

Pinning lattice: Effect of rhenium doping on the microstructural evolution from Tl-2212 to Hg-1212 films during cation exchange

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In a cation exchange process developed recently by some of us, epitaxial $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ films can be obtained by diffusing volatile Tl cations out of, and simultaneously diffusing Hg cations into, the crystalline lattice of epitaxial $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (Tl-2212) precursor films. When a large number of Tl cations diffuse out from the same local area of the precursor lattice simultaneously, it causes lattice collapse locally and leads to formation of pores of micrometer dimension. To eliminate such large-scale lattice collapse, "lattice pins" were introduced on the original Tl-2212 lattice by partially replacing volatile Tl cations with nonvolatile Re ones. Since the Re cations remain on the lattice during the Tl-Hg cation exchange, they pin the lattice around them. $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ films obtained from these Re-doped Tl-2212 precursor films have much improved microstructures with the pore dimension reduced by an order of magnitude. © 2004 American Institute of Physics.

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I. INTRODUCTION

$\text{HgBa}_2\text{CaCu}_2\text{O}_6$ (Hg-1212) has a high superconducting transition temperature (T_c) around 125 K and is one of the most promising candidates in the family of the Hg-based cuprates^{1,2} for various applications in both electronics and electrical power-related devices. This has motivated considerable efforts in growth of epitaxial Hg-1212 films.^{3–11} Hg-1212 is, however, highly volatile due to the presence of Hg and thus extremely difficult to grow into high-quality epitaxial films. In order to overcome the difficulties in epitaxy of Hg-1212 films, our group has developed a simple diffusive cation exchange process recently in which epitaxial Hg-1212 films can be obtained from epitaxial $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (Tl-2212) "precursor" films by replacing Tl cations on the lattice with Hg ones.¹² Using this method, high-quality epitaxial Hg-1212 thin and thick films have been obtained on both oxides and metal substrates with high critical current densities (J_c)'s exceeding 10^6 A/cm² at temperatures near 100 K.^{13–15} In addition, superior microwave properties, including low surface resistance and high power handling capability comparable to that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 77 K, have been achieved on Hg-1212 films at temperatures near 100 K or higher.^{16,17}

Although the cation-exchange process provides a simple and highly reproducible method for epitaxy of Hg-1212 films, these films are by no means optimized. One major problem is the formation of voids of micrometer dimension during the Tl-Hg cation exchange, which occurs when a large number of Tl-O planes collapse in the same area of the Tl-2212 lattice as Tl cations diffuse out, resulting in porous microstructure in and rough surface morphology on the Hg-1212 films.¹⁵ This may explain the lower microwave power handling capability of Hg-1212 films in the normalized temperature scale as compared to its yttrium barium

copper oxide and Tl-2212 counterparts.¹⁷ Moreover, these voids provide entrance channels for moisture and other contaminants, making Hg-1212 films vulnerable even in standard characterization and device fabrication processes. This problem may be partially solved by lowering cation-exchange processing temperature so as to reduce the probability that many Tl cations are thermally excited out of the lattice simultaneously from the same local area. Indeed, the void population was reduced¹⁵ when the processing temperature was decreased from ~ 800 °C to ~ 700 °C but the dimension of the voids remained more or less the same. This is not surprising since simply lowering the processing temperature does not imply a fine control over the Tl diffusion pattern at a microscopic scale. In addition, the cation exchange becomes much less efficient at temperatures close to the binding energy of Tl cations (~ 700 °C) to the Tl-2212 lattice.¹⁵

Chemical doping/substitution may provide a direct solution to the voids problem by modifying diffusion patterns of Tl cations out of the lattice at a microscopic scale. In the cation exchange process, the thermal energy provided to the crystal lattice causes deflection of atoms. The weakly bonded volatile elements, such as Tl, may acquire enough energy to break their bonds from the lattice while other elements remain. This lattice deformation may occur at a macroscopic scale if a large number of volatile elements leave the lattice simultaneously. If the volatile elements, such as Tl in Tl-2212, are replaced partially with nonvolatile elements, the nonvolatile cations remain on the lattice during the cation exchange so as to pin the lattice and to minimize macroscopic lattice deformation. Many elements, such as Re,^{18–20} Bi,²¹ and Pb,²² may be chosen to replace Hg in the Hg-1212 lattice. Among others, Re is of special interest because of its benefits to Hg-1212. First of all, the material stability of Hg-based films can be remarkably improved through doping Re to the Hg sites.¹⁸ In addition, the irreversibility field was also reported improved in Re-doped

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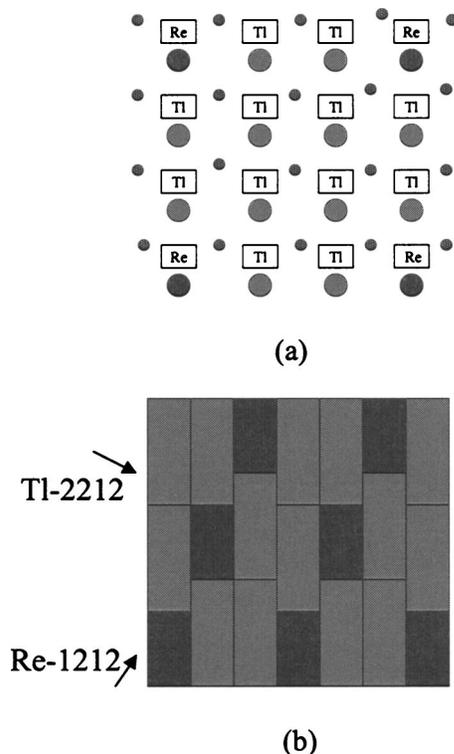


FIG. 1. Schematic diagrams of the lattice structure of (Tl,Re)-2212 film when 6% of Tl-2212 unit cells (textured symbols) are replaced with Re-1212 ones (solid): (a) a plan view, and (b) a cross-sectional view.

Hg-1223, despite a slightly lower T_c .^{19,20} In the cation exchange process, the nonvolatile dopants need to be inserted in the precursor lattice. This is illustrated schematically in Fig. 1 with Re taken some of the Tl sites in the Tl-2212 unit cells. In this work, we have successfully synthesized the doped $(\text{Tl}_{1.88}\text{Re}_{0.12})$ -2212 [(Tl,Re)-2212 in the rest of the text] films on LaAlO_3 substrate and converted them to $(\text{Hg}_{0.94}\text{Re}_{0.06})$ -1212 [(Hg,Re)-1212 in the rest of the text] using the cation-exchange process. Indeed, a dramatic improvement in the film microstructure was observed on Re-doped Hg-1212 films. In this paper, we report our experimental results.

II. EXPERIMENT AND DISCUSSION

A. Sample preparation

Sample fabrication consisted of two steps: preparation of epitaxial (Tl,Re)-2212 precursor films was followed by conversion to epitaxial (Hg,Re)-1212 films via Tl-Hg cation exchange. In the first step, the precursor (Tl,Re)-2212 thin films were deposited on single crystal (100) LaAlO_3 substrate at room temperature using dc magnetron sputtering from a pair of $(\text{Tl}_{1.88}\text{Re}_{0.12})$ -2212 superconducting targets. A gas mixture of argon and oxygen at a ratio of 4:1 was used for sputtering process. The as-deposited (Tl,Re)-2212 films were amorphous and nonsuperconducting. Superconductivity and epitaxy were obtained after these films were annealed in a closed Al_2O_3 crucible together with a pressed undoped Tl-2212 pellet (Tl vapor source) and annealed at 820 °C for 1 h. In the second step, the (Tl,Re)-2212 superconducting films obtained from the previous step were sealed in an

evacuated quartz tube together with two pellets. One pellet was an unreacted $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ pellet (Hg vapor source) and the other, a $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ pellet (Hg vapor absorber). The weight ratio between the former and the latter was 3:1. The entire assembly was kept in a furnace at 700 °C for 12 h. The (Hg,Re)-1212 films were then annealed in flowing oxygen at 300 °C for 3 h to optimize their oxygen composition.

B. Crystalline structure

The crystalline structure and phase purity of the films were analyzed using x-ray diffraction (XRD). Figure 2 depicts the XRD θ - 2θ spectra of (a) Hg-1212, and (b) (Hg,Re)-1212 films and their precursor (c) Tl-2212, and (d) (Tl,Re)-2212 films, respectively. All films are c -axis oriented and the amount of impurity phases is negligible. The (Hg,Re)-1212 film has a nearly identical structure to the undoped Hg-1212 as shown in Figs. 2(a) and 2(b). Interestingly, their precursor films had a subtle difference in structure. Without doping, only “2212” lattice structure is visible [see Fig. 2(c)]. In the case of Re doping [see Fig. 2(d)], some additional peaks marked with * are clearly visible. A comparison of Fig. 2(d) with Figs. 2(a) or 2(b) suggests that these peaks are from “1212” phase. This means that certain amount of 1212 phase was formed in the Re-doped Tl-2212 precursor films. Theoretically speaking, both Tl-1212 and Re-1212 structures are possible. We, however, argue that the latter may occur at a much higher probability based on the following reasons. First, the processing condition used was favorable to Tl-2212, which has been confirmed by the fact that no Tl-1212 was formed in the undoped case [see Fig. 2(c)]. On the other hand, Re-2212, similar to Hg-2212, is much less stable than Re-1212 (Hg-1212) and special processing condition, such as high vapor pressure plus chemical replacement on the Hg or/and Ca sites, is required to form “double-layer” structure.^{23,24} Based on these considerations, we propose that the Re-doped Tl-2212 is composed of pure Tl-2212 and Re-1212 phases. If no phase segregation occurs, Re-1212 unit cells should be present uniformly in the lattice of Tl-2212. Since the c -axis lattice constant of Re-1212 is ~ 1.27 nm while that of Tl-2212 is 1.48 nm, the mixing of the Re-1212 phase in Tl-2212 lattice will result in antiphase grain boundaries, as schematically illustrated in Fig. 1(b), in the first several to several tens of monolayers. These antiphase grain boundaries have been observed on $\text{YBa}_2\text{Cu}_3\text{O}_7$ films grown on miscut substrates and they later develop into dislocation type of growth defects at larger film thickness.^{25,26}

C. Surface morphology

The scanning electron microscopy (SEM) micrographs of the Tl-2212 and (Tl,Re)-2212 precursor films are shown in Figs. 3(a) and 3(b), respectively. The surface morphology of the latter [Fig. 3(b)] is nearly featureless, much smoother than that of the undoped Tl-2212 film [Fig. 3(a)]. In addition, the impurity phases (mostly the intermediate oxide compounds) typically observable on undoped Tl-2212 films due to contamination of the simple oxides precursor materials in air [see Fig. 3(a)] disappeared in the case of Re doping. This

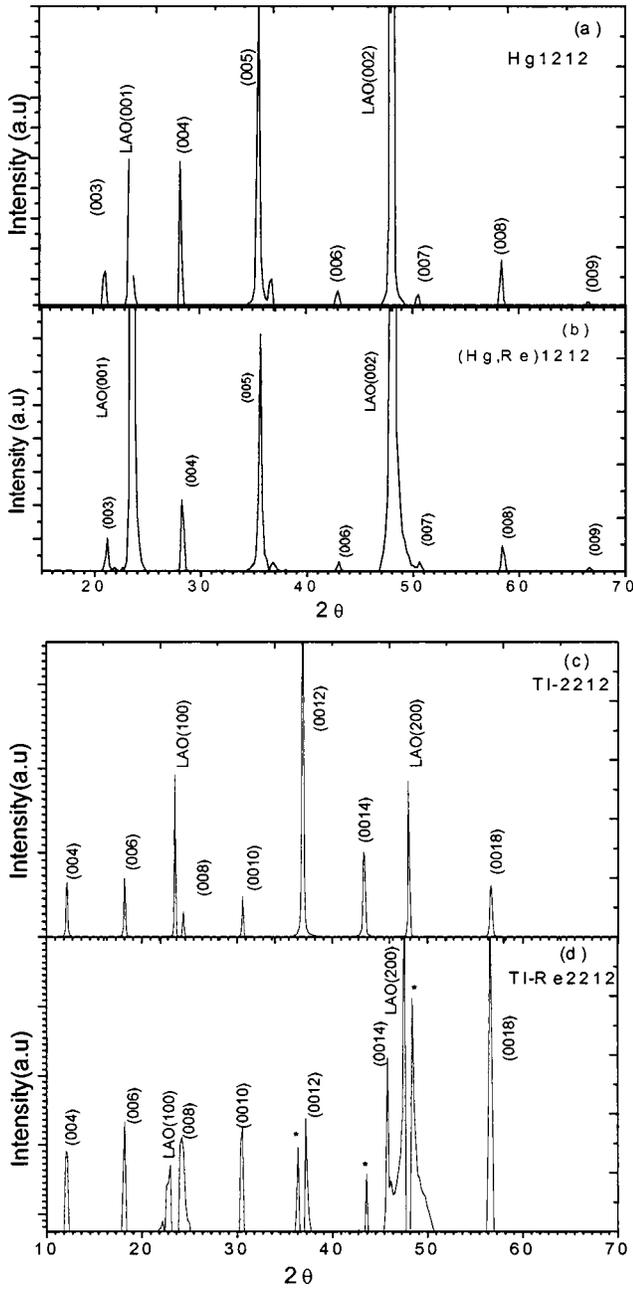


FIG. 2. XRD $\theta-2\theta$ spectra of (a) a Hg-1212 film fabricated using cation exchange process; and (b) a (Hg,Re)-1212 film made under the same condition as (a). The XRD $\theta-2\theta$ spectra of their precursor films are also shown, respectively, in (c) and (d). Both precursor films were about $0.25 \mu\text{m}$ thick. After cation exchange, the film thickness reduced to $\sim 0.21 \mu\text{m}$ when the 2212 unit cells ($c=1.48 \text{ nm}$) were transferred to 1212 cells ($c=1.27 \text{ nm}$). All films were on (100)LaAlO₃ substrates.

suggests Re doping reduces air contamination of the TI-2212, which is similar to what has been observed for Hg-1212 and Hg-1223 cases. On Fig. 3(b), many small size “holes” of tens of nanometers in diameter can be clearly seen. By carefully examining the surface of undoped TI-2212 [Fig. 3(a)], we conclude that this is unlikely related to Re doping since the holes are present also on the undoped TI-2212 films. Nevertheless, those holes are not as obvious on the undoped TI-2212 films simply because they are covered by many surface impurity particles. The mechanism of the hole formation remains unclear at this point. One possi-

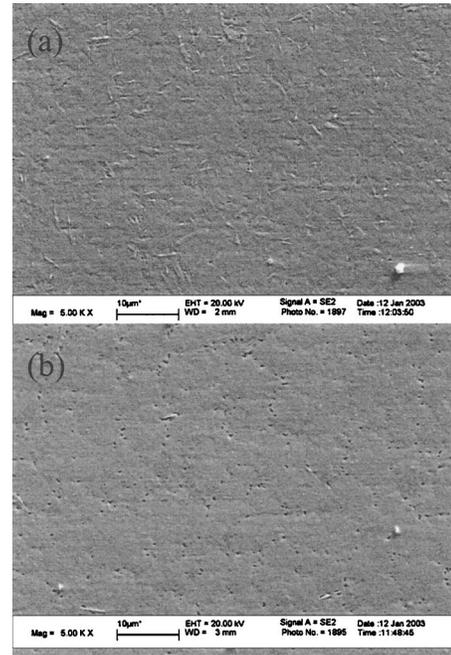


FIG. 3. SEM micrographs of (a) a superconducting TI-2212 precursor film; and (b) a (TI,Re)-2212 precursor of film both annealed in Thallium vapor at 820°C for 1 h in an Al₂O₃ crucible in flowing oxygen gas.

bility is that they may be the pathways for TI diffusion during the TI vapor processing. Further experiments are necessary to pinpoint this mechanism.

Figures 4(a) and 4(b) depict the SEM micrographs of Hg-1212 and (Hg,Re)-1212 films obtained via cation-exchange process from TI-2212 and (TI,Re)-2212 precursor films, respectively. A remarkable difference between these two films is the reduced void dimension with Re doping, suggesting that the crystalline lattice deformation pattern was indeed modified by doping Re on TI-2212 lattice. In the un-

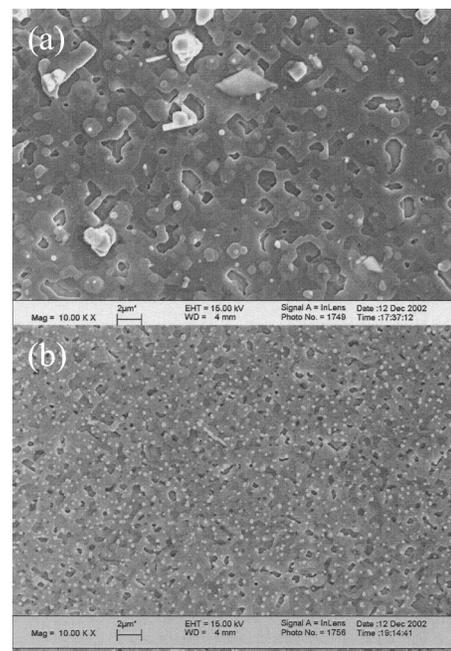


FIG. 4. SEM micrographs of (a) Hg-1212 film, and (b) (Hg,Re)-2212 film both made using cation-exchange process in Hg vapor at 700°C for 12 h.

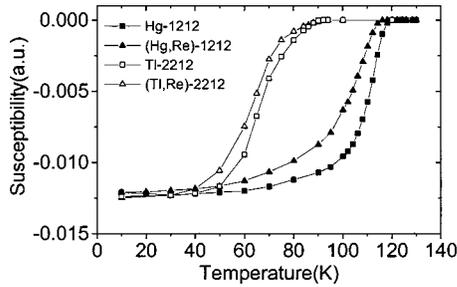


FIG. 5. Magnetic susceptibility as a function of temperature measured in zero-field-cool mode on Hg-1212, (Hg,Re)-1212 films, and their precursor films. The magnetic field was 10 Oe applied along the normal of the film.

doped case, the dimension of the voids is in the range of submicrometer to several micrometers [see Fig. 4(a)] while with Re doping, it reduced by an order of magnitude [see Fig. 4(b)]. It should be realized that this reduced void dimension is two orders of magnitude larger than what is expected theoretically. When 6% of unit cells of Tl-2212 are replaced with Re-1212 ones, the void dimension should be less than 1.6 nm (both Re-1212 and Tl-2212 have their *a* axes around 0.4 nm) if the two types of unit cells formed an alloy. The observation of the much larger dimension of the voids suggests that phase segregation may occur in (Tl,Re)-2212. This argument is supported by the observed Re-1212 phase in XRD data [Fig. 1(b)]. This phase segregation is in fact not unexpected because of large lattice mismatch between Tl-2212 and Re-1212 along the *c* axis. The strain generated by this lattice mismatch may serve as the driving force for the phase segregation. Another fact consistent with this argument is the difficulty we have encountered in doping higher percentage Re in Tl-2212 lattice. Dramatically roughened surface morphology was observed when the Re-doping level was doubled. The size of Re-1212 colonies after the phase segregation can be estimated by assuming that the collapsed Tl-2212 colonies are a hundred times bigger in dimension than the theoretically expected value of 1.6 nm. A simple-minded calculation suggests $\sim 10^4$ unit cells of Re-1212 in each Re-1212 colony with dimension ~ 40 nm along each side if the colony is a square. Transmission electron microscopy with adequate spatial resolution would be ideal to confirm this and will be certainly a topic of future research (unfortunately, such a facility is not available locally at this point).

D. Superconducting properties

Figure 5 depicts the temperature dependence of the magnetic susceptibility of Hg-1212 (solid squares) and (Hg,Re)-1212 (solid triangles) films measured in a 10 Oe magnetic field (*H*) applied along the normal of the film. Both films showed superconducting transition above 110 K. The T_c of (Hg,Re)-1212 films was typically in the range of 114–118 K, slightly lower than that of the undoped Hg-1212 films (~ 120 –124 K). Interestingly, lower T_c 's were also reported previously on most chemically doped Hg-1212, including Re-doped ones.^{18–20} The susceptibility vs temperature curves for the Tl-2212 (open squares) and (Tl,Re)-2212 (open triangles) measured under the same ex-

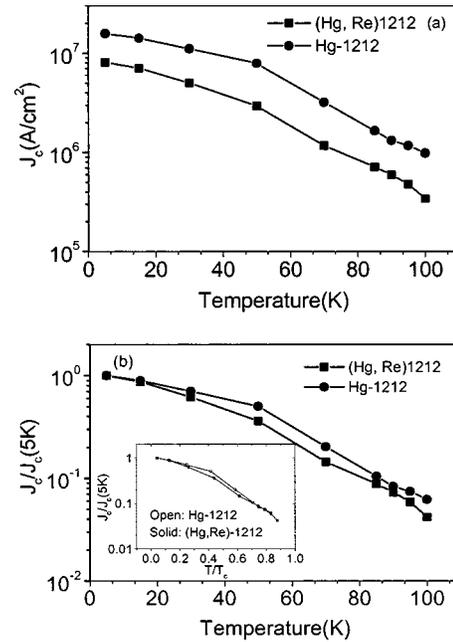


FIG. 6. Temperature dependence of J_c of the Hg-1212 film (circle solid symbol) and the (Hg,Re)-1212 film (square solid symbol) plotted (a) in the original J_c scale and (b) normalized J_c scale [$J_c/J_c(5\text{ K})$]. The inset of (b) replots the data in (b) on the normalized temperature scale [T/T_c].

perimental conditions were also included in Fig. 5. It has been noticed that T_c 's of the Tl-2212 films were also slightly higher than that of (Tl,Re)-2212 films. Since post oxygen anneal did not improve the T_c 's of Re-doped Tl-2212 and Hg-1212 films, we speculate that Re dopants may disturb the local oxygen distribution in both the 2212 and 1212 lattice, which in turn lowers the T_c of the material.

J_c 's were calculated using the Bean model from the magnetization vs magnetic field hysteresis loops measured at different temperatures. The magnetic field was applied along the normal of the film. Figure 6 shows a typical comparison of the self-field J_c as function of temperature for a pair of representative Hg-1212 and (Hg,Re)-1212 films. The J_c in the former is typically higher by a factor of 1.5–3 than that of the latter in the whole temperature range from 5 K to 100 K. For example, the J_c 's of the undoped Hg-1212 are 15.6, 3.2, and 1.0 MA/cm² at 5 K, 77 K, and 100 K respectively, while those for the (Hg,Re)-1212 are 8.0, 1.2, and 0.38 MA/cm² at the same temperatures [see Fig. 6(a)]. This represents the typical behavior among all the films we have studied. The J_c ratio between the Hg-1212 and (Hg,Re)-1212 films increases slightly with increasing temperature, as shown in Fig. 6(b). This slightly higher J_c ratio at higher temperature may be attributed to the lower T_c of the (Hg,Re)-1212. Indeed, the two J_c curves almost coincide when Fig. 6(b) is replotted on the normalized temperature scale (T/T_c) as shown in the inset of the Fig. 6(b). It is, however, unclear why the overall J_c is lower in the Re-doped Hg-1212 films.

Figure 7 compares the magnetic field dependence of J_c in the two types of films at 5 K, 77 K, and 100 K. Subtle difference is visible. Despite an overall higher values as shown in Fig. 7(a), the J_c in the undoped Hg-1212 film de-

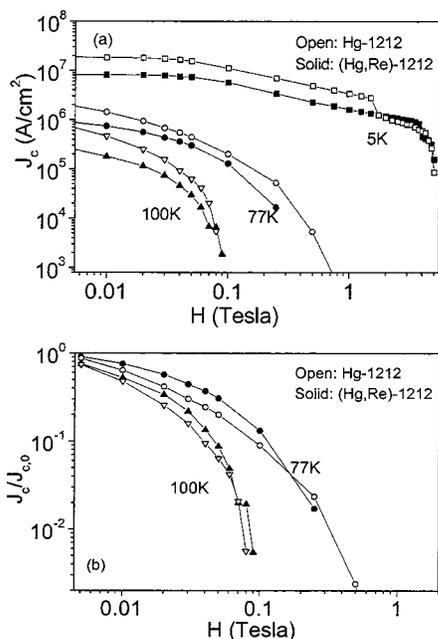


FIG. 7. (a) J_c - H curves at different temperatures of 5 K, 77 K, and 100 K for Hg-1212 and (Hg,Re)-1212 films. (b) replots the same J_c 's at 77 K and 100 K on the normalized J_c scale ($J_c/J_{c,0}$). $J_{c,0}$ is the J_c at zero applied magnetic field.

increases faster with increasing field in the low field range. This can be better demonstrated when the same curves are plotted on the normalized scale ($J_c/J_{c,0}$) in Fig. 7(b). This indicates the magnetic flux pinning is enhanced with Re doping, consistent with what was previously reported by other groups.^{19,20} At higher field, the two J_c - H curves cross over and both drop sharply when the field is further increased.

III. CONCLUSION

In conclusion, we have fabricated epitaxial c-axis oriented $(\text{Hg}_{0.94}\text{Re}_{0.06})\text{Ba}_2\text{CaCu}_2\text{O}_6$ films by replacing the Tl cations from an epitaxial $(\text{Tl}_{1.88}\text{Re}_{0.12})\text{Ba}_2\text{CaCu}_2\text{O}_x$ precursor films in the cation-exchange process. It was found that the presence of nonvolatile Re on the precursor lattice pins the lattice locally so as to reduce the large-scale lattice collapse, which occurs on undoped Tl-2212 precursor lattice and typically results in micrometer size voids in Hg-1212 films after the cation exchange processing. By pinning the lattice with Re doping, the void size has been reduced by an order of magnitude and the surface morphology has been improved dramatically. In addition, this result has also demonstrated for the first time that Tl-2212 precursor lattice doped with

nonvolatile elements on the volatile Tl sites can be employed for epitaxy of chemically doped Hg-1212 films in cation exchange process, enabling tailoring microstructure and physical properties of Hg-1212 films in a much controllable fashion.

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