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Microstructural evolutions in converting epitaxial $Tl_2Ba_2CaCu_2O_x$ thin films to epitaxial $HgBa_2CaCu_2O_{6+\delta}$ thin films

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Superconducting $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) thin films were obtained from $Tl_2Ba_2CaCu_2O_x$ (Tl-2212) precursor films using a cation–exchange process. In this process, Tl cations on the precursor lattice were thermally excited and then replaced with Hg cations. The mechanism of such an atomic perturbation process has presented an interesting topic in material research. This work investigated the evolution of the crystalline structure and surface morphology of the film during such a conversion. It has been found that the Hg-1212 films may inherit epitaxy and surface morphology from their $Tl_2Ba_2CaCu_2O_x$ precursor films at the low perturbation energy limit. Although the *c*-axis lattice constant was reduced from 1.48 nm for Tl-2212 to 1.27 nm for Hg-1212 during the cation exchange, the in-plane texture of the film remains. The inverse conversion from Hg-1212 to Tl-2212 has also been investigated. Hg-1212 is found to be energetically preferred so that a perturbation above a threshold is required to convert it back to Tl-2212. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1529305]

I. INTRODUCTION

Since the discovery of Hg-based high-temperature superconductors (Hg-HTSs)[1,2] a number of processes have been applied for fabrication of $HgBa_2Ca_{n-1}Cu_nO_x$ (Hg-1212 at $n=2$ and Hg-1223 at $n=3$) superconducting thin films.[3–11] One of such processes, the cation–exchange process developed recently by some of us,[12] employs an epitaxial precursor matrix that is then subjected to cation exchange—replacing certain cations unwanted with others desired via atomic perturbation of the lattice—to form the desired Hg-HTS thin films. Although many other precursors may work equally well, Tl-based high-temperature superconductors (Tl-HTSs) were selected first since they have similar crystal structures and chemical compositions to Hg-HTSs. Tl-HTS's have two series: One contains a single Tl–O plane in a unit cell and the other, two Tl–O planes. The former is described as $TlBa_2Ca_{n-1}Cu_nO_x$ (so Tl-1212 at $n=2$, Tl-1223, at $n=3$,... etc.) and the latter, as $Tl_2Ba_2Ca_{n-1}Cu_nO_x$ (so Tl-2212 at $n=2$, Tl-2223, at $n=3$,... etc.). We have shown that epitaxial Hg-1212 films can be obtained from both Tl-1212 (Ref. 13) and Tl-2212 (Ref. 14) films after the precursor matrices are annealed in Hg vapor. We have also obtained Hg-1223 films[15] and bulks,[16] respectively, from Tl-1223 (or Tl-2223) film and bulk precursors. Besides having high superconducting transition temperatures (T_cs) typically above 120 K, the cation–exchange processed Hg-HTS films have high critical current densities (J_cs) and superior microwave performance, many of these remain as the best so far achieved for HTS films.[17,18]

The mechanism of the cation exchange presents an interesting topic in materials processing and has not been studied thoroughly so far. The conversion from Tl-1212 to Hg-1212 seems to be more straightforward as the two "1212" systems have nearly identical crystalline structures and chemical compositions. One may speculate that such a conversion is reversible if no phase transition is involved. Indeed, this reversibility has been confirmed in a recent experiment by Xing *et al.*,[19] indicating that the direction of the conversion, either from Tl-1212 to Hg-1212, or vice versa, is solely controlled by the partial pressure of Hg and Tl. On the other hand, when the Tl-2212 is employed as the precursor, the two Tl–O planes collapse into one Hg–O plane and the *c*-axis lattice constant is shortened.[12,14] Such a microscopic structural change in the conversion from "2212" to 1212 structure suggested a different growth mechanism from that in the conversion between the 1212 system. The question is how exactly this conversion occurs at a microscopic scale and how the microscopic growth mechanism correlates to the macroscopic physical properties of the sample. Motivated by this, we have carried out an experimental investigation on the microstructural evolution during the 2212 to 1212 conversion. We show that the Hg-1212 is energetically preferred so that a perturbation above the threshold energy is required to convert it back to Tl-2212. The details of our experimental results are described next.

II. SAMPLE PREPARATION

The Tl-2212 precursor films were prepared on $LaAlO_3$ (001) substrates using dc-magnetron sputtering and postannealing process.[20,21] Films of nominal composition were off-axis sputtered at room temperature from a pair of superconducting Tl-2212 targets. A gas mixture of 80% Ar and 20% O_2 was used for sputtering. The as-deposited films were amorphous with the cation composition ratio Tl:Ba:Ca:Cu

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$=2{:}2{:}1{:}2$. These films were placed in an Al_2O_3 crucible together with a reacted Tl–Ba–Ca–Cu–O pellet and annealed at 760 °C for 6 h in pure argon of ambient pressure to obtain superconducting Tl-2212 films. These Tl-2212 films were then sealed in an evacuated quartz tube together with $Hg_xBa_2Ca_2Cu_3O_y$ or $Hg_xBa_2Ca_2Cu_3O_y/Ba_2Ca_2Cu_3O_y$ annealing pellets. The $Ba_2Ca_2Cu_3O_y$ powder was prepared by thoroughly mixing high-purity $Ba(NO_3)_2$ of 99% (or BaO_2 of 95%), CaO of 99.9%, and CuO of 99+% powders and annealing them at 910 °C for 48 h. The $Hg_xBa_2Ca_2Cu_3O_y$ pellet was used for the Hg source and was prepared by mixing HgO of 99+% and Ba_2 $Ca_2Cu_3O_y$ powders. The whole sample assembly was then annealed in a furnace at $T_a=650\,°C–820\,°C$ for 1–12 h to convert the Tl-2212 phase to the Hg-1212 phase via Tl–Hg exchange. At the final stage, the Hg-1212 films were annealed at 350 °C for 1 h in flowing O_2 to optimize the oxygen concentration. It should be mentioned that, since both the amorphous as-deposited Tl–Ba–Ca–Cu–O films and the superconducting Tl-2212 films are stable in air, all the samples reported here were prepared in air.

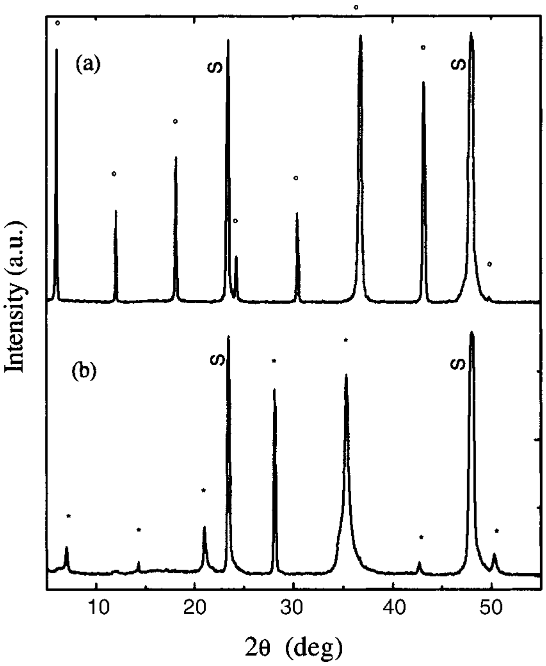

FIG. 1. XRD θ–2θ patterns of (a) a Tl-2212 precursor film and (b) Hg-1212 films processed via cation exchange at 700 °C for 12 h.

III. EXPERIMENTAL RESULTS

The crystalline structure and phase purity of the samples were characterized using x-ray diffraction (XRD) θ–2θ spectroscopy and pole figures. Scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) was employed for analysis of the film surface morphology and chemical distribution. Superconducting properties, such as T_c, and J_c, were studied both electrically with standard four-point transport measurements and magnetically using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The results are discussed next.

A. Structural Variation

Figure 1 shows the XRD θ–2θ spectra of a precursor Tl-2212 film [Fig. 1(a)] and the Hg-1212 film [Fig. 1(b)] converted from this Tl-2212 film. The conversion was processed at 700 °C for 12 h. The (00l) peaks (marked as "○") in Fig. 1(a) show that the precursor film is pure Tl-2212 phase and highly textured with *c*-axis perpendicular to the substrate surface. After the cation exchange, the film became purely Hg-1212 phase and is also *c*-axis oriented as indicated by the (00l) peaks [marked as "*" in Fig. 1(b)]. The reduction of the *c*-axis lattice constant during conversion from Tl-2212 to Hg-1212 is evidenced from the XRD data. The *c*-axis lattice constants calculated for Tl-2212 and Hg-1212 are ~1.48 nm and ~1.27 nm, respectively. Since the *c*-axis of Hg-1212 is shorter than that of Tl-2212, the film experienced a volume reduction of approximately 14% along the *c* axis, or the normal of the film, during the cation exchange. This has been confirmed recently in film thickness measurements, in which a 300 nm thick Tl-2212 film, for example, was found to be approximately 260 nm thick after the conversion to Hg-1212 film.

The in-plane texture of a precursor Tl-2212 film and the converted Hg-1212 film processed at 700 °C for 12 h in the cation–exchange process have been studied using XRD pole figures (not shown in this article). The sharp (105) poles for the Tl-2212 film observed indicate that the film grew epitaxially with its (100) axis aligned with the (100) axis of the $LaAlO_3$ substrate. After the conversion, the Tl-2212 (105) poles disappeared while the four (103) poles of Hg-1212 appeared at the same φ angles, illustrating that the (100) axis of the Hg-1212 is aligned with the (100) axis of the $LaAlO_3$. This observation suggests an interesting procedure during the Hg–Tl cation exchange: While the Tl-2212 lattice is collapsing along the *c* axis, the in-plane texture remains, allowing Hg-1212 films to inherit epitaxy from their Tl-2212 precursor films. In fact, the full width half maximum of the (105) poles for this Tl-2212 film is nearly the same as that of the (103) poles of the Hg-1212 film. The former is about 0.57° and the latter is about 0.71°. These values suggest that the Tl–Hg cation exchange occurs uniformly at microscopic scales and the relative grain tilting or rotation is minimal. Similar in-plane structural replication from Tl-2212 to Hg-1212 was also observed on films cation–exchange processed at a higher temperature below ~800 °C, while degradation of epitaxy occurred at higher processing temperatures (we will discuss this later in this article). It should be pointed out that quality of epitaxy in Hg-1212 films obtained via cation exchange from Tl-2212 (or Tl-1212) precursor films is much better than that of the same films made from amorphous precursor films.

B. Surface Morphology

Generally speaking, the surface morphology of the Hg-1212 films made in the cation–exchange process, whether from Tl-1212 or from Tl-2212 films, is also much smoother

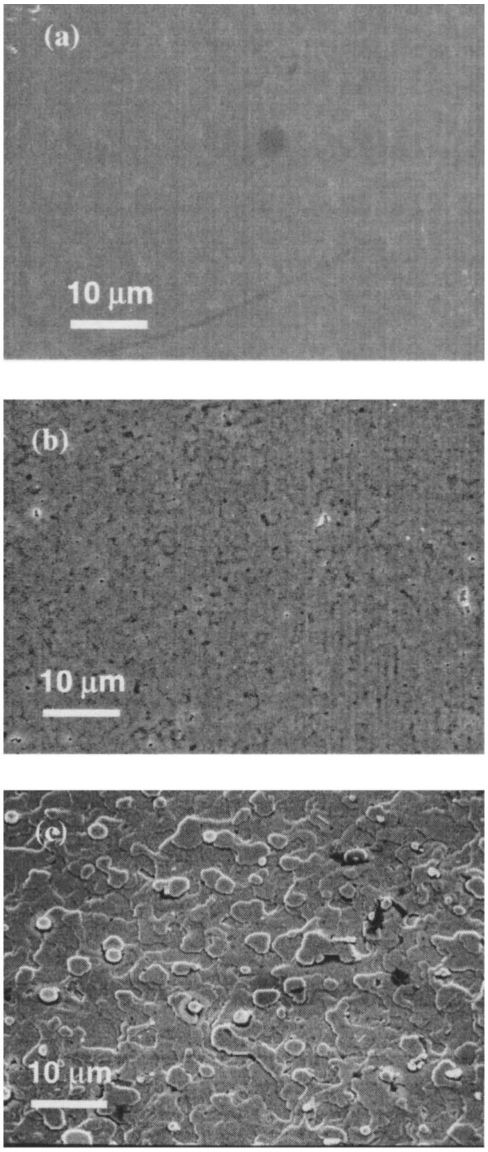

FIG. 2. SEM images of: (a) a precursor Tl-2212 film, (b) a Hg-1212 film processed via cation exchange at 700 °C for 12 h, and (c) a Hg-1212 film processed via cation exchange at 780 °C for 3 h. The precursor films for the two Hg-1212 films were Tl-2212 films made under the same processing condition.

than that of the same films made from amorphous precursor films. One of the remarkable features associated with the improved surface morphology is the much lower microwave surface resistance on the cation–exchange processed Hg-1212 films.[17,18] Figures 2(a)–2(c) depict the SEM images of a Tl-2212 precursor film and two Hg-1212 film cation–exchange processed from this Tl-2212 film. Unlike the surface of Hg-1212 films made from Tl-1212 precursor films, where the smooth surface morphology transferred from Tl-1212 to Hg-1212, the surfaces of Hg-1212 films made from Tl-2212 become rougher after the cation exchange. Especially, voids of up to submicron dimensions are visible on the surface of the Hg-1212 films whether the cation exchange was processed at low temperatures [700 °C for Fig. 2(b)] or high temperatures [780 °C for 2(c)]. It should be pointed out that such features are not present on the original Tl-2212 film. In order to understand how the voids are formed during the cation–exchange process, several samples were quenched after a short period of cation–exchange process and subjected to a chemical mapping using SEM/EDS. Interestingly, a high density of Hg cations was observed near the voids in the initial stage of the cation exchange, indicating that the voids may be formed as the vertical channels for Tl–Hg exchange. Since no voids were observed on Hg-1212 films converted from Tl-1212 films, one may speculate that the extra Tl cations in Tl-2212, by making a way out, are the major reason for the formation of the voids.

The low-temperature cation–exchange processed Hg-1212 film [Fig. 2(b) for $T_a = 700\,°\mathrm{C}$] has a very different surface morphology compared to that processed at high temperatures [$T_a = 780\,°\mathrm{C}$ in Fig. 2(c)]. The former replicated that of Tl-2212 precursor except the additional voids as we have discussed here, while the latter showed terracelike features all over the surface, indicating the possibility of melting or localized melting during the cation exchange. Nevertheless, both low-temperature and high-temperature processed Hg-1212 films show comparable XRD pole figures, high T_cs and J_cs (see Sec. III C), and microwave surface resistance. In fact, the high-temperature processed films have dense surfaces with minimal impurity phases. This suggests that the crystal lattice may melt during cation exchange at high processing temperatures close to 800 °C, leading reconstruction of the lattice. Such reconstruction of the lattice may be fairly localized below 800 °C, yielding mainly point defects that are neither detectable by XRD pole figures, nor affect the superconducting properties.[12] This argument is supported by the higher minimum yield (χ_{min}) of Rutherford backscattering spectroscopy/channeling in higher-temperature cation–exchange processed Hg-1212 films. For example, χ_{min} is about 10%–12% for Hg-1212 films processed at around 700 °C. It increases to about ~40% for Hg-1212 films processed at 780 °C, and 100% when the processing temperature is raised to 810 °C. Above 810 °C, no channeling axis could be identified and serious degradation of T_cs and J_cs were also observed, indicating the replication of the crystalline structure from the precursor matrix may no longer be the case.

C. Superconducting properties

The T_c and J_c of the films were obtained from the measured dc magnetization (M) as functions of temperature and applied magnetic field (H) using a Quantum Design SQUID magnetometer. Figure 3 shows the superconducting transition curves of some fully converted Hg-1212 films. For comparison the transition curve of a precursor Tl-2212 film is also presented in Fig. 3. The T_c of the 0.3 μm thick Tl-2212 precursor film was 105 K. Samples b, c, and d were cation–exchange processed at 810 °C for 10 min, 780 °C for 3 h and 700 °C for 12 h, respectively. The annealing pellets for samples b and c are $\mathrm{Hg_{0.5}Ba_2Ca_2Cu_3O}_x$ and that for sample d is $3\mathrm{HgBa_2Ca_2Cu_3O}_x/\mathrm{Ba_2Ca_2Cu_3O}_x$. The T_cs of samples b, c, and d are 121 K, 121.5 K, and 122 K, respectively, although the samples were annealed at different T_a for different times and with different annealing pellets. The T_cs of

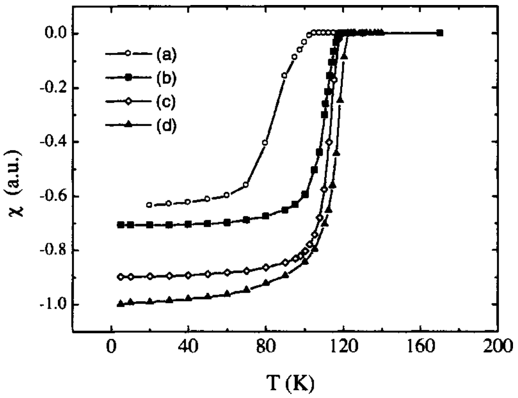

FIG. 3. *M* vs. *T* curves of (a) a precursor Tl-2212 film and three fully converted Hg- 1212 films annealed at (b) 810 °C for 10 min, (c) 780 °C for 3 h, and (d) 700 °C for 12 h, respectively.

Hg-1212 films were typically in the range of 120–124 K for most samples that were fully converted into Hg-1212 phase. These T_cs are about 16–17 K higher than that of the Tl-2212 film.

The J_c of the film was calculated using the critical state Bean model, $J_c = 20\ (M^{+}\text{-}M^{-})/R$.[22,23] Here M^{+} and M^{-} are, respectively, the upper and lower branches of the M–H hysteresis loop. R is estimated for a rectangular film sample using $R = b(1 - a/3b)$, where a and b represent the short and long dimensions of the sample, respectively. In the calculation, the entire area of the film is used rather than the grain size. Figure 4 shows the temperature dependence of the self-field J_cs for a 0.3 μm thick Tl-2212 precursor film (solid circles), and a 0.26 μm thick Hg-1212 film (solid squares). The Hg-1212 film was annealed at 700 °C for 12 h using an $Hg_{0.5}Ba_2Ca_2Cu_3O_x$ pellet and had T_c of 123 K. J_cs of the Hg-1212 film and Tl-2212 film are almost the same at very low temperatures. For example, the J_cs (5K) are 1.9×10^{7} A/cm^2 and 2.2×10^{7} A/cm^2, respectively, for the Tl-2212 and Hg-1212 films. The $J_c$of Tl-2212 film, however, is much more susceptible to temperature and, therefore, at higher temperatures the J_cs of the Hg-1212 film are much higher than that of the Tl-2212 film. At 77 K, Hg-1212 film had a J_c of 3.4×10^{6} A/cm^2 that is about three times higher than that of the Tl-2212 film at the same temperature. At 100 K, the J_c of the Hg-1212 film is 1.5×10^{6} A/cm^2 which is 75 times higher than that of the Tl-2212 film. This is mainly because the T_c of Hg-1212 film is much higher than that of Tl-2212 film. For comparison, the J_c versus T curve of a 0.2 μm thick Hg-1212 film converted from Tl-1212 film is also included in Fig. 4 (solid triangles). It is interesting that the J_cs of the Hg-1212 film converted from Tl-2212 film are much higher than that converted from Tl-1212 film, especially at higher temperatures. At 100 K, the latter only has a $J_c = 3.6\times10^{5}$ A/cm^2, that is about four times smaller than that of the former. Since the M versus T curves for Hg-1212 films made from either Tl-2212 or Tl-1212 precursors showed comparable superconducting transitions, incomplete conversion may not be the reason for the lower J_cs observed on Hg-1212 films converted from Tl-1212. We speculate that more pinning centers were formed in the Hg-1212 film converted from Tl-2212 film during the cation–exchange process, leading to a higher temperature susceptibility of J_cs in these films. Further investigation is certainly necessary to confirm this speculation.

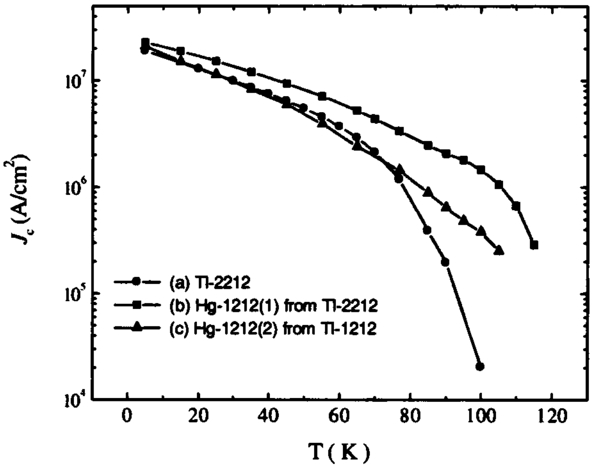

FIG. 4. Temperature dependence of J_cs of (a) a precursor Tl-2212 thin film, (b) a Hg-1212 thin film converted from a Tl-2212 thin film, and (c) a Hg-1212 thin film converted from a Tl-1212 thin film.

IV. MECHANISM OF CATION–EXCHANGE PROCESS IN CONVERTING Tl-2212 TO Hg-1212

Although the cation–exchange process provides a simple way to obtain high-quality epitaxial Hg-HTSs films, the mechanism of this process has not been investigated systematically and, hence, is barely understood. Nevertheless, several important pieces of evidence have been obtained in this experiment. First, it is confirmed that the cation exchange is a perturbation process that can be performed in a large window of the processing temperature. In fact, the Tl-Hg cation exchange was observed at the temperature as low as 620 °C, that is substantially lower than that required for the conventional process (typically ~800 °C or higher for the Hg-1212 phase). It should be pointed out that HgO powder was employed in this experiment and its sublimation temperature is about 570 °C. We suspect that even lower temperatures may be applied for cation exchange if a more volatile Hg-vapor source is employed. The rate of cation exchange, however, increases monotonically with the processing temperature T_a. For example, when the Tl-2212 film was annealed at 660 °C for 12 h, Tl was partially replaced by Hg, which resulted in two phases of Tl-2212 [marked with '○'] and Hg-1212 [marked with "*"] as shown in Fig. 5(a). At a higher $T_a = 690\,^{\circ}$C for 12 h [Fig. 5(b)], the replacement rate of Tl by Hg was evidently increased. At $T_a = 700\,^{\circ}$C for 12 h, Tl-2212 phase was replaced completely by the Hg-1212 phase [Fig. 1(b)]. When T_a was 810 °C, the Tl-2212 phase can be completely converted into Hg-1212 phase in only 5 minute as shown in Fig. 5(c).

For a thermal perturbation process such as the cation–exchange process in this experiment, one may expect the probability of cation exchange to be proportional to $\sim\exp(-U_{\text{th}}/kT)$, where $U_{\text{th}} = kT_{\text{th}}$ is the crystal lattice decomposing energy and k is the Boltzmann's constant. The efficiency of the cation exchange increases monotonically

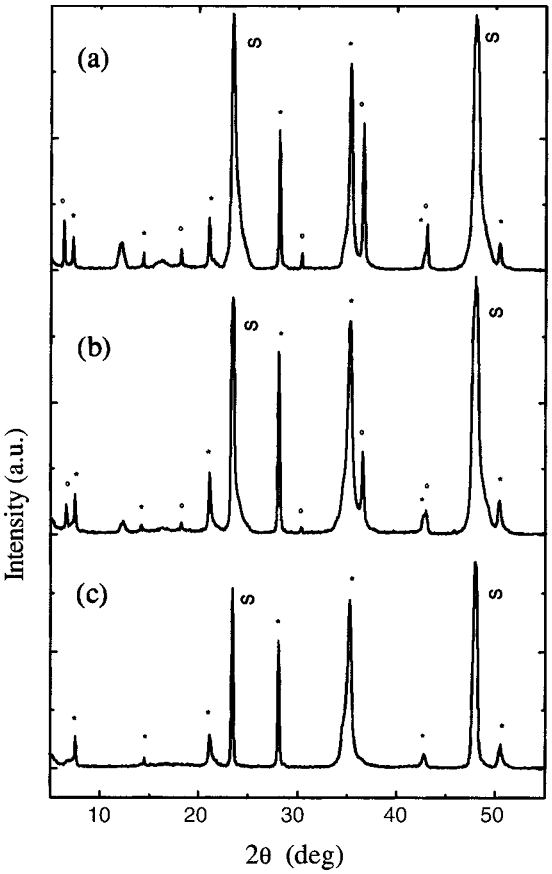

FIG. 5. XRD θ–2θ patterns of the Hg-1212 films annealed at (a) 660 °C for 12 h, (b) 690 °C for 12 h, and (d) 810 °C for 5 min.

with the processing temperature, which agrees qualitatively with the experiment. To find out U_{th}'s for Tl-1212, Tl-2212, and Hg-1212 films, we heated Tl-2212, Tl-1212, and Hg-1212 films in 0.8 atm O_2 to different temperatures and stayed for 1 h and cooled back to room temperature. After each thermal cycle, the XRD θ–2θ spectra, T_cs and J_cs of the samples were measured. The normalized J_cs at 77 K are shown in Fig. 6. Remaining more or less constant at lower temperatures, the normalized J_cs for all three types of films experienced a sharp drop above certain temperatures ($T_{\mathrm{th,onset}}$) and reached zero at slightly higher temperatures ($T_{\mathrm{th,zero}}$). In addition, the sharp drop in J_cs at the $T_{\mathrm{th,onset}}$'s was found to be accompanied by diminishing of (00l) peaks in the XRD spectra of the film, signaling collapse of the crystal lattice. If we take the midpoint between the $T_{\mathrm{th,onset}}$ and $T_{\mathrm{th,zero}}$ as the T_{th}, the T_{th}s for Tl-1212, Tl-2212 [see Fig. 6(a)] and Hg-1212 films [see Fig. 6(b)] will be, respectively, 620 °C (890 K), 680 °C (950 K), and 780 °C (1050 K). Since lattice collapse is due to evaporation of Tl in Tl-2212 and Tl-1212 or Hg in Hg-1212 films, one may estimate the binding energies of Tl or Hg to the lattice to be near 890 K for Tl-1212, 950 K for Tl-2212, and 1050 K for Hg-1212. The T_{th} defines the upper limit of the perturbation energy one may provide to a precursor matrix without destroying it. Indeed, our experiment confirmed that there is an upper limit for T_a. For Hg-1212 films converted from Tl-2212 precursor films, this limit is around 800 °C. Beyond this limit, the quality of epitaxy in Hg-1212 films degrades dramatically as we

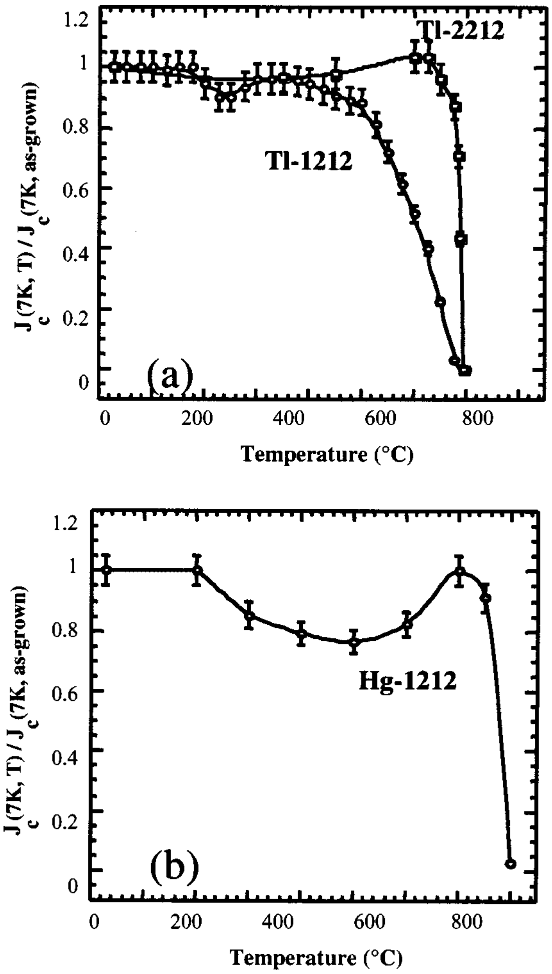

FIG. 6. Normalized critical current densities at 77 K and self-field of (a) Tl-2212, Tl- 2212 and (b) Hg-1212 thin films after annealing at different temperatures for 1 h in 0.8 atm O_2.

discussed in our earlier sections. It should be realized that these T_{th} values were obtained in 0.8 atm O_2, while cation exchange is usually carried out in mixed vapors of Hg and oxygen of higher total pressures. A quantitative fitting is still difficult at this point due to inadequate data available.

Interestingly enough, the T_{th} for Hg-1212 is slightly higher than that of Tl-1212 and Tl-2212. This raises a question on whether the conversion from Tl-2212 to Hg-1212 is a phase transition. We have shown recently that the conversion between Tl-1212 and Hg-1212 is reversible and the direction of the cation–exchange process can be controlled by the ratio between the Tl and Hg cation populations.[19] In a similar attempt, several Hg-1212 thin films, made from Tl-2212 in cation–exchange process, were used as precursor films for Tl-2212 thin film. These Hg-1212 films were sealed in an alumina crucible together with a $Tl_2Ba_2Ca_2Cu_3O_x$ pellet, and annealed at temperature of 740 °C to 830 °C for 30 min to 2 h in flowing O_2. The $Tl_2Ba_2Ca_2Cu_3O_x$ pellet provided a Tl-rich atmosphere during the annealing process. The Hg-1212 films annealed at temperatures below 800 °C turned into Tl-1212 with a negligible trace of Tl-2212. Those processed at above 800 °C, however, were predominantly converted back to Tl-2212. Figures 7(a) and 7(b) show, respectively, the XRD spectra of the Hg-1212 precursor film and

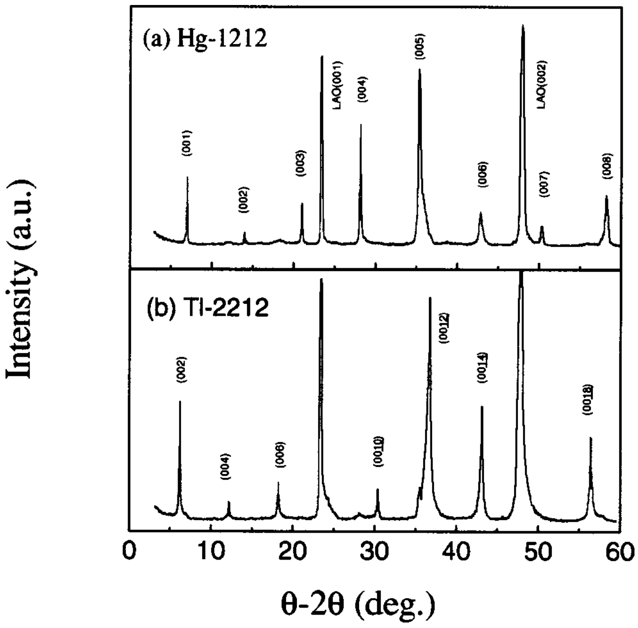

FIG. 7. XRD θ–2θ patterns for (a) precursor Hg-1212 film, and (b) Tl-2212 film converted from this Hg-1212 film.

the resulting Tl-2212 film cation exchange processed at 830 °C for 30 min. The precursor film was almost pure Hg-1212 phase and the resulting film was identified to be about 87% Tl-2212 phase and only 13% Hg-1212 phase left. If the annealing temperature is higher or the annealing period is longer the Hg-1212 phase could be completely converted into Tl-2212 phase (not shown here). The results suggest that a phase transition occurs during the conversion from Tl-2212 to Hg-1212, which is not surprising as the two materials have different lattice structures. In the reversed process, the perturbation energy must be above the U_{th} for Hg-1212, that is ~800 °C to unstable the Hg-1212 lattice and to form Tl-2212. This is different from the conversion between Tl-1212 and Hg-1212, where at a given T_a the direction of the cation–exchange process can be controlled solely by the ratio between the Tl and Hg cation populations.

V. CONCLUSIONS

In conclusion, the microstructural evolution in converting epitaxy Tl-2212 films to Hg-1212 thin films has been investigated in the developed cation–exchange process. It has been found that such a perturbation process can be carried out in a large temperature window below the crystal lattice decomposition energy. This conversion allows Hg-1212 films to inherit high-quality epitaxy and surface morphology from their Tl-2212 precursor films. The fully converted Hg-1212 thin films show high T_cs in the range of 120–124 K and high J_cs in the self-field. At 77 K, the J_c is up to 3.4×10^6 A/cm^2 and 100 K, 1.5×10^6 A/cm^2. In comparison with the conversion between Tl-1212 and Hg-1212, where the conversion can be controlled solely by the populations of Tl and Hg cations, we have shown that a phase transition may occur in the conversion between Tl-2212 and Hg-1212.

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