Effects of post-annealing in different gas atmospheres on the properties of Tl-2212 films fabricated by sol-gel method

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Abstract. Tl-2212 superconducting thin films were fabricated on LaAlO_3 (001) substrates by sol-gel method. In the process, the precursor films were annealed in various gas atmospheres. XRD and EDX testing results showed that the precursors annealed in O_2 converted into pure Tl-2212 superconducting phase, and the nominally stoichiometric cation ratio of TlBaCaCu was close to 2:2:1:2. The Tl-2212 film had a layered morphology and medium-quality superconductive parameters, which included the critical temperature $T_c$ of 105.5 K, and the critical current density $J_c$ of 0.8 MA/cm$^2$ (self-field, 77K).

1. Introduction

The discovery of high-temperature copper-based superconductors (HTSCs) in 1986 brings about an extensive research and application in superconducting electronics. In practical applications of HTS thin films, Tl$_2$Ba$_2$CaCu$_2$O$_8$ (Tl-2212) superconducting films are especially noticeable in superconducting families for various high-frequency electromagnetic applications such as superconducting filter, because of their high $T_c$ and $J_c$, low microwave surface resistance, excellent chemical stability[1-3], and easy to form pure (001) phase than other thallium-based superconducting phases, such as Tl-1223 and Tl-2223. With thallium oxide easily evaporated during high temperature heat treatment, the primary methods to grow Tl-2212 films are physical methods including magnetron sputtering, electron beam evaporation, etc. Seldom chemical preparation technology, except for MOCVD and aerosol, were used to grow Tl-2212 films. The chemical deposition method like sol-gel and MOD is a low cost preparation of HTS films. The method has a very high deposition rate and does not require expensive vacuum equipment [4].

In recent years, the sol-gel method was widely used to grow YBCO films with the rapid development of the application of superconducting thin films. The process includes fluorine-free and fluorine-containing sol-gel method [5]. In the present work, we reported the fabrication of Tl-2212 films by fluorine-free process and the effect of various post-annealing atmospheres on Tl-2212 films containing their orientations, chemical compositions, surface morphologies and superconductivities.

2. Experiments

The TBCCO precursor solution, corresponding to the TiBaCaCu cation ratio of about 3:2:1:2, was prepared starting from four solutions obtained from Ti-, Ba-, Ca- and Cu-acetates, respectively. Thallium acetate was dissolved in methanol using methylacetic and diethylenetriamine (DETA) as a
chelating agent to prepare stable solution 1, barium and calcium acetate were dissolved in methanol and methylacetic with a small amount of lactic acid as solution 2 and 3, respectively. Solution 4 was prepared by dissolving copper acetate in the mixture of methanol, methylacetic and triethylene tetramine. The four solutions above were mixed together with formamide under stirring and concentrated by the removal of solvent at 70 °C. The as-prepared solution was spin-coated on a c-axis oriented LaAlO₃ (LAO) wafer at a spin rate of 4500 rpm for 15 s to get gel films.

The amorphous precursor films were prepared by the coated gel films dried in vacuum oven at 90 °C for 2 h, and then heated to 370 °C keeping for 35 minutes at a speed of 1 °C /min under the humidified (dew point 25 °C) flowing Ar atmosphere. The restricted temperature raising rate ensured the slow rate of organic decomposition. The moist Ar gas used in the process produced mirror-like surface morphology. Repeating the above process twice, thicker precursor film can be obtained.

The post-annealing process was carried to transform amorphous materials into superconducting phases[6]. In this process, the precursors were enclosed in a corundum crucible, along with a superconducting bulk material providing thallium vapor, and sintered at 750 °C for 4 h in Ar atmosphere (named sample 1) or 820 °C for 2 h in oxygen (named sample 2), then naturally cooled down to normal temperature.

3. Results and Discussion

The structure characteristic of the films with the same thickness grown on LAO substrates, which were post-annealed in various gas atmospheres, was tested by XRD, as shown in figure 1. Figure 1(a) showed that the precursor film was annealed at 750 °C for 4 hours in argon atmosphere. Obviously, The film was mainly composed of 440-oriented BaCuO₂ grains, with a small quantity of other oriented particles such as (105), (0014), (1110) for Tl-2212, (444), (640), (732), (622) for BaCuO₂. As a comparison, after the precursor film was annealed in oxygen atmosphere at 820 °C for 2 hours, the whole film consisted of crystalline grains with out-of-plane texture as only Tl-2212 phase (00l) diffraction peaks could be observed, as shown in figure 1(b). In addition, the intensity of diffraction peaks for sample 2 was 100 times than that for sample 1, implying that the precursor annealed in Ar mainly consisted of amorphous material.

![Figure 1. XRD patterns for Tl-2212 films prepared by precursor films annealed in (a) Ar; (b) O₂](image)

To study the difference in crystal structure, the microscopic composition of above films were evaluated by EDX. As can be seen clearly in Figure 2(a), the component of the film annealed in Ar was Tl:Ba:Ca:Cu = 0.5:2:1.05:2.1, which confirmed rather low thallium content in the film. This was because that under Ar atmosphere, the volatilization temperature of thallium in precursor, which was fabricated by sol-gel solutions with the various materials mixed at molecular level, was much lower.
than that of disc used as a source of thallous vapor and made of powder. It meant that the difference of volatilization temperature in Ar resulted in the loss of thallium in precursor having insufficient compensation from disc during the annealing process. By contrast, the component ratio of the sample 2 prepared by $O_2$ was about 2:2:1:2 (figure 2(b)), indicating that the post-annealing precursor in $O_2$ restricted the thallous volatility at low temperature, or increased the volatilization temperature of thallium in precursor.

Figure 2. EDX patterns for Tl-2212 films prepared by precursor films annealed in
(a) Ar; (b) $O_2$

The SEM images of the samples mentioned above were presented in figure 3. The film prepared by the thalliation of precursor in Ar evidently showed much poorer surface morphology with many $BaCuO_2$ grains on the film in different directions, as shown in figure 3(a). In contrast, the film prepared using $O_2$ clearly demonstrated a layered morphology with smooth platform, which manifested the classic features of Tl-2212 film grown on LAO substrate. Additionally, there were some holes and varisized granules on the film. The holes were proven to be only pits without stretching to the interface between film and substrate. These particles are composed of thallium, barium, calcium and copper, with the molar ratio of 1:1:2:3.2:4.6. Notice that the XRD measurements revealed the film consisted of purely c-axis oriented grains of Tl-2212 phase with no other oriented crystal particles (figure 1(b)). We can draw a conclusion that during the thalliation of precursor film, the superfluous calcium and copper oxides were expelled from the interior of the lattice and accumulated on the outside surface.

Figure 3. Secondary electron images of samples prepared by precursor films annealed in
(a) Ar; (b) $O_2$

The in-plane texture of the sample prepared using $O_2$ on LAO substrate was tested by $\phi$-scans. The diffraction plane of (1019) was corresponding to the reflection angle of $2\theta=64.86^\circ$ and incident angle of $\alpha=10.65^\circ$, see Figure 4 (a). The in-plane texture was apparent from the patterns with fourfold symmetrical peak. The $\phi$-scan data obtained from the (101) diffraction plane of substrate were also presented for the substrate (Figure 4(b)). It was obvious that the b-axis of superconducting phase Tl-
2212 was parallel to the b-axis of substrate, indicating the film was epitaxially grown on the LAO wafer.

![Figure 4. XRD Phi-scan patterns for sample2](image)

Also, the superconducting parameters of the samples were tested. The $T_c$ of both sample 1 and sample 2 showed in figure 5, were around 97.5 K and 105.5 K, their transition widths (Δ$T_c$) were 11.3 K and 2.3 K, respectively. The $J_c$ of sample 2 was close to 0.8 MA/cm² (self-field, 77K), but without critical current density was observed for sample 1.

![Figure 5. Superconducting transition temperatures $T_c$ (K) for (a) sample 1; (b) sample 2](image)

4. Conclusion

A sol-gel method was introduced in the preparation of Tl-2212 films on LAO wafers. In the process, purely (00l)-oriented Tl$_2$Ba$_2$CaCu$_2$O$_8$ thin films were fabricated by sintering Tl-Containing precursors at 820 °C for 2 h in oxygen. The Tl-2212 films exhibited layered morphology, and compact structure. The $T_c$ of sample was about 105.5 K, its $J_c$ (self-field, 77K) was close to 0.8 MA/cm². The further improvement to $J_c$ of Tl-2212 thin films prepared by sol-gel method is under way.

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