

The Progress on Low-Cost, High-Quality, High-Temperature Superconducting Tapes Deposited by the Combustion Chemical Vapor Deposition Process

Shara S. Shoup, Marvis K. White, Steve L. Krebs, Natalie Darnell, Adam C. King, Dave S. Mattox, Ian H. Campbell, Ken R. Marken,¹ Seung Hong,¹ Bolek Czabaj,¹ M. Paranthaman,² Hans M. Christen,² Hong-Ying Zhai,² and Eliot Specht²

MicroCoating Technologies, Inc., 5315 Peachtree Industrial Blvd., Atlanta, GA 30341

¹Oxford Superconducting Technology, 600 Milik Street, P.O. Box 429, Carteret, NJ 07008-0429

²Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831

ABSTRACT

The innovative Combustion Chemical Vapor Deposition (CCVD) process is a non-vacuum technique that is being investigated to enable next generation products in several application areas including high-temperature superconductors (HTS). In combination with the Rolling Assisted Biaxially Textured Substrate (RABiTS) technology, the CCVD process has significant promise to provide low-cost, high-quality lengths of YBCO coated conductor. Over 100 meter lengths of both Ni and Ni-W (3 at. Wt.%) substrates with a surface roughness of 12-18 nm were produced. The CCVD technology has been used to deposit both buffer layer coatings as well as YBCO superconducting layers. Buffer layer architecture of strontium titanate (SrTiO₃) and ceria (CeO₂) have been deposited by CCVD on textured nickel substrates and optimized to appropriate thicknesses and microstructures to provide templates for growing PLD YBCO with a J_c of 1.1 MA/cm² at 77 K and self-field. The CCVD buffer layers have been scaled to meter plus lengths with good epitaxial uniformity along the length. A short sample cut from one of the lengths enabled high critical current density PLD YBCO. Films of CCVD YBCO superconductors have been grown on single crystal substrates with critical current densities over 1 MA/cm². In addition, superconducting YBCO films with an I_c of 60 A/cm-width ($J_c = 1.5$ MA/cm²) were grown on ORNL RABiTS (CeO₂/YSZ/Y₂O₃/Ni/Ni-3W) using CCVD process.

INTRODUCTION

High-temperature superconductors hold great promise for offering tremendous energy and cost savings to the electric power industry. Over the past several years, scientists have investigated the potential YBCO coated conductors have to offer and have achieved very high current densities on single crystal substrates as well as coupon-sized flexible metallic substrates. Efforts are turning towards scaling the deposition process to obtain practical lengths of coated conductor to begin investigating "real product" usage. Once these trials have succeeded, the focus will be on achieving long length, large volume production at a cost that will be competitive with copper. Scaling is a task in itself with many factors to consider in maintaining the high quality over the long length while providing coated conductor at a viable cost.

The CCVD technology has considerable potential to overcome many of the shortcomings of traditional vapor deposition techniques while yielding equal or better quality coatings at a lower cost. As a result, capital requirements and operating costs are reduced at least tenfold when compared to competing vacuum-based technologies (e.g. sputtering and MOCVD). The ability to

deposit thin films in a non-vacuum atmosphere enables continuous, production line manufacturing. Consequently, throughput potential is far greater than with conventional thin-film technologies, most of which are generally restricted to batch processing. Such advantages can help decrease the cost of fabricating HTS tape over traditional deposition technologies and thus help meet DOE's target cost goals for making HTS tape competitive with copper.

EXPERIMENTAL DETAILS

In the traditional CCVD process (Fig. 1), precursors are dissolved in a solvent which typically acts as the combustible fuel. This solution is atomized to form submicron droplets by means of the Nanomiser technology, proprietary to MCT (patent pending). These droplets are then convected by an oxygen stream to the flame where they are combusted. A substrate is coated by simply drawing it through the flame plasma. The heat from the flame provides the energy required to evaporate the droplets and for the precursors to react and to vapor deposit on the substrates. Substrate temperature is an independent process parameter that can be varied to actively control the film's microstructure, epitaxy, and oxidation of the nickel substrate. In the case of the buffer layer depositions, a localized reducing atmosphere is also used to prevent nickel oxidation, and a solvent system with lower carbon content is used to minimize carbon deposition in such an atmosphere. Dynamic seals allow for continuous substrate passage between the open air and the localized reducing atmosphere.

One of the largest challenges in tailoring the CCVD system for deposition of YBCO was the removal of all carbon sources from the process. Once formed, barium carbonate is difficult to remove and detrimental to the performance of the superconductor coating. The process was modified to allow for use of aqueous solutions in the deposition of YBCO. A new Nanomiser for the atomization of aqueous solutions and the use of a hydrox flame resulted in successful YBCO depositions on single crystal substrates.

DISCUSSION

Buffer Layers: Optimization and Scaling

Buffer layer depositions were initiated on single crystal substrates to prove the viability of using CCVD to deposit layers that could be used as suitable templates for the growth of high-performance YBCO. Critical current densities $> 3.5 \text{ MA/cm}^2$ were obtained on CCVD buffer layers on single crystal substrates. The focus then moved to depositing layers onto textured metal substrates. MCT partnered with Oxford Superconducting Technology who supplies the substrates and is in the process of scaling the textured metal to 100 plus meter lengths. Several architectures of buffer layers have been deposited by CCVD using SrTiO_3 , CeO_2 , YSZ, and LaAlO_3 , with SrTiO_3 and CeO_2 being the only layers to be grown epitaxially directly on Ni. The architecture enabling the highest performance PLD YBCO has been a 250 nm SrTiO_3 layer with a 40 nm CeO_2 cap layer. Phi scans performed on an architecture of SrTiO_3 with a CeO_2 cap layer yield an average full width at half maximum (FWHM) phi value of 8.3° and 8.7° for SrTiO_3 (111) and CeO_2 (111), respectively, while (002) omega values are 9.8° and 8.0° . MCT

has continued to refine the deposition temperature, thickness and microstructure of the buffer layers and, in conjunction with ORNL, has demonstrated that PLD YBCO with a $J_c > 1 \text{ MA/cm}^2$ can be deposited onto CCVD RABiTS (Figure 2).

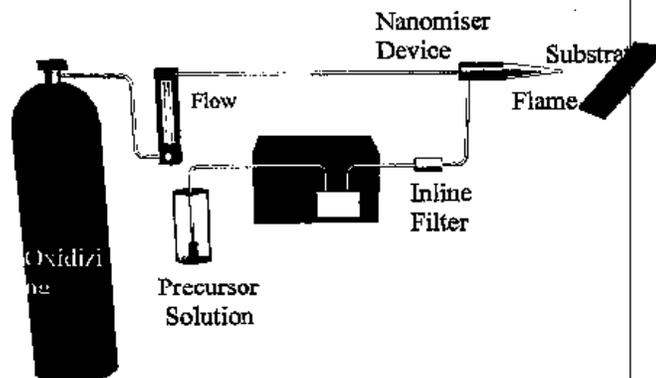


Figure 1. Schematic representation of CCVD technique.

Ceria seed layers can also be grown on Ni and yield ~1% of misorientation. Alternative architectures will be explored using this seed layer in the future. Sulfur content on the surface has been found to be an important factor in determining the amount of misorientation that is grown in the initial seed layer. X-ray Photoelectron Spectroscopy (XPS) has been used to detect the amount of surface sulfur, and a correlation has been drawn between sulfur percentage and percentage of misorientation. XPS is now used as a diagnostic technique to screen batches of Ni, and Oxford is investigating the metal rolling and heat treatment processing steps required to achieve consistent diffusion of sulfur to the surface.

With successful coupon-sized samples of CCVD RABiTS fabricated, MCT focused on scaling this technology to meter lengths of tape. A meter length of tape was first made using the same single Nanomiser system used to produce the small samples. A thin layer of SrTiO_3 (estimated to be ~ 5 nm based on time and solution concentration ratios) was deposited in two passes to provide the seed epitaxial layer. A higher concentration of SrTiO_3 solution was then used to deposit a growth layer of the desired thickness (~ 250 nm) in the second pass. A third pass deposited the CeO_2 cap layer (~40 nm). X-ray diffraction analyses (Table 1) taken from small samples on each end of the meter indicate that there is a minor amount (< 3.5%) of both in-plane and out-of-plane misorientation in the SrTiO_3 layer but no detectable misorientation in the CeO_2 cap layer. PLD YBCO deposition performed by the Oak Ridge National Lab onto one of these end pieces resulted in a critical current density of 1.1 MA/cm^2 as measured by ORNL.

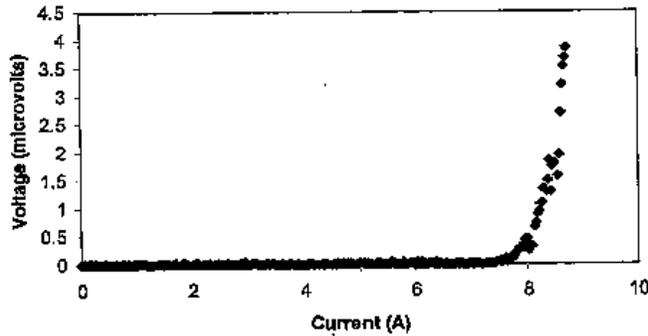


Figure 2. I_c as a function of applied voltage for PLD YBCO/CCVD Buffer/Ni: $I_c = 7.944$ A, 0.44 cm wide sample and 170 nm thick YBCO translates into a J_c of 1.06 MA/cm².

Reel-to-reel XRD analyses (Figure 3) indicate fairly good uniformity along the length with a higher degree of misorientation seen in CeO₂ in- and out-of-plane and SrTiO₃ in-plane around 50 cm. The cause of this is unknown but the uniformity rebounds slightly after this position. This figure is the XRD analyses showing the uniformity of the CeO₂ in-plane along three different lengths of tape (different deposition runs) that have been spliced together for ease of analysis. The first segment is the piece made from the single Nanomiser system described above.

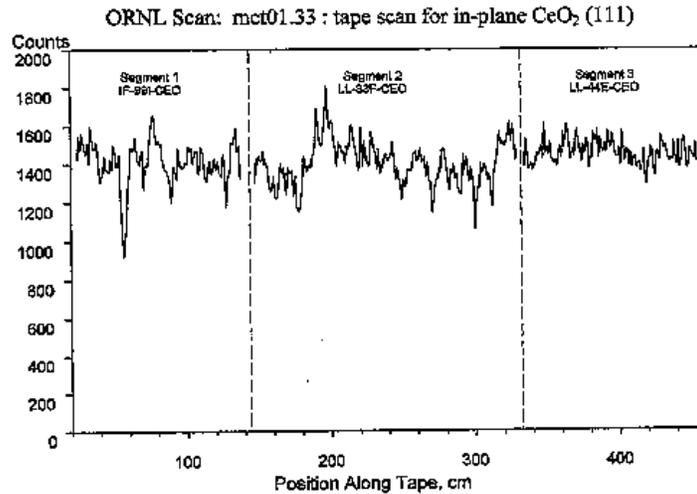


Figure 3. CeO₂ cap in-plane texture uniformity for three meter-plus buffered lengths.

The next scaling step was to replicate the current set-up to yield a multi-Nanomiser system made up of four units to decrease deposition time and thus increase throughput. In most cases, two of the Nanomisers provided the seed layer and then the tape was rewound and traversed through the system again with three Nanomisers delivering the growth SrTiO₃ layer and the last Nanomiser providing the CeO₂ cap. Several runs have been made using this system with XRD analyses performed (Table I). Slight changes in deposition parameters including the rate at which the tape moved (and thus the number of Nanomisers providing the layer) and the concentration of the solution account for the varying degree of misorientation and FWHM changes among the different tapes. The second and third segments in Figure 3 are tapes made using the multi-Nanomiser system. The last segment shown has the lowest FWHM values and is the most uniform along the length. Coupons of the ends of this segment will be coated with PLD YBCO to determine their effectiveness as buffer templates. Attempting to deposit the desired thickness and architecture in a single pass through four Nanomiser systems required increasing the concentration of the solution providing the SrTiO₃ growth layer to 1.5 x. This resulted in the largest amount of misorientation, as can be seen for the tape with the ID number LL-50D. Ideally, a five Nanomiser system would be required to deposit a desired thickness in a single pass under the current deposition conditions. Further increasing the number of Nanomisers would increase the rate.

Table I. Epitaxy characterization for meter lengths.

Run ID	Out-of-Plane				In-Plane			
	CEO		STO		CEO		STO	
	% Misorient.	(002) Omega FWHM	% Misorient.	(002) Omega FWHM	% Misorient.	(111) Phi FWHM	% Misorient.	(111) Phi FWHM
IF-99I	0.00	9.51 ^a	2.15	7.23 ^a	0.00	7.92 8.34 ^a	3.36	8.49 9.10 ^a
LL-22D	26.01	∞	23.35	11.25	47.0	14.73	-0	10.15
LL-33F	2.93	9.56 ^a	3.48	7.35 ^a	0.00	10.77 8.33 ^a	0.00	8.60 8.32 ^a
LL-44E	0.00	8.80 ^a	1.82	6.97 ^a	7.96	8.69 7.98 ^a	9.91	8.62 8.30 ^a
LL-49D	0.00	12.46	1.36	11.09	0.00	8.64	0.00	7.46
LL-50D	11.39	8.84	4.53	7.59	6.75	9.21	13.86	7.75

Superconductors – Optimization on single crystals and CCVD RABiTS

YBCO deposited onto single crystals by CCVD has achieved the benchmark performance, critical current density value (J_c) of 1 MA/cm² (Figure 4). This was performed in the open atmosphere using an aqueous solution of nitrates. Although additional oxygen can be entrained during deposition from the surrounding air, the best critical current densities were obtained when the sample was annealed in flowing oxygen for 50 minutes in an in-line furnace at 500 °C immediately after deposition and then quenched to room temperature. Without the anneal, J_c values were around 850,000 A/cm². Critical transition temperatures for such samples are typically between 85 and 91 K (Figure 5).

Depositing CCVD YBCO on CCVD RABiTS is currently under investigation. A localized reducing atmosphere, or at the least an inert atmosphere, is still required even in the presence of

the buffer layer to minimize the oxidation of the metal substrate. Not only have the traditional challenges of abating NiO formation during YBCO growth along with epitaxy and compositional control been prevalent, but some deposition conditions cause breakdown of the buffer layer and thus formation of excessive, random BaCeO₃ or BaTiO₃ when SrTiO₃ and CeO₂ layers are used. In these cases, the original buffer layers have been randomized or appear with significantly reduced intensities.

Conditions have been identified where the buffer layer remains intact and functional and thus minimal NiO formation is seen. Work will continue in this area as composition, deposition rate, formation temperature, etc. will be investigated further. It may also be necessary to modify the architecture or thickness of the CCVD RABiTS from that used with PLD YBCO to obtain the highest performance CCVD YBCO possible.

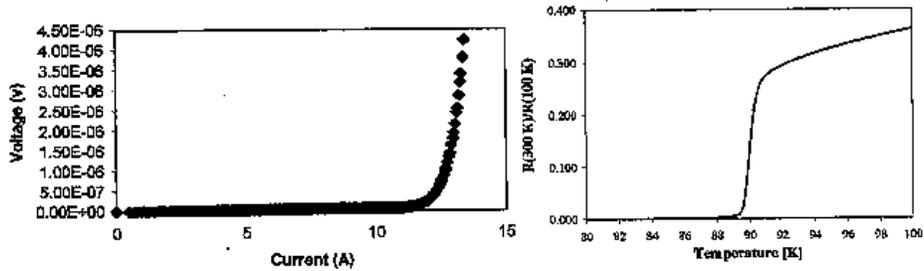


Figure 4 (left). I_c as a function of applied voltage for CCVD YBCO/LAO single crystal: $I_c = 12.22$ A, 0.3 cm wide sample, and 380 nm thick YBCO translates into a J_c of 1.07 MA/cm^2 .

Figure 5 (right). Resistance as a function of temperature for a YBCO coating deposited by CCVD.

In addition, superconducting YBCO films with an I_c of 60 A/cm-width ($J_c = 1.5 \text{ MA/cm}^2$) were grown on ORNL RABiTS (CeO₂/YSZ/Y₂O₃/Ni/Ni-3W) using CCVD process. The I-V plot for the same film is presented in Figure 6.

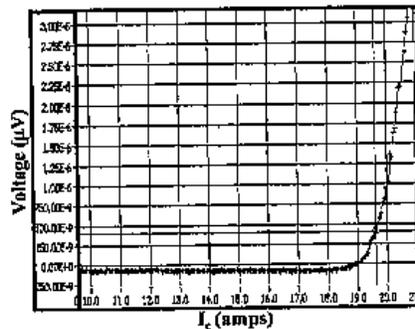


Figure 6. I-V plot for CCVD YBCO/ORNL RABiTS (CeO₂/YSZ/Y₂O₃/Ni/Ni-3W): $I_c = 19.6$ A (60 A/cm-width).

CONCLUSIONS

Scaling the CCVD buffer layer deposition process to longer and longer lengths was a preeminent focus for MCT. CCVD buffer layer depositions onto alloy substrates have yielded promising results. Research on CCVD YBCO on CCVD RABiTS is encouraging and this could be a path towards achieving low-cost YBCO coated conductors..