

Diffusion Mechanism of Cations and Anions in Cation-Exchange Process for Fabrication of High- T_c Superconducting $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ Films

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ABSTRACT

We have investigated the diffusion mechanism of Hg and Tl cations in cation-exchange process that has been used successfully for fabrication of Hg-based high- T_c superconducting films. Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) was employed to map the distribution of Tl and Hg cations in films quenched at different stages of the cation exchange process. SEM/EDS mappings showed that the nonuniform distribution of Hg is visible in micrometer size on the surface of samples quenched after short-time (~10min) Hg-annealing, but this nonuniformity disappears for longer-time (~45 min) Hg-annealing samples. This change could be ascribed to different stages in Hg diffusion -- the former is the early stage when Hg is concentrated in the channels and the latter Hg-cations have already diffuse to grains. Our experimental results hence suggest that Hg-cations channel through defects in the films then diffuse into grains along a-b planes and vice versa for Tl-cations. The diffusion mechanism of anions (oxygen) in post annealing has also been discussed. Fluorine-doped Hg-1212 films were post annealed in flowing oxygen at 300 °C for several hours. Magnetic measurement has shown these samples are comprised pure overdoped Hg-1212 phase with smooth and sharp transition below 120 K, but resistivity vs. temperature measurement shows a kink at ~123 K. This implies that the optimally doped Hg-1212 phase with higher T_c might be surrounded by overdoped Hg-1212 phase and their contribution to magnetization is minimized, thus the possible diffusion mechanism for anions is also through grain boundaries at a much larger time scale compared to the cations.

INTRODUCTION

Hg-based high- T_c superconductors (Hg-HTSs) are of great interest for electrical and electronic applications above the liquid N_2 temperature because of their high T_c values up to 135 K [1-3]. In order to fulfill the requirements in practical applications, epitaxy in Hg-HTSs must be achieved for the films to carry high critical current density (J_c), low microwave surface resistance (R_s) and etc. To overcome the difficulties associated with the development of epitaxy in Hg-HTSs in conventional processes in which amorphous precursor contains mixture of Ba, Ca and Cu oxides, and Hg oxide in some cases, we recently developed a cation-exchange process [4,5] in which epitaxial Tl-based HTSs are used as precursor and the formation of Hg-HTSs is through a Tl to Hg cation exchange at lowered annealing temperatures without changing the overall crystalline structure of the precursor. Using this cation-exchange process, high J_c , low R_s and high microwave power handling capability have been obtained in epitaxial $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Hg-1212) films on oxide substrates [6-8]. In addition, Hg-1212 has also been epitaxially coated on metal substrates such as Ni [9]. An example of this cation-exchange process is to use epitaxial $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$ films to fabricate Hg-1212 films. In principle, a Hg-O layer replaces

two Tl-O layers in each crystalline cell therefore the conversion from Tl-2212 to Hg-1212 is a process of Hg cations diffusing in and Tl cations diffusing out. In addition Hg has chemical valence +2 and Tl +3, thus oxygen also needs to diffuse out from the film. Since there are many grains in a film and each grain contains hundreds of unit cells, how this diffusion process takes place is rather complicated. A dynamic picture of this process involves the pathway of Hg cations from the ambience of the films into every crystalline cell and vice versa for Tl cations. Knowledge about such a dynamic picture is crucial to the precise control of the experimental parameters, the minimization of thermal budget and the optimization of the quality of Hg-HTS films.

Recently, we proposed a diffusion mechanism of cation-exchange process with emphasis on the pathway of cations, in which Hg cations channel through defects in the films such as voids, growth defects and grain boundaries then diffuse into grains along a-b plane, and vice versa for Tl cations [10]. One can speculate that Hg cations should be concentrated on the channels at the early stage of this diffusion process, and this nonuniformity should diminish after Hg cations diffuse into grains. In this report, we will present the experimental data from a scanning electron microscopy/ energy dispersive spectroscopy (SEM/EDS) study. We will also discuss the diffusion mechanism of anions (oxygen) in post annealing since it is a very important process to optimize the sample superconductivity.

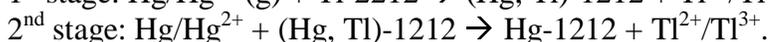
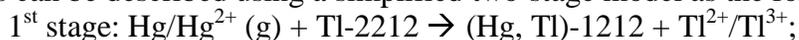
EXPERIMENTAL DETAIL

Tl-2212 HTS films on $\text{LaAlO}_3(100)$ single-crystal substrates were synthesized from dc magnetron sputtered Tl-containing amorphous precursor by annealing them at 800-830 °C for 30-90 min in flowing oxygen using a crucible technique[11-12], and then subjected to Hg-vapor annealing. In Hg-vapor annealing, the traditional torch-sealing quartz technique was employed [1-9]. The Hg-vapor source includes two pellets: 1.5-gram Hg-containing mixture with nominal composition $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and 0.5-gram non-Hg one with composition $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. The evacuated-then-sealed quartz ampoules with one or two Tl-2212 HTS films and Hg-vapor source were heated to 780 °C in a ramping rate of 50 °C/min, kept for different periods: 10 and 45 min. The 10 min Hg-annealed sample was quenched, and the 45 min one was cooled down in a rate of 20 °C/min. Samples were then studied by EDS mapping to determine the uniformity of Hg cation distribution.

To study the diffusion mechanism of anions during post annealing, same Hg-vapor annealing was carried out on several Tl-2212 HTS precursor films but different post oxygen annealing conditions were used on the converted samples. For Hg-annealing, 15% HgF_2 was used to replace part of HgO as part of the Hg-vapor source, and the heat treatment was 700 °C for 12 h to complete cation exchange, thus the samples are fluorine doped Hg-1212 and nearly optimally doped in terms of anion concentration [13,14]. The post annealing was done in flowing oxygen at 300 °C for different periods: 2 h and 4 h, respectively, to drive to overdoped region [13,14]. The as-converted and oxygen-annealed samples were finally characterized using QUATUM DESIGN SQUID magnetometer and four-probe transport measurement to determine the superconducting transition behavior.

RESULTS AND DISCUSSION

The two pictures in Figure 1 are the EDS mapping of Hg element on the surface of two samples annealed in Hg-vapor at 780 °C. The contrast in the pictures indicates the variation in Hg concentration – the more Hg there is and the darker it is. The left panel represents the one quenched after 10 min Hg-annealing, and the right panel is the other Hg-annealed for 45 min. It is clearly shown that Hg is non-uniformly distributed in the former sample and the nonuniformity is visible in ~ μm size. The Hg distribution is overall uniform in the latter one. These phenomena imply that the distribution of Hg changes as cation-exchange process goes on at different stage. According to the diffusion mechanism we proposed recently [10], the whole process can be described using a simplified two-stage model as the following.



In the first stage, Hg channels through all kinds of defects into films, then diffuses into grains. This diffusion of Hg into grains is accompanied by the diffusion of Tl out of grains. At the mean time, 2212 structure collapses into 1212. Such a structural change is visible from XRD θ -2 θ spectra. Since Tl is still diffusing out even at the end of this stage, one can speculate that some Tl is left in the 1212 structure. This hybrid 1212 structure can be represented by an alloy form (Hg,Tl)-1212. Hg distribution is expected to be nonuniform at the beginning and becomes uniform at the end of the 1st stage. This is consistent with our EDS mapping results. 45 min is very close to the time constant for the 1st stage we found through other characterization methods [10]. Such a pronounced uniformity change in Hg serves as a piece of evidence for the validity of our proposed diffusion mechanism of cation-exchange process. In the second stage, more Hg/Tl cations diffuse in/out, which would finally result in pure Hg-1212 phase. There is no substantial structural change in the 2nd stage, but superconductivity such as T_c and J_c changes as Hg-annealing goes on [10]. At this point, chemical analysis is still needed for the confirmation of the transient 1212-type compound: (Hg,Tl)-1212 and the thorough understanding of the diffusion mechanism of cation-exchange process.

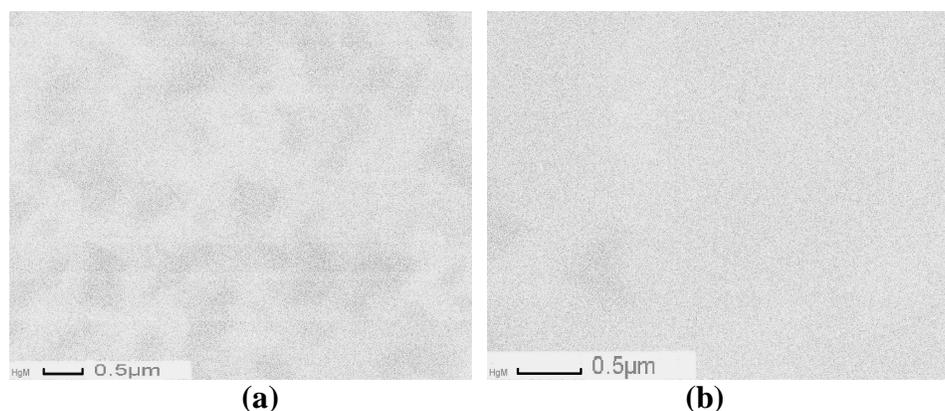


Figure 1. EDS mapping on the surface of two samples: (a) quenched after 10-min Hg-annealing and (b) 45-min Hg-annealed. The contrast in the pictures indicates variation in Hg concentration: the more Hg there is and the darker it is. For the former, nonuniform distribution of Hg is visible in ~ μm size. For the latter, Hg concentration is overall uniform.

The temperature (T) dependence of resistivity (ρ) of a fluorine-doped Hg-1212 film (Sample “B”) measured on a 0.2 mm \times 1 mm bridge is shown in Figure 2. This sample has been oxygen-annealed at 300 °C for 2 h. Zero resistance temperature is \sim 115 K. A kink at \sim 123 K is shown on this ρ - T curve, implying the coexistence of two superconducting phases -- one has T_c \sim 115 K and the other \sim 123 K. It is likely these two phases are corresponding to overdoped and optimally doped Hg-1212, respectively. The optimally doped Hg-1212 does not form a path throughout the whole bridge to conduct supercurrent. The T dependence of magnetization per cm³ volume (M) of three fluorine-doped Hg-1212 films: “A”, “B” (the one shown in the main figure) and “C”, is shown in the insert. “A” is an as-converted sample, “C” was oxygen-annealed at 300 °C for 4 h. T_c is about 123 K, 115 K and 114 K for “A”, “B” and “C”, respectively. T_c for “B” is consistent with the magnetic measurement. This result indicates “A” is optimally doped, and “B” and “C” are overdoped. It should also be noticed that superconducting transition become sharper after oxygen annealing. For Sample “B” and “C”, the transition is sharp and smooth. There is no indication for the existence of other phases with higher or lower T_c . The puzzle here is why the optimally doped Hg-1212 phase indicated in resistive measurement is not observed in magnetic T_c measurement. To explain this, one may

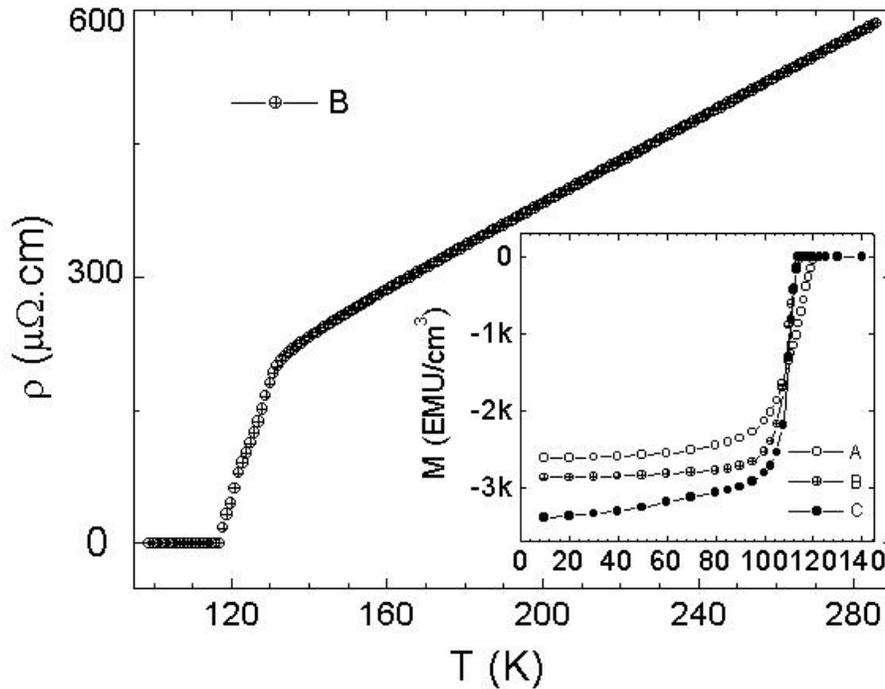


Figure 2. ρ (Resistivity) - T (temperature) curve of a fluorine-doped Hg-1212 film (Sample “B”) measured on a 0.2 mm \times 1 mm bridge. This sample has been oxygen-annealed at 300 °C for 2 h. Zero resistance temperature is \sim 115 K, and a kink at \sim 123 K is shown on the curve. The insert is the T dependence of magnetization per cm³ (M) of three fluorine-doped Hg-1212 films: “A”, “B” (the one shown in the main figure) and “C”. “A” is as-converted and “C” has been oxygen-annealed at 300 °C for 4 h. T_c is about 123, 115 and 114 K, for “A”, “B” and “C”, respectively. M – T curves for “B” and “C” show sharp and smooth transition with no indication for other phases of higher or lower T_c .

assume that the pathway for oxygen to diffuse into grains is through grain boundaries (GBs) since GBs provide more space. In a single grain, as post oxygen annealing goes on, the outer part of this grain contain more oxygen than the inner part. At some stage, the outer part is overdoped but the inner part is left optimally overdoped. Since the inner parts (cores) of grains are isolated and form islands, their contribution to magnetization is minimized. If the total amount of the optimally doped inner parts is sufficiently small, magnetic measurement will not detect them. However, when these cores become superconducting at ~ 123 K, the second drop in resistance may still appear on $\rho - T$ curve.

CONCLUSIONS

In summary, a SEM/EDS mapping study on the surface of samples at different stages of Hg diffusion in cation-exchange process showed that the Hg distribution changes throughout the process. The nonuniform distribution of Hg was visible in $\sim \mu\text{m}$ size on the surface of samples quenched after short-time (~ 10 min) Hg-annealing, but this nonuniformity disappears for longer-time (~ 45 min) Hg-annealing samples. This EDS result provided an important piece of evidence for the proposed diffusion mechanism of cation-exchange process: Hg-cations channel through defects and grain boundaries in the films then diffuse into grains along a-b planes and vice versa for Tl-cations.

Transport measurement results show the coexistence of overdoped and optimally doped Hg-1212 phases in fluorine-doped Hg-1212 films after 2 h oxygen annealing at ~ 300 °C. The magnetic T_c measurement, however, does not detect the optimally doped Hg-1212, which reveals a picture that the optimally doped Hg-1212 is surrounded by the overdoped phase thus their contribution to magnetization is minimized. This implies the possible diffusion mechanism of anions (oxygen) in post annealing is through GBs.

ACKNOWLEDGEMENT

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