

## Microwave surface resistance of $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ thin films

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(Received 27 July 1999; accepted for publication 24 January 2000)

Microwave surface resistance ( $R_s$ ) has been measured on *c*-axis-oriented superconducting  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (Hg-1212) films. A cavity perturbation method was employed using a high- $Q$  Nb cavity cooled at 4.2 K. For the best film, an  $R_s$  as low as  $\sim 0.3$  m $\Omega$  was observed at 10 GHz up to  $\sim 120$  K on Hg-1212 films that have smooth surface morphology and high critical current density near 2 MA/cm<sup>2</sup> at 100 K and self-field. This result suggests that Hg-1212 films are very promising for microwave applications above 100 K. © 2000 American Institute of Physics.  
 [S0003-6951(00)01012-3]

High-temperature superconductors (HTSs) are very attractive for microwave applications due to their low-loss performance in this frequency range. Generally, a microwave loss is characterized with the surface resistance ( $R_s$ ) of a superconductor defined as dissipation per unit area at a given power level. Results of  $R_s$  measurements have been reported on many HTS thin films.<sup>1</sup> Low  $R_s$ s in the range of 0.1–0.5 m $\Omega$  at 77 K and 10 GHz have been observed on several HTSs including  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [YBCO, with superconducting transition temperature ( $T_c$ )  $\sim 90$  K],  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  (Tl-2212,  $T_c \sim 110$  K), and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (Tl-2223,  $T_c \sim 125$  K).<sup>1–3</sup> This  $R_s$  value is nearly an order of magnitude lower than that of the copper ( $R_s \sim 0.87$  m $\Omega$ )<sup>2</sup> at the same temperature and frequency. During the past few years, many efforts have been put forth to optimizing HTS thin films, such as YBCO and Tl-2212 films, on low-loss substrates and microwave passive devices fabricated on these films show very encouraging results for practical applications. For example, planar filters with up to 11 poles have been produced with an insertion loss lower than 0.05 dB at 2 GHz and 77 K.<sup>1</sup> Operation of these devices at temperatures  $\sim 77$  K has been demonstrated by many groups.

Recent discovery of superconductivity near 135 K on Hg-based high-temperature superconductors (Hg-HTSs) makes them very attractive for microwave applications since higher  $T_c$ s imply higher operation temperatures. This could significantly ease the cooling requirement that has been one of the major obstacles in commercialization of HTS microwave devices. The high critical current densities ( $J_c$ s) achieved recently on Hg-HTS thin films suggest that adequate microwave power handling capability may be obtained on Hg-HTS films at temperatures above 100 K.<sup>4–10</sup> It is therefore necessary to investigate the microwave  $R_s$  of Hg-HTS films. In this letter, we report our recent experimental study of microwave  $R_s$  of  $\text{HgBa}_2\text{CaCu}_2\text{O}_6$  (Hg-1212) thin films. We show that, by optimizing the processing conditions, low  $R_s$ s can be obtained on Hg-1212 films at temperatures above 100 K. At 10 GHz, the  $R_s$  of the best film is as low as  $\sim 0.3$  m $\Omega$  at temperatures as high as 120 K, which

improves the previous results on other HTSs by more than 20 K.

Hg-1212 thin films used for this experiment were fabricated using two different processes: conventional thermal-reaction process<sup>4–8</sup> and cation-exchange process.<sup>9,10</sup> The first process involves deposition of Ba–Ca–Cu–O precursor films followed by thermal annealing at high Hg-vapor pressures. In the cation-exchange process, Tl-based HTS films (either Tl-2212 or Tl-1212) are employed as precursors. They are converted to Hg-1212 films by Hg-vapor annealing. The dimension of Hg-1212 films, as well as that of Tl-2212 and YBCO films used in this experiment for comparison, was typically 2 mm  $\times$  3 mm. Although many samples have been measured, the data shown in this letter were from: four Hg-1212 film made using cation-exchange process (labeled as sample Ia–Id), a Hg-1212 film by conventional thermal reaction process (labeled as sample II), and a Tl-2212 precursor film (labeled as sample III). All these films were grown on (100) single crystal  $\text{LaAlO}_3$  substrates. Several YBCO films, with their  $R_s$ s measured at the Los Alamos National laboratory by cavity wall replacement technique, were used to calibrate our system.

X-ray diffraction (XRD) was used to determine the orientation of the film, which shows that all samples used have their *c* axis perpendicular to plane of the substrate. XRD pole figure measurements indicate that samples Ia–Id and III are highly epitaxial, with their *a* axis aligned with the (010) axis of the substrates. Sample II is predominantly epitaxial with a small volume portion of unaligned grains in the plane of the substrate. To characterize  $T_c$  and  $J_c$  of the films, magnetization ( $M$ ) was measured as function of temperature ( $T$ ) and magnetic field ( $H$ ) in a Quantum Design superconducting quantum interference device (SQUID) magnetometer.  $J_c$ s were estimated using Bean model:  $J_c = 20(M_+ - M_-)/R$ , here  $M_+$  and  $M_-$  are the upper and lower branch of the H– $M$  hysteresis loop, respectively, and  $R$  is the effective radius of the induced current loop in the film. Figure 1 shows  $J_c$  vs  $T$  curves for samples Ia, II, and III at zero field. It seems that  $J_c$ s of the two Hg-1212 samples are comparable while that of Tl-2212 is higher at low temperatures. For example, at 5 K, samples Ia, II, and III have  $J_c$  values of 22, 23, and 33 MA/cm<sup>2</sup>, respectively. It should be realized that

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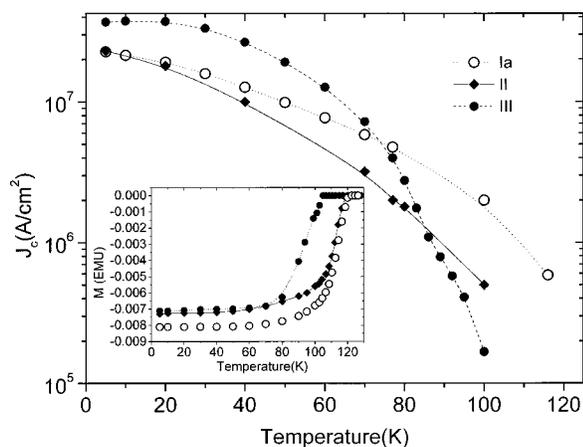


FIG. 1. Zero-field  $J_{c,s}$  as a function of temperature of Hg-1212 made in cation-exchange process (open circle), Hg-1212 by conventional thermal reaction process (solid diamond) and Tl-2212 precursor film (solid circle) which have dimension of  $2 \times 3$  mm. Inset: Plot of magnetic susceptibility vs temperature showing the  $T_{c,s}$  of the samples.

these Hg-1212 films have not been fully optimized. In several Hg-1212 films we made recently,  $J_{c,s} \sim 40$  MA/cm<sup>2</sup> have been obtained at 5 K and self-field. Tl-2212 film displays slightly better  $J_c$  in the low temperature regime but it has also the most rapid decrease with increasing temperature. At 77 K,  $J_c$  of the Tl-2212 film drops to  $\sim 4$  MA/cm<sup>2</sup>, which is in between that of sample Ia ( $\sim 5$  MA/cm<sup>2</sup>) and II ( $\sim 2$  MA/cm<sup>2</sup>). The decrease of  $J_c$  of the Tl-2212 film is significant at 100 K as the  $T_c$  ( $\sim 103$  K as shown in the inset of Fig. 1) of the sample is approached. Both Hg-1212 films still show moderate  $J_{c,s}$  at 100 K due to their higher  $T_{c,s} \sim 120$  K (inset of Fig. 1). The  $J_c \sim 2$  MA/cm<sup>2</sup> of sample Ia, however, is four times higher than that of sample II, suggesting poorer quality epitaxy is a major current limiting factor. This  $J_c$  difference is even enlarged at higher temperatures. For example, sample Ia still has a  $J_c$  of  $0.5$  MA/cm<sup>2</sup> at 115 K while that of sample II is not measurable. This result indicates that high-quality epitaxy is the key to achieve high  $J_{c,s}$  at temperatures close to the  $T_{c,s}$  as weak-link effect from high-angle grain boundaries becomes a dominant factor to suppress current flow. By comparison between samples Ia and II, it has been noticed that the quality of film epitaxy has been greatly improved in the cation-exchange process, although their  $T_{c,s}$  are nearly the same.

Surface features of the three samples are shown in the scanning electron microscopy (SEM) pictures in Fig. 2. A comparison between the upper (sample Ia) and lower (sample III) panel reveals changes in film surface morphology during the Tl-Hg cation-exchange process. The number of voids or holes increases on Hg-1212 and the surface becomes rougher after the cation exchange. The surface of sample Ia, however, is much smoother than that of sample II. It is interesting to notice the presence of finely dispersed impurity particles on the surface of sample Ia, which are Hg rich from an analysis using energy dispersive x-ray spectroscopy (EDS) and most of them can be wiped away with tissues. Since no impurity phases were visible in XRD data, we suspect that most of these Hg-rich particles present on the surface of the film and their volume portion is negligible. In contrast, massive impurity particulates can be identified on

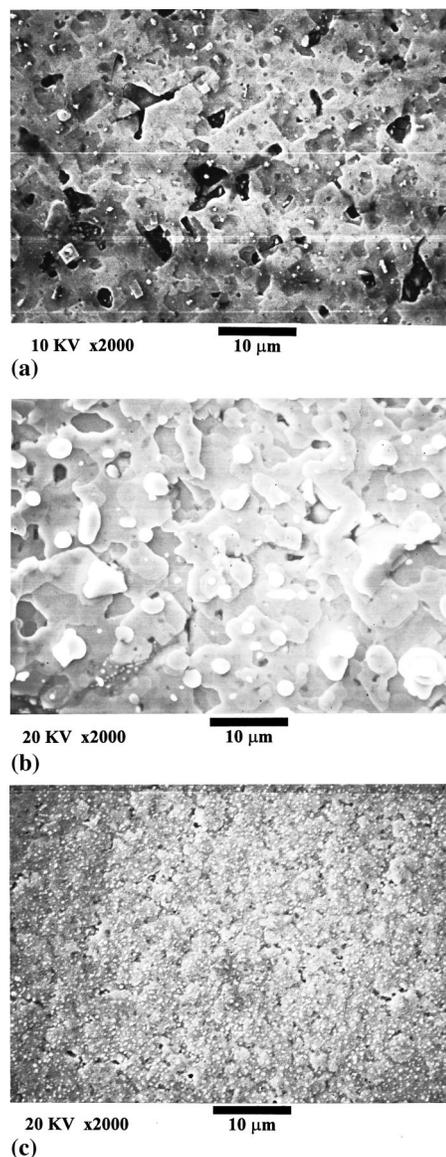


FIG. 2. Surface morphology of (a) Hg-1212 by cation exchange (sample Ia), (b) Hg-1212 by conventional (sample II), and (c) Tl-2212 precursor (sample III) taken by scanning electron microscope.

the surface of sample II (middle panel of Fig. 2). The dimension of these impurity particulates is much larger than that of Hg-rich particles on sample Ia so that the surface of sample II is much rougher than that of sample Ia. Consistent with the XRD results, these impurity particulates are either Hg (possibly HgCaO<sub>2</sub>) or Ba-Cu-Ca rich phases as suggested by the EDS analysis. Since in most Hg-1212 films, the impurity phases have finite volume portion in the XRD spectra, it is plausible to speculate that the observed impurities on the surface of the films may also exist on the film. This presence of impurities could thus be another reason for the degraded  $J_c$  and  $R_s$ , which is to be discussed in the following paragraphs, of sample II. Reducing impurity phases of Hg-HTS films is hence a very important success of the cation-exchange process.

$R_{s,s}$  of films were characterized using a cavity perturbation technique, which is discussed in detail elsewhere.<sup>11</sup> The  $R_{s,s}$  of samples Ia–Id and III are plotted as function of temperature in Fig. 3. Since the  $R_s$  of sample II is much higher,

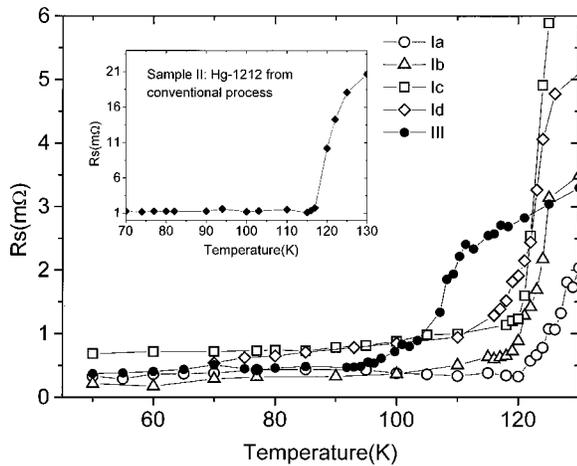


FIG. 3. Surface resistance ( $R_s$ ) scaled at 10 GHz against temperature of the Hg-1212 samples from cation-exchange (open shapes) and a TI-precursor (solid circle). Inset:  $R_s(T)$  of Hg-1212 made from conventional process.

the same plot for sample II is shown in the inset of Fig. 3 in order to show the details. The  $T_c$ 's of these films can be determined from the transition of  $R_s$ . For samples Ia–Id, the  $T_{c,s}$  are all around 120 K.  $T_{c,s}$  of samples II and III, are  $\sim 118$  and 100 K, respectively. These  $T_{c,s}$  agree very well with the values obtained in magnetization measurements. The 20 K difference in  $T_{c,s}$  between samples Ia–Id and III is a typical  $T_c$  increase after the TI-Hg cation-exchange process. The  $R_s$  of samples Ia–Id and III lies between 0.3 and 0.7 m $\Omega$  in the temperature range below 100 K. The scattering of the  $R_s$  from sample to sample is attributed to fluctuation in processing parameters and it is expected to be reduced when a fine control of processing parameters is reached. Sample Ib has the minimum  $R_s$  in this temperature range. At 77 K, its  $R_s$  is as low as  $\sim 0.2$  m $\Omega$  and at 100 K, it increases to 0.3 m $\Omega$ . It has been noticed that sample Ia has nearly a constant  $R_s \sim 0.3$  m $\Omega$  below  $T_c$  while  $R_s$  of other samples show more or less temperature dependence. Above 100 K, sample Ia shows the lowest  $R_s \sim 0.3$  m $\Omega$ , which remains the same up to 120 K. It should be pointed out that the  $R_s$  of sample II is much higher than that of samples Ia–Id. At 77 K, it is up to five times higher than that of sample Ib although the two films have similar  $T_{c,s}$ . In fact, the  $R_s$  of sample II is the lowest  $R_s$  we have observed on Hg-1212 films made in the conventional process. The  $R_s$  of sample III ( $\sim 0.45$  m $\Omega$ ) is comparable with that of samples Ia–Id, but slightly higher than the best  $R_s$  reported for TI-2212 at the same condition.<sup>3</sup> Since the  $R_{s,s}$  of all the films remain nearly constant in a wide temperature range below their  $T_{c,s}$ , an increase of 20 K in the operation temperature seems to be possible in Hg-1212 microwave devices over their TI-2212 counterpart.

Our results show significant improvement of  $R_s$  on Hg-1212 films made in cation-exchange process. This improvement may be explained by better phase purity, better quality epitaxy, and smoother surface morphology obtained in cation-exchange processed Hg-1212 films. Formation of impurity phases has been a common problem of Hg-HTS films made in the conventional process due to difficulties in controlling processing parameters and detrimental effect of air as confirmed by both XRD and SEM/EDS studies. In the

cation-exchange process, however, Hg-HTS films inherit high phase purity from their TI-HTS precursors. Most TI-HTSs can now be routinely made highly pure in air. Over a wide processing window, the TI-HTS precursor can be completely converted to Hg-HTSs via TI-Hg cation exchange, yielding minimized impurities in the Hg-HTS films as supported by XRD and SEM/EDS results. Hg-1212 films made in the cation-exchange process also inherit high-quality epitaxy from their TI-based HTS precursor films.<sup>10</sup> Since TI-related compounds are much less volatile, epitaxial growth of TI-HTS films has been obtained on many different substrates in many laboratories. This epitaxial structure can be well kept, as shown in both XRD pole figure and RBS/channeling measurements, during the Hg-TI cation exchange unless the thermal perturbation energy is so high so that the lattice collapses.<sup>9,10</sup> Moreover, Hg-HTS films made in cation-exchange process show minimal film/substrate interface reactions/diffusions as the TI-HTS precursor serves as a barrier to prevent direct interaction between Hg vapor and substrates. The cation-exchange processed Hg-HTS films have much better surface morphology as compared to those processed in the conventional process. We did notice, however, film surfaces become rougher during the cation-exchange process (from sample III to Ia–Id) although  $R_s$  seems “insensitive” to this degradation. Further study of this issue is certainly necessary and it is anticipated that better  $R_s$  may be achieved as the Hg-1212 films are further optimized in terms of epitaxy and surface morphology.

In summary, microwave surface resistance  $R_s$  has been measured on *c*-axis oriented, epitaxial Hg-1212 films synthesized in both the conventional thermal reaction process and the cation-exchange process. With comparable  $T_{c,s} \sim 120$  K, the Hg-1212 films made in the cation-exchange process, however, show much lower  $R_s$  than that of the same films made in the conventional process. This difference was attributed to higher phase purity, better quality epitaxy, and smoother surface morphology observed on the cation-exchange processed Hg-1212 films. On these films, the  $R_s$  is as low as 0.2 m $\Omega$  at 10 GHz and 77 K, and  $\sim 0.3$  m $\Omega$  at 120 K, suggesting Hg-1212 films are very promising for microwave device applications operated at temperatures above 100 K.

This work is supported in part by AFOSR, NSF, NSF EPSCoR, and DEPCoR.

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