Integrated pinning centers in $\text{YBa}_2\text{Cu}_3\text{O}_x$ thick films on single-crystalline and textured metal substrates

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Abstract. The second-generation coated tapes of high temperature superconductors (HTS) deposited on textured metal substrates strongly rely on the introduction of extended nano-defects in order to enhance their critical current. A proven effective way to introduce such defects is growing $\text{BaZrO}_3$ (BZO) nano-rods and an alternative way is to generate HTS columnar growth using nanoparticles of noble metals. Here we report the combination of these methods. It allows achieving controlled pinning and high critical current in $\text{YBa}_2\text{Cu}_3\text{O}_x$ films deposited on single crystal substrates and significantly improves critical current in coated conductors deposited on rolling-assisted biaxially-textured metal substrates (RABiTS). The superconducting properties of thick (up to 5 micron) conductors are analysed using DC-magnetisation, AC-susceptibility and angle-dependent transport measurements. TEM imaging is used to confirm the presence of extended defects in the tapes.

1. Introduction

The tapes of high temperature superconductors (HTS) deposited on textured metal substrates known as second-generation HTS wires promise to revolutionise applications of superconductivity. Strong research efforts to develop cheap and effective way of the introduction of extended defects to enhance pinning and critical current in these wires is under way. A proven effective way to introduce nano-defects in films deposited on single-crystal and technical metal substrates is growing $\text{BaZrO}_3$ (BZO) nano-rods [1,2]. An alternative way already applied to films on single crystal substrates is to use nanoparticles of noble metals to generate columnar growth of $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) films [3]. This method allows depositing thick films without strong decrease in critical current density with thickness.

Recently a new method has been introduced for YBCO films deposited on single crystalline SrTiO$_3$ substrates that combined the two methods described above [4]. It allows to achieve controlled pinning and high critical current in low magnetic fields along the $c$-axis, which is important for cable applications, and high magnetic fields in the $ab$-plane of YBCO, crucial for magnet application of superconductivity. The transmission electron microscopy (TEM) revealed entangled nano-threads of BZO and YBCO in these films. In a 5 $\mu$m-thick film, large critical current per centimetre of width $I_{c-w}$ (the actual important parameter for practical applications) at 77.3 K in high fields has been obtained. The achieved value of $I_{c-w}$ was 170 A/cm-w in 1 T, 90 A/cm-w in 1.5 T, and 60 A/cm-w in field of 2 T [4]. A combination of high $I_{c-w}$ with suitable behaviour in magnetic field of different orientation

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promises to make it a valuable method for films deposited on metal substrates. Here we clarify its potential by growing integrated films on rolling-assisted biaxially textured substrates (RABiTS).

The texture in the metal substrates is necessary to eliminate high-angle grain boundaries in HTS films since they strongly affect critical current [5]. The critical current density ($J_c$) decreases exponentially with misorientation angle, and an average misorientation of about $7^\circ$ is sufficient to suppress $J_c$ by an order of magnitude [5,6]. The texturing of long-length metal tapes is not a trivial issue [7] and the process significantly contributes to the price of coated conductors. Especially difficult is to promote grain misorientations with the angle below $7^\circ$ that would allow to achieve the highest possible critical current in the tapes. Preliminary to the growth of HTS films, tapes require deposition of a buffer layer that would prevent diffusion of metal ions into HTS. The buffer layer preserves orientation of the metal tape and the local HTS misorientations are typically close to those in the buffer layer. There is currently no reliable mechanism that would allow the reduction of misorientations in HTS film below those in the RABiTS tape. The integrated method developed in [4] has a specific mechanism of film growth in which nanoparticles of noble metals coherently move perpendicularly to the film surface. Such a motion is not linked to the local misorientations and could reduce them in the film, thereby increasing $J_c$ in the coated conductor. In order to clarify whether it is possible and whether it could work for thick HTS films, we have grown a wide range of YBCO films on RABiTS substrates with and without nanoparticles of noble metals and additions of BZO.

2. Experimental
A range of experimental techniques was used in this investigation. The crystallography of the RABiTS substrates, supplied by 3C-s Ltd., was mapped by electron backscatter diffraction (EBSD) on a scanning electron microscope (SEM) JEOL7000. The buffer layer in the form of a trilayer: CeO$_2$ (0.1 µm), yttria-stabilised zirconia (YSZ, 0.6 µm) and CeO$_2$ (0.1 µm) was deposited on the substrate by pulsed laser deposition (PLD). In the integrated method, the buffer layer was densely covered by Ag nanoparticles (also using PLD) and after that a YBCO/BZO layer was laser-deposited from a YBCO target with 2% of nano-dispersed BZO. All depositions were done in-situ by an excimer KrF 248 nm laser with pulse duration of 30 ns. The substrate temperature was 700 °C for the buffer layer, 780 °C for Ag and 800 °C for YBCO/BZO. The repetition rate of the laser was 8 Hz for the buffer layer and Ag and 5 Hz for YBCO/BZO. For the latter, the repetition rate is lower and the substrate temperature is higher than in preparations of pure YBCO films (6-10 Hz and 780 °C). Such conditions were chosen to promote growth of BZO nanorods [2].

A variety of Ag/YBCO/BZO films of different thickness have been grown in configurations as described above or in the form of quasi-superlattices, in which deposition of the quasi-layer of Ag nanodots was periodically repeated after the growth of YBCO/BZO layer of a certain thickness. The total thickness of the films and quasi-superlattices was between 0.75 and 5 µm.

The critical current density in magnetic field along the c-axis of YBCO was determined from DC magnetization loops of rectangular samples measured on a Quantum Design Magnetic Properties Measurement System MPMS-XL in DC field $\mu_0H$ up to 4.4 T. For a film of planar dimensions $a, b$ ($a>b$), critical current density $J_c$ was calculated from the averaged magnetic moment ($\bar{m}$) using equation:

$$J_c = \frac{4\bar{m}}{a^2bd(1 - \frac{a}{3b})}.$$

This equation represents a critical state model, in which current is constant and equal to $J_c$ in every point of the cross-section of the sample. The $J_c$ is considered to be field-dependent and the gradients of magnetic field are not taken into account when considering $J_c(H)$. Equation (1) can easily be obtained by simple integration from the definition of $\bar{m}$. However, gradients of magnetic field can
be ignored at high fields only, and this equation is not applicable below a certain characteristic field \[8\]. In low fields, \(J_c\) can be calculated by an extrapolation from the higher magnetic fields. For non-magnetic substrates the characteristic field usually does not exceed 0.1 T, but the magnetism of RABiTS substrate shifts it to a higher value. This restricts the ability to correctly determine \(J_c\) from DC measurements in zero magnetic field. In this field we calculated \(J_c\) from temperature \((T)\) dependence of AC magnetic moment, which is measured at frequency of 100 Hz and excitation fields \((h)\) from 5 \(10^{-6}\) T to 4 \(10^{-4}\) T.

In this technique, the imaginary part of AC magnetic moment \(m''(T)\) shows a maximum at certain temperature \(T_{\text{max}}\) and \(J_c\) at this temperature is connected with the excitation field \(h\) by the equation:

\[
J_c(T_{\text{max}}) = \frac{h}{\alpha d},
\]

where \(d\) is the film thickness and \(\alpha\) is a constant between 0.8 and 0.9 that slightly depends on the geometry of the film \[9\]. Due to the low value of \(h\) available in MPMS and the high value of \(d\) in our samples, only small values of \(J_c\) are accessible at temperatures close to critical temperature \((T_c)\).

These magnetisation techniques are only suitable for magnetic field along the c-axis of YBCO or perpendicular to the surface of the film. In magnetic fields of arbitrary orientation, \(J_c\) was derived from the angle-dependent transport measurements on 550 µm long and 18-30 µm wide micro-bridges produced by conventional photolithography and chemical etching. The measurements have been done on a Quantum Design Physical Properties Measurement System (PPMS).

The micro and nanostructure of the samples was analysed on scanning (SEM, JEOL 7000) and transmission (TEM, TECHNAI F20 operated at 200 kV) electron microscopes. The samples for TEM were prepared by focused ion beam milling (FIB) on a FEI Quanta 3D FEG.

3. Results and discussion

Figure 1 shows EBSD grain maps of a typical section of Ni5%W RABiTS substrate tape. The grains are shown by different colour if they are misoriented with neighbour grains by an angle above 1°, 3°, 5°, and 7° for plots a, b, c and d, respectively. If a superconducting film copies the grain map of RABiTS tape, the superconducting current flowing in this section would need to cross several grain boundaries with misorientations at least up to 7°. The misorientation of the last boundary between the blue and green areas in figure 1c is 7.4°. Each grain boundary restricts supercurrent and the final \(J_c\) is expected to be \[6\] of about one order of magnitude below \(J_c\) of the film without grain boundaries. The supercurrent may flow around highest-angle grain boundaries, which would keep an intermediate value of \(J_c\).

The \(J_c\) can be derived from DC magnetisation measurements. In addition to DC signal from superconductor, the RABiTS substrate gives a strong magnetic signal. Figure 2 shows magnetisation loops of the RABiTS substrate at two temperatures: 77.3 K (black squares) and 20 K (red circles). These temperatures are important for applications in liquid nitrogen and hydrogen, respectively. The Ni5%W is a soft magnetic material with weak amplitude dependence of magnetic moment below 77.3 K. The amplitude of magnetic moment from RABiTS tape is large comparable with the magnetic moment of most superconducting films, and to obtain magnetisation loop of the superconductor, it is necessary to accurately subtract magnetic moment of the substrate. Figure 3 shows total \(m\) as function of field for a 3.75 µm-thick integrated Ag/YBZO film deposited on RABiTS at 77.3 K (black squares) and 20 K (red circles).
Figure 1. EBSD grain maps of a section of RABiTS substrate in which grains are shown by different colour if they are misoriented with neighbour grains by an angle above a) 1°, b) 3°, c) 5° and d) 7°.

Because the loops in figures 2 and 3 belong to the samples of slightly different size, an adjustment is necessary to subtract the magnetic moment of the substrate. It was done by recording the temperature dependence of the magnetic moment of the substrate (filled black squares in figure 4) and film on substrate (filled red squares in figure 4) at an intermediate field of 1 T. These dependencies were plotted together and the former was multiplied by a coefficient of 0.765 to match values of magnetic moment above $T_c$ as shown by open black squares in figure 4. This coefficient was further used for this film to reduce magnetisation loops in figure 1 and subtract them from the loops in figure 2. The result of subtraction is shown in figure 5. The unusual drop in magnetic moment in the loop at 77.3 K and tilted to the right loop at 20 K reflect the influence of the field gradients enhanced by the magnetic substrate. Using equation (1), the loops in figure 5 were used to calculate $J_c$ and total critical current density per centimetre of width $I_{c-w}$ for the film at two temperatures are shown in figure 6.

The difference between the lines represented by filled red squares and open black symbols in figure 4 gives the net magnetic moment of the superconducting film and can be used for calculation of the temperature dependence of $J_c$ or $I_{c-w}$ at field of 1 T. We performed these calculations using equation (1) for several key samples deposited on RABiTS substrates.

The example given in figure 6 shows that $I_{c-w}$ in the film of moderate thickness can reach a high value above $10^3$ A/cm at 20 K, which is the operating temperature in liquid hydrogen applications.
Figure 2. Magnetisation loops of the Ni5%W RABiTS substrate at two temperatures: 77.3 K (black squares) and 20 K (red circles).

Figure 3. Magnetisation loops of a 3.75 µm thick integrated Ag/YBZO film deposited on RABiTS substrate at 77.3 K (black squares) and 20 K (red circles).
Figure 4. Temperature dependence of the DC magnetic moment of the substrate (filled black squares) and YBCO integrated film on the substrate (filled red squares) at magnetic field of 1 T. The open black squares show the reduced $m$ of the substrate adjusted to $m$ of integrated film at $T$ above $T_c$.

Figure 5. Subtracted magnetisation loops for a 3.75 µm thick integrated Ag/YBZO film at 77.3 K (black squares) and 20 K (red squares).
Figure 6. Magnetic field dependence of total critical current per centimetre of width for Ag/YBZO film at 77.3 K (black) and 20 K (red) derived from the magnetisation loops in figure 5. Thin solid line shows an extrapolation for high-field $I_{c-w}(H)$.

The field dependence of $I_{c-w}$ for 20 K is weak and the $I_{c-w}$ at this temperature can only be determined from equation (1) at fields above 0.5 T as shown by the extrapolation line from higher magnetic fields. The underestimation of $I_{c-w}$ at low fields from (1) is significant. The $I_{c-w}$ at 77.3 K is more than an order of magnitude below $I_{c-w}$ at 20 K and it has a strong dependence on magnetic filed.

Figures 7 and 8 show the temperature dependence of $J_c$ and $I_{c-w}$ for a range of the films at a magnetic field of 1 T, important for applications. It is also the field at which (1) can reliably be used to determine $J_c$ and $I_{c-w}$ from DC measurements. The black filled squares show $J_c$ and $I_{c-w}$ for pure YBCO film deposited on RABiTS substrate. As expected, for the misorientations of substrate shown in figure 1, $J_c$ and $I_{c-w}$ are well below that of pure YBCO film deposited on single crystal SrTiO$_3$ substrate: two examples are shown by open black triangles and squares. The ratio of $I_{c-w}$ in these films is about one order of magnitude. There is little improvement in $J_c$ and $I_{c-w}$ by the deposition on RABiTS substrate of YBCO with added 2% of BZO (red filled squares), and the highest values of $J_c$ and $I_{c-w}$ are achieved in Ag/YBCO+2%BZO single-layer (olive and dark cyan spheres) and quasi-multilayer (blue) films.

As seen in figure 7, $J_c$ in integrated films reaches that in the YBCO films deposited on single-crystal substrates. It is likely to be due to the correlated growth of BZO and YBCO nano-columns, which could even reduce misorientations in the superconducting film comparable with misorientations in the substrate. As seen from figures 7 and 8, the BZO nanorods alone are not able to improve the crystallinity of the film. The slightly different relative arrangement of the lines in figures 7 and 8 is due to different thickness of the films.

In zero field, $J_c$ was measured by the AC method. Figure 9 shows the temperature dependence of imaginary AC magnetic moment $m''$ for one of the best pure YBCO samples (open squares) deposited on single-crystal SrTiO$_3$ (STO) substrate and integrated Ag/YBCO+2%BZO sample (filled squares) deposited on RABiTS substrate. $m''(T)$ was measured at four different values of $h$: 0.05 Oe (black), 0.1 Oe (red), 0.5 Oe (green) and 1 Oe (blue) and in the plot it is reduced by the value of $h$. 
Figure 7. Temperature dependence of $J_c$ for a range of films at magnetic field of 1 T. Black filled squares show $J_c$ for Ag/YBCO film deposited on RABiTS substrate. Open black triangles and squares are for pure YBCO films deposited on SrTiO$_3$ substrate. Red filled squares show $J_c$ for YBCO+2% BZO film on RABiTS substrate and blue, olive and dark cyan symbols are for three different integrated Ag/YBCO+2%BZO films on RABiTS substrate.

Figure 8. Temperature dependence of $I_{c,w}$ for a range of the films at magnetic field of 1 T. The symbols are the same as in figure 7.
Figure 9. Temperature dependence of reduced by excitation field imaginary AC magnetic moment $m''$ for one of the best pure YBCO samples (open squares) deposited on single-crystal SrTiO$_3$ substrate and integrated Ag/YBCO+2% BZO sample (filled squares) deposited on RABiTS substrate. The inset shows $m''/h(T)$ of the main plot in the vicinity of $T_c$. $m''(T)$ has been measured at four different values of $h$: 0.05 Oe (black), 0.1 Oe (red), 0.5 Oe (green) and 1 Oe (blue).

The position of the maximum on each curve gives the temperature at which $J_c$ is equal to a certain value defined by $h$ according to equation (2). It is the motion of the maximum to lower $T$ with the increase of $h$ that characterises the temperature dependence of $J_c$. Figure 9 shows that in both films the maximum remains close to $T_c$ in spite of significant increase in $h$. Although the film deposited on STO has a higher $T_c$ than in the Ag/YBCO+2%BZO film on RABiTS substrate, the rate of the peak motion is comparable in both films, as can be seen in the inset. The wider peaks in Ag/YBCO+2%BZO film reflect the less homogeneous distribution of current and/or the influence of misorientations between grains enhanced by the deformations developed at cutting samples for magnetisation measurements. The measurements similar to those shown in figure 9 have been performed for several samples grown on RABiTS and STO substrates and their $J_c(T)$ are shown in figure 10.

In this figure, the open triangles show $J_c(T)$ for two representative YBCO films deposited on single-crystal STO substrates. Filled blue squares are for a pure YBCO film deposited on RABiTS substrate. It shows somewhat lower $J_c$ than in films on STO substrate at low temperatures. The YBCO+2%BZO film deposited on the tape (black diamonds) shows even lower $J_c$. The Ag/YBCO+2%BZO film deposited on Ni5%W RABiTS (red stars) shows the highest $J_c$ among other samples except when comparing with higher-$T_c$ YBCO tape shown by open down triangles. The Ag/YBCO film on the metal tape with YBCO nanocolumns [4] (orange circles) is an exceptional sample with very high $T_c$. However, the rate of decrease in $J_c$ with decrease of $T$ is higher in this sample comparable with others, and it cannot compete with Ag/YBCO+2%BZO at low temperatures.
Figure 10 confirms that the superconducting properties of the samples deposited on RABiTS substrates, the best being the integrated Ag/YBCO+2%BZO, are comparable with properties of the samples on STO substrates.

Figure 10. Temperature dependence of $J_c$ for several samples deposited on single-crystalline STO substrates (open symbols) and RABiTS flexible metal tape (filled symbols). The blue squares are for pure YBCO film deposited on RABiTS substrate. The YBCO+2%BZO film deposited on the tape is shown by filled black diamonds and the Ag/YBCO+2%BZO film on Ni5%W is shown by red stars. The Ag/YBCO film on metal tape with YBCO nanocolumns is shown by orange circles.

The DC measurements discussed above were performed in a magnetic field perpendicular to the substrate, which is the direction of field with the strongest suppression of $J_c$. The extended defects like BZO nanorods or YBCO columns reduce the effect of magnetic field and the best way to clarify how it is done is to measure the angle ($\Theta$) dependent transport $J_c$ or $I_c$-$w$. The $I_c$-$w$ ($\Theta$) for integrated Ag/YBCO+2%BZO sample on RABiTS tape at temperature of 77.3 K and magnetic field of 2 T is shown in figure 11. The angle dependence clearly demonstrates the increase of $I_c$-$w$ in the direction perpendicular to the substrate or along the $c$-axis of YBCO (maxima at angles of 0°, 180° and 360°). However, the pinning along the $c$-axis is not dominant in this sample as it is in the integrated samples deposited on STO substrates [4]. This indicates that there is still room for improvement in the properties of superconducting films deposited on RABiTS substrates.

Finally, the presence of extended defects responsible for the increase in $I_c$-$w$ along the $c$-axis of YBCO is confirmed by TEM imaging of the cross-section of an Ag/YBCO+2%BZO sample deposited on Ni5%W RABiTS tape as shown in figures 12 and 13. Figure 12 is focused on the buffer layer composed of two layers of CeO$_2$ and one layer of YSZ in-between, while figure 13 is a TEM image of the YBCO+2%BZO (YBZO) layer. The extended vertical nano-defects perpendicular to the substrate are clearly seen in this layer.

The described method of deposition features double additions to YBCO: Ag and BZO nanoparticles. Similar methods, for example, with nano-additions of BZO and Y$_2$O$_3$ are already described in the literature [10,11]. The difference between our method and methods described in
Figure 11. Angle dependence of transport $I_{c-w}$ for integrated Ag/YBCO+2%BZO sample deposited on Ni5%W RABiTS tape.

Figure 12. TEM image of the cross-section of an Ag/YBCO+2%BZO sample deposited on Ni5%W RABiTS tape in the vicinity of the buffer layer.

Figure 13. TEM image of YBCO+2%BZO layer of the sample shown in figure 12. The extended nano-defects perpendicular to the substrate are clearly seen in the layer.
[10,11] is that Ag nanoparticles do not pin directly the magnetic flux. Instead, they promote the growth of YBCO nanocolumns. The motion of Ag nanoparticles perpendicularly to the substrate may decrease the misorientations in YBCO films and reduce costs of texturing metal substrates.

4. Conclusions
The integrated method for the deposition of superconducting films that unites the growth of BaZrO$_3$ nano-rods and generation of HTS columns by nanoparticles of noble metals is applied to rolling-assisted biaxially-textured metal substrates with relatively high misorientations between grains. The YBa$_2$Cu$_3$O$_x$ superconducting coatings of the thickness up to 5 µm show strong increase in total critical current per centimetre of width in comparison with pure YBa$_2$Cu$_3$O$_x$ films. The method can be considered as a way to overcome the negative effect of strong grain misorientations in the flexible metal substrates and may lead to a cheap technology for the deposition of coated conductors.

5. References
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