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C-axis oriented (Hg,Ti)-based superconducting films with T_c>125 K

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Thin films with mostly $(Hg,Tl)_1Ba_2Ca_3Cu_2O_{8+\delta}$ [(Hg,Tl)-1223] phase have been fabricated by radio frequency magnetron sputtering of precursor films and post-annealing method. The doping of a small amount of thallium in the film is helpful to the formation of the three-layer CuO_2 compound. These films have a highly oriented structure with the *c*-axis perpendicular to the film surface. Resistivity measurements show that the films after annealing at 300 °C for 1 h in O_2 have the superconducting transition temperature of T_c(onset)=133 K and T_c(zero)=127 K. Scanning electron micrographs of the film reveal platelike micrometer-size grains coalesce to cover the substrate surface. © *1996 American Institute of Physics.* [S0003-6951(96)00608-7]

Since the discovery of superconductivity in the $Hg_1Ba_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ family,[1–3] the three-layer CuO_2 compound $Hg_1Ba_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) has attracted considerable interest due to the high superconducting transition temperature (T_c).[4–6] In order to explore the intrinsic properties of these materials, high-quality films and single crystals are often needed. There are several reports in the growth of $Hg_1Ba_2Ca_1Cu_2O_{6+\delta}$ (Hg-1212) films with T_c of 120–125 K.[7–9] So far, there is no report on the growth of Hg-1223 films. One of the main difficulties in synthesizing Hg-based cuprates is the high vapor pressure of Hg and Hg-based compounds. Therefore, an enclosed or high-pressure environment is needed to maintain the Hg content during the high-temperature treatment. From past experience with the synthesis of Tl- and Bi-based cuprates, phases with three CuO_2 layers need a longer reaction time or higher annealing temperature than phases with two CuO_2 layers.[10,11] If the same trend exists in the Hg-based cuprates, it will be more difficult to synthesize the Hg-1223 films compared to the Hg-1212 films.

In view of the severe difficulties encountered in making Hg-1223 films due to the above reasons, we investigated the substitutions of other cations for Hg that promote the formation of the Hg-1223 phase. Several studies have demonstrated the substitutions of thallium, lead, and bismuth for mercury in the Hg-1223 superconductor.[12–18] The effect of lead doping in the Hg-1223 superconductor was demonstrated by Isawa *et al.*[12] This is similar to the cases of Bi–Sr–Ca–Cu–O and Tl–Sr–Ca–Cu–O superconductors, where lead was used for the stabilization of the higher-T_c phase.[13,14] It is known that Hg(II) and Tl(III) have identical electronic configurations (both are $5d^{10}$ cations). Goutenoire *et al.*[15] have shown that mercury can substitute thallium in the $Tl_2Ba_2Ca_2Cu_3O_{10-y}$(Tl-2223) cuprate. They found the disordered distribution of thallium and mercury in the thallium bilayers does not change the critical temperature of the mercury-doped Tl-2223 phase. However, Sun *et al.* and Dai *et al.*[16,17] reported a T_c enhancement to 138 K for a sample with a nominal composition of $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$. This difference in observations has not been resolved. In addition, a continuous solid solution in the $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ [(Hg,Tl)-1223] system has been demonstrated.[18] Partial mercury ion replacement by thallium ions in the (Hg,Tl)-1223 oxide superconductors was shown to greatly increase the volume fraction and change the density of oxygen vacancies.[18] Liu *et al.*[18] argued that Tl doping produces partial melt in the mixture that would prevent the rapid evaporation of mercury during the reaction. Clearly, (Hg,Tl)-1223 is an interesting system to study and is also a more suitable material for producing thin films with T_c above 125 K.

Thin films of (Hg,Tl)–Ba–Ca–Cu–O have been fabricated using radio frequency (rf) magnetron sputtering and post-annealing method. Thin precursor films of the Ba–Ca–Cu–O were made by rf magnetron sputtering onto (100) $LaAlO_3$ single crystal substrates. The sputtering was carried out in a 10:1 mixture of Ar and O_2 gases at total pressure of 10 mTorr. The precursor films ~0.5 μm thick were moved immediately into a plastic bag filled with argon gas, to minimize the exposure to moisture CO_2 in the air. The films were placed in an alumina tube with several pressed and unreacted pellets of nominal composition $Hg_{0.9}Tl_{0.2}Ba_2Ca_2Cu_3O_y$. The pellets were made from high purity HgO, Tl_2O_3, BaO, CaO, and CuO. The alumina tube with the contents and a quartz rod (7 mm o.d.×30 mm length) were introduced into a quartz tube (8 mm i.d.×12 mm o.d.), which was then evacuated and sealed (60 mm length). The quartz rod was used to reduce the empty space in the quartz tube. The typical annealing schedule was slow heating to 750–860 °C in 3 h and maintaining that temperature for 1 h and then furnace cooling to room temperature. After the sintering, some films were further annealed at 300 °C for 1 h in O_2.

Figure 1 shows the x-ray diffraction patterns for the (Hg,Tl)–Ba–Ca–Cu–O films annealed at 830 °C. The (00*l*) peaks as indexed to the (Hg,Tl)-1223 phase in the figure indicates that the film grew *c*-axis oriented and perpendicular to the substrate surface. The lattice parameter *c* was determined to be 15.83 Å, very close to the reported (Hg,Tl)-1223 bulk value of ~15.85 Å.[18] A second minor phase present was (Hg,Tl)-1212, which also has a *c*-axis orientation, as shown by the (00*l*) peaks indexed in Fig. 1. Above

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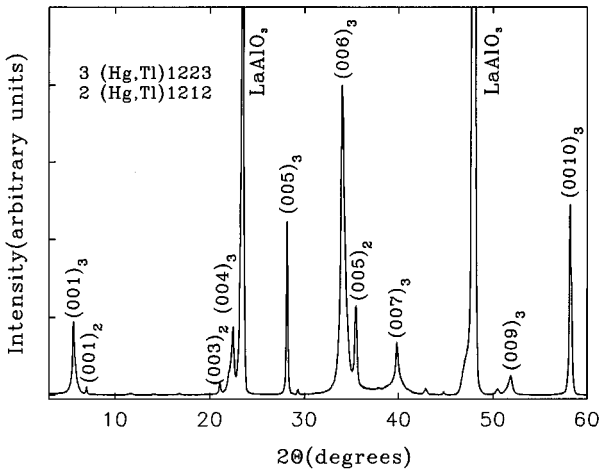

FIG. 1. The x-ray diffraction pattern for the (Hg,Tl)–Ba–Ca–Cu–O film annealed at 830 °C for 1 h. The indexed peaks are for the (Hg,Tl)-1223 phase and (Hg,Tl)-1212 phase.

the annealing temperature of ~800 °C, most films consist of more than 80% (Hg,Tl)-1223 phase, less than 20% (Hg,Tl)-1212 phase and with very little other phases that were detected from the x-ray diffraction patterns. Below 800 °C (Hg,Tl)-1212 phase becomes the major phase and a small amount of $HgCaO_2$ phase emerges.

The surface morphology of the film was observed by scanning electron microscopy (SEM) as shown by the micrograph in Fig. 2. We can see well-connected and irregular platelike crystals, but it is difficult to discern their orientations. The features such as rounded grains and grain coalescence are very similar to the Tl-based superconducting films,[10,19] suggesting that the grain growth process in both cases is similar. The analysis of the energy dispersive x-ray spectrum indicates that the composition of most platelike crystals was very close to $(Hg_{0.7},Tl_{0.3})Ba_2Ca_2Cu_3O_{8+\delta}$. However, the actual ratio of Hg, Tl, Ba, Ca, and Cu is always off from ideal stoichiometry. The observed variation of the composition in these films may be due to the incomplete phase formation, the presence of both phases or intergrowths. We can also see a very small amount of bright particles and other substance between the platelike crystals. Microprobe analysis showed that the content of Cu was higher in these areas; perhaps they were impurity phases of Cu-rich compounds which contribute to the background in x-ray diffraction patterns.

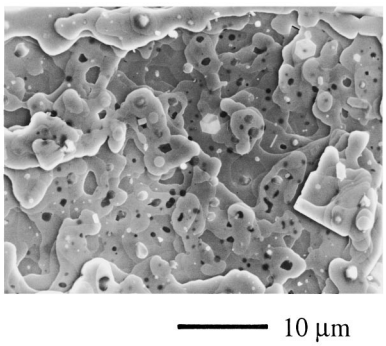

FIG. 2. Platelike grains are observed in the SEM micrograph of the (Hg,Tl)–Ba–Ca–Cu–O film annealed at 830 °C for 1 h.

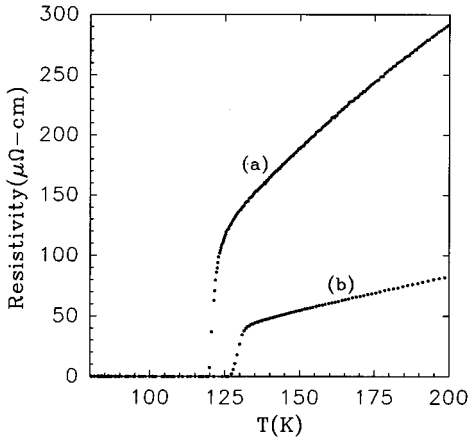

FIG. 3. Resistivity vs temperature for the (Hg,Tl)–Ba–Ca–Cu–O film (a) before and (b) after annealing in oxygen at 300 °C for 1 h.

The resistivity versus temperature of the films was measured by the dc four-probe method. Figure 3 shows the temperature dependence of the resistivity for the as-prepared and oxygen annealed films. The resistivity of the as-prepared film begins to drop at temperature T_c(onset)=125 K and goes to zero at T_c(zero)=120 K. After annealing in O_2 at 300 °C for 1 h, as shown in Fig. 3, the onset superconducting transition temperature increases to 133 K and the zero resistivity to 127 K. The rather sluggish and a large rounding of signatures near the transitions on both as-prepared and annealed films suggest that there are the intergrowth of (Hg,Tl)-1212 and (Hg,Tl)-1223 phases or a large thermodynamic fluctuation regime. A linear decrease from room temperature to about 200 K, with a negative interpolated intersection unlike most other high T_c materials, is observed in these films. The highest value of zero-resistance T_c that has been obtained is 127 K. To the best of our knowledge this is the highest T_c reported for superconducting films.[9] Estimated resistivity in the normal state for these two kinds of films were in the range of ~80–400 $\mu\Omega$ cm, which is comparable with the other high-temperature superconductors. The results indicate that there are good connections between the superconducting grains in these (Hg,Tl)-1223 films. Most of the films we prepared showed similar electrical transport properties with T_c(zero) around 120–127 K.

In summary, we have successfully fabricated (Hg,Tl)–Ba–Ca–Cu–O superconducting films with more than 80% (Hg,Tl)-1223 phase determined from x-ray diffraction patterns. They grew with the *c*-axis oriented perpendicular to the surface of the film, and the grains are connected very well, thus showing a low resistivity of the normal state. The films annealed in oxygen for 1 h show the highest superconducting transition temperature, with T_c(onset)=133 K and T_c(zero)=127 K as determined from resistivity measurements. At present, the phase reproducibility of these films is good, but the composition variation is still large. In order to achieve a higher T_c, a better control of phase formation in these films is needed.

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