Nanotechnologies to enable high-performance superconductors for energy applications

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Abstract

High Temperature Superconductors (HTS) wires or coated conductors (CC) hold promise to revolutionize the transmission of electricity enabling the present electric grid to meet the world's growing energy needs. Although superconducting wires can carry 150 times more power than copper wires of the same cross section, further performance improvements are necessary for the superconducting technology to become cost-competitive. This objective can be achieved by introducing and controlling nano-sized defects and non-superconducting phases within the superconducting film's matrix. Such nanostructures, when carefully engineered, significantly increase the loss-free current sustained by the superconductor through a mechanism known as flux pinning. This chapter is a review of the various types of nanostructures that are artificially introduced in superconducting films to enhance the superconductor's performance. Different approaches, materials, and techniques are discussed and the most recent results in this field compared. The last section of this chapter discusses an additional example of

nanotechnology employment in superconducting wires. This nanotechnology can be regarded as an atomic surface treatment designed to enable the right crystallographic orientation of the superconducting film deposited on the metal template.

Overcoming limitations to superconductors' performance

Efficient transport and storage of energy are two key factors in the formidable quest to meet the world's growing energy needs. Because electricity is the energy form of choice for most uses, and the most effective way to transport energy from and to different locations, addressing the energy problem means necessarily addressing the shortcomings of the present electric power grid. Capacity and reliability of the present grid are entirely inadequate to accommodate an expected growth in energy demand of 50% by the year 2030, most of which will be concentrated in urbanized areas whose infrastructures are already severely congested. In addition, 7 – 10 % of the electricity generated is lost in the grid by heat dissipation, and transmission limitations have already caused black outs throughout the world. Superconducting cables made with high critical temperature (T_c) cuprate superconductors have the potential to transform the grid to meet the 21st century demands. Such cables can carry five times more power than copper cables with the same cross section and exhibit considerable lower losses (loss-free dc transmission). Because lower losses enable longer transmission lengths, superconductors provide the best choice for building a new, non-fragmented, super grid that will enable massive long-distance power transmission, interconnect entire continents, and provide widespread, local energy storage. In such a grid, renewable source power plants in the most remote areas can deliver power anywhere in the continent according to real time demands, and episodic

surpluses are readily stored for future use. High temperature superconducting (HTS) cables can in fact be exploited in conjunction with solar and wind power for building “green power superhighways” or used to serve congested urban agglomerates replacing copper in existing underground transmission conduits. In addition, HTS can provide oil-free transformers, compact motors and generators, superconducting magnetic-energy storage (SMES) units, and fault current limiters, all with much improved efficiency and reliability and more environmentally friendly as compared to the present infrastructure. All these applications require that the high T_c superconductor of choice, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO), be formed into long and flexible conductors that can replace copper wires. By itself, this is already a formidable obstacle because all high T_c superconductors are brittle ceramics, and the large anisotropy of their physical and transport properties requires that all the crystallites in the conductors be very closely aligned along the three principle crystal axes, with the current flowing in the basal (ab) plane. Only ten years ago, there were still serious doubts about whether YBCO could be shaped in the form of kilometers-long wires with the required performance for commercial applications. This doubt has now been lifted thanks to tremendous advances in nanotechnology and the consequent ability to control and engineer oxide/metal interfaces and multilayers of various thicknesses. Successful technology partnerships between research institutions and industrial companies has allowed for the newest scientific achievements to be promptly transferred from the laboratory to large-scale production. Currently, HTS wires are fabricated using the second generation (2G), also called coated conductors (CC) wire technology. They utilize YBCO or similar cuprate oxides with the chemical formula $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ where R is a rare earth or a mixture of rare-earth ions (Nd, Sm, Gd, Dy,

etc.). The superconductor is processed in the form of an epitaxial film deposited by different methods on a near single-crystal flexible template comprising a metal substrate and epitaxial oxide buffer layers. The template is manufactured using two major technologies: the rolling assisted biaxially textured substrate (RABiTS) technology [1-3], and the ion beam assisted deposition (IBAD) technology [4–6]. As shown in Fig.1, the RABiTS approach relies on producing a biaxially textured Ni-5%W alloy template on which oxide buffer layers and the superconductor are epitaxially deposited. In the IBAD approach, the metal alloy substrate is polycrystalline and the biaxial texture is developed in an MgO thin film by the assisted ion beam deposition, and then transferred by epitaxy to the subsequent layers. Wires of 100-500 meters in length carrying currents of over 300 A/cm-width at 77 K (LN₂ boiling temperature) can now be made [7]. Since 2003, several pilot projects sponsored by the Department of Energy – Office Electricity and Energy Reliability (DOE-OE) have been successfully carried out at utility substations in the US, such as the Long Island superconductor transmission cable system, capable of transmitting 574 MW of electric power.

Figure 1 goes here

Despite the tremendous progress made in this area, in order for superconducting cables to become reality, their cost/performance ratio needs further improvement. The critical objective today is to increase the amount of current the superconductor can carry without dissipation in a range of magnetic fields required by the specific application. This can be achieved by carefully playing on two different and related fronts—trying to push the dissipation-free current density (J_c) as close as possible to the theoretical limit, and at the

same time, increasing the thickness of the superconductive layer as much as possible without degrading performance. It is in this final challenge that the newest achievements in nanotechnology come into play as J_c enhancements in thick superconducting films can only be obtained by introducing and engineering extrinsic nano-sized defects within the film.

Flux pinning by nanoscale defects

The importance of nanoscale defects derives from the concepts of magnetic flux lines and flux pinning in the superconductor. The current carried by a type II superconducting film, such as a YBCO film, generates a magnetic field (self field) that penetrates the superconductor in the form of tubular structures called vortices or flux lines, each of them carrying one unit of magnetic field, the flux quantum ϕ_0 . The current interacts with the magnetic flux lines generating a Lorenz-type force (equal to $\mathbf{J} \times \phi_0$) that pushes the vortices across the conductor [8-12]. Because the material within the vortex core is in the normal state, this motion generates dissipation and the superconductor ends up resembling a low resistance conductor. Fortunately, naturally occurring nano-sized defects and secondary phases provide spatial variations in the thermodynamic free energy that act like potential wells for the flux lines. A flux line has a lower free energy when it is positioned in the energy well of the defect than it does in the bulk matrix. This energy difference acts as a pinning force constraining the vortex to remain within the well [13-16]. Figure 2 is a schematic that illustrates the interaction between flux lines and different types of defects in a superconducting film. As the current increases, so does the Lorenz

force and when this exceeds the pinning force (at $J = J_c$) dissipation begins. Therefore, the higher the pinning force, the higher the current the superconductor can sustain without dissipation.

Figure 2 goes here

The picture gets more complicated in presence of an external magnetic field, which is the case for several power applications. In this case, as more flux lines are generated within the superconductor, the density of pinning sites, in addition to their strength, becomes important. The most effective pinning sites are defects whose size is close to the vortex's normal core diameter 2ξ where ξ , the superconducting coherence length, is a few nanometers for the superconductors of interest. This is why artificially introduced nanostructures play a dramatic role in optimizing pinning without destroying an unnecessary volume fraction of the superconductor, thereby allowing for a significant increase in J_c .

The grain boundary problem

Although flux pinning has been the object of numerous studies for many years, efforts aimed at increasing flux pinning in coated conductors by means of extrinsically added defects and nanostructures started only around 2004. The reason for this late interest is that early efforts to optimize coated conductors performance had to face more pressing issues. One of the greatest quandaries was that, even after more ordinary materials issues,

such as interdiffusion of chemical species between the different layers and non-epitaxial growth were addressed, early CC's still showed reduced J_c 's as compared to the J_c of YBCO films of the same thickness on single crystal substrates (e.g. SrTiO_3). The reason for this discrepancy resided in the imperfect texture of the metal-based template, which showed grain boundaries as high as 10 degrees. From early studies of YBCO films on bi-crystals, scientists had learned that grain boundaries of this magnitude dramatically suppress J_c across the grain boundary region (intergrain J_c) [17]. Therefore, strategic research on CC's towards the end of the 90's focused mainly in studying J_c across YBCO grain boundaries in the low angle regime ($2^\circ - 10^\circ$) to establish the critical angle at which the intergrain J_c started departing from the J_c within the grain (intragrain J_c), and in improving CC's texture. The grain boundary problem, and related role of weak links in YBCO, casted a doubt on the technological application of CC's for many years but was finally resolved for both major routes of fabricating CC's through the improvement of the superconducting film texture [18, 19]. Today both techniques are able to produce long wires with a true in-plane texture full-width-half-maximum (FWHM) in the YBCO film of $\sim 4^\circ$. J_c 's comparable to those obtained on single crystals are obtained for wires with such sharp textures. While FWHM's less than 4° are routinely obtained in IBAD coated conductors, RABiTS conductors still show some margin for improving the in-plane texture in the YBCO film. However, comparable J_c values in IBAD and RABiTS conductors suggest that grain boundary meandering during YBCO growth on RABiTS might reduce the current-suppressing grain boundary effect in these conductors [20]. Grain boundaries less than 2° do not essentially affect the performance of YBCO films and actually might be beneficial since their widely spaced dislocation cores provide

additional pinning in magnetic fields. As a result of the study of low angle grain boundaries, it was found that the intergrain $J_c(H)$ curve, although lower than the intragrain $J_c(H)$ curve always joined the latter at a certain field value (see Fig. 3), which increased as the grain boundary angle increased [21]. For fields larger than this crossover field the grain boundary can in principle sustain a higher current density than the grain itself. This finding implies that 1) since all applications of CC's involve some magnetic field, a substrate with a texture of 3° - 4° is equivalent to a single crystal substrate in terms of current performance. In addition, because for fields larger than the crossover field, J_c is limited by the intragrain component, further J_c improvements in this regime can only be achieved by optimizing bulk flux pinning. Additional fixes on the grain boundaries, such as, for example, Ca doping [22] will not produce any observable benefit. Once the limitations imposed by the grain boundaries were reduced, the efforts turned to improving flux pinning by introducing atomic-scale and nano-scale defect structures in addition to those naturally occurring during YBCO processing.

Figure 3 goes here

It is worth noting that while the performance of YBCO films on single crystal was considered an upper limit in early CC's days, such performance lies well below the theoretical limit. The critical current density at which superconductivity viewed as pairing of electrons is destroyed in the absence of any extrinsic material issue is named the depairing current and is roughly 3-4 times higher than the best J_c values obtained today on any YBCO film. Therefore, CC's with performances well above those of thin

YBCO films on single crystal are in principle possible. The questions to be addressed at this point are 1) what kind of nanostructures will offer the best pinning properties, and 2) how can these nanostructures be implemented in various YBCO processing techniques.

Anisotropic current properties

Since the deposition of the first YBCO films on single crystals, many studies have been conducted to investigate the origin for the high J_c of epitaxial films as compared to melt textured and single crystal YBCO samples. The discovery of a well defined type of defect that would dramatically increase flux pinning throughout the H,T phase space has however eluded scientists and the picture that gradually emerged was that of a multitude of point-like and extended defects that acted synergistically producing different outcomes in different regimes. The reason for this complex behavior is that the pinning force depends on many characteristics of a single defect (size, shape, composition) and is not additive for different types of defects. In addition, pinning is affected by vortex-vortex interactions, which become more prominent at higher magnetic fields (the vortices are more numerous and closer together), by thermal activation processes, which can induce depinning of vortices, and by the electronic mass anisotropy, which is due to the layered crystal structure. As a result, the objective is not to increase pinning in general but to target the enhancement in particular H,T regions of interest and for specific orientations of the magnetic field relative to the sample. Often, the pinning enhancement might be very significant in some H,T regions and completely negligible or even deleterious in others. For example, a highly crystalline YBCO film with very few but strong columnar

defects along the c axis might have a record high J_c in self-field [23] because all the vortices produced by the small self magnetic field can be accommodated in deep narrow potential wells, which take away very little superconducting material from the nearly perfect surrounding matrix. However, once the vortices exceed the number of columnar defects, they cannot be effectively pinned and J_c decreases so rapidly with field that the film performance becomes completely inadequate for any real application. .

As a consequence of the anisotropic crystal structure and the presence of many point-like random defects, J_c in as grown YBCO films obtained by various techniques is always maximal when the magnetic field is directed parallel to the ab planes, a situation which is not preferred in all power applications. Figure 4 shows a typical curve for J_c as function of magnetic field orientation for an YBCO film grown by pulsed laser deposition (PLD) on SrTiO_3 . Superimposed to the data points is a curve that represents the contribution to J_c from uncorrelated pinning, produced by randomly distributed localized defects. The random pinning contribution is obtained by fitting the $J_c(\theta)$ data to the scaling curve predicted for electronic mass anisotropy effects alone, according to the analysis of Civale *et al.* [24]. The difference in J_c between the data and the random pinning component is due to correlated pinning provided by extended, parallel pinning centers, either linear or planar, which naturally arise during growth. These defects are usually oriented both along the c axis (especially for PLD films) and parallel to the ab planes. A final contribution to the peak at $H//ab$ is given by intrinsic pinning, also due to the layered crystal structure.

From the point of view of meeting power applications criteria, the goal would be to introduce artificial pinning sites that enhance J_c for orientations close to $H//c$ near to the level of J_c at $H//ab$, giving rise to a more isotropic angular dependence.

Figure 4 goes here

Another way to quantify desirable pinning effects is to analyze the $J_c(H)$ curve for the least favorable field orientation ($H//c$). Typically, in YBCO with only naturally occurring defects, $J_c(H)$ shows a plateau at small fields of the order of 0.1 T, where the defects outnumber the vortices (see Fig. 5). Generally, added pinning sites produce a small effect in this regime because there are already enough defects to pin all the vortices produced by the small field. Although some added defects (such as impurity nanophases) may produce stronger pinning forces than other naturally occurring defects, they are also made of non-superconducting material and necessarily reduce the superconducting areal section and often T_c as well. At intermediate fields, J_c decreases like $H^{-\alpha}$ where α is an exponent ranging between 0.5 and 0.7. However, in the case of strong pinning, such as that produced by nanoparticles/nanorods additions, the α exponent decreases, reflecting a smaller J_c degradation with increasing magnetic field. This is the regime where the introduction of artificial pinning sites plays the largest effect. For fields larger than 2 T a rapid decay of J_c toward zero at the irreversibility field H_{irr} is observed because of depressed vortex line tension and strong thermal activation. Improved performance in this regime can also be observed with added pinning sites, as observed for strong linear defects with high areal density.

Figure 5 goes here

5. Enhancing naturally occurring nanoscale defects

It is well known from flux pinning studies that only defects that are to some degree extended or correlated along the c direction can give rise to enhancement of J_c when $H//c$. Similar to earlier heavy ion irradiation studies on single crystals [25], the best performance results from columnar structures of non-superconducting material that accommodate the vortex core over the entire thickness of the film with a certain amount of splay [26, 27]. On the other hand, randomly distributed localized defects (uncorrelated pinning centers) can produce very strong pinning, but do not give rise to a peak for $H//c$ in the J_c angular dependence at 77 K. One of the first attempts of correlating J_c performance for $H//c$ with the density of extended pinning centers along the c axis was carried out in 1999 [28]. The defects targeted by this study were threading edge and screw dislocations normally occurring during the YBCO growth process, especially in PLD films with their columnar growth mode. Subsequently, another type of strong, naturally occurring, pinning defects, known as antiphase boundaries, were studied in detail using controlled vicinal substrate surfaces to tailor their density [29, 30]. Figure 6 shows a collection of various defects usually occurring in YBCO films as imaged by high resolution transmission electron microscopy (HRTEM).

Figure 6 goes here

One approach to optimize flux pinning is to try to tune deposition conditions and/or the substrate morphology in order to increase the most effective naturally occurring crystal defects. For example, by controlling the size of the YBCO growth islands and the mosaic

spread within a single substrate grain, additional threading dislocations along the c axis can be introduced. However, the increase in defect density obtained through this route is modest and limited to low magnetic fields. Moreover, such an approach is highly dependent on the YBCO deposition method.

By decorating the substrate surface with chemically compatible nanoparticles one can try to disrupt the subsequent YBCO growth just enough to introduce low angle grain boundaries or dislocations of another nature that might tread to the film surface. This approach has been pursued by various research groups in the last few years using different materials deposited in the form of nanoparticles on the substrate (Ir, Ag, Y_2O_3 , ZrO_2 , MgO, $BaZrO_3$) or processing the oxide template so that it develops outgrowths of nanoscale size [31-36]. However, the pinning induced by the defects and strain fields stemming from the surface particles is generally of a random nature and does not provide the desirable enhancement of J_c for $H//c$. Figure 7 shows an example of surface decoration on a $SrTiO_3$ (001) substrate by PLD deposited ZrO_2 nanodots. The YBCO growth is disturbed by the presence of the nanodots, and antiphase boundaries terminating in stacking faults are produced in the growing film. In two cases c -axis correlated defects with consequent significant J_c enhancement for $H//c$ were reported using Y_2O_3 nanoparticles and nanometer sized $SrTiO_3$ outgrowths [34, 37]. Nevertheless, an understanding of the correlation between nanoparticles or outgrowths and the type of defects they generate is lacking and similar nanostructures on the surface of the substrate give rise to different pinning mechanisms within the superconductor. On the other hand, a recent result obtained on *ex situ* YBCO films that did not contain artificially introduced pinning sites shows that the relation between defects and resulting pinning landscape is

still not well understood and *c*-axis correlated defects might not be the only route for enhanced performances [38]. In that study, crystal defects that were not unambiguously identified, gave rise to very strong pinning, yielding an almost isotropic $J_c(\theta)$ curve at magnetic fields as high as 3 T.

Figure 7 goes here

Artificial introduction of flux pinning nanostructures

A different approach, that has produced overall better results, is to introduce nanosized particles of chemically compatible, non-superconducting material throughout the superconductor matrix. This can be accomplished by deposition from multiple sources, in the case of *in situ* methods, or by adding excess elements to the superconductor precursor, in the case of *ex situ* methods. *In situ* ablation from a superconductor pellet already containing the nanoparticle material in a disperse form is another option. Although the uncorrelated pinning from randomly distributed point-like defects is generally weak, randomly dispersed finite size particles can provide strong pinning with significant enhancements throughout the H,T phase space. As several research groups worked on this approach, several examples of impurity additions in the form of nanoparticles and/or nanodots are available. In the first attempts an YBCO non-superconducting phase Y_2BaCuO_5 , also known as 211 was added by intermittently depositing YBCO layers and discontinuous 211 layers by PLD using two deposition targets [39, 40]. This approach resulted in pancake-like 211 particles with an average size of 15 nm distributed in the YBCO film, which produced some enhancement in pinning

along c and much higher improvements for $H//a,b$. Correlated pinning along the c -axis was also observed when seemingly randomly distributed 10- nm -wide $BaZrO_3$ (BZO) particles were inserted in the YBCO film by ablating from a PLD target synthesized using Ba excess and added Zr [41]. In the last study the observed correlated pinning along the c -axis was related to misfit dislocations between the nanoparticles and the superconducting matrix, which aligned along the c direction, with an areal density of $400\ \mu m^{-2}$ compared to $80\ \mu m^{-2}$ for undoped YBCO films. Figure 8 shows high resolution Z-contrast scanning transmission electron microscope (STEM) images of a YBCO film with incorporated Y_2O_3 nanoparticles obtained with the multilayer approach (depositing from a YBCO and a Y_2O_3 target alternately) [42]. In this case, the Y_2O_3 nanodots (3 to 10 nm in size) grew epitaxially aligned with the YBCO in a coherent fashion, without obvious signs of lattice distortions, stacking faults or strain fields. Therefore, the observed pinning enhancement can be assumed to derive from the nanodots themselves and not from defects induced by the nanodots. The films in this study showed strong flux pinning characterized by a better J_c retention in magnetic field compared to pure YBCO films, as indicated by a lower value (0.3 vs. 0.5) for the α exponent. However, the dependence of J_c on the orientation of the magnetic field was typical of random pinning and showed no correlation or preferential direction for the pinning.

Figure 8 goes here

Nanoparticle addition has the great advantage of being applicable to all YBCO deposition methods, including solution-based *ex situ* processes. For example, nanocomposite YBCO

films containing randomly oriented, non-coherent BZO nanoparticles in their matrix were recently processed from complex metal–organic solutions [43]. These films showed strong isotropic flux pinning generated by stacking faults and other lattice defects emanating in the YBCO from the embedded nanoparticles.

Self-assembled nanostructures

When BZO nanoparticles are epitaxially oriented within the YBCO matrix a significant strain field is expected in the growing film due to the large mismatch between the two lattices, which is about 9% when BZO(001)/YBCO(001) and BZO(100)/YBCO(100). Such strain, if properly tuned, can induce a remarkable self-assembly of the nanoparticles resulting in the growth of almost continuous and uniform BZO nanorods in the YBCO matrix. The mechanism responsible for self-assembly has been explored for semiconducting heteroepitaxial structures and is quite complex. Tersoff, *et al.* [44, 45] have demonstrated that in multilayer structures with large mismatch, buried dots can influence the nucleation in subsequent layers, leading to self-organization of a more ordered and uniform array. Formation of an island on the surface is most favorable where the strain at the surface reduces the mismatch between the surface and the island. Because the nucleation rate is an exponential function of the nucleation barrier, which in turn depends sensitively upon the strain, islands nucleate wherever this strain gives a local minimum in the misfit. Strain mediated self-assembly of nanodots is therefore more prominent for large mismatched heteroepitaxial systems. Analogous to semiconductor heterostructures, a multilayer approach in which continuous YBCO layers and BZO

nanodots are deposited sequentially is expected to produce a near ideal regular array of linear defects embedded within the HTS film matrix, when the layers thickness is properly controlled.

Goyal [46, 47] and MacManus-Driscoll [48] were able to produce such an ordered array of BZO nanodots in YBCO by simply performing laser ablation from a single target comprising a mixture of YBCO powder and BZO nanoparticles. During simultaneous deposition of YBCO and BZO, the two phases were found to separate in the growing film and interact through the strain field similar to consecutively deposited phases. Goyal [49] and Varanasi [50] were able to produce similar nanostructures using different oxides in addition to BZO (CaZrO_3 , YSZ, MgO, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, BaSnO_3) and therefore demonstrate the general validity of this approach. In addition to the strain field that develops around the nanoscale second phases embedded in the matrix, reduction of phase boundary energy also plays an important role for simultaneous deposition of YBCO and BZO, causing the morphology of the second phases to resemble continuous nanorods instead of a stack of nanodots. The nanorods can in some cases extend for the entire film thickness or consist of stacks of shorter nanorods. Theoretical formulations based on energetic and kinetic arguments specify an optimal range of 4 - 12 % for the lattice mismatch of the embedded phase with respect to the REBCO matrix.

Figure 9 shows a HRTEM image obtained from an YBCO/BZO composite films deposited from a YBCO target doped with 2 vol. % BZO nanoparticles. The BZO columns produced by stacking of nanodots and continuous nanorods are clearly visible in the TEM cross-section. The contrast of the BZO rods is generally enhanced in the TEM images by tilting the sample along the $\mathbf{g} = 001$ vector of YBCO. The nanocolumns extend

throughout the thickness of the film, have a diameter of 2 - 3 *nm*, and are aligned along the *c* axis of YBCO.

Figure 9 goes here

Figure 10 shows a plan view TEM image in low magnification with the electron beam directed parallel to the YBCO *c* axis. It is interesting to note that the areal distribution of nanocolumns as shown in this image is not random and the spacing between nearest neighboring columns is fairly uniform, suggesting an interaction-mediated self-organization in the basal plane of the film. The degree of order in the areal distribution of columns can be probed by plotting the autocorrelation function for a bidimensional plot of the nanocolumn positions in Fig 10a. The autocorrelation function of an image *I* is defined as the inverse Fourier transform of $F(I) \times F^*(I)$, where $F(I)$ indicates the Fourier transform of the Image and $F^*(I)$ is the complex conjugate. As the autocorrelation determines the self-similarity of an image, the result always shows a peak in the center (each image point is correlated to itself) and an additional structure that ranges from an amorphous background, for a random distributions of dots, to an ordered peak array, for an ordered lattice of dots. As shown in Fig. 10b, several distinct peaks are observed for the BZO columns distribution around the central maximum and their symmetry resembles that of a square lattice with constant $a \cong 15$ *nm*. From this average spacing we can estimate a maximum pinning force scenario for an applied magnetic field $B_\phi = \phi_0/a^2$ of 8 – 10 T, known as the matching field, corresponding to the ideal situation of each nanocolumn accommodating one flux line. According to this value, significant J_c

enhancement is expected in these films for all field regimes that relevant for certain power applications.

Figure 10 goes here

The high-resolution Z-contrast STEM image of Fig. 11 is a plan view of a single BZO nanorod. Different atomic columns are distinguishable thanks to a dependence of the image intensity on the atomic number. In the YBCO matrix the Ba/Y columns appear brighter than the Cu/O columns and within the BZO, BaO columns appear brighter than ZrO. The image shows that the BZO is epitaxially oriented and coherent with the YBCO matrix, and misfit dislocations form to accommodate mismatch at the corners of the BZO nanorod. Since the nanorods are aligned along the YBCO c direction, the strain from the misfit dislocations is also aligned and extended along this direction. Both the arrays of dislocations and the nanorods themselves are therefore expected to form ideal flux pinning columns, similar to damage tracks by heavy ion irradiation [51, 52].

Figure 11 goes here

The pinning enhancement is evident in Fig.12, which compares J_c dependencies on field magnitude and orientation for an undoped YBCO film on RABiTS and a BZO-doped YBCO film on the same substrate. Both films have a thickness of $0.2 \mu m$. In particular, we notice that the correlated c axis peak in the angular dependence of J_c is very pronounced for the YBCO film containing the BZO nanodots, indicative of strong

pinning defects along the c axis. Although the J_c 's shown in Fig. 12 are large, for practical application of HTS it is also essential to increase the overall current carrying capacity of the coated conductor. The figure of performance of a coated conductor is not the J_c of the YBCO film but the engineering current density J_E of the whole conductor, which is the total current carried by the superconductor, I_c , divided by the total cross section of the conductor. Because the thickness of the superconducting film is only a small fraction (2-3%) of the total conductor thickness, including the substrate and the stabilizing metal overlayer (see Fig. 1), YBCO films with a thickness of a few microns, and therefore larger I_c 's are in fact preferred, provided their J_c is similar to that of 0.2- μm -thick films. Unfortunately, gradual deterioration of the critical current density occurs with increasing superconductor thickness, and in some cases, a dead layer, which provides no contribution to the current carrying ability, forms after a critical thickness of $\sim 1.5 \mu m$.

Figure 12 goes here

This effect has been attributed both to extrinsic material issues, such as roughening of the film/vapor interface, coarsening of precipitates, secondary outgrowths, etc., and the intrinsic healing with thickness of threading misfit dislocations originating at the substrate interface. A first solution to this problem was found by fabricating multi-layered films with alternating YBCO layers less than 1.5 μm thick and intervening CeO_2 interlayers [53]. More recently, several group were able to overcome the extrinsic issues involved with the J_c decay in thick films by optimizing PLD YBCO deposition conditions, and/or using a mixture of Y and Eu instead of pure Y to obtain a smoother and denser film

microstructure [54]. Goyal *et al.* have recently demonstrated record-high critical current values by incorporating 3D self-assembled BZO nanodots, like the ones shown above, in films as thick as 4 μm . The achievement of 3D self-assembly throughout such large thickness was obtained by careful control of the PLD target concentration, homogeneity, and surface roughness, and by optimization of deposition repetition rate and substrate temperature [55]. Figure 13 shows cross-section TEM images of the 4 μm -thick film, illustrating the BZO nanorod structure in the film. It appears that the columns of self-assembled BZO nanodots are not perfectly aligned along the *c*-axis of YBCO at the high deposition rate used to grow the film. The columns show a range of angles with respect to the *c*-axis of YBCO and resemble a ‘splayed’ defect microstructure. Such a ‘splayed’ microstructure appears to be more favorable for flux-pinning at all field orientations [27]. The performance of this 4 μm -thick film on a short section of CC template (I_c of 353 A cm^{-1} at $T = 65$ K, $H = 3$ T) is higher than record values previously reported and exceed minimum requirements for transmission cables, electric ship propulsion systems, large-scale motors, and generators. This result is even more impressive when considering that the BZO nanodots technology was successfully transferred from ORNL to SuperPower, one of the leading US Company in 2G coated conductors manufacture. Interestingly, the self-assembly of BZO dots is not confined to the PLD process but also occurs, with proper processing tuning, during YBCO growth by MOCVD, a highly scalable technique used by Superpower to produce kilometer long superconducting cables [56].

Figure 13 goes here

Effect of local strain fields in nanocomposite films

In composite superconducting films, the incorporated nanocolumns give rise to local strain modulations, which have important effects not only on pinning but also on oxygen stoichiometry and T_c . Differently from (and in addition to) the macroscopic, unidirectional strain that arises in YBCO films due to epitaxial growth on a substrate with slightly different lattice parameter, the array of vertical interfaces between BZO nanocolumns and YBCO matrix produces a much more localized, non-monotone strain field, which varies on the nanoscale and produce measureable broadening of XRD peaks. XRD analysis shows that such a local strain increases with increasing BZO concentration and thus nanocolumns density, as shown by the square symbols in Fig. 14b for both PLD- and MOCVD- deposited films [55, 57, 58]. Finite element strain distribution calculations for the YBCO-BZO system (Fig. 14c) deviate significantly from the XRD measurements, as shown by the triangular symbols in Fig. 14b. Such a discrepancy originates from misfit dislocations present at the vertical YBCO/BZO interfaces, which render these interfaces non-coherent. Modeling dislocations within the finite element calculation does indeed produce microstrain estimates closer to the experimental values, as shown by circles in Fig 14b for the less computational intensive case of diluted nanocolumns, for which the ratio between nanocolumn length, d , and distance between nanocolumns, L ; $d/L = 1$. The experimental films considered in this study fall in the more concentrated limit $d/L \sim 20$.

Figure 14 goes here

In addition to an increase in local strain, an increasing BZO concentration above ~ 4 vol % also produces a significant drop in T_c with a linear trend of ~ 0.4 K/ vol %.

Understanding the cause of such unexpected drop in T_c and reconciling microstrain measurements with theoretical predictions was possible using aberration-corrected Z-contrast STEM coupled with EELS, which allows lattice displacement and chemical concentration analysis at the nanoscale [59]. Figure 15 shows a single BZO nanorod sectioned for TEM using the focus ion beam (FIB) technique. The nanorod is embedded in a REBCO film (RE is a mixture of Y and Gd) grown by MOCVD and having a BZO volume fraction of 4.1%. The Z-STEM image shows that tilt and misfit between the relative lattices of rod and matrix is accommodated by tilt dislocations with Burgers vector $1/2(100)$, as indicated by circles, and misfit dislocations with Burgers vector $1/2(101)$, which are active in relieving misfit strain (indicated by arrows). The average spacing between dislocations is ~ 3 YBCO unit cells (3.5 nm). A similar average spacing D can be calculated using the equation $D = b_z/(f_o - \varepsilon_o)$, where f_o defines the original misfit between lattices, ε_o is the residual misfit strain, and b_z is the Burgers vector component along the interface plane. Choosing $\varepsilon_o = 1.9\%$, as suggested by Fig. 14 comparing theoretical and measured microstrain¹ gives $D = 2.7$ YBCO unit cells, showing excellent agreement between STEM and XRD. The local strain can be quantified directly through the Z-STEM images by measuring the variation of the REBCO c axis parameter. The variation in c axis spacing shown in Fig. 15b is derived by finding the center of mass for the intensity distribution of each Ba and Y/Gd column in the desired region (dashed box in the figure) and then averaging the calculated c spacings in the direction parallel to the

¹ Fig 14 b shows that the experimental slope is reduced to nearly 24% of the simulation for the case $d/L = 20$ and coherent interface, indicating that 76% of the original misfit has been relieved and the effective residual misfit strain is $\sim 24\% \times 8\% = 1.9\%$. This reduction is caused by misfit dislocations that form at the YBCO/BZO interface, giving rise to a semicoherent REBCO/BZO phase boundary.

interface. The quantity shown in the figure is the difference between this average and the bulk lattice spacing c_0 well within the matrix, $(c-c_0)/c_0$. The data are compared in the same figure with the theoretical prediction obtained by analytically solving the anisotropic elastic boundary value problem of the bimaterial interface dislocations [60].

Fig. 16 goes here

The theoretical trend is similar to the data extracted by Z-STEM with some difference in the location and magnitude of the peak, which can be attributed to an additional mechanism for strain relief unaccounted for by the theoretical model: the presence of oxygen vacancies. The existence of a relationship between film stress and oxygen nonstoichiometry has been reported in the literature for perovskites at interfaces [61, 62] and grain boundaries [63]. In REBCO/BZO nanocomposite films, the local O stoichiometry was investigated by electron energy loss (EELS) elemental maps of film regions incorporating the rod, as shown in Fig 16. The simultaneously acquired, Z-sensitive annular dark field (ADF) signal shows a bright contrast in the REBCO region immediately adjacent to the BZO rod, which is indicative of lattice distortions. The region showing the brightest shade in the ADF map appears as darkest in the O-K map. That is, the O signal shows a minimum in the REBCO region immediately surrounding the rod, which is highly strained according to the discussion above. In contrast, the Ba and Cu maps show maximum and minimum values, respectively, within the BZO rod and exhibit a constant contrast level everywhere else in the surrounding REBCO matrix. Since the heavier atoms show a constant concentration outside the BZO rod, the dark

contrast in the O map cannot be caused by electron beam dechanneling and is correlated to lattice strain. Local probing of the Cu valence using the Cu-L_{2,3} edge is another way to assess oxygen deficiency. As shown by the ratio of the L₃ and L₂ lines, the Cu valence is lower in region 1, adjacent to the BZO rod than in region 2, within the REBCO matrix, indicating lower O coordination at the interface with the nanorod. The same behavior for the Cu-L_{2,3} edges is observed in all of the spectrum images acquired, indicating that the oxygen deficiency is present everywhere within the strained region surrounding the nanorods and is not localized in certain points. A picture then emerges in which the strain surrounding the nanorods hinders proper REBCO oxygenation, and the resulting substoichiometry reduces somewhat the strain at the phase boundary, partially explaining the discrepancy with analytical calculations (Figure 15b). Oxygen deficiency readily suppresses T_c in REBCO and the observed distribution of oxygen depleted regions explains the reduced T_c in REBCO films with self-assembled BZO nanorods for concentrations of 4 vol% and above. The diameter of the BZO rods is 6 - 8 nm and the average spacing between BZO rods is ~20 nm for a BZO concentration of 4 vol %. The observed spatial extent of oxygen depletion is 3 - 4 times the BZO rod diameter; therefore an overlap of oxygen-depleted REBCO regions surrounding BZO nanocolumns is expected to occur near or above this concentration, leading to the disruption of current percolation through the high T_c phase and to a lower measured T_c. On the other hand, nanostrain modulations are highly effective in pinning vortices, and, in the case of randomly oriented BZO nanoparticles, the resulting pinning force is found to be isotropic [64], leading to an almost constant J_c as a function of magnetic field orientation, which is highly desirable for applications involving superconducting coils. Dislocations and strain

at REBCO grain boundaries also produces oxygen depletion, which, however, can be mitigated by impurity additions (e.g., Ca) [63,65]. Therefore, doping might be effective in locally raising T_c while, at the same time, maintaining the positive pinning effect of nanostrain, hence further improving the critical current in nanocomposite superconducting films.

Fig. 17 goes here

Control of epitaxy-enabling atomic sulfur superstructure

In addition to the nanostructures added to the superconductor to enhance its performance, the successful processing of long lengths of 2G HTS wires is based on the employment of several other nanotechnologies. A great example of nanotechnology use in coated conductors is given by the atomic surface treatment of the Ni-W surface prior to the deposition of oxide buffer and superconductor layers in RABiTS coated conductors. Before 2001, it seemed natural to assume that a deposited oxide layer nucleated on a clean and pure Ni or Ni-W surface. Before deposition, the native metal oxide was removed by an *in situ* reducing heat treatment, and unwanted re-oxidation of the Ni surface was prevented by choosing an oxide layer thermodynamically more stable than NiO (e.g., CeO_2 or Y_2O_3) and by depositing it in reducing conditions for Ni. At this point, the lattice match between metal and oxide buffer layer was supposed to be the main factor influencing epitaxial growth. This picture, however, ultimately proved to be inadequate, particularly after the introduction of continuous reel-to-reel processes for fabricating kilometers-long buffered tapes. In fact, irreproducibilities in the oxide layer

texture and unwanted crystal orientations threatened to stop further development of coated conductors in the early stage of industrial scale-up. Careful structural and chemical investigations subsequently revealed the existence of a $c(2 \times 2)$ sulfur superstructure on the textured Ni surface that formed after diffusion and surface segregation of sulfur contained in the metal bulk at a level less than 30 wt ppm [66]. It was found that a fully developed atomic sulfur superstructure on the Ni surface, corresponding to half monolayer of S atoms, enabled the epitaxial nucleation of the oxide buffer layer and consequently the right crystal orientation for the superconductor. In cases where the bulk S contents of particular batches of Ni or Ni-W were much lower than 30 wt ppm, and therefore inadequate to spontaneously produce the surface superstructure, the buffer layer deposition process produced films with degraded texture or mixed crystal orientations. However, annealing the Ni-W substrate at 800 °C in the presence of a small amount of H₂S was sufficient to produce a stable $c(2 \times 2)$ -S with the desired coverage of 0.5 ML [67]. This simple step allowed creating a complete S template independently of the coverage obtained through segregation. Implementing this step in a continuous RABiTS fabrication process provided a solution to the irreproducibility issues and enabled subsequent stages of development. The role played by the S superstructure can be partially explained on the basis of structural and chemical considerations. The S layer behaves like a template that matches and mimics the arrangement of the oxygen atoms of particular (001) sublattice planes of YSZ, CeO₂, or STO. Sulfur belongs to the VI group and is chemically very similar to oxygen, often exhibiting the same electronic valence. Therefore, it is plausible that during the oxide buffer layer deposition the cations easily bond to the S atoms already present on the

substrate surface, giving rise to the desired (001) epitaxial growth of the film, which otherwise would not take place. Such structural argument for the effect of the S template on buffer layer nucleation is supported by the observation that other oxides with crystal structures very similar to perovskites and fluorites, like LaMnO_3 , and Gd_2O_3 or Y_2O_3 also grow epitaxially on (100) Ni (or Ni-W) only in presence of an intervening $c(2 \times 2)$ -S superstructure. Figure 14 illustrates the above proposed model of epitaxial growth on a S-terminated (001) Ni surface for SrTiO_3 and CeO_2 . Today, Y_2O_3 is used instead of CeO_2 or SrTiO_3 as first oxide buffer layer for its improved structural and diffusion properties. However, the Y_2O_3 crystal structure is very similar to that of CeO_2 and the model applies to Y_2O_3 as well.

Figure 17 goes here

Acknowledgments

The authors would like to thank Prof. L. Civale, Dr. D. Christen, and Dr. M. Varela for providing some of the figures. Research supported by the US Department of Energy, Office of Electricity Delivery and Energy Reliability and by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. The Research was performed in part at the Shared Research Equipment User Facility, a DOE-BES user facility.

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Figure captions

Fig. 1. Schematic of the two major technologies for HTS wires. The RABiTS architecture, (a), involves a sharply textured, single-crystal-like Ni-W alloy substrate on which Y_2O_3 , YSZ, and CeO_2 are epitaxial deposited to provide chemical and structural compatibility for the superconductor (YBCO) deposition. In the IBAD architecture, (b), the metal tape is polycrystalline Hastelloy. The texture is developed in the MgO film and transferred to the YBCO through a LaMnO_3 layer. The Al_2O_3 layer serves as a diffusion barrier between oxides and metal. In both techniques the superconductor is capped with a $\sim 1 \mu\text{m}$ -thick Ag layer followed by a $\sim 50 \mu\text{m}$ -thick Cu layer for electrical, thermal, and environmental stability.

Fig. 2. Schematic diagram illustrating unpinned and pinned magnetic flux lines and random and extended defects. Columnar defects are capable of pinning the flux lines over the full length and, therefore, provide strong pinning effects.

Fig. 3. J_c dependence on magnetic field for YBCO thin films on a single crystal, representing the intragranular J_c (black line), and SrTiO_3 bicrystals with [001] tilt or in-plane tilt angles of 2° , 4.5° , 7° , 15° , 20° , and 24° . YBCO films grown on single crystal SrTiO_3 are expected to show a mosaic spread of at least 1.8° as a consequence of twinning domains [20]. The schematic to the right of the figure illustrates the direction of magnetic field, current, and pinning force in the measurements.

Fig. 4. Angular dependence of J_c for a $1.55\ \mu\text{m}$ -thick YBCO film on SrTiO_3 at 5 T. Note that the largest current density is obtained when the field lies in the a,b plane. The solid line represents the random pinning contribution. The various angular ranges of pinning are indicated. Courtesy L. Civale. The schematic on the right illustrates the geometry used in the measurements.

Fig. 5. Magnetic field dependence of J_c . Three regions are distinguishable: a plateau at very small fields, a power law dependence at intermediate fields, and a rapid decay for fields larger than 1-2 T.

Fig. 6. Nanosize defects typically observed in YBCO films for coated conductors: (a) antiphase boundaries (the crystal cells of two adjacent grains are out-of-registry along the c -axis); (b) stacking faults; (c) second phase spherical nanoparticles; (d) elongated, platelet-like intergrowths; (e) a -axis grains (the YBCO grows with the $[100]$ perpendicular to the substrate); (f) low angle grain boundaries formed when slightly misoriented grains coalesce during growth.

Fig. 7. (a) SrTiO_3 substrate decorated with ZrO_2 nanodots deposited by PLD. (b) antiphase boundaries, stacking faults and plane buckling developed around a surface nanoparticle in the YBCO film grown on the decorated substrate shown in (a). In this particular sample J_c was enhanced by a factor of 2 at $H = 1\text{ T}$ and $T = 40\text{ K}$ with respect to a control YBCO film on bare SrTiO_3 .

Fig. 8. Cross-section high-resolution STEM of a YBCO/Y₂O₃ composite film deposited with the multilayer approach. (a) Nanoparticles (indicated by arrows) are clearly discernible, with sizes ranging from 3 to 10 nm and about 5 to 20 nm apart. (b) High-resolution image of a Y₂O₃ nanoparticle, coherent with the YBCO matrix.

Fig. 9 Cross-section TEM image of a YBCO film on RABiTS with self-assembled BaZrO₃ (BZO) nanodots and nanorods. The image shows that the BZO nanodots are aligned along the *c* axis of YBCO and are about 2-3 nm in diameter.

Fig. 10. Low magnification, plan view TEM image of a YBCO film on RABiTS with self-assembled nanodots of BaZrO₃ (BZO) showing some degree of order in the areal distribution of the nanocolumns (a). Corresponding autocorrelation function plot for an image derived from (a) by highlighting the BZO columns (b). The appearance of peaks around the central (auto-correlation) peak indicates a degree of ordering among the BZO columns.

Fig. 11. Z-contrast STEM image of a single BZO nanodot. Four misfit dislocations can be seen around the BZO nanodot. The extra semiplane in the edge dislocation cores are marked in blue. Different sets of planes in the YBCO and BZO are indicated.

Fig. 12. Left: log-log plot of normalized J_c as a function of applied field showing that the power law exponent in the relation $J_c \sim H^{-\alpha}$ is lower in the YBCO film with self-assembled nanodots than for the control, undoped YBCO film. Right: angular

dependence of J_c at 77 K, 1T for an undoped YBCO film on RABiTS compared to a YBCO film with 2 vol. % BZO nanodots. Significant enhancement of J_c is seen at all angles, particularly at $H//c$ (angle = 0°). Both superconducting films have a thickness of 0.2 μm .

Fig. 13. Cross-section HRTEM images of BZO nanocolumns in a 4- μm -thick YBCO film. The columns extend through the entire thickness of the film and show small deviations in their direction from the YBCO c direction.

Fig. 14. (a) TEM micrograph illustrating the morphology of a 4 vol % BZO nanocolumn array embedded in the YBCO matrix. (b) Volumetric average of the out-of-plane strain (ϵ_{33}/f_0 ; f_0 = lattice misfit) calculated through finite element method for the case $d/L = 1$ (d) Strain versus BZO concentration as calculated by the finite element method for the cases $d/L = 20$ coherent interface (triangles), $d/L = 1$ coherent interface (black dots), $d/L = 1$ incoherent interface (circles), and measured by X-ray diffraction for PLD films (open squares) and MOCVD films (filled squares). Adapted from ref. 57.

Fig 15. (a) High-resolution Z-STEM image of a sectioned BZO nanocolumn. dashed circles indicate pure tilt dislocations; white arrows indicate misfit dislocations. (d) Comparison between analytically calculated strain (dots) and experimentally derived strain (squares). Adapted from ref. 57.

Fig 16. (a) EELS maps of O-K, Ba-M4,5, Cu-L2,3, and Gd-M4,5. The top map is the signal from the ADF detector acquired simultaneously to each spectrum. (b) Comparison of Cu-L_{2,3} edges after removal of plural scattering by deconvolution for the regions labeled 1 and 2 in (b).

Fig. 17. Schematic model for the nucleation of CeO₂ and STO on a (001) Ni surface with chemisorbed $c(2 \times 2)$ sulfur superstructure. The dashed lines indicate correspondence between oxygen sites in (001) planes of the seed layer and sulfur sites on the Ni surface. The seed layer cations impinging on the Ni surface bond easily to the sulfur atoms present on the metal surface, promoting the (001) orientation of the growing film. In the STO case, there is a 1:1 correspondence between oxygen atoms in the SrO plane and sulfur atoms on the Ni surface. Therefore, it is plausible that Ti ions initially bond to the S surface atoms to form the first TiO₂ plane of the STO structure. In the CeO₂ case, two of four oxygen ions/unit cell match the sulfur atoms of the $c(2 \times 2)$. During nucleation of CeO₂, oxygen atoms may fill in the empty fourfold Ni hollows and the Ce cations subsequently bond to the template formed by S and O.

Fig. 1

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Fig 14

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Fig 16

Fig. 17