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Promotion of phase transformation and single-phase formation in silver-doped Tl–Ba–Ca–Cu–O superconducting thin films

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Phase transformation and physical characteristics of the spray-pyrolyzed Tl–Ba–Ca–Cu–O superconducting films with 3 mol% silver dopant have been studied using electrical resistivity, x-ray diffraction, and scanning electron microscopy. The major phase formed in the resultant film, annealed at a temperature of 885 °C for 3 min, was found to be the nearly single-phase, high-T_c $Tl_2Ba_2Ca_2Cu_3O_y$ (Tl-2223). The multiple phase of $Tl_2Ba_2Ca_2Cu_3O_y$ and $TlBa_2Ca_2Cu_3O_y$ (Tl-1223) appeared at annealing temperatures lower and higher than 885 °C. It was also observed that Ag dopant effectively reduces normal resistivity at 300 K and enhances the phase transformation of single-Tl-layer Tl-1223 to double-Tl-layer Tl-2223 phases and further helps to form the nearly single-phase Tl-2223 within a short duration. Critical transition temperature ($T_{c,\text{zero}}$) and current density (J_c, 77 K, 0 Tesla) of the best resultant film were shown to be 123 K and 5.7×10^4 A/cm^2, respectively.

I. INTRODUCTION

It is well known that the addition of various metallic dopants in superconducting oxides exhibits not only the improvement of physical characteristics of superconductors but also the realization of the mechanism of superconductivity. Among these metallic dopants, noble metals such as silver, platinum, and gold have been proved as the friendly elements in the superconducting oxides including Y- and Bi-based bulks, thin films, and wires.[1–3] The advantages of the noble metallic dopants in the Y- and Bi-based superconductors are an increase in the critical transition temperatures and critical current density, improvement of surface morphology and formation temperature of superconducting phases, and so on. Jodoit *et al.*[4] reported that the doping effect of various metallic elements of Zn, Cd, Al, In, Pb, and Bi in the Tl–Ba–Ca–Cu–O system can control the rate of solid-state reaction and the volatility of Tl components and increase the electrical conductivity at room temperature and the volume fraction of the superconducting phase. It is also observed that metallic dopants promote the intergranular coupling of the superconductive particles and annihilate the pores in the sintering process.

It was reported[5] that Ag_2O-doped $Tl_2Ca_2Ba_2Cu_3O_y$ bulk with Ag molar ratio ≦ 1.0 was prepared by a solid-state reaction, which indicated that the normal-state resistance decreased and the critical transition temperature increased with an increase in the content of Ag_2O for the doped bulks. Doping of the silver oxide as indicated from the results of the x-ray diffraction (XRD) pattern, is favorable for the formation of the high T_c $Tl_2Ca_2Ba_2Cu_3O_y$ (Tl-2223) phase in the Tl-based bulk. Morphology transformation from a plate-like grain in the undoped sample to a needle-like grain in the Ag-doped sample was observed. Tachikawa *et al.*[6] demonstrated that Ag addition and F addition to the coating layer of the Tl–Ba–Ca–Cu–O composites enhance the diffusion reaction and decrease the optimum reaction temperature. Many reports had demonstrated the addition of various metallic dopants in the high T_c superconductor bulks.[7,8] However, the doping effect of noble metals on the physical characteristics of the Tl-based superconductor is not studied in detail, and the observation of phase transformation and single-phase formation of the Ag-doped Tl-based film is still infrequent and inconsistent.

In this paper, the phase transformation of the Ag-doped Tl–Ba–Ca–Cu–O superconducting films prepared by spray pyrolysis as well as the effects of Ag additive on the physical characteristics of the resultant films will be systematically studied in detail, and the formation of single-phase Tl-2223 thin film was also observed.

II. EXPERIMENTAL PROCEDURE

Silver-doped and undoped Ba–Ca–Cu–O films were prepared from a glycerol solution mixture with high purity reagents of $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $Ag(NO_3)$, and $Cu(NO_3)_2 \cdot 3H_2O$. The metal stoichiometric ratios of silver-doped and undoped precursor solutions are shown to be Ba : Ca : Cu : Ag of 2 : 2 : 3 : 0.3 and Ba : Ca : Cu of 2 : 2 : 3. The as-sprayed films were formed on the MgO substrates heated at ~300 °C by spraying the solution mixture using a spray gun. The typical thickness of the as-sprayed films was about

20–30 μm. The thallination process was performed and described in detail as follows: the as-sprayed films were post-annealed at temperatures of 865, 875, 885, and 900 °C for 3 min to find the optimal conditions for the preparation of superconducting oxide films with high T_c. All as-sprayed films were processed in the closed system with $Tl_2Ba_2Ca_3Cu_3O_y$ bulk sources. Superconducting $Tl_2Ba_2Ca_3Cu_3O_y$ bulks were prepared by the solid state reaction process.[9] The closed system means that the as-sprayed film and bulk source were put together inside a metal foil of Au. With careful control of the annealing temperature and duration, thin film with a majority of a single superconducting phase may be obtained by such a closed processing system, although the nominal composition of the resultant superconducting phase may not be directly related to the starting composition. The phases in the as-sprayed and resultant films were identified using a Philips PW1700 x-ray diffractometer with nickel-filtered Cu K_α radiation (40 kV, 300 mA) at a scan rate of 0.04°/s with scan angles (2θ) ranging from 3 to 60°.

The thickness, surface morphology, and composition of the as-sprayed and resultant films were examined under a Hitachi S-400000 scanning electron microscope (SEM) operated at 20 kV/10 μA and inductively coupled plasma-atomic emission spectrometer (ICP-AES). For the electrical resistance measurement, a standard four-point probe technique was employed. Electrical contacts to the films were made using fine copper leads attached to the films with a conductive silver paste. The resistance limit measured was 10^{-6} Ω. The critical current densities of the resultant films were measured with a nanovoltmeter Model 181 and a voltage/dc current power supply source Model 228 from Keithley Inc. Similarly, a four-point technique was also employed to measure transport critical current density with a criterion of 1 μV/cm.

III. RESULTS AND DISCUSSION

Figure 1 shows an XRD pattern of the silver-doped film annealed at 885 °C for 3 min and the nearly single phase of $Tl_2Ba_2Ca_2Cu_3O_y$ (Tl-2223) with strong (001) orientation. In fact, the characteristic peaks of Tl-2223, $TlBa_2Ca_2Cu_3O_y$ (Tl-1223), and Ag phases appeared in the films annealed at 865, 875, and 900 °C for 3 min, and the relative intensity of the characteristic peaks of Tl-2223 and Tl-1223 is different while that of the silver phase is similar. From the result of XRD patterns, it was found that the addition of silver was favorable for the formation of superconducting phases of Tl-2223 and Tl-1223. The undoped Tl-based superconducting film annealed at 885 °C for 3 min showed the appearance of Tl-1223 and Tl-2212 phases and the formation of the single phase of Tl-1223 at the annealing temperature of 900 °C for 3 min. The addition of silver on the Tl-based superconducting film showed that the formation temperature of the superconducting phase can be reduced and the formation of Tl-2223 phase is superior to the Tl-1223 phase. In fact, silver has been proved to lower the melting point of Ba–Ca–Cu-containing precursor film[8,14] and promote the formation of crystalline Tl–Ba–Ca–Cu–O thin film at lower temperatures. On the other hand, the doping amount of silver affected the amount of liquid phase formed and resulted in the nucleation and/or the phase transformation between Tl-1223 and Tl-2223.

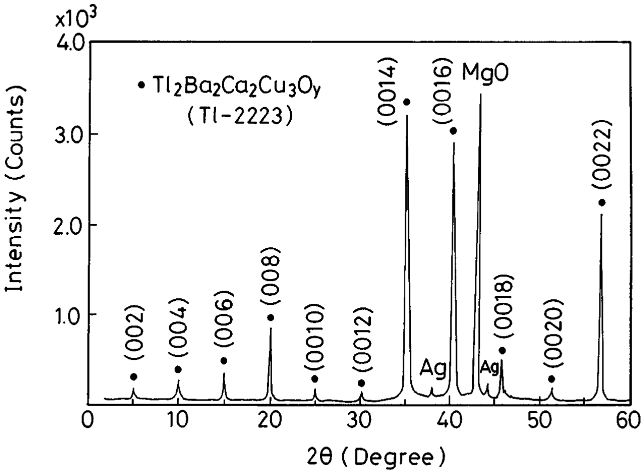

FIG. 1. X-ray diffraction pattern of Tl-2223 superconducting phase in the Ag-doped resultant film which annealed at 885 °C for 3 min.

Figure 2 shows the volume fraction of Tl-2223 (i.e., Tl-2223/Tl-2223 + Tl-1223) of the silver-doped and undoped films annealed at 865, 875, 885, and 900 °C

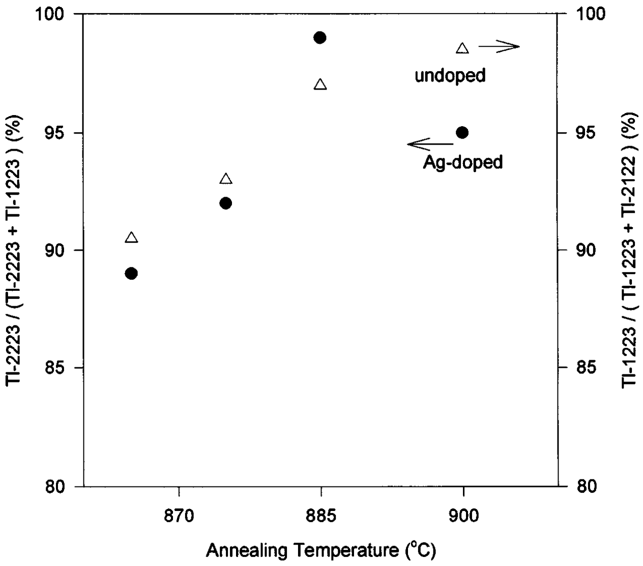

FIG. 2. The volume fraction of Tl-2223/(Tl-2223 + Tl-1223) and Tl-1223/(Tl-1223 + Tl-2122) for the Ag-doped and undoped resultant films which annealed at 865, 875, 885, and 900 °C for 3 min.

for 3 min. The volume fraction of the Tl-2223 phase in the samples was evaluated from the relative intensity of XRD peaks in (0014) Tl-2223, (006)Tl-1223, and (0014)Tl-2212 phases, respectively. For the Ag-doped Tl-based superconducting film annealed at 865 °C, the XRD pattern shows the existence of both major phase of Tl-2223 and minor phase of Tl-1223. When the annealing temperature was increased, the relative intensity of the Tl-2223 phase gradually increased and that of Tl-1223 phase decreased. The maximum volume fraction of the Tl-2223 superconducting phase would reach nearly 100% at the annealing temperature of 885 °C for 3 min. The volume fraction of Tl-2223 decreased to 95% when the annealing temperature was 900 °C. These indicate that the sequential transformation of Tl-1223 + Tl-2223 (at annealing temperatures lower than 885 °C) → Tl-2223 (at annealing temperatures of 885 °C) → Tl-1223 + Tl-2223 phases term (at annealing temperatures higher than 885 °C), a reaction route for the preparation of Ag-doped Tl-based superconducting film. On the other hand, both Tl-2212 and Tl-1223 phases appear in the undoped Tl-based superconducting films. The amount of Tl-1223 phase in the undoped films increased with increasing annealing temperatures, and the nearly single-phase Tl-1223 was formed at a temperature of 900 °C for 3 min.[10] The phase transformation can be realized either by increasing the annealing temperature and duration or by reducing the Tl content in the starting composition and in the Tl-source bulk.[11] Phase transformation of double-Tl-layer compounds into single-Tl-layer ones are useful in prolonging the annealing duration. Similarly, an appropriate short duration of annealing processing was also found to result in the reversible transformation reaction.[12]

The full-width at half-maximum (FWHM) of Tl-2223 (0014) in the Ag-doped Tl-based superconducting films and that of Tl-1223 (006) in the undoped films as a function of annealing duration is shown in Fig. 3. The values of FWHM decrease with increasing annealing duration and then remain constant at a value of about 0.4. This indicates that the improvement of the Tl-based superconducting film in quality at longer annealing duration is no longer remarkable. The silver addition is favorable to the formation of liquid phase and leads to the change in orientation behavior of the grain and texturing of thin films.

Figure 4 shows the relationship between electrical resistivity, critical transition temperature ($T_{c,\text{zero}}$), and various annealing temperatures for 3 min. The critical transition temperature of the Ag-doped resultant films increases from 110 and 118 up to a maximum value of 120 K and then decreases to 115 K with increasing the annealing temperatures from 865 to 900 °C. The similar variation of T_c was also found in the undoped thin film. The optimum annealing temperature for the formation of high T_c Tl-2223 film should be 885 °C. In general, the preparation of high T_c Tl-based superconductors with single phase is at temperatures of 900–920 °C and depends on the stoichiometric ratio of the constituents. Excess amounts of calcium and copper in the preparation of Tl-based superconductor bulk can also promote the formation of a single-phase superconductor.[9] Too high or too low temperatures and inappropriate treatment during processing will result in the formation of the multiple phases. Additionally, the electrical resistivity, at 300 K, of the resultant films decreases linearly with increasing

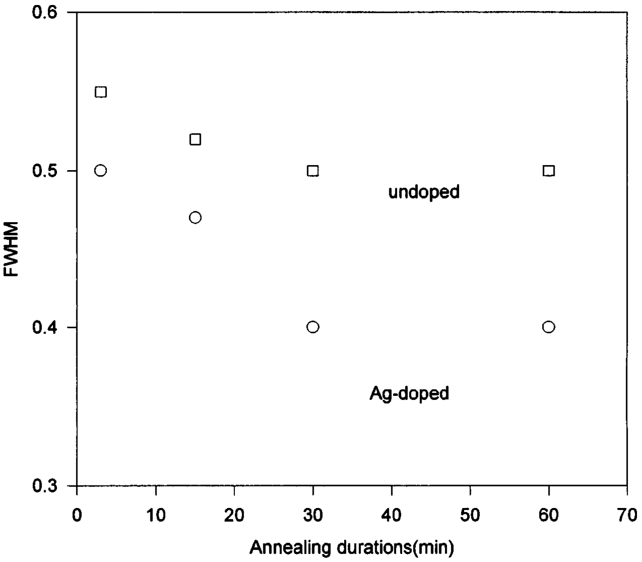

FIG. 3. The full-width at half-maximum (FWHM) of Tl-2223 (0014) in the Ag-doped and Tl-1223 (006) in the undoped resultant films as a function of annealing durations.

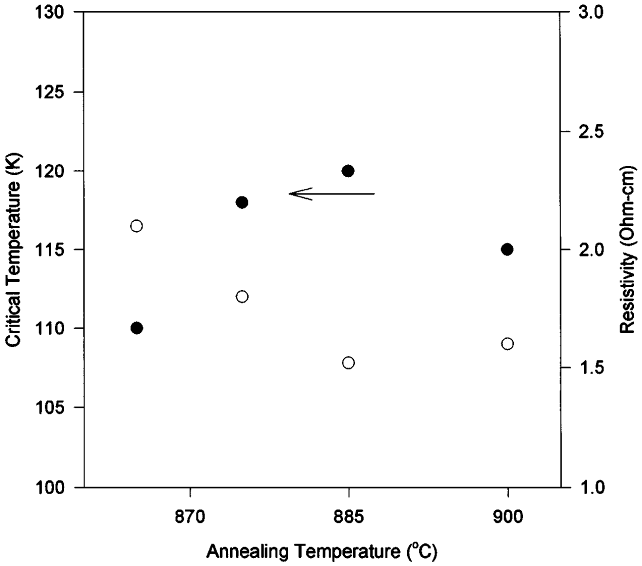

FIG. 4. Relationship between electrical resistivity (○), critical transition temperature (●), and various annealing temperatures for 3 min for the Ag-doped resultant films.

the annealing temperatures. Silver has excellent thermal and electrical conductivities. The doping effect of silver in the preparation of superconducting film exhibits the promotion of electrical characteristics of the superconducting Tl–Ba–Ca–Cu–O film. This indicates that an extremely good connectivity existed in the intergrains.

Electrical resistivity and critical transition temperature ($T_{c,\mathrm{zero}}$) of the films annealed at 885 °C for various durations are shown in Fig. 5. Critical transition temperature of the Ag-doped Tl–Ba–Ca–Cu–O films was markedly improved and increased for long-term annealing. The $T_{c,\mathrm{zero}}$ of 123 K as shown in the present study is one of the highest critical transition temperatures of the spray-pyrolyzed silver-doped Tl–Ba–Ca–Cu–O superconducting film that was annealed at 885 °C for 30 min. The films annealed at 885 °C for 3, 15, and 60 min showed the critical transition temperatures of 120, 122, and 120 K, respectively. A typical relationship between temperature and electrical resistivity of the Ag-doped and undoped resultant films is also shown in Fig. 6. In the case of the superconducting films, the variation of the electrical resistivity with increasing annealing duration is small. Comparing with the results in Fig. 4, it is to be noted that the effect of annealing temperature on the electrical resistivity is more apparent than that of annealing duration on the electrical resistivity. This may be due to the occurrence of silver diffusion in the thin film at higher annealing temperatures which leads to the accumulation of Ag in grain boundaries; consequently, improvement of electrical characteristics is due to the important changes in the electrical behavior of the grain boundaries. This phenomenon were also proved in the case of Y-based and HgTl-based systems.[1,13]

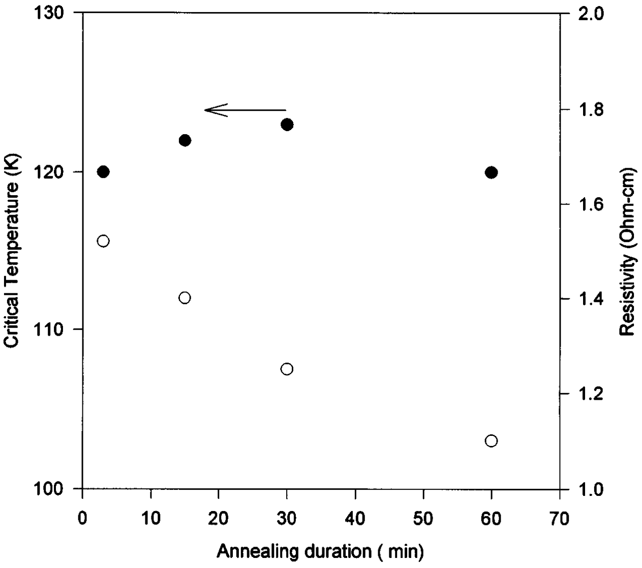

FIG. 5. Electrical resistivity (○) and critical transition temperature (●) of the Ag-doped resultant films as a function of annealing duration at 885 °C.

The SEM micrographs of the films annealed at 875 (a) and 885 °C (b) for 3 min are indicated in Fig. 7 and reveal the presence of round-like and plate-like microstructures consisting of crystallites having different

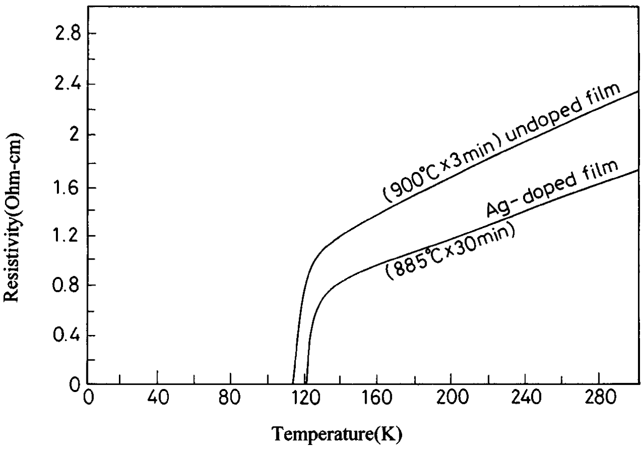

FIG. 6. Typical relationship between temperature and electrical resistivity of the Ag-doped and undoped resultant films.

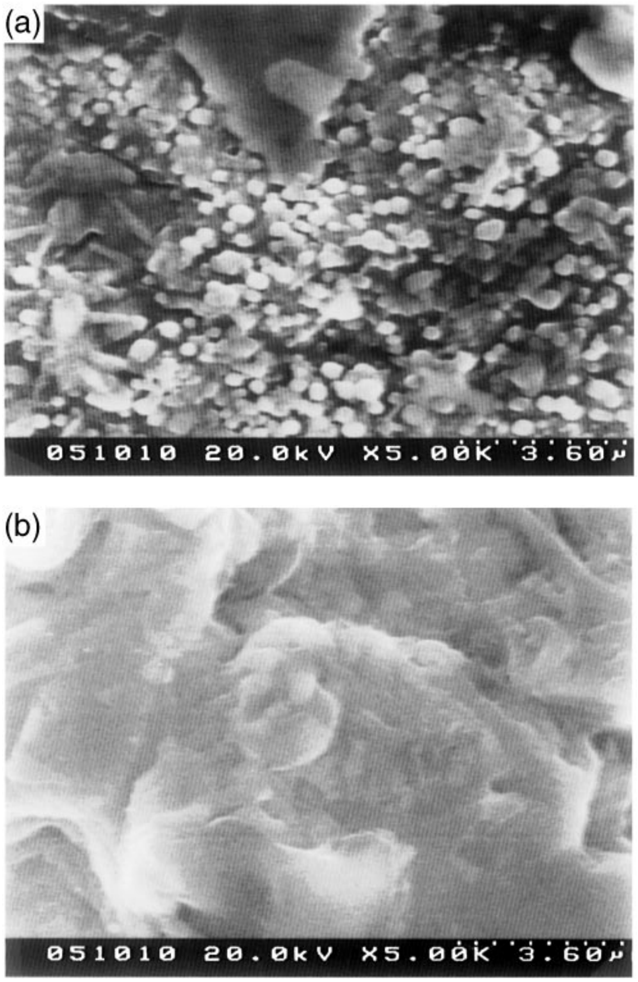

FIG. 7. Typical micrographs of the Ag-doped resultant films which annealed at (a) 875 °C and (b) 885 °C for 3 min.

TABLE I. Chemical composition, critical transition temperature, critical current density, and superconducting phases in the Ag-doped resultant films which annealed at 885 and 900 °C for 3 min and 885 °C for 30 min.

Films	Annealing condition (temp./time)	Phases in the resultant film	T_c (K) and J_c (A/cm^2)	Chemical compositions				
				Tl	Ca	Ba	Cu	Ag
A	885 °C/3 min	Tl-2223	120 K 2.3×10^4 A/cm^2	2.13	2.14	1.95	3.08	0.29
B	885 °C/30 min	Tl-2223	123 K 5.7×10^4 A/cm^2	2.08	2.11	1.93	3.05	0.28
C	900 °C/3 min	Tl-1223 + Tl-2223	115 K 8.6×10^3 A/cm^2	1.96	1.94	1.93	2.88	0.28

sizes. The plate-like microstructure, Fig. 7(b), has been demonstrated to be a microstructural characteristic of the Tl-2223 phase. No remarkable impurity phase appeared in the Ag-doped films except for the phases of Tl-2223 and Tl-1223.

Table I lists chemical compositions, critical transition temperature, critical current density, and superconducting phases of the resultant films. In the case of chemical composition analysis, the nominal compositions of Ba, Ag, Ca, and Cu in the resultant films are apparently different from the starting compositions of the as-sprayed films. It is found that the nominal compositions of Ba and Ag in the resultant films A, B, and C are less than those in the as-sprayed films. On the contrary, chemical compositions of Ca and Cu in the films A, B, and C are more than those in the as-sprayed films and indicates that the excess amount of Ca and/or Cu is favorable for the preparation of single-phase Tl-2223. However, the amount of thallium, supplied from the Tl-bulk source, is also crucial for the formation of superconducting phases. In the case of thallium, nominal composition in the films A and B is larger than that in the film C and starting composition in the as-sprayed film. The nearly single-phase Tl-2223 appears in the films A and B while the phase of the film C is thus both Tl-1223 and Tl-2223. Additionally, the critical current densities of films A and B are one order of magnitude larger than that of film C. In the present investigation, the optimum annealing temperature for the formation of single-phase Tl-2223 is 885 °C. It is also indicated in the present study that the existence of silver in the film facilitates the incorporation of Tl into the precursor film and promotes the formation of single-phase Tl-2223.

IV. CONCLUSIONS

Phase transformation of Tl-1223 to Tl-2223 and formation of single-phase Tl-2223 were observed in the preparation of Tl–Ba–Ca–Cu–O superconducting thin films containing 3 mol% Ag under the appropriate reaction condition. The Ag-doping effect, which may be due to the catalysis reaction, in the present study results in not only lowering the formation temperature of Tl-2223 phase but also in improving the crystallinity, transition temperature, and critical current density of the Tl-based thin films. Silver in the Ba–Ca–Cu–O precursor film is beneficial to the incorporation of more Tl constituent into the precursor film and the stabilization of single-phase superconducting Tl-2223 in the resultant films.

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REFERENCES

1. Dhananjay Kumar, M. Sharon, R. Pinto, P. R. Apte, S. P. Pai, S. C. Purandare, C. P. D'Souza, L. C. Gupta, and R. Vijayaraghavan, J. Appl. Phys. **76**, 1349 (1994).
2. M. Satou, Y. Yamada, S. Murase, T. Kitamura, and Y. Kamisada, Appl. Phys. Lett. **64**, 640 (1994).
3. N. Vasanthamohan and J. P. Singh, Supercond. Sci. Technol. **10**, 113 (1997).
4. K. Jodoit, A. Sonoda, S. Yasuyama, and A. Ohyoshi, Jpn. J. Appl. Phys. **30**, L221 (1991).
5. H. S. Koo, W. M. Hurng, W. H. Lee, T. Y. Tseng, M. Chen, and J. R. Lo, Appl. Phys. Lett. **62**, 3354 (1993).
6. K. Tachikawa, K. Zama, and A. Kikuchi, Jpn. J. Appl. Phys. **32**, L654 (1993).
7. J. A. Deluca, P. L. Karas, J. E. Tkaczyk, P. J. Bednarczyk, M. F. Garbauskas, C. L. Briant, and D. B. Sorensen, Physica C **205**, 21 (1993).
8. H. K. Singh, A. K. Saxena, and O. N. Srivastava, Supercond. Sci. Technol. **8**, 448 (1995).
9. H. S. Koo, J. R. Lo, T. Y. Tseng, and C. S. Lin, Jpn. J. Appl. Phys. (in press).
10. H. S. Koo, G. C. Tu, and T. Y. Tseng, J. Am. Ceram. Soc. **77**, 27 (1994).
11. R. Sugise, M. Hirabayashi, N. Terasa, M. Jo, M. Tokumoto, T. Shimomura, and H. Ihara, Physica C **157**, 131 (1989).
12. Y. Q. Tang, Z. Z. Sheng, W. A. Lou, Z. Y. Chen, Y. N. Chan, Y. F. Li, F. T. Chen, G. J. Salamo, and D. O. Pederson, Supercond. Sci. Technol. **6**, 173 (1993).
13. H. K. Singh, A. K. Saxena, and O. N. Srivastava, Physica C **273**, 181 (1997).
14. H. S. Koo and T. Y. Tseng, unpublished.