

Characterization of suitable buffer layers on Cu and Cu–alloy metal substrates for the development of coated conductors

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Abstract

A novel buffer layer architecture consisting of LaMnO₃/MgO/TiN is proposed as a suitable structural and chemical template for the epitaxial growth of high-*T_c* superconductors on Cu metal surfaces. For the first time, high *J_c* values are reported for YBCO films grown by laser ablation on (001) Cu single crystals, {100}<100> textured Cu surfaces and {100}<100> textured Cu–48% Ni–1% Al alloys, without intervening metal coatings. The *J_c* for single-crystal-like substrates is as high as 3.5 MA cm⁻² and values of 2 MA cm⁻² were obtained on the Cu–alloy tape substrates.

1. Introduction

As progress in fabricating lengths of coated conductors brings the development of second generation wire technology closer to industrial manufacturing, new specifications emerge which are dictated by practical applications. Among these are requirements for a totally non-magnetic substrate tape and for cryogenic and/or adiabatic stabilization of conductors during thermal transients. At the same time, studies of the superconducting properties of thick YBCO films and intergranular *J_c* behaviour have highlighted the importance of substrate texture for achieving targeted critical currents per unit width. These issues indicate that significant improvement of overall performance using the RABiTS technique [1] can be achieved by the careful choice of substrate metal tape.

In power applications where ac fields are required, hysteretic losses in coated conductors are dominated by the irreversible magnetization of the superconducting film and the hysteretic movement of magnetic domains in the ferromagnetic substrate. Recent measurements by others [2] indicate that, in those current regimes typically used for practical applications, the ferromagnetic losses in Ni–5% W-based wires are a significant fraction of the total losses. Consequently, the use of a non-magnetic substrate such as Cu is highly desirable. The use of Cu for coated conductors can bring additional advantages, such as larger thermal and electrical conductivity,

and lower cost (Cu and commercial Cu alloys can be up to six times less expensive than Ni alloys).

While the Ni–W alloy used in today's demonstration tapes cannot contribute to thermal stability because of its low thermal and electrical conductivity, a Cu substrate can serve as a stabilizer whenever a suitable electrical connection is implemented between YBCO and substrate, for example by using electrically conducting buffer layers, or a thin Cu coating around the superconducting tape. This would in turn eliminate or greatly reduce the thickness of the required stabilizing Cu overlayer, substantially increasing the engineering critical current (*J_E*). We note that the combination of high yield stress (necessary for tape handling) and low resistivity can be achieved in Cu alloys where the alloying elements form precipitates within the Cu matrix [3].

2. Choice of buffer layers for Cu-based substrates

We investigated several issues associated with the development of buffer and superconducting layers directly on Cu substrates, including poor Cu oxidation resistance, high Cu thermal expansion and surface sulfur-mediated buffer layer epitaxy.

The fast Cu oxidation is due to the very high diffusivity of Cu ions through CuO/Cu₂O and the consequent inability of the native metal oxide to be self-protective (at YBCO processing conditions). This poses stringent requirements on the buffer

layers to be used on Cu. Such layers need to block cation and oxygen diffusion more efficiently than the $\text{Y}_2\text{O}_3/\text{YSZ}/\text{CeO}_2$ buffer combination on Ni–W alloys, for which self-passivation of the native oxide at the buffer/substrate interface does occur [4].

Another concern related to the use of a Cu–RABiT substrate is the large strain imposed by the substrate on the YBCO film during cool-down. In fact, the thermal expansion coefficient of Cu can be estimated as $18 \times 10^{-6} \text{ K}^{-1}$ in the temperature region of interest (the same parameter for Ni is $16 \times 10^{-6} \text{ K}^{-1}$). On the sole basis of the difference between Cu and YBCO thermal expansion ($a_{\text{YBCO}} = 12 \times 10^{-6} \text{ K}^{-1}$), a residual strain of $\sim 0.45\%$ in the YBCO film can be calculated. This value is very close to the failure limit of 0.5% for compressive strain, as experimentally derived by bending tests in coated conductors [5].

Although an ordered sulfur superstructure is necessary on the Cu surface (just as for Ni) to nucleate and grow many cubic oxides [6, 7], such a superstructure cannot be formed on Cu by controlling sulfur adsorption, as is done for Ni and Ni alloys. Therefore, the choice of possible buffer layers on Cu is limited to materials that can be grown on a clean fcc metal surface.

Among the possible oxides used today in coated conductor technologies, MgO is certainly a good candidate as a barrier layer for oxygen in buffer layer architectures intended for Cu. Previous O^{18} transport studies indicate that the oxygen diffusion coefficient of MgO at 800°C is roughly $10^{-20} \text{ cm}^2 \text{ s}^{-1}$, nearly 13 orders of magnitude smaller than that for YSZ at the same temperature [8, 9]. Although MgO is known to grow on clean fcc metal surfaces, this layer alone is not a suitable buffer layer due to rapid Cu diffusion. For this reason a seed layer of TiN was introduced as a Cu diffusion barrier between MgO and the metal substrate. TiN is one of the most widely investigated barrier materials in Cu metallization for integrated circuit technology [10] and is also structurally compatible with MgO, having the same rock-salt crystal structure and a lattice mismatch of only 0.5%. Further, we found that TiN could be easily grown epitaxially on Cu without the need for a sulfur template. Finally we deposited LaMnO_3 (LMO) as a cap layer on MgO for good lattice match and chemical compatibility with YBCO. LMO was selected from among other perovskites (SrTiO_3 , SrRuO_3) because of its wide window of deposition conditions for single-oriented (100) films on MgO and large critical currents reported using LMO as a buffer layer on Ni–3% W alloys and ion-beam-assisted deposition MgO substrates [11, 12].

3. Experimental details

The Cu substrates used for this study include Cu(001) single crystals, Cu(001) epitaxial films deposited on (001) MgO or (001) SrTiO_3 (STO) single crystals, {100}<100> textured Cu tapes and {100}<100> textured Cu–48% Ni–1% Al tapes. All the oxide buffer layers were grown in an ultra-high vacuum (UHV) pulsed laser deposition (PLD) chamber equipped with a load lock for loading samples and targets, a reflection high-energy electron diffraction (RHEED) system, a residual gas analyser and a Kauffman-type ion source for sputter cleaning. The laser used for ablating target materials was a KrF excimer laser with a power of 150 W and a wavelength of 248 nm. The

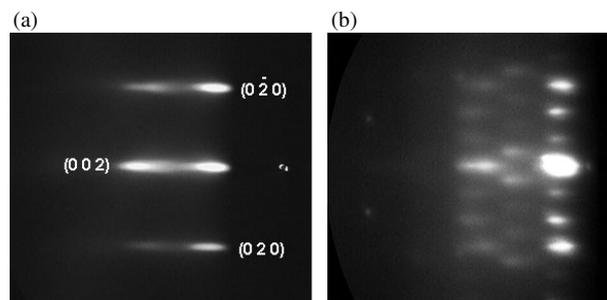


Figure 1. RHEED patterns of an as-grown epitaxial TiN film on (001) Cu, in a vacuum background (a) and when exposed to an oxygen partial pressure of 8×10^{-6} Torr at a temperature of 600°C (b).

laser fluence varied between 4 and 5 J cm^{-2} and the repetition rate was between 10 and 20 Hz.

Fully (100)-oriented, epitaxial TiN films were grown using a TiN target in a nitrogen background pressure of $3.0\text{--}10 \times 10^{-5}$ Torr and a substrate temperature of 580°C . The film nucleation and growth was monitored by RHEED and a cube-on-cube epitaxial relationship was observed between the Cu substrate and TiN film. After a nearly 200 nm-thick TiN film was grown, the nitrogen was pumped out, the substrate temperature was increased to 600°C and oxygen was introduced into the chamber with a partial pressure of $0.8\text{--}1.0 \times 10^{-5}$ Torr for the growth of the MgO layer. At such oxygen pressures, the TiN RHEED pattern exhibited spots in addition to those typical of a clean (001) surface. Figure 1 shows the RHEED pattern produced by a clean TiN surface and that of a TiN film when exposed to the oxygen pressure and temperature indicated above. The latter suggests the presence of a 6×6 superstructure, likely formed by oxygen adatoms bonded onto film surface lattice sites. This superstructure was stable at the deposition condition employed for the MgO buffer layer and fully (001) oriented MgO films could be grown on this surface. Thermodynamic data of the free energy of formation for MgO and TiO indicate higher stability of the former oxide compared to the latter. The formation of MgO is thus favoured over the formation of TiO and the O adatoms initially present on the TiN surface at the time the MgO deposition starts are likely to be incorporated in the growing MgO film. Once a 100 nm-thick MgO film was grown, an additional LMO cap layer was deposited *in situ* at a temperature of 620°C and a H_2O partial pressure of 5–8 mTorr.

4. Results and discussion

Figure 2 shows the critical current density of a YBCO film grown by PLD on a buffered Cu(001) epitaxial film on a MgO single crystal. The critical current was measured by electrical transport as a function of the applied magnetic field at 77 K. The thickness of the laser-ablated YBCO film (180 nm) was measured by Rutherford back-scattering (RBS) and the corresponding J_c in a self-field was 3.5 MA cm^{-2} . Such a value is comparable with those obtained on YBCO films deposited directly on single-crystal STO substrates. The behaviour of J_c in a field and the value of the irreversibility field ($H_{\text{irr}} = 7 \text{ T}$) are also typical of YBCO films on STO or LAO single crystals.

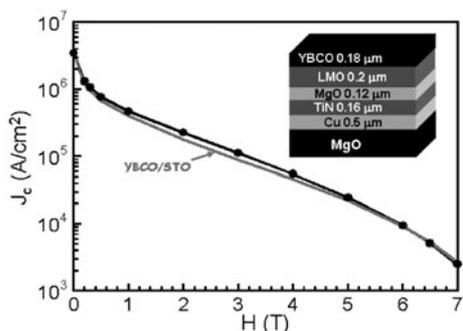


Figure 2. Critical current density versus applied magnetic field for a YBCO film deposited on LMO/MgO/TiN/Cu/MgO (crystal) (black curve and dots), and a typical YBCO film deposited on single-crystal STO (grey curve).

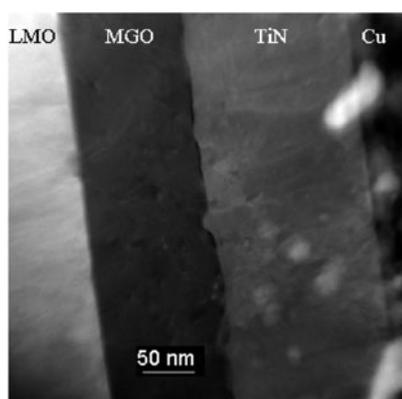


Figure 3. STEM image of a YBCO/LMO/MgO/TiN/Cu multilayer structure on a MgO single crystal acquired with a high-angle annular dark field detector. This technique provides direct compositional contrast and the heavier elements appear brighter.

Figure 3 shows a low-magnification Z-contrast STEM image of the multilayered LMO/MgO/TiN structure grown on the Cu film on a MgO single crystal, after deposition of the YBCO top film. All the interfaces appear clean and there is no evidence of reactions or interdiffusion between the different layers. Further, the oxygen presence at the Cu/TiN interface was not detected from *in situ* electron energy loss spectroscopy (EELS) measurements.

To estimate the actual residual strain induced by the Cu substrate in the superconductor, we deposited the same buffer layer architecture and YBCO film described above onto a 1.5 mm-thick Cu crystal. The Cu crystal was nearly a single crystal with a FWHM of 0.28° for the (001) rocking curve and a [001] tilt of 1° . The critical current density was derived in this case by measuring the sample magnetic moment hysteresis in a SQUID magnetometer as a function of temperature and field. The observed sharp T_c transition and the high value of J_c at low temperatures ($J_c(5\text{ K}) = 1.42 \times 10^7\text{ A cm}^{-2}$) were indicative of the absence of weak links. The value of J_c at 77 K and low magnetic field was 1 MA cm^{-2} . We used high resolution x-ray diffraction to measure the lattice parameters of the layers composing our heterostructure. By using (002) and (111) type reflections, we calculated a lattice distortion of $(a-c)/a = -1.31\%$ in the TiN film and 0.04% for MgO. The YBCO lattice constants were evaluated using (005), (006) and (113) reflections and the residual strain was estimated to be

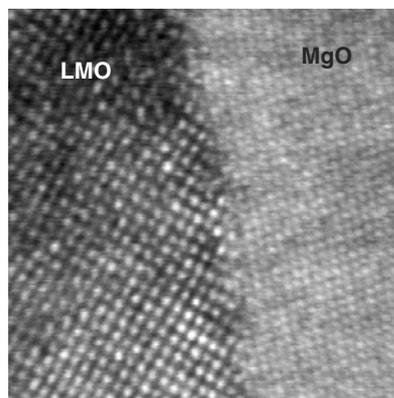


Figure 4. High resolution STEM micrograph of the LMO/MgO interface.

$\varepsilon_{zz} = 0.25\%$. This value is significantly lower than the 0.45% calculated on the basis of differences in thermal expansion, and closer to the residual strain measured on the $50\text{ }\mu\text{m}$ -thick Ni-3% W substrate (0.08%). This result indicates that strain is released by the introduction of dislocations within the buffer layers or at their interfaces. An example of such a mechanism is illustrated in figure 4, which shows a high-magnification Z-contrast STEM image of the interface between MgO and LMO. The large lattice mismatch between the two oxides (7.3%) is accommodated in the early stages of film nucleation with the introduction of disorder and misfit dislocations in the very first atomic planes of LMO, leading to virtually unstrained growth of the rest of the film. Another strain relief mechanism that can occur when stiff and brittle films are deposited on soft and ductile metals is the insertion (and motion) of dislocations in the underlying metal substrate rather than the film.

To complete our study we grew the LMO/MgO/TiN buffer layer heterostructure and the YBCO film on 99.99% pure Cu tapes, which were thermo-mechanically processed to obtain a biaxial texture with XRD FWHMs of 6° and 5° for the in-plane and out-of-plane alignment. In this case, the magnetically determined J_c at 77 K and low magnetic field was 0.7 MA cm^{-2} , corresponding to a transport value J_c of nearly 1.5 MA cm^{-2} . Although this is a very encouraging value, it is not consistent with the optimal degree of texture of the buffered substrate which, according to previous studies on the dependence of transport J_c on grain boundary distribution in coated conductors, should correspond to a J_c around 2.5 MA cm^{-2} [13]. These samples also showed a lower T_c ($T_c = 88.5\text{ K}$) than typical YBCO films on coated conductors, which suggests the possibility of chemical contamination of the YBCO film by outward Cu diffusion. SEM measurements were consistent with this hypothesis and, in particular, showed sparse Cu_2O outgrowths in the form of large particles and, sometimes, straight lines aligned with the substrate rolling direction. We attributed the formation of these outgrowths to oxidation that occurs during the YBCO deposition on the unprotected back side and edges of the substrate, and that propagates towards the front. Outgrowths form preferentially in correspondence to defects, such as pinholes or scratches, introduced onto the substrate surface during the rolling process. EDX measurements performed before and after subsequent high-temperature vacuum anneals on TiN/Cu bi-layers deposited on 7° STO bi-crystals indicated no detectable

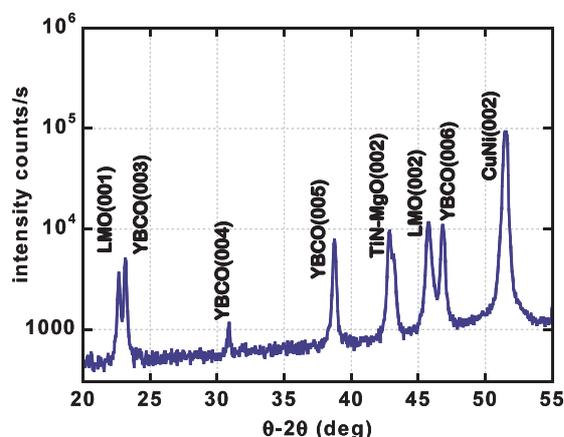


Figure 5. θ - 2θ XRD scan of a YBCO/LMO/MgO/TiN/CuNiAl sample.

(This figure is in colour only in the electronic version)

Cu diffusion through the TiN grain boundary. This experiment suggests that the occurrence of the Cu_2O outgrowths is not related to the presence of low-angle grain boundaries in the textured substrate. No such Cu_2O eruptions were, in fact, observed along the Cu substrate grain boundaries, whose traces are still visible through the YBCO film.

One of the possible ways to avoid oxidation from the back side is to alloy Cu with a more oxidation-resistant metal. We investigated the performance of non-magnetic Cu-48% Ni with 1-1.5% Al using the same buffer layer architecture used on pure Cu and a 0.3 μm -thick YBCO film grown by pulsed laser deposition. The small percentage of Al in such a substrate is very effective in passivating the CuNi alloy, which otherwise can oxidize nearly as fast as pure Cu. Passivation occurs by formation of a thin surface Al_2O_3 layer at extremely low oxygen partial pressure. Such an alumina layer is very desirable for protecting the back side, but not a suitable template for well oriented buffer or superconducting layers. Therefore, the Al_2O_3 layer that had formed on the substrate front surface during the texturing anneal was removed by ion sputtering prior to the deposition of the seed layer. Although the TiN deposition occurs without introduction of oxygen in the deposition chamber, the Al present in the substrate can readily diffuse up to the surface at temperatures greater than 400 °C and oxidize in the presence of residual background oxygen, thus corrupting the buffer layer epitaxy. To avoid this problem an initial 100 Å-thick TiN layer was deposited at 400 °C. The cube epitaxial growth, which does not normally occur at such low temperatures, was achieved by locally increasing the energy of the impinging species with an Ar^+ ion beam of 400-500 eV in energy. The rest of the TiN film and the subsequent buffer layers were deposited at the conditions

used for pure Cu substrates. Figure 5 shows the XRD θ - 2θ pattern acquired on a YBCO/LMO/MgO/TiN/CuNiAl sample that showed a transport J_c of 2 MA cm^{-2} . We note that only YBCO and substrate peaks are present and there is no evidence of unwanted oxide peaks. Four circle diffractometer measurements revealed the optimal alignment of the YBCO film with a FWHM of 2.8° for the out-of-plane texture (in the rolling direction) and 6.5° for the in-plane texture.

In conclusion, we have shown that a multilayered structure consisting of LMO/MgO/TiN acts as a good diffusion barrier and structural template for the deposition of a high J_c YBCO film on pure Cu and Cu-alloy substrates. Each of the three buffer layers has a unique property that is essential to suppress Cu oxidation, keep the interfaces clean and accommodate strain. TiN is a barrier to outward Cu diffusion, while MgO is a barrier to inward oxygen diffusion and is stable enough thermodynamically to be grown on TiN. LMO provides structural compatibility with the YBCO lattice.

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