Growth of Superconducting Hg-1212 Very-Thin Films

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***Abstract*—High quality epitaxial $HgBa_2CaCu_2O_{6+\delta}$ (Hg- High 1212) films with thickness less than 100 nm have been successfully synthesized using cation-exchange process. The films show the superconducting transition up to ~ 118 K which is close to the intrinsic value of 124 K for Hg-1212 phase, and critical current densities up to $1.1\times10^7 A/cm^2$ at 5 K, $1.14\times10^6 A/cm^2$ at 77 K and $2.59\times10^5 A/cm^2$ at 100 K in zero field.**

I. INTRODUCTION

The discovery of superconductivity in Hg-based high-T_c superconductors (Hg-HTSs: $HgBa_2Ca_{n-1}Cu_nO_{2n+2+d}$, n=1-5) has attracted considerable interest due to the high critical temperature (T_c) of these materials [1,2]. Despite the difficulties associated with the high volatile nature of the Hg-based compounds, considerable progress has been made recently in fabrication of high-quality Hg-1212 and Hg-1223 films [3-7]. Typically, the thickness of these films is in the range of 0.5-1 μm and the minimum thickness is still above 200 nm. For many microelectronic applications, such as optical devices, high-quality very-thin films with their thickness less than 100 nm are necessary. The major difficulty in fabrication of thinner films of the Hg-based HTSs rises from the liquefying of the material during the film crystallization in the post Hg-vapor annealing, resulting in unconnected islands when the film thickness is below certain threshold. In addition, the severe air-sensitivity of the cuprate precursor ($Ba_2Ca_{n-1}Cu_nO_x$) used in the currently adopted two-step process further complicates the processing and results in poor sample reproducibility even for thick films. In order to solve these problems, we have recently developed a new precursor film scheme. Instead of using un-reacted $Ba_2Ca_{n-1}Cu_nO_x$ precursor, a pre-reacted $Tl_yBa_2Ca_{n-1}Cu_nO_x$ film (y=1 or 2, n=2 or 3) is subjected to the same Hg-vapor annealing [8] to replace Tl by Hg. In this cation-exchange process, an epitaxial template can be formed in the precursor film. This allows growth of very-thin Hg-HTS films through a completely different mechanism and eliminates the air-detrimental effect since the $Tl_yBa_2Ca_{n-1}Cu_nO_x$ precursor films are stable in air. In this article, we report fabrication of epitaxial Hg-1212 very thin film with their thickness less than 100 nm on (001) $LaAlO_3$ substrates using the cation-exchange process. Epitaxial Tl-1212 thin films were used as precursor films, which were annealed in Hg vapor to form Hg-1212 thin film.

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II. EXPERIMENT

Tl-1212 precursor films were prepared using dc-magnetron sputtering and post-annealing method. Non-superconducting precursor films were sputtered from a pair of superconducting Tl-1212 targets onto $LaAlO_3$ (001) single-crystal substrates in a mixture of Ar and O_2 gases (Ar/O_2=4/1) at total pressure of 20 mTorr. The as-deposited film was amorphous with the metal composition of Tl:Ba:Ca:Cu = 1:2:1:2. The thickness of the films is dependent on the sputtering time and is typically controlled in the range from 50-200 nm. The as-deposited films were annealed in 1 atm O_2 using crucible process at temperatures ranging from 800-850°C.

The precursor films of Tl-1212 were then sealed in a pre-cleaned and evacuated quartz tube with bulk pellets of $Ba_2Ca_2Cu_3O_x$ and $HgBa_2Ca_2Cu_3O_x$ and annealed in Hg vapor at high temperature, typically 760-780°C for 3-4 hours to form Hg-1212 films. The mass ratio between the two bulk pellets was adopted to be 1:2.5~3 in order to maintain proper Hg vapor pressure. After the sintering, the films were further annealed at 300°C in a flowing O_2 atmosphere for 1 hour to optimize the oxygen content of the films.

Material phase(s) and orientation were determined using x-ray diffraction (XRD) θ-2θ scans from Cu Kα radiation. Scanning electron microscopy (SEM) was used to determine film surface morphology. T_cs of the Tl-1212 films and Hg-1212 films was determined by both electrical transport four-probe method and magnetic measurement. The critical current density (J_c) can be estimated from magnetic measurements with the magnetic field applied perpendicular to the plane of the film.

III. RESULTS

The precursor thin films of Tl-1212 films are superconducting with T_c about 80 K. The surface morphology of the films observed by SEM is typically smooth and uniform. Fig. 1(a) shows the XRD spectrum of a 80 nm thick Tl-1212 thin film annealed at 825°C. As indicated in Fig. 1(a), the sample is dominated by Tl-1212 phase with a negligible portion of impurity phases. The Tl-1212 phase grows with c-axis orientation perpendicular to the substrate surface as indicated by the (00l) peaks. The XRD θ-2θ pattern of the film after Hg-vapor annealing process is presented in Figure 1(b), which shows a nearly unchanged spectrum as expected from the same crystalline the Tl-1212 and Hg-1212 phases have. The transformation from Tl-1212

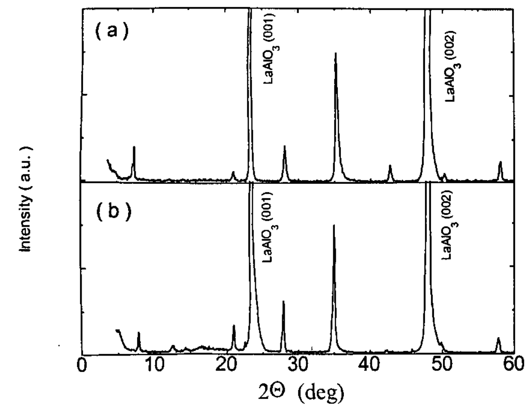

Fig. 1. The x-ray diffraction patterns for (a) the Tl-1212 film 80nm thick annealed at 825°C and (b) the Hg-1212 film (80 nm thick) annealed at 780°C for 3 h.

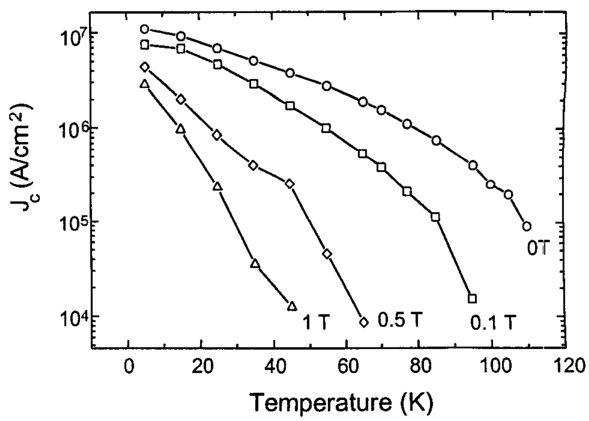

Fig. 3. J_c of Hg-1212 film (80 nm thick) as function of temperature and magnetic field.

to Hg-1212 is, however, confirmed by T_c measurement. Fig. 2 shows the temperature (T) dependence of the zero-field-cooled (ZFC) dc magnetization (M) of the same Hg-1212 film in a 5 Gauss magnetic field measured in a superconducting quantum interference device (SQUID) magnetometer. The T_c of the Hg-1212 film is as high as 118 K, which is close to the intrinsic value of 124 K for Hg-1212 phase and is comparable to the T_c (120-124 K) obtained on thick (thickness > 200nm) Hg-1212 films [8]. It has been noticed that this T_c value is about 38 K higher than that of the precursor Tl-1212 film. In addition, the smooth transition near T_c indicates a nearly complete transformation from Tl-1212 to Hg-1212 phase after the Hg-vapor annealing.

To estimate the magnitude of J_c from the M-H loops measured at different temperatures for the same Hg-1212 film, the Bean formula was used: $J_c = 20(M_+ - M_-)/R$. Here M_+ and M_- are the upper and lower branches of the M-H hysteresis loop, respectively. R, the circulation radius of the current, 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. The calculated J_cs are shown in Fig. 3 as functions of the magnetic field and temperature. In calculation of the J_c values, the total film area (5 mm by 2.4 mm) was used so that the calculation gives a lower bound estimates for J_c. At zero field, J_c is 1.1×10^7 A/cm^2 at 5 K and drops to 1.14×10^6 A/cm^2 at 77 K. These values are lower than the best obtained on thicker films by a factor of 2-4 [9]. At higher temperatures, the reduction of J_c becomes more significant. At 100 K and 110 K, J_cs are, respectively, 2.59×10^5A/cm^2 and 9.1×10^4 A/cm^2, which are a factor of 5-7 lower than the best reported for a thick Hg-1212 film. Further optimization of processing conditions is necessary to improve

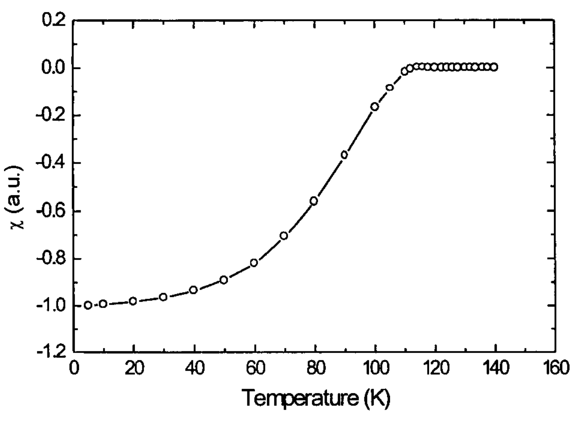

Fig. 2. Zero-field-cooled dc magnetization of (80 nm-thick) Hg-1212 film as a function of temperature in a 5 G magnetic field.

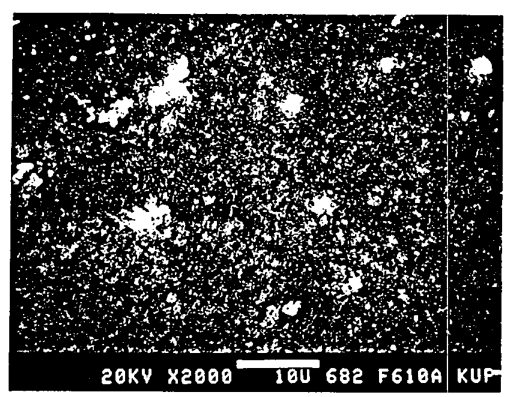

Fig. 4. SEM pictures of 80nm-thick Hg-1212 film made by cation-exchange process.

the quality of the very-thin Hg-1212 films. On the other hand, it should be mentioned that such reduction in T_c and J_c is not uncommon and has been reported on other high-T_c superconducting (HTS) very-thin films [10]. Since a protection layer could considerably decrease this reduction, it is argued that oxygen depletion near the film surface may be responsible for the degraded superconducting properties of HTS very-thin films. A comparative investigation of sample quality with or without protection layer would provide insights in this issue.

Figure 4 shows a typical SEM image of 80 nm-thick Hg-1212 films. Smooth morphology and dense crystal structure can be seen clearly on the surface. No evident grain boundary structure or cracks are visible, indicating a well-connected film at the thickness of 80 nm.

IV. CONCLUSIONS

Superconducting Hg-1212 films with their thickness less than 100 nm have been fabricated on $LaAlO_3$ substrates by annealing epitaxial Tl-1212 precursor films in a controlled Hg-vapor. The T_c up to 118K was obtained in these films. At zero applied field, J_c is up to 1.1×10^7 A/cm^2 at 5 K and close to 1×10^5 A/cm^2 at 110K. These very-thin films are very promising for various microelectronic applications.

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