We explored ways both to enhance Jc and to optimize/simplify the manufacturing procedures for coated YBa2Cu3Ox (YBCO) conductors. For Jo-enhancement, we found that the nano-size interface-irregularity through inserting a (Nd 1/3Eu1/3Gd1/3) Ba2Cu3Ox sublayer is an effective way to enhance the critical current density (Jc). Enhancements up to 50% have been observed, especially under high magnetic fields. We also found that the Ca-substituted overlayer on YBCO films with poor crystalline structure can significantly improve the grain misalignment and Jc. Partial substitution of Y by rare earth elements as previously suggested, however, does not lead to better performance in our synthesis conditions. For manufacturing, copper-metal with electroplated Ni-layer and Ce02-buffer layer has been tested as a cheaper and more convenient alternative for the traditional textured Ni. High crystalline texture has been achieved. The in-plane misalignment angle, 5-10°, is comparable to those on traditional rolling-assisted biaxially textured substrate (RABiTS). Photo-assisted MOCVD has also been tested in synthesizing both the buffer layer and YBCO films. Reasonable Jc (77 K) up to 10 6 A/cm2 has been achieved with a very fast process rate.
Summary

We explored ways both to enhance $J_c$ and to optimize/simplify the manufacturing procedures for coated YBa$_2$Cu$_3$O$_x$ (YBCO) conductors. For $J_c$-enhancement, we found that the nano-size interface-irregularity through inserting a $(\text{Nd}_{1/3}\text{Eu}_{1/3}\text{Gd}_{1/3})\text{Ba}_2\text{Cu}_3\text{O}_x$ sublayer is an effective way to enhance the critical current density ($J_c$). Enhancements up to 50% have been observed, especially under high magnetic fields. We also found that the Ca-substituted overlayer on YBCO films with poor crystalline structure can significantly improve the grain misalignment and $J_c$. Partial substitution of Y by rare earth elements as previously suggested, however, does not lead to better performance in our synthesis conditions. For manufacturing, copper-metal with electroplated Ni-layer and CeO$_2$-buffer layer has been tested as a cheaper and more convenient alternative for the traditional textured Ni. High crystalline texture has been achieved. The in-plane misalignment angle, $\Delta \phi \sim 5$-$10^\circ$, is comparable to those on traditional rolling-assisted biaxially textured substrate (RABiTS). Photo-assisted MOCVD has also been tested in synthesizing both the buffer layer and YBCO films. Reasonable $J_c$ (77 K) up to $10^6$ A/cm$^2$ has been achieved with a very fast process rate.

Achievements

A. Enhanced Pinning in YBCO Films through NEG Sublayer

We have enhanced pinning in films of YBa$_2$Cu$_3$O$_y$ (YBCO) by inserting a superconducting Nd$_{1/3}$Gd$_{1/3}$Eu$_{1/3}$Ba$_2$Cu$_3$O$_x$ sublayer, which possesses a nano-undulated interface (Fig. 1). $J_c$ enhancement up to 50% is observed over a wide range of fields and temperatures (Table 1, Fig. 2). Transmission electron microscopy shows a high density of dislocations and stacking faults, which lead to nano-domains with sizes of 20x20 to 25x40 nm$^2$ (Fig. 3). The atomic planes in such domains rotate 2-5$^\circ$ against the surrounding matrix, as shown in moiré patterns. They distribute randomly and uniformly without noticeably changing the epitaxial nature of the matrix as suggested by the rather slow decrease of $J_c$ under field (Fig. 4). We attribute the enhanced flux pinning to these nanostructures.
Fig. 1: AFM image of surface area of an NEG film deposited on STO, serving as a sublayer for subsequent deposition of a YBCO film. The NEG growth granules with diameters of 80–100 nm and heights of 20–25 nm appear nearly mono-disperse in $5 \times 5 \, \mu\text{m}^2$ scale.

Table 1: The table shows $J_c$, in units of $10^7 \, \text{A/cm}^2$ for the YBCO film grown on a NEG sublayer at different temperatures. Shown also is the $J_c$ of a reference YBCO film.

<table>
<thead>
<tr>
<th></th>
<th>5 K</th>
<th>60 K</th>
<th>77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO/NEG/STO</td>
<td>7.2</td>
<td>1.8</td>
<td>0.46</td>
</tr>
<tr>
<td>YBCO/STO</td>
<td>4.7</td>
<td>1.2</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Fig. 2: Critical current density in YBCO films as a function of applied magnetic field. The solid symbols represent YBCO/NEG (100 nm/50 nm) film, and open symbols show 100 nm YBCO on the bare STO substrate.
Fig. 3: (a) TEM image of the two-layer film cross-section taken under mass contrast imaging conditions. (b) Conventional TEM bright-field image of the interface. In both panels, the arrow points at the undulated YBCO/NEG interface. (c) Selected area diffractogram representing the full YBCO/NEG/STO structure. (d) High resolution TEM of the YBCO layer showing several areas (see arrows) with rotational moiré patterns.

Fig. 4. The field effect of the transport $J_e$ of a film at 5 K.
B. \(J_c\) Enhancement through Rare-Earth Substitution

We have studied the substitution of rare earth Ho, Nd, and Sm. The results are shown in Figures 5-7. In most cases, the enhancements are small. In some cases (e.g. the Ho-doped one in Fig. 6), the \(J_c\) is even two times lower than that of YBCO films. Previously reported \(J_c\) enhancement by rare-earth substitution in melt-textured and polycrystalline bulk YBCO samples was not observed here.

Fig. 5. The effects of Nd substitution.

Fig. 6. The effect of Ho substitution.
C. Healing Weak-Links through Ca-Substituted Over-layers

It was first pointed out by Mannhart et al. that a thin over-layer of Ca-doped YBCO can improve the supercurrent carrying capability, or critical current density ($J_c$) of YBCO across a grain-boundary caused by a crystal-misalignment. We have therefore examined the effects of YCBCO on the grain alignment and microstructures of and on the doping to the grain-boundaries of YBCO. YBCO films on an MgO-substrate with poor crystal orientation (so poor initial $J_c$) were used as the starting base. Our results demonstrate unambiguously that a YCBCO over-layer can greatly improve the overall crystallinity of the poorly aligned YBCO films and that there exists an optimal layer-number ($n$) of the multi-layer YBCO($n$ layers)/YCBCO($n$-1 layers) for maximum $J_c$-enhancement while keeping the total YBCO/YCBCO film thickness constant (Fig. 8). The observations suggest that an YBCO/YCBCO multi-layer healing technique for low-cost high-performance YBCO-coated conductors can be developed by relaxing the stringent and costly requirements for precise atomic alignment employed in the previous fabrication methods.

To explore the origin, the pole-figures of the multi-layer YBCO/YCBCO films with $n = 1, 2$ and $3$ were determined and are shown in Fig. 9. All the films are well c-oriented.
The (00l) rocking curves show very little difference. However, the (103) pole figures shows that the in-plane grain alignment is different for films of different n’s. In Fig. 9, Film A shows the (103) pole figure for the single layer YBCO thin film on a MgO substrate and indicates that most grains in plane are aligned along the MgO (100) direction. A small amount of grains are aligned along the MgO (110) direction. Some grains are randomly oriented in the plane. Fig. 9 Film B shows the (103) pole figure for a YBCO/YCBCO film with n = 3. It is evident that most in-plane grains are aligned along MgO (100) direction. Only a small amount of the grains orient at a 45-degree angle. No randomly oriented in-plane grain was observed. Fig. 9 Film C shows the (103) pole figure for a YBCO/YCBCO film with n = 5. All the in-plane grains are aligned along the MgO (100) direction. The n = 7 YBCO/YCBCO film pole figure is basically similar to that for the n = 3 film. A correlation of \( J_c \) with the in-plane alignment induced by YCBCO over-layer is therefore established and the existence of an optimal n for maximum \( J_c \)-enhancement demonstrated.

![Graph: \( J_c \times 10^7 \) A/cm² vs. Number of layers](image)

Fig. 8. \( J_c \) versus layer number.
D. Texturing of Ni and Ni alloy Substrates
Deposition of YBCO thick films on biaxially textured metallic substrates represents one of the most promising technologies for fabrication of high current superconducting tapes. One of the most advanced techniques to produce appropriate substrates is the rolling-assisted biaxially textured substrate (RABiTS) process that involves mechanical rolling and subsequent heat treatment to develop the \{100\}<100> or cube texture. Nickel and Ni alloys are the most widely used substrates.

A study regarding the role of mechanical deformation in texturing of coated conductor composites has been carried out. Mechanical deformation per pass and total deformation have determinant roles on texturing of Ni substrate. The degree of cube texture increases with increasing the percentage of total mechanical deformation and using a smaller percentage reduction per pass. To obtain pure cube textured substrate after recrystallization, it is essential to have uniaxial deformation during the mechanical deformation treatment. Thus lateral spread during mechanical deformation should be avoided because the amount of lateral spread, which depends on the deformation per pass, strongly influences the quality of the cube texture obtained after recrystallization.

The pure Ni substrate has an in-plane alignment of 6.9° and out-of-plane alignment of 6.1°. We have also fabricated the Ni3%atW alloy substrates with sharp cube texture in-plane alignment of 7.5° and out-of-plane alignment of 4.5°. AFM measurements show the substrate with very smooth surface. The roughness value \(R_{rms}\) is about 0.343 nm. In addition, these texture characteristics are found to be reproducible.

E. Electroplated Ni Layer on Textured Cu Substrate for Cu-based HTS Coated Conductors
Alternative Cu-based coated conductors have been developed, in which textured Cu is used as the substrate. In general, such substrates have the advantages of easy formation of a sharp cube texture, no ferromagnetic contribution to hysteretic AC losses, low cost compared to nickel or nickel alloy substrates and low resistivity. The primary disadvantage, however, is that Cu has poorer resistance to oxidation than Ni and Ni alloy substrates, especially in an oxygen atmosphere at the high temperatures necessary for the fabrication of YBCO superconducting layers. One potential solution for overcoming this problem is to deposit a metal protective layer over the textured Cu substrate to reduce the...
Cu oxidation rate and protect its diffusion to YBCO. Electroplating has been used for many years to fabricate decorative and protective metallic films. It is non vacuum, low cost, fast and easily scalable, which gives the promise for the production of long length Cu-based coated conductor tapes.

The Cu substrates were mechanically deformed by rolling followed by annealing at temperature 800 °C for 60 minutes. The FWHM values of these substrates were typically found to be 4.2° and 6.5° for out-of-plane and in-plane alignments, respectively. A low cost, non vacuum and easily scalable technique of electroplating was developed for the production of long-length RABiTS-based coated conductor tapes. Smooth, crack-free and continuous 1-4 μm thick electroplated Ni overlayers were deposited on cube textured Cu substrate without any intermediate layers. After high temperature heat treatment, both the Cu substrate and Ni overlayer retain the cube texture and chemical stability. Fig. 10 shows the 0-20 x-ray scans for 3 μm Ni overlayers electroplated on textured Cu substrate after heat treatment at 750 °C for 30 minutes. The FWHM values of electroplated Ni for in-plane and out-of-plane alignments to be 6.40° and 4.66°, respectively. Sharp cube textured Sm-doped CeO\textsubscript{2} buffers have been grown on Ni plated Cu substrate using pulsed laser deposition with in-plane and out-of-plane FWHM values of 6.50° and 5.25°, respectively. The superconducting quality of this template was tested with YBCO deposition. X-ray studies shown in Fig. 4 indicate that YBCO films have good out-of-plane and in-plane textures with full-width-half-maximum values of 6.5° and 8.1°, respectively.

![Fig. 10. The 0-20 x-ray scans for 3μm Ni overlayers electroplated on textured Cu substrate after heat treatment at 750 °C for 30 minutes.](image)

**F. MOD approach to fabricate buffer layers**

Metalorganic decomposition (MOD) techniques use high molecular weight precursors and water insensitive carboxylates, 2-ethylhexanoyates, etc. These chemical processes offer many desirable aspects such as precise control of metal oxide precursor stoichiometry and composition, ease of formation of epitaxial oxides, and the ability to be scaled-up at low cost.

The application of the MOD process to buffer layer deposition has resulted in highly oriented epitaxial SrTiO\textsubscript{3} and CeO\textsubscript{2} thin films. The Ω scans show both the SrTiO\textsubscript{3} and CeO\textsubscript{2} buffer layers have a good out-of-plane alignment on rolled Ni substrate. The pole
figures indicate a single cube-on-cube texture and SEM observations reveal a continuous, dense, and crack-free microstructure. The average FWHM for out-of-plane alignment is about 6-7° and for in-plane alignment about 7-8°. AFM studies show a smooth surface with an average roughness value of 3 nm that is suitable for deposition of further layers. Efforts are underway to grow YBCO directly on SrTiO$_3$ and CeO$_2$ buffered Ni substrates.

**G. A New Precursor for High Quality CeO$_2$ Buffers**

Metal alkoxide complexes are attractive metal oxide precursors because of the ease at which their properties (e.g., boiling point and thermal stability) can be tuned by changing the alkoxide-ligand substituent. In the present study, the cerium(IV) alkoxide complex Ce(OCMe$_2$-i-Pr)$_4$, a volatile, non-fluorinated source of cerium, was used as a chemical vapor deposition precursor to cerium oxide films. A conventional thermal chemical vapor deposition process rapidly deposited cerium(IV) oxide films from Ce(OCMe$_2$-i-Pr)$_4$ on silicon, glass, quartz, lanthanum aluminum oxide (001), and roll-textured nickel (001) substrates at low substrate temperatures (<550 °C). The films were highly oriented when the depositions were carried out on the lanthanum aluminum oxide and textured nickel substrates (e.g., Fig. 11). An X-ray crystallographic study of Ce(OCMe$_2$-i-Pr)$_4$, which melts at just below room temperature, shows that it is a loosely bound dimer in the solid state with five-coordinate cerium centers and two bridging alkoxide ligands (Fig. 12). The successful deposition of films on textured nickel suggests the possibility of using these cerium oxide films as buffer layers in YBCO-based coated conductor applications. Further studies to demonstrate the practicality of using the films for these applications are needed.

![Fig. 11. Electron backscatter diffraction pattern for the film deposited at 500 °C on a roll-textured nickel (001) substrate.](image1)

![Fig. 12. The structure of [Ce(OCMe$_2$-i-Pr)$_4$)$_2$ from a single-crystal X-ray crystallographic study.](image2)

**H. Photo-assisted MOCVD for rapid deposition of YBCO**

Photo-assisted MOCVD (PhAMOCVD) has been successfully used to enhance MOCVD growth rate of YBCO and buffer layers for the development of second generation coated
conductors. YBCO thick films were deposited by using PhAMOCVD technique with a single liquid precursor delivery system. The metalorganic precursors of Me(TMHD)$_n$ (Me=Y, Ba, Cu; TMHD=2,2,6,6-tetramethyl-3,5-heptanedionate) were dissolved in tetrahydofuran (THF). During deposition, the precursor solution was pumped into a preheated evaporator, and the precursors were instantaneously evaporated and transported by the carrier gas to the reactor. Films of several thicknesses (1.2 μm, 2.2 μm, and 4.2 μm) were grown on LaAlO$_3$ substrates at a film growth rate of 0.3–0.4 μm/min. SEM cross-section micrographs of these three YBCO films show very solid and uniform films with no visible signs of pinholes or grain boundaries. The thick YBCO films are strongly textured with c-axis perpendicular to the substrates. X-ray ω-scan and φ-scan measurements show that both the out-of-plane and in-plane texture is of high quality with (for the 2.2μm thick film) the θ-2θ scan reveals a fully c-axis-oriented film, and a φ-scan through the YBCO (113) peak showing an in-plane FWHM of ~1.6° and an out-of-plane FWHM of only 0.21°. The results of these XRD analyses confirm further that these YBCO thick films obtained by PhAMOCVD technique possess very high crystalline quality.

For Coated Conductor application, however, the high quality thick film YBCO needs to be integrated with a metal substrate through appropriate buffer layers. We have chosen to investigate a single buffer layer for this purpose and have focused on the CeO$_2$ system. We have found that doping of the CeO$_2$ with Sm (Sm$_0.2$Ce$_{0.8}$O$_{2.5}$ - SCO) resulted in films grown on textured nickel substrates that were generally biaxially ordered over the range of deposition temperatures of 500-800 °C under 500 mTorr forming gas (4% H$_2$ with 96% Ar) pressure. However, good (100) orientation was obtained for the Sm-CeO$_2$ film in temperature range of 600 °C to 700 °C as indicated by strong SCO (200) diffraction lines and low SCO (111) diffraction lines in the XRD data. A more important advantage of adding the dopant to the CeO$_2$ buffer layer is that the oriented SCO buffer layer can avoid the cracking problems seen in undoped CeO$_2$ layer, even for SCO buffer of several hundred nanometers thick. YBCO films of ~0.5μm thickness were grown on 0.6μm thick SCO buffer layers on roll-textured nickel by PhAMOCVD. The YBCO film was dense and crack free. The XRD θ-2θ scan of the sample after YBCO deposition indicated that the buffer layer was primarily (100) oriented, and the YBCO film was (001) oriented. XRD pole figure and φ-scan analysis on the YBCO sample indicated an SCO (111) FWHM of 7.8° and a YBCO (103) FWHM of ~11° (Fig. 13). The in-plane azimuthal orientation of SCO was rotated 45° relative to the substrate and the YBCO film due to the ~$\sqrt{2}$ lattice parameter difference for the buffer layer with the substrate and the YBCO. $J_c$ for the YBCO film was measured at 77K, with the result of 1.06 x10$^6$A/cm$^2$. 
Fig. 11. The YBCO pole figures for the YBCO/CeO$_2$/Ni/Cu coated conductors.

Publications


Presentations
