Enhanced flux pinning by $BaZrO_3$ and $(Gd,Y)_2O_3$ nanostructures in metal organic chemical vapor deposited GdYBCO high temperature superconductor tapes

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We have formed $BaZrO_3$ nanocolumns and $(Gd,Y)_2O_3$ nanoprecipitates in reel-to-reel metal organic chemical vapor deposition (MOCVD) processed $(Gd,Y)Ba_2Cu_3O_{7-x}$ coated conductors and increased the critical currents (I_c) of the conductors in applied magnetic fields to remarkable levels. A $(Gd,Y)Ba_2Cu_3O_{7-x}$ tape of 1 m in length with 6.5% Zr-additions and 30% composition rich in both Gd and Y showed I_c values of 813 A/cm width at (self-field, 77 K) and above 186 A/cm width at (1 T, 77 K). The strongly enhanced flux pinning over a wide range of magnetic field orientations can be attributed to the bidirectionally aligned defect structures of $BaZrO_3$ and $(Gd,Y)_2O_3$ created by optimized MOCVD conditions. © *2009 American Institute of Physics*.
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Remarkable advancements have been made in the fabrication technology of second generation high temperature superconductor (2G HTS) tapes or $REBa_2Cu_3O_{7-x}$ (REBCO, where RE=Y or rare earth) coated conductors in the past 3 years.[1–4] Improvements in their in-magnetic-field performance and critical current density (J_c) in thick films have recently become topics of the most intense research on HTS coated conductors. In many applications, HTS wire will operate in moderate-to-high magnetic fields and high critical currents (I_c) are required.

Magnetic field and field-angle dependences of I_c can be modified through materials engineering, such as varying the composition ratio RE:Ba:Cu and introducing additional dopants, which form nonsuperconducting extrinsic defects in the REBCO film to pin magnetic flux lines. However, to be effective in pinning the flux, the defects should be of appropriate size, geometry, and density in the film.

$BaZrO_3$ (BZO) particles in REBCO films grown by pulsed-laser deposition (PLD) using $BaZrO_3$-doped REBCO targets were shown to be effective pinning centers.[5] In particular, columnar structures of 5–100 nm in diameter comprised of BZO nanodots, aligned along the *c*-axis of REBCO, can be formed in the PLD REBCO films.[6–9] These *c*-aligned columnar defects were found to be very effective in pinning, especially when the magnetic field *B* is applied parallel to the *c*-axis of REBCO. However, the aligned nanometer sized columnar defects were not previously observed in REBCO films grown by metal organic chemical vapor deposition (MOCVD), and the Zr doping was not substantially proven to enhance performance of MOCVD grown REBCO films until we recently demonstrated that the I_c at 77 K and 1 T for MOCVD grown Zr:GdYBCO tapes could be of a factor of two higher than those for GdYBCO tapes without Zr-additions.[1,2,10] In all of these conference presentations, however, we simply reported the record performance of Zr-added GdYBCO tapes but did not describe the MOCVD conditions and microstructures for such a performance.

Unlike the BZT-containing REBCO target used in PLD, precursors of individual elements are used in MOCVD. So, the formation and distribution of the defects in a chemical vapor deposition process may be very different from those in the physical deposition process. The Zr ions in MOCVD REBCO films may not form $BaZrO_3$ particles or the sizes, shapes, or distribution required for effective pinning centers. A key objective of the present work was to establish MOCVD conditions for effective pinning by Zr doping in REBCO films.

Our MOCVD process uses a liquid precursor delivery system, which was described in our previous publication.[11] The fabrication details of the buffered substrate architecture, Hastelloy substrate\$Al_2O_3$\$Y_2O_3$\IBAD-MgO\MgO\$LaMnO_3$, were also described in our previous publications.[1,2]

The MOCVD conditions to optimize the sizes, shapes, and distributions of $BaZrO_3$ and RE_2O_3 particles required for effective pinning centers include ratios of Ba/RE and Cu/RE, growth temperature, growth rate, and layer thickness in each pass of multipass deposition process, as described below.

It is found that J_c is impacted mostly by the composition of the film specified by atomic ratios of Ba/RE and Cu/RE. Our experiments indicated that the composition for optimized J_c should be rare earth rich. A nominal ratio of RE:Ba:Cu in our REBCO films is 1.3:2:3, which is far off from the stoichiometric ratio of 1:2:3. The additional rare-earth ions in the film have been found to result in abundant nanometer-sized precipitates of RE_2O_3, which are effective pinning centers to increase the I_c in self-field as well as in an applied magnetic field.[12] Furthermore, Y-rich or RE-rich phases can reduce the formation of CuO and $BaCu_3O_4$, which are deleterious to the I_c of the film.

The amount of Zr dopants needs to be high enough to generate the density of defects to enhance the flux pinning in a strong magnetic field. However, too large an amount of the nonsuperconducting content will suppress the self-field and

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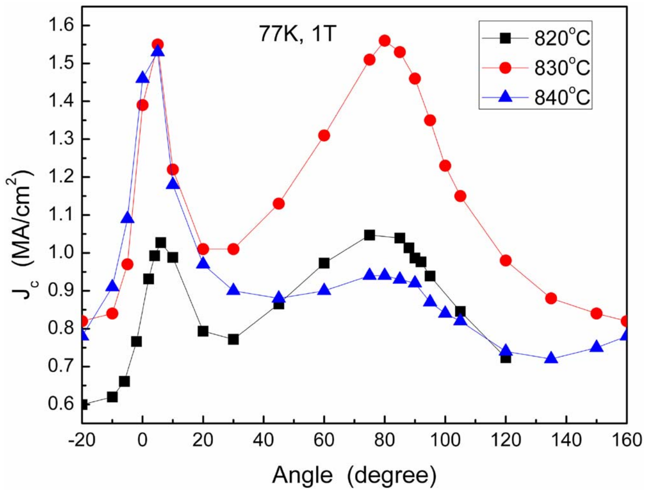

FIG. 1. (Color online) Critical current density J_c as a function of angle between the magnetic field and the film surface at 77 K and 1 T for $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ films with thicknesses of about 0.35 μm grown at different temperatures. 90° is the direction of magnetic field perpendicular to the film surface.

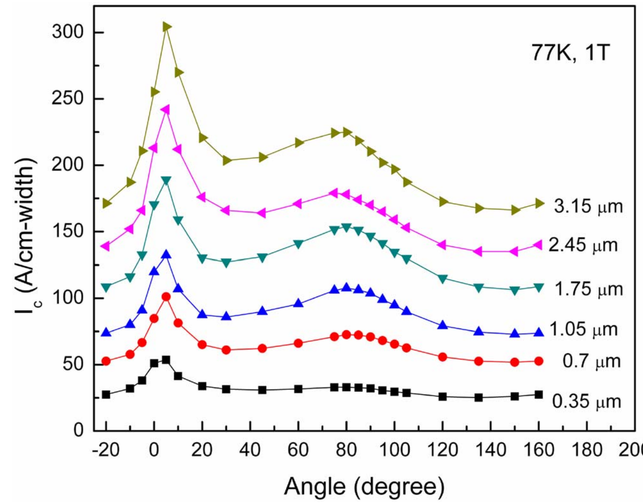

FIG. 2. (Color online) Critical current I_c as a function of angle between the magnetic field and the film surface at 77 K and 1 T for $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ films with various thicknesses grown in a multipass process. 90° is the direction of magnetic field perpendicular to the film surface.

low field J_c significantly. Our experimental results showed that Zr mol ratio below 6.5% did not significantly suppress the self-field J_c. In the present work, we used 0.065:0.65:0.65:2:3 for the ratio of Zr:Gd:Y:Ba:Cu in the films and denoted the composition as $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$.

Deposition rate was proved to be an important parameter in forming effective Zr related pinning centers in the Zr:GdYBCO films. At a growth rate above 0.5 μm/min, which was the rate we regularly used in growing REBCO films without Zr-additions, it was difficult to establish a MOCVD condition that yielded significant improvement in performance of the films. The possible reason may be that the growth rate of crystalline BZO columns is low. In this work we reduced the deposition rate for Zr:GdYBCO films to $\sim$0.13 μm/min.

The temperature window for high $J_c(B)$ in growth of Zr-added GdYBCO films is narrow. Figure 1 shows the magnetic-field angle dependences of critical current densities at 77 K, 1 T for three $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ films with thicknesses of about 0.35 μm deposited at different temperatures. The self-field J_c values for the three samples were 5.1, 6.2, and 5.4 MA/cm^2 for the growth temperatures (temperatures at the growth surface) of 820, 830, and 840 °C, respectively. As seen from the figure, a higher deposition temperature resulted in a suppression of the J_c peak at $B \| c$. This finding is in contrast to that reported in BZO doped YBCO films fabricated by PLD where higher temperatures yield better performance at $B \| c$.[13] At lower temperature, J_c was low over the whole angular range.

Multipass deposition has been proven to be effective in growing thick REBCO films with high critical current. In this technique, a thick film is fabricated by growing multiple thinner films one atop each other in distinct MOCVD runs. This approach enables high tape speed in each run as well as the capability to modify process conditions in each run separately to achieve higher J_c in thick films. It should be noted that no nonsuperconducting interlayer is used between the multiple superconducting films, unlike Foltyn *et al.*[14] who employed a YBCO/CeO_2 multilayer structure. In multipass-processed REBCO thick films, the sizes of secondary-phase particles were found to be smaller compared to those in single-pass processed thick films. In this work, the film thickness increment in each pass was 0.35 μm. The fabrication of sample tapes of $Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ and $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ started with buffered substrate tapes of 2.5 m in length and 12 mm in width. The tapes were moved at a speed of 5 m/h to pass through the deposition zone (22 cm in length) multiple times in our research MOCVD reactor. After each pass, about 10 cm of the tape was cut off for I_c testing and microstructural characterization. After multiple passes were completed, over 1 m in length remained with the final thickness for I_c testing and other characterizations.

Figure 2 shows the magnetic-field angle dependences of the I_c at 77 K and 1 T for $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ tapes processed in a nine-pass process. The film growth tempera-

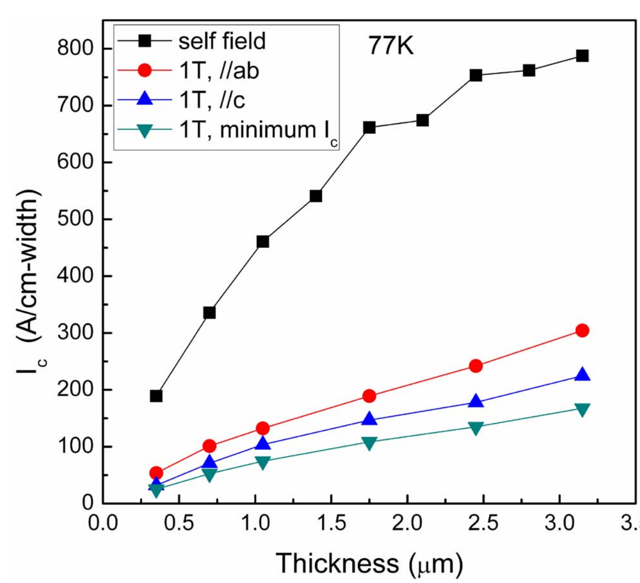

FIG. 3. (Color online) Thickness dependences of I_c for $Zr_{0.065}Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ films at 77 K, 0 T and 77 K, 1 T with $B \| ab$, $B \| c$, and B in a direction resulting minimum I_c.

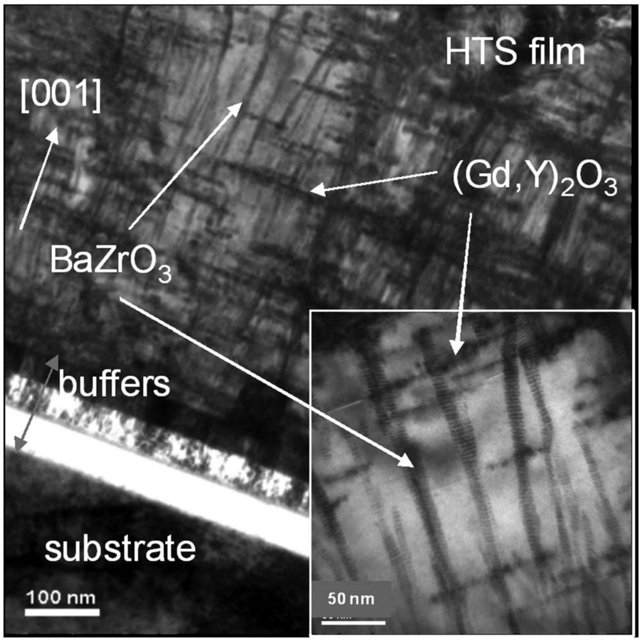

FIG. 4. Cross-section TEM of $Zr:Gd_{0.65}Y_{0.65}Ba_2Cu_3O_7$ film showing the BZO nanocolumns distributed in the film in addition to $(Gd,Y)_2O_3$ nanoprecipitates.

ture was about 830 °C in every pass except the first pass. In the first pass of this series, the growth temperature was about 840 °C, being higher than the best set point. It can be seen from Fig. 2 that the I_c at 1 T shows a peak at $B \| c$ for every pass except the first pass. The final tape with 3.15 μm thick Zr:GdYBCO film obtained from the nine-pass process was 1.3 m in length with end-to-end I_c of 788 A/cm width at 77 K and self-field. At 77 K and 1 T, the I_c value was above 168 A/cm width. The 1.75 μm thick Zr:YBCO obtained in the fifth pass showed a minimum I_c(77 K,1 T) of 108 A/cm width, which was as high as the highest I_c(77 K,1 T) obtained in GdYBCO (2.8 μm) films without Zr-additions. The thickness dependences of $I_c(77\ \mathrm{K}, B\|c=1\ \mathrm{T})$, $I_c(77\ \mathrm{K}, B\|ab=1\ \mathrm{T})$, minimum of I_c(77 K,1 T) and I_c(77 K,sf), are plotted in Fig. 3.

It should be noted from Fig. 3 that the $I_c(B=1\ \mathrm{T})$ increases near linearly with the film thickness for every field direction, though the self-field I_c tends to be saturated when the thickness approaches 3 μm. The results indicate that increasing film thickness can be a way to improve in-magnetic-field performance.

The multipass processes described above were repeated twice and obtained comparable results. In a ten-pass process, 1.2 m in length of Zr:GdYBCO (3.5 μm) tape with I_c(77 K,0 T) of 803 A/cm width was obtained. Achieved in another ten-pass process was a 1 m in length of Zr:GdYBCO (3.3 μm) tape with I_c(77 K,0 T) of 813 A/cm width and I_c(77 K,1 T) of 186 A/cm width. These are the highest reported values for meter-long 2G HTS tapes.

A typical cross-section transmission electron microscopy image of the thick Zr:GdYBCO film is shown in Fig. 4. As seen from the figure the BZO columns are aligned primarily along the *c*-axis but also splayed over an angular range. Such an array of *c*-aligned columnar defects should be responsible for the improved I_c in the orientation of $B\|c$ as well as other intermediate angles.

A high density of $(Y,Gd)_2O_3$ nanoprecipitates was also found in the Zr:GdYBCO films with an average size of ~9 nm as determined via x-ray diffraction peak-broadening analysis. The RE_2O_3 nanoparticles are highly oriented with respect to the RE-123 matrix. Some of them formed layers parallel or at a small angle to the *a-b* plane of the GdYBCO film. The planar structures of RE_2O_3 crystallites may be responsible for the strong peak in $I_c(B)$ at $B\|ab$, beyond the contribution of intrinsic pinning from the modulated Cu–O planes. The $I_c(B)$ peak at $B\|ab$ for Zr:GdYBCO was found to be lower than that for GdYBCO, though both had similar self-field I_c values. This was possibly due to the disruption of the aligned nanocrystalline RE_2O_3 by the columns of BZO in Zr:YGdBCO.

In summary, the MOCVD conditions derived in the present work have resulted in the formation of a microstructure with a unique combination of vertically aligned BZO nanocolumns and horizontally aligned layers of RE_2O_3 nanoprecipitates in GdYBCO matrix, which has led to substantial enhancement in the in-magnetic-field performance of the HTS tapes.

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