Processing Dependence of Texture, and Critical Properties of YBa$_2$Cu$_3$O$_{7-\delta}$ Films on RABiTS Substrates by a Non-Fluorine MOD Method

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YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO or Y123) films on rolling-assisted biaxially textured substrates (RABiTS) were prepared via a fluorine-free metalorganic deposition (MOD) through spin coating, burnout, and high temperature anneal. The effects of substrate texture and surface energy of the CeO$_2$ cap layer were investigated. Except for the commonly accepted key factors, such as the textures of substrate and buffer layers, we found some other factors, for example, the deposition temperature of the cap layer, are also critical to the epitaxial growth of Y123 phase. With the CeO$_2$ cap layer deposited at relative high temperature of 700°C, a critical current density, $J_c$, over 1 MA/cm$^2$ has been demonstrated for the first time on Ni-RABiTS by a fluorine-free MOD method. Whereas for samples with CeO$_2$ cap layers deposited at a lower temperature of 600°C, even though XRD data showed a better texture on these buffer layers, texture degradations of YBCO grains under the optimized processing conditions were observed and a lower oxygen partial pressure around 40 ppm was necessary for the epitaxial growth of Y123 phase. As a result, $J_c$ fell to 0.45 MA/cm$^2$ at 77 K. The observed phenomena points to the change of surface energy and reactivity of the CeO$_2$ cap layer with respect to the CeO$_2$ deposition temperature. In this paper, the YBCO phase diagram was also summarized.

I. Introduction

Soon after the discovery of the cuprate high temperature superconductor (HTS), chemical solution depositions (CSD) were developed to grow YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) films. Now three major CSD approaches are in use for the ReBCO (Re, rear earth) deposition\textsuperscript{6–9}. (1) sol–gel processes that use 2-methoxyethanol as reactant/solvent, (2) hybrid processes that use chelating agents such as acetylatedonate or diethanolamine to reduce alkoxide reactivity, and (3) metal organic decomposition (MOD) techniques that use high-molecular weight precursors and water-insensitive carboxylates, for example 2-ethyl-hexanoates, etc. These CSD routes have been used for growing both oxide buffer layers and HTS films. Whereas the critical current density, $J_c$, was usually very low and it was believed that the carbon-contained precursor might have resulted in the formation of stable BaCO$_3$ at grain boundaries. In 1988, Gupta et al.\textsuperscript{10} reported a new method of using metal trifluoroacetate (TFA) precursors to grow textured YBCO films on single crystal substrates. McIntyre et al.\textsuperscript{11} further developed this method and high $J_s$ over 1 MA/cm$^2$ had been demonstrated on thin YBCO films. As the stability of BaF$_2$ is greater than that of BaCO$_3$, fluorine can be removed in a humid environment at temperature above 650°C. Hence, the use of TFA salts appears to avoid the formation of barium carbonate. Now, the MOD using TFA is a well-established CSD route for the coated conductor development.\textsuperscript{12–14} Nevertheless, the interest in the fluorine-free MOD approach remains. The most important being is that the removal of fluorine in the form of HF at the conversion temperature is a non-trivial process. There appear to be many issues related to the fluid-flow and complicated reactor designs. Moreover, the HF release as a byproduct in the TFA approach is a major environmental concern especially for a large-scale production.

YBCO films prepared through the fluorine-free precursor\textsuperscript{16} of trimethylacetates in amylamine and propionic acid (TMAP) have shown $J_c$ over 1.6 MA/cm$^2$ at 77 K on single crystal substrates.\textsuperscript{20} In this paper, $J_s$ over 1 MA/cm$^2$ at 77 K for 0.2 µm YBCO films have been successfully demonstrated on rolling-assisted biaxially textured substrates (RABiTS).\textsuperscript{21} The data in this research show that the fluorine-free TMA MOD approach is promising for the YBCO coated conductor fabrication. Moreover, in this paper, the YBCO phase diagram was summarized.

II. Experimental Procedure

(1) Preparation of Coating Solution

Y(C$_4$H$_9$COO)$_3$ and Cu(C$_4$H$_9$COO)$_2$ were home-made compounds by reacting metal nitrates with ammonium trimethyl acetate at room temperature (RT), respectively. All other chemicals were from Alfa Aesar (Ward Hill, MA). Steps of the solution preparation is shown in the flow chart (Fig. 1). Usually the solution’s viscosity was adjusted to 30–100 cross polarizations and the oxide contents were around 10–12 wt% with a total ionic concentration of 1.0 ~ 1.2 mol/L.\textsuperscript{20}

(2) Preparation of Ni and Ni-3W Substrates with Buffer Layers

Architectures of the RABiTS used in this experiment are shown in Fig. 2. Biaxially textured Ni and NiW substrates were prepared through the standard RABiTS process.\textsuperscript{9,21,22} The buffer stack of Ni-RABiTS includes a 12 nm CeO$_2$ seed layer, a 300 nm...
YSZ barrier, and a 20 nm CeO2 cap. The seed layer was grown by reactive e-beam deposition at 700°C. The barrier and the cap were deposited by radio frequency sputtering at 700°C in 5–10 mTorr forming gas. For Ni–RABiTS, the major difference in the buffer deposition is that the CeO2 cap was grown at 600°C, 100°C lower than did on Ni–RABiTS.

3) Coating, Burnout, and High Temperature Anneal
Precursor films were prepared by spin coating at 2000 rpm for 30 s at ambient temperature and pressure. The as-coated film, green film, of about 2 μm were condensed to 0.2 μm through burnout and high temperature anneal. All samples were burnout at the same conditions as reported previously. After high temperature conversion, silver contacts around 1 μm in thickness were sputtered onto YBCO films at RT. The oxygen anneal was performed at 500°C for 1 h followed by a cooling ramp of 2°C/min to 350°C to diffuse oxygen into the YBCO perovskite structure and to establish good contact of Ag with YBCO films.

4) Characterization
Critical transition temperature, \( T_c \), and critical current, \( I_c \), were measured with the direct four-probe transport method. The criterion for the \( I_c \) measurement is 1 μV/cm and \( J_c \) is calculated based on \( I_c \) value and the cross-sectional area of YBCO films. X-ray diffractions (XRD) of the 0-20 scan (A Philips XRG3100 diffractometer with CuKα radiation) were used for the phase examination. O-scans, φ-scans, and pole-figures were performed on four-circle diffractometer (dilfractometer 3488M-401 with CuKα radiation, \( λ = 1.54 \) Å) to characterize in-plane and out-of-plane textures. We use volume fraction of cubic phase (VFCP) as one of the reference criterion for the texture characterization, which is defined as follows: we collect one pole figure (note: the pole figure was collected on (111) plane for NiW, YSZ, and CeO2; on (222) plane for \( Y_2O_3 \), and on (113) plane for YBCO) and one background pole figure, offset in 20. We take the difference. Because the background pole figure may contain reflections from other phases, giving spurious negative values in the difference pole figure. We set all negative values to zero, then normalize the pole figure. Most often we see only a single (twinned) (001) \( <100> \) orientation, giving four peaks with only noise at other directions. We integrate the cube peaks and express this as a fraction of the total intensity. For example, a volume fraction of 90% says that we see only one orientation, but concedes that other more weakly textured orientations may be present at ~10% volume fraction. Surface morphology was observed by scanning electron microscopy (SEM). The cross-sectional interface structure was examined with transmission electron microscopy (TEM) and selected area diffraction (SAD). Thickness and stoichiometry were determined by Rutherford backscattering spectroscopy (RBS) with 5 MeV He\(^{++}\) ions near normal incidence and detected at 160° scattering angle. By using RBS, the thickness could be measured down to 0.5–1 nm, and errors for the composition measurement should be within 5%.

III. Experimental Results and Discussions
Texture data in transverse direction of RABiTS and buffer layers are listed in Table I. Usually, peaks in the rolling direction are sharper and the full-width at half-maximum (FWHM) values are 1–2 smaller than those in the transverse direction. In-plane and out-of-plane texture, and especially VFCP of RABiTS and buffers, are the key factors that affect YBCO alignment. The FWHM in the rocking curve (Δω) of CeO2 cap layer on NiW–RABiTS is about 3–3.5° smaller than that on Ni–RABiTS. Although the broader rocking curve may be from the added combination of the seed and the cap layers on Ni–RABiTS, the fact that the value of VFCP is 5.9% smaller than that on NiW–RABiTS indicates the inferior texture of the CeO2 cap layer on Ni–RABiTS compared with those on NiW–RABiTS.

In addition to the texture effect, the deposition conditions of the cap layer, such as the deposition temperature, should be considered as well. Because the activity of the cap layer is a control factor for the nucleation and growth of Y123 phase in terms of barrier energy and reactivity. Table II shows typical results of YBCO films deposited on Ni–RABiTS and NiW–RABiTS under different conditions. RBS analysis shows that the composition as well as the film thickness are comparable for those samples prepared under the similar conditions. Figure 3 is a typical RBS spectrum on sample N-180. Apparently, RBS data shows no observable macroscopic compositional difference from the stoichiometry of the solution. Thickness data in RBS analysis agree well with that in cross-sectional TEM observations. The processing conditions used for samples listed in Table II are based on a large number of experiments. Under optimized conditions (745°C, 30 min, D.P. = 45°C, and \( ρO_2 = 180 \) ppm), YBCO films had shown a \( J_c \) over 1.6 MA/cm² on LAO substrate, and this work, a \( J_c \) of 1.02 MA/cm² (sample N-180) has been demonstrated on RABiTS. Nevertheless, under the same processing condition, YBCO films on NiW–RABiTS show no \( J_c \) (sample NW-180). Only when partial pressure of oxygen (\( ρO_2 \)) was reduced to a low level of, in this case, 40 ppm (sample NW-40) a \( J_c \) of 0.45 MA/cm² was shown on NiW–RABiTS. It is well known that once the \( ρO_2 \) approaches to the unstable line in the YBCO phase diagram, the driving force of YBCO formation is greatly reduced and the growth of Y123 phase slows down or even stops on the regular base as shown on sample N-40. Hence, the results in this group of experiments indicate that the texture of buffer layers is not the only decisive factor for the nucleation and growth of YBCO phase.
factor for high quality YBCO growth, other factors had played roles either. To make a better understanding, α-scan and φ-scan were performed on these samples. For Ni-RABITS with higher CeO2 deposition temperature of 700°C, when converted at lower P02 (40 ppm) intensities in both rocking curve and φ-scan drop about 25% compared with samples that processed in P02 = 180 ppm (Fig. 4). In addition, Δα increased 1.5° and the VFCP decreased 8.6% as well. Tc has very small drop of about 5 K. However, Jc drops more than 88%. The rapid loss in Jc may result either from the reduction in the VFCP or the degradation in texture.

On the other hand, for NiW-RABITS with a lower CeO2 deposition temperature of 600°C, better texture was shown for YBCO films processed at pO2 = 40 ppm while YBCO films converted at pO2 = 180 ppm showed very broad FWHM. Figures 5 and 6 are the α-scan and φ-scan showing the out-of-plane and in-plane texture of YBCO films on NW-40 and NW-180, respectively. These results indicate that Y123 phase has not very well nucleated on the CeO2 cap layer especially for the conversion in a relatively higher pO2 of 180 ppm. To further investigate the texture, the pole figure analysis was performed on sample NW-180 and N-180 (Fig. 7). Compared with sample N-180, YBCO films on NW-180 showed poor texture with large amount random oriented grains. Obviously, these polycrystalline grains were not formed by interface nucleation, but they may have originated from nuclei that initiated from second phase or other defects in the precursor film. The data in Table II show that, for sample NW-180, the value of VFCP is only 1.5%, which means almost half of YBCO grains were misoriented. In this instance, weak links exist at large angle grain boundaries and superconducting networks are frustrated.

<table>
<thead>
<tr>
<th>Architecture Layers</th>
<th>NiW/YSZ/YSZ/CeO2</th>
<th>Ni/YSZ/YSZ/CeO2</th>
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<tr>
<td>Δα (°)</td>
<td>8.2  8.0  6.9</td>
<td>6.8</td>
</tr>
<tr>
<td>Δφ (°)</td>
<td>8.0  7.7  8.3</td>
<td>7.7</td>
</tr>
<tr>
<td>VFCP (%)</td>
<td>95.2 82.2 97.5</td>
<td>86.1</td>
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For Y2O3, Δα was collected from (004) plane and Δφ from (222), but for NiW, YSZ, and CeO2 the Δα values were from (002) planes and Δφ from (111).

Table II. Texture Data and Electrical Properties of YBCO Films Converted in Different Conditions

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Annealing condition (ppm)</th>
<th>Δα (°)</th>
<th>Lα (Counts)</th>
<th>Δφ (°)</th>
<th>Lφ (Counts)</th>
<th>VFCP (%)</th>
<th>Tc (K)</th>
<th>Jc (× 10^6 A/cm^2)</th>
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<tr>
<td>N-180</td>
<td>Ni, 180</td>
<td>11.5</td>
<td>1830</td>
<td>10.2</td>
<td>2110</td>
<td>78.2</td>
<td>89.6</td>
<td>10.2</td>
</tr>
<tr>
<td>N-40</td>
<td>Ni, 40</td>
<td>13.0</td>
<td>1521</td>
<td>10.1</td>
<td>1345</td>
<td>69.6</td>
<td>89.0</td>
<td>1.2</td>
</tr>
<tr>
<td>NW-180</td>
<td>Ni3W, 180</td>
<td>13.5</td>
<td>649</td>
<td>7.2</td>
<td>454</td>
<td>52.5</td>
<td>65.5</td>
<td>0</td>
</tr>
<tr>
<td>NW-40</td>
<td>Ni3W, 40</td>
<td>6.5</td>
<td>1867</td>
<td>7.4</td>
<td>1692</td>
<td>64.3</td>
<td>88.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The Δα and Δφ were collected from YBCO (003) and (113) planes, respectively. Pole figure was performed on YBCO (113) plane. VFCP, volume fraction of cubic phase.
(r^*) increases with the CeO2 deposition temperature. On the other hand, based on the phase diagram, the driving force for the YBCO formation increases with Po2. For sample of NW-180, as the CeO2 was deposited at lower temperature of 600°C, so the r^* should be smaller than those deposited at 700°C. Relatively high Po2 (180 ppm) applied a high driving force for the YBCO formation. As a result, in addition to the interface nucleation, nuclei on relative larger defects such as voids and second phase precipitations prevailed and polycrystalline film was formed. A smaller driving force with low Po2 should suppress the unwanted random nuclei on defects. Sample NW-40 is just the case with interface nucleation dominating. Because of the low driving force, YBCO grains lost their tracks during the epitaxial growth, ended up half way, and left the upper portion

Fig. 4. YBCO (113) φ-scans showing the change of in-plane texture with the partial pressure of oxygen (Po2). Processing condition: (a) 745°C and Po2 = 180 ppm; and (b) 745°C and Po2 = 40 ppm.

Fig. 5. YBCO (003) ω-scans showing out-of-plane texture change of YBCO on NiW and Ni substrates. Samples were converted at 745°C in a furnace gas of one atmosphere contained (a) 180 ppm oxygen and (b) 40 ppm oxygen.

Fig. 6. YBCO (113) φ-scans showing the change of in-plane texture with oxygen partial pressure at 745°C. Samples were converted at (a) Po2 = 180 ppm, and (b) Po2 = 40 ppm.
polycrystalline. The low performance of N-40 is because the combination effect of the high energy barrier and low driving force that rendered low nucleation rate and large grains with weak link at grain boundaries.

Figure 9 shows cross-sectional TEM image taken in the vicinity of the interfaces of YBCO/CeO2/YSZ/Y2O3/NiW of sample NW-40. A c-axis oriented YBCO layer with in-plane alignments is observed on the CeO2 cap layer, which is a robust layer and can carry high current density. But YBCO grains on the upper portion of the film tends to tilt and form large angle grain boundaries. So the current carrying ability for the upper portion is very limited. This TEM image is in good agreement with the previous analysis. The degradation in the upper portion of YBCO films, called “dead layer,” has also been observed in other approaches, and usually appears in a relatively thick film.22,28–32 The characteristics of this layer includes the development of misoriented YBCO grains or porosity,28,33,34 formation of second phases,29,35,36 oxygen deficiencies, changes in stoichiometry,37 a-axis oriented grains,38 and other defects. For sample NW-40, if we count out the dead top layer, $J_c$ should be double and comparable to that of sample N-180.

The reason why YBCO grains lost their tracks of epigrowth under small driving force and formed a polycrystalline layer on the upper portion is still unclear. Whereas even at very low $p_{O_2}$, the compositional change at the growth front and random-oriented nuclei should be responsible for the formation of polycrystalline at the upper portion of the film. The RBS analysis in Fig. 3 does not show observable macroscopic changes in the composition. If the compositional change is one of the reasons for the polycrystalline nucleation, it must be a locally compositional aggregation formed before or during the crystallization. For example, the formation of BaCO3 phase24 will cause barium aggregations.

Figure 10 shows the $J_c$ measurement of sample N-180 in self-field and in fields up to 0.5 T. The inset is a plot of $J_c$ versus magnetic field. This is the first demonstration of critical current density at 77 K in self-field above 1 MA/cm² for a non-fluorine MOD approach. However, its performance in a magnetic field is inferior to those films prepared by PLD or e-beam BaF2 approaches, which generally give a ratio of $J_c(0T)/J_c(0.5T) = 4–5$.39 The high ratio of $J_c(0T)/J_c(0.5T) in this measurement has a good agreement with the large angle grain boundaries either from the upper dead layer or from the texture of Ni–RABiTS, or both. Because the broad texture of the Ni substrate (Δω = 10.3°, ΔΦ = 10.7°) and the CeO2 cap layer (Δω = 10.1°, ΔΦ = 10.5°) weak links exist in the YBCO film.
Fig. 9. TEM image taken at the vicinity of the interfaces of YBCO/CeO$_2$/YSZ/Y$_2$O$_3$/Ni of sample NW-40. (a) A reaction layer of BaCeO$_3$ and all other buffer layers are clearly visible. YBCO grains outgrew from the interface and formed $c$-axis oriented texture with $a$-$b$ in-plane alignment. The upper portion shows the feature of polycrystalline films. (b) $a$-axis oriented grains are usually observed at interface.

Fig. 10. The magnetic field dependence of current density at 77 K for sample N-180. The high ratio of $J_c(0.5)$/$J_c(0.5)$ indicates weak links at YBCO grain boundaries. The inset plot shows the magnetic field dependence of $J_c$. The magnetic field, $H$, was applied parallel to the $c$-axis direction ($H/c_\perp$) and 1 $\mu$V/cm was used as the criterion of $I_c$.

IV. Summary

Superconducting YBCO films with a $J_c$ of 1.02 MA/cm$^2$ at 77 K were prepared on Ni/CeO$_2$/YSZ/CeO$_2$ substrates. This is the first report of YBCO films on a RABiTS substrate that can carry a critical current density over 1 MA/cm$^2$ through a fluoride-free MOD approach. Experimental data and analysis show that the deposition temperature of the CeO$_2$ cap layer is one of the key factors that affect the nucleation process in terms of the energy barrier and reactivity. By reducing the $p$O$_2$ we realized epitaxial growth of Y123 phase on NW series substrates, even though the growth was not that robust and ended up half way in the film. YBCO films with better performance can be expected only when the polycrystalline nucleation is suppressed and the $c$-axis oriented grains from interface nucleation and epitaxial growth dominate. Based on our experiments and data from previous publications, a revised YBCO phase diagram is reported, which will especially fit for the YBCO conversion in the ex situ MOD process.

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