substrate distance was about 40 mm. Under these conditions, precursor films of composition $Ba_2Ca_{1.3}Cu_{2.1}O_x$ could be obtained. The second step was the incorporation of Tl into the precursor film, i.e. thalliation, which was performed by annealing in a Tl_2O/O_2 atmosphere. For this purpose, the precursor film and a sintered Tl-2212 pellet acting as the source of Tl_2O were placed together inside an alumina crucible covered with a lid. This crucible was put inside an alumina tube inserted in the furnace. The film was first annealed at 760–790°C for 6–10 h and then at 830°C for 30 min. For comparison, another precursor film was annealed at 830°C for 30 min and then cooled with the furnace to room temperature. After each thalliation process, due to the evaporation of Tl_2O gas, the weight of the Tl-2212 pellet decreased about 0.15–0.2 g, and the film thickness decreased to about 1.2 μm.

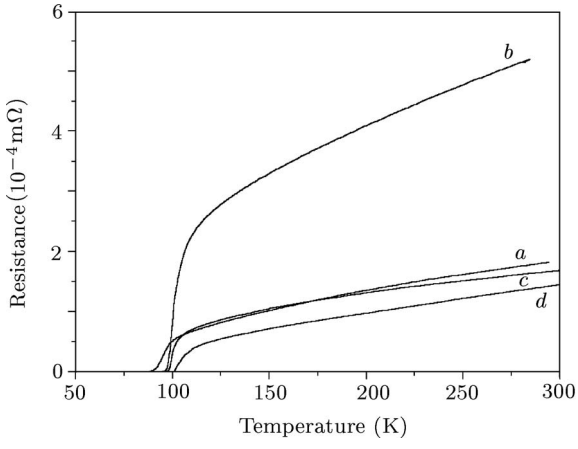

Fig. 1. Resistance versus temperature for film samples: (a) T_{C0} = 88 K, (b) T_{C0} = 92 K, (c) T_{C0} = 96.6 K and (d) T_{C0} = 101 K.

The films were investigated by scanning electron microscopy (SEM) including microanalysis (EDX) and x-ray diffraction (XRD). T_{C0} was measured by the standard four-probe resistance method. The experimental results show that T_{C0} of the films depends

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obviously on the morphology, composition and orientation of the films.

Figure 1 shows the resistance versus temperature (R–T) of the films after thalliation. In the two-step annealing process, the temperature was increased at a rate of 10°C/min to both the annealing temperature intervals. Curve a in Fig. 1 shows the $R-T$ behaviour of the film annealed at 780°C for 10 h and then at 830°C for 30 min, $T_{C0} = 88$ K. Curve b shows the $R-T$ behaviour of the film annealed at 790°C for 6 h, and then at 830°C for 30 min, $T_{C0} = 92$ K. Curve c shows the $R-T$ behaviour of the film annealed at 780°C for 8 h, then at 830°C for 30 min, $T_{C0} = 96.6$ K. For the one-step annealing process, the temperature was increased to 830°C at a rate of 5°C/min. Curve d shows the $R-T$ behaviour of a film annealed for 30 min at 830°C, $T_{C0} = 101$ K. The typical XRD spectrum of these films is shown in Fig. 2, in which the peaks pertain to {001} of Tl-2212 and the substrate. This indicates that the films are c-axis oriented, but some anomalous phases are always presented, shown by the $*$ symbols. Figures 3(a)–(d) show the SEM micrographs of the films with $T_{C0} = 88$, 92, 96.6 and 101 K, respectively. It can be seen from Fig. 3(a) that the morphology of the film is erratic, which consists of a variety of phases. Surface scanning of EDX shows that the substrate is not fully covered by the film, so T_{C0} is rather low and ΔT_C is rather wide, i.e. 88 and 14 K, respectively. Figure 3(b) exhibits a much regular microstructure, in which the film matrix consists of re-crystallized crystallites and morphology of the self-assembled structure, i.e. long streaks with a length of a few hundred micrometres and a radius of a few micrometres inter-crossed with each other.

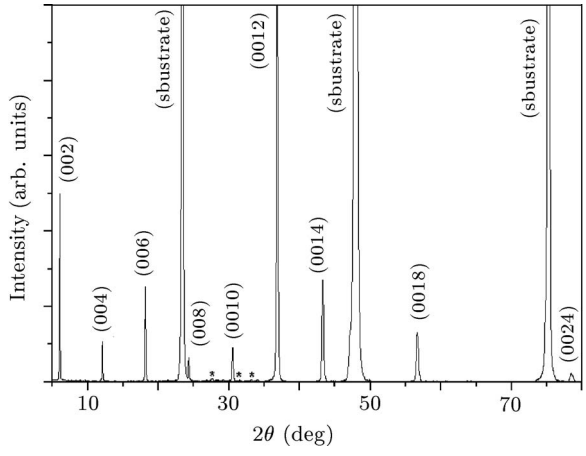

Fig. 2. Typical XRD spectrum of the film showing the {001} peaks of Tl-2212 and the substrate with the three symbols $*$ representing the anomalous peaks.

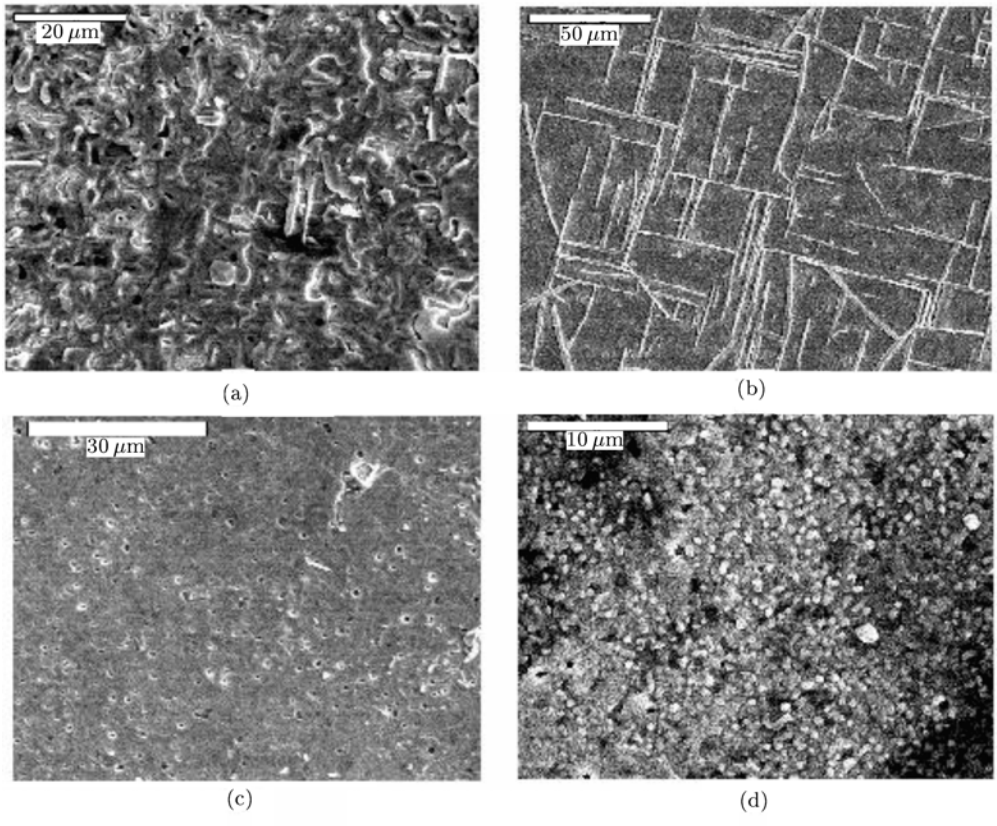

Fig. 3. SEM morphology of the film samples: (a) annealed at 780°C for 10 h and then at 830°C for 30 min, $T_{C0} = 88$ K; (b) annealed at 790°C for 6 h, and then at 830°C for 30 min, $T_{C0} = 92$ K; (c) annealed at 780°C for 8 h, then at 830°C for 30 min, $T_{C0} = 96.6$ K; (d) annealed for 30 min at 830°C, $T_{C0} = 101$ K.

The EDX analysis indicates that the film matrix composition is nearly Tl:Ba:Ca:Cu = 2:2:1:2. T_{C0} is 92 K and ΔT_C is 10 K. With a slight adjustment of the annealing conditions, a film with a more ordered self-assembled structure is obtained, as shown in Fig. 4. This film is extraordinarily smooth so that it is suitable for the use of multilayer devices. Figure 3(c) shows a uniform microstructure without well-defined grain boundaries. The surface is porous but not pinholed, which could enhance the pinning so that the film should have a high critical current density.[7] Figure 3(d) shows that the microstructure consists of re-crystallized small grains with a size of a few hundred nanometres and is distributed uniformly in the film. EDX indicates that the composition of the small grains is Tl:Ba:Ca:Cu = 2:2:1:2 and there are many large voids in the film. Although the one-step annealing process can obtain a film with a high critical temperature of $T_{C0} = 101$ K but ΔT_C is wide, and the surface is rough. During the thalliation, the volatility of Tl_2O dominates the fabrication of thin films,[8] which means that Tl_2O_3 decomposes to Tl_2O, i.e. $Tl_2O_3 \leftrightarrow Tl_2O(g) + O_2(g)$, and Tl_2O is volatile. Therefore, the reaction is

$$2Tl_2Ba_2CaCu_2O_8 \leftrightarrow 4BaCuO_2 + 2CaO + 2Tl_2O(g) + 2O_2(g).$$

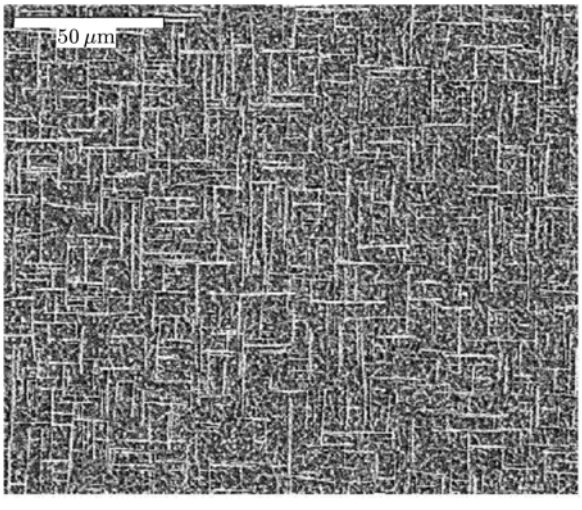

Fig. 4. SEM image of the film annealed by the two-step process with a more ordered self-assembled structure.

Therefore, when thalliation is carried out at low temperature, the surface of the precursor film is piled up with thallium oxide, most of which diffuses into the film during the long-time annealing process. When we obtain films by thalliation at high temperature, due to the decomposition of Tl_2O_3 to Tl_2O, most of Tl_2O_3 evaporates away from the film surface during the annealing process and leaks out from the crucible lid, finally depositing at the cool end of the alumina tube as Tl_2O_3 powder. The Oxford Group has observed this phenomenon previously when they fabricated large-area Tl-2212 films.[9]

In summary, we have experimentally determined that Tl-2212 films obtained by thalliation with the two-step annealing process are better than those obtained by the one-step process. The films are denser and smoother. EDX analysis has determined that the film matrix has an almost '2212' composition, and XRD shows that the Tl-2212 films are *c*-axis in orientation. However, it is not easy to obtain a pure Tl-2212 phase. We have found from SEM and EDX analyses that the different morphologies of the two-step annealed films stems from the pre-existence of voids, particles and the compositional heterogeneity of the precursor films. Thus, it is essential to fabricate precursor films with homogeneous $Ba_2Ca_{1.3}Cu_{2.1}O_x$ composition, and to avoid the occurrence of voids or particles.

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