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Physica C 363 (2001) 107–112

PHYSICA C

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Growth characteristics of $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ superconducting films on CeO_2 -buffered YSZ single crystals: an assessment for coated conductors

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Received 19 March 2001; received in revised form 27 April 2001; accepted 27 April 2001

Abstract

Superconducting $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ (Hg-1212) films have been fabricated on CeO_2 -buffered YSZ single-crystal substrates using a two-step cation-exchange process. X-ray diffraction analyses show that the Hg-1212 films are highly crystalline and grow epitaxially on these CeO_2 /YSZ substrates. Although the superconducting transition temperatures (T_c) of these films are approximately 122 K, the critical current densities (J_c) fall far below the expected values. The reason for these low- J_c values is explained by the observations of a cracked surface morphology in the superconducting layers. The likely mechanism for formation of the cracks and implications for the development of Hg-based coated conductors are discussed. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 74.72.Gr; 74.76.Bz

Keywords: High-temperature superconductors; Hg-1212; Buffer layers; Coated conductors

1. Introduction

Recently, development of a coated-conductor technology employing rolling-assisted biaxially textured substrates (RABiTS) has emerged as a most promising method for practical, high-current superconducting wires/tapes [1,2]. These tapes offer great potential for electric utility and power applications of high-temperature superconductors (HTS) operating in the liquid nitrogen tempera-

ture range (64–77 K). The RABiTS approach utilizes biaxially textured metallic substrates, Ni or Ni-alloys, as a template for deposition of epitaxial buffer layers, such that these buffer layers provide a barrier to chemical interactions with Ni. At the same time, these buffers yield a chemically and structurally compatible surfaces for the subsequent growth of HTS films. So far, the most successful and hence preferred buffer architecture for the RABiTS technique has been the combination of yttria stabilized zirconia (YSZ) and CeO_2 . Significant progress towards coated conductor development has been demonstrated by the fabrication of high-quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films on CeO_2 /YSZ/ CeO_2 buffered Ni or Ni-alloy substrates [2–6]. These YBCO coatings show high-critical

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current densities (J_c) exceeding 1×10^6 A/cm² at 77 K. This success stimulated substantial interest towards the use of Tl- and Hg-based HTS materials for coated conductors. While some progress has been achieved on Tl-based HTSs [7–9], development of Hg-based coated conductors has just begun [10].

Among the HTS materials, Hg-based HTSs with nominal composition $\text{HgBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+4}$ ($n = 0, 1, \text{ or } 2$) hold great promise due to their high-critical temperatures ($95 \geq T_c \geq 135$ K) and high- J_c values ($>10^6$ A/cm² at 100 K). Particularly, these high- T_c and J_c values provide additional flexibility and stability for power applications operating at temperatures higher than 77 K. However, the highly volatile and chemically reactive natures of Hg and Hg-related compounds make the fabrication of high-quality, reproducible Hg-based HTS films [11–16] extremely difficult. Generally, Hg-vapor reacts with most materials at elevated temperatures, resulting in deterioration of the interface between the HTS layer and the substrate material. This in turn prohibits the epitaxial growth of Hg-HTS films on technologically compatible substrates, including most metals and single-crystal oxides [11]. In addition, since the precursor films are highly sensitive to the detrimental effects of air exposure [17–22], synthesis of Hg-based superconductors requires extraordinary care during all steps of sample preparation. Recently, all the above mentioned inherent problems have been overcome by the development of a novel diffusive technique involving a Tl-to-Hg cation-exchange process [23–25]. The epitaxial and surface morphological quality of such samples are found to be superior to those made by conventional, direct reaction methods [11,26,27]. For instance, a significant, factor-of-four improvement in J_c (100 K and self-field) from 5×10^5 up to 2×10^6 A/cm², has been achieved for Hg-1212 films formed on single-crystal oxide substrates using cation-exchange applied to $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$ (Tl-2212) precursor films [23]. These J_c values are comparable to those of epitaxial YBCO films at 77 K and much higher than achieved in other HTS systems. Coated conductors utilizing such Hg-based HTS materials could provide robust operation at temperatures above where the YBCO

materials are no longer superconducting, when implemented in electric utility and power applications.

In this study, we extend the cation-exchange process to fabricate Hg-1212 films on CeO_2 -buffered YSZ single-crystal substrates. In this way, we gain a fundamental understanding of the epitaxy of Hg-1212 on this prototype buffer layer, since high-quality growth of YBCO films has been realized on textured Ni substrates employing the standard buffer layer sequence of $\text{CeO}_2/\text{YSZ}/\text{CeO}_2$. While we have previously demonstrated fabrication of Hg-1212 films on biaxially textured Ni substrates [10], the present study of growth and characterization provides a baseline whereby interactive effects of the textured Ni base metal can be assessed.

2. Experimental

Deposition of CeO_2 buffer layers on YSZ substrates was performed with a rf-magnetron sputtering system of base pressure 1×10^{-6} Torr. The 95 mm diameter sputtering target was composed of pressed and sintered CeO_2 powder. The YSZ substrates were mounted onto a heated substrate block assembly using conductive silver paste, in an on-axis sputter geometry. Typical sputtering conditions consist of 10 mTorr Ar and a substrate temperature in the range of 650–700°C. Typical thickness of the CeO_2 layer was 30 nm.

Growth of Hg-1212 films on CeO_2 -buffered YSZ substrates was composed of two major steps, which are (1) synthesis of Tl-2212 precursor films, (2) replacement of Tl by Hg through a Hg-vapor post-annealing process to form Hg-1212. The precursor Tl-2212 films were first deposited on CeO_2/YSZ substrates at room temperature using dc-magnetron sputtering, in an off-axis sputter geometry. Superconducting Tl-2212 films were then synthesized by enclosing the as-deposited films, together with a Tl-source pellet of chemical composition $\text{Tl}_{2+\delta}\text{Ba}_2\text{CaCu}_2\text{O}_x$, inside a covered alumina crucible at temperatures ranging from 800°C to 830°C in 1 atm Ar. The Tl-2212/ CeO_2/YSZ samples were then sealed in an evacuated quartz tube with bulk pellets of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$

and $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. The entire assembly was annealed at 720–780°C for 3–12 h. After this cation-exchange processing, the resulting Hg-1212 films were further annealed at 300°C for 1 h in a flowing oxygen atmosphere to optimize the oxygen content. Typical film thickness was 400 nm. X-ray diffraction (XRD) was employed to analyze phase, structure and texture of the films. A powder diffractometer with CuK_α radiation was used to record θ – 2θ diffraction patterns. Pole figures were collected by a four-circle diffractometer. Surface morphological characterizations were conducted using scanning electron microscopy (SEM). A standard four-point electrical technique was applied to measure the T_c of the Hg-1212 films. The J_c values were calculated using the Bean model from the magnetization (M) hysteresis measured in a SQUID magnetometer.

3. Results and discussion

Fig. 1 plots the XRD θ – 2θ diffraction patterns for a 400 nm thick Hg-1212 film and its precursor Tl-2212 film on a CeO_2 -buffered YSZ substrate. It is clear from the figure that all major peaks are indexed as $(00l)$ peaks for Tl-2212 and Hg-1212, indicating good c -axis orientation of the films.

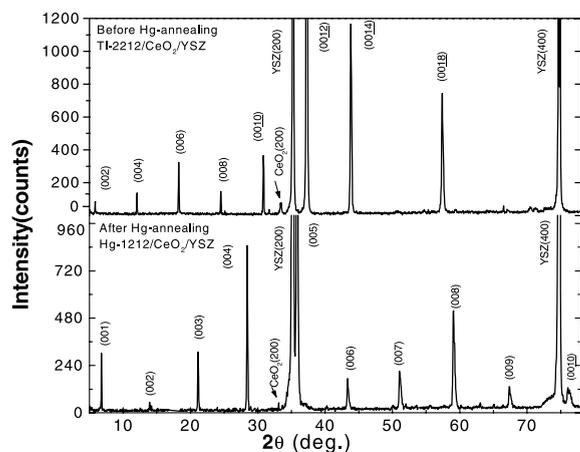


Fig. 1. XRD θ – 2θ patterns for a 400 nm thick Hg-1212 film grown by a cation-exchange process on a CeO_2 -buffered YSZ substrate. Also shown is the precursor Tl-2212 film, prior to conversion.

Complete conversion of Tl-2212 into Hg-1212 through Tl–Hg-exchange, with no trace of non-superconducting impurity phases, is also evident from the figure. The quality of epitaxy of Hg-1212 films as examined by XRD pole figure analysis of the (102) reflection is shown in Fig. 2. The four poles are 90° apart, which verifies that the a - and b -axes of the film are aligned in the plane of the substrate, but rotated 45° with respect to CeO_2/YSZ . The out-of-plane (ω -rocking curve) and in-plane (ϕ -scan) scans through the Hg-1212 (005) and Hg-1212 (102) peaks yielded peak width FWHM values of 1.1° and 0.9°, respectively. The narrow peak widths are comparable to those of epitaxial Hg-1212 films grown on LaAlO_3 substrates and reiterate the highly textured microstructure of the Hg-1212 films on CeO_2/YSZ . This indeed should be anticipated because of the small lattice mismatch (0.89%) between the superconducting film and the top CeO_2 layer.

In contrast to the good-quality epitaxy of the films, the J_c values are found to be poor. The magnetic field dependence of J_c , estimated using the Bean model, $J_c = 20(M_+ - M_-)/R$, from the magnetic-hysteresis loop measurements at 5 K, is shown in Fig. 3, where the field was applied normal to the film plane. Here, M_+ and M_- are the upper and lower branch of the M – H hysteresis loop, respectively. It should be noted that in calculation of J_c , the sample size ($3 \times 4 \text{ mm}^2$) instead of the grain size was used. The circulation radius, R , of the current is estimated using $R = b(1 - a/3b)$, where a and b are the short and long dimensions of the sample, respectively. We assumed that the critical current in the ab -basal plane of the Hg-1212 film is isotropic and the total area covered by the film is used as the relevant loop dimension. The J_c for this film in the absence of applied magnetic field was around $3 \times 10^5 \text{ A/cm}^2$ at 5 K, which is about two orders of magnitude lower than the typical J_c values ($2 \times 10^7 \text{ A/cm}^2$ at 5 K) obtained using the same method for epitaxial Hg-1212 films fabricated on LaAlO_3 substrates [23]. It should be mentioned that the T_c values of these films, as shown in the inset of Fig. 3, are around 122 K, which is typical of the best reported for Hg-1212 films. An explanation for the observed low- J_c behavior is the presence of cracks

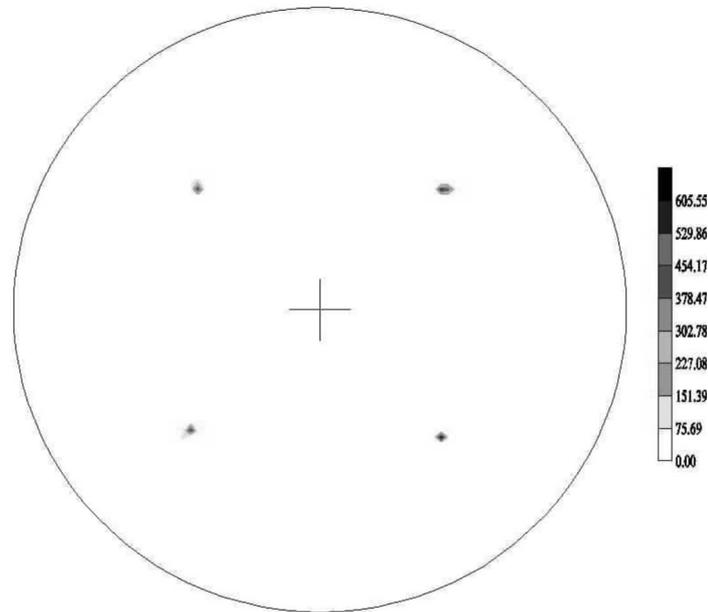


Fig. 2. XRD (102) pole figure for the Hg-1212 film shown in Fig. 1, indicating epitaxial growth on the CeO₂/YSZ substrate.

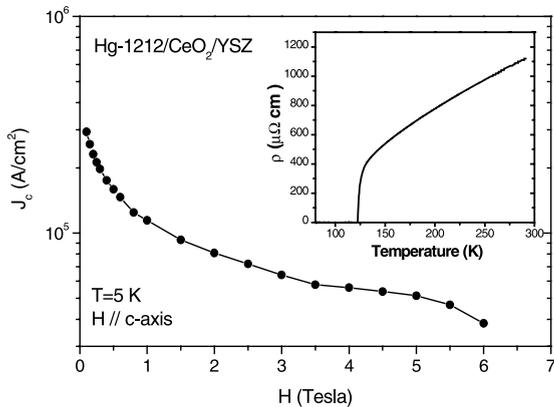


Fig. 3. Magnetic field dependence of J_c , determined magnetically, for a Hg-1212 film fabricated on a CeO₂/YSZ substrate, with the field applied parallel to the c -axis. The inset plots the temperature dependence of resistivity for the same sample.

in both the Tl-2212 precursor and the converted Hg-1212 films. The surface morphology was investigated using SEM, and the results are shown in Fig. 4a and b. It should be mentioned that, in order to make a consistent observation, a large piece of Tl-2212 film was cut into two pieces; one

piece was used for SEM analysis and the other was converted to Hg-1212. Fig. 4a and b revealed pronounced crack formation, accounts for a large-scale reduction in current flow. Since the cracks pre-existed in the precursor film, their replication in the converted Hg-1212 is not surprising. The network of orthogonal cracks indicates cleavage along symmetry planes. The most likely cause of crack formation is stress generated by differential thermal expansion between the film and the substrate. Since the thermal expansion coefficient of YSZ (8.8 ppm/deg) is smaller than that of Tl-2212 (≈ 11 – 13 ppm/deg), the Tl-2212 layer undergoes tensile stress during the cool down cycle after deposition. As far as we know, detailed thermal expansion coefficient measurements of Tl-2212 or Hg-1212 have not been reported; however, because of the structural similarities, we expect comparable thermal expansion coefficients to the well documented values of YBa₂Ca₃O_{7- δ} (11–13 ppm/deg) [28]. On the other hand, one may argue that the cracks could have been first initiated in the CeO₂ layer (rather than formed in Tl-2212) and then propagated to the subsequent Tl-2212 during the film growth. However, this is unlikely because

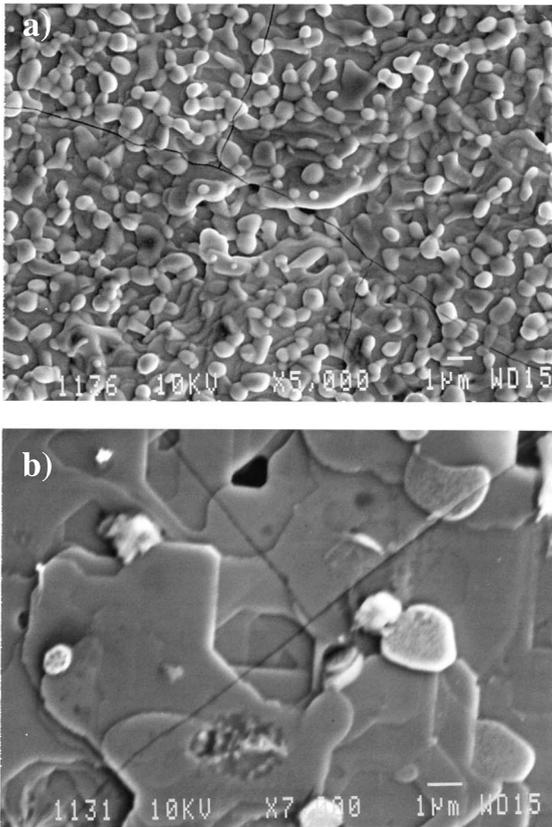


Fig. 4. SEM micrographs of (a) precursor Tl-2212 film on CeO₂/YSZ and (b) Hg-1212 film after the cation-exchange conversion. Both films show a cracked surface morphology.

CeO₂ exhibits an excellent thermal expansion (8.9 ppm/deg) and good lattice match (5.4%) with YSZ, minimizing the possibility of crack formation in CeO₂ buffers during or after the growth. In fact this was also confirmed by SEM observations, which revealed no evidence of cracks in CeO₂ layers grown on YSZ substrates. Despite these cracks, it is important to realize that the SEM micrograph of Hg-1212 showed a smooth surface morphology, with well-connected superconducting phase and traces of HgCaO₂ surface impurities. Moreover, both the Tl-2212 and Hg-1212 films are dense and have flat terrace-like surfaces, characteristic of *c*-axis-oriented grains. Such features are similar to those observed for epitaxial Hg-1212 films grown on LaAlO₃ substrates by the cation-exchange process [23]. Based on these observa-

tions, the use of a metal substrate, such as biaxially textured Ni, should effectively eliminate the crack formation since Ni has a similar thermal expansion coefficient (13 ppm/deg) that would impose slight compression to the HTS layers. Since it is well known that tensile, not compressive stress, is the primary cause of film crack formation, then in principal Hg-1212 films should grow effectively on RABiTS having the standard architecture of CeO₂/YSZ/CeO₂/Ni.

4. Summary

In summary, this study investigated the growth characteristics of Hg-1212 films on CeO₂-buffered YSZ single-crystal substrates, aimed at implementation of Hg-1212 HTS materials to RABiTS-based coated conductor technology. In this approach, the substrate structure simulated the standard buffer layer configuration of CeO₂/YSZ/CeO₂ used on Ni tapes. A two-step cation-exchange process was used to fabricate Hg-1212 films. Property characterizations revealed that even though the Hg-1212 films exhibit excellent epitaxy and high-*T_c* values of 122 K, the *J_c* values of the films were found to be poor. Surface morphological observations showed pronounced crack formation for both the precursor Tl-2212 and the converted Hg-1212 films. The cause of crack formation is attributed to the thermal expansion coefficient differences between the HTS film and the substrate material. This work, together with our previous successful demonstration of crack-free Hg-1212 films on RABiTS support the use of thermal expansion matched Ni substrates for fabrication of crack-free Hg-based coated conductors.

Acknowledgements

This work was supported by the US Department of Energy, Division of Materials Sciences, Office of Science, Office of Power Technologies-Superconductivity Program, Office of Energy Efficiency and Renewable Energy. The research was performed at the Oak Ridge National Laboratory,

managed by UT-Battelle, LLC for the USDOE under contract no. DE-AC05-00OR22725. T. Aytug and J.Z. Wu would like to acknowledge NSF grant no. DMR-9901460 and AFOSR grant no. F49620-96-1-0358.

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