Filamentization of YBCO Coated Conductors by Microcontact Printing

Minsoo Kim, Herbert C. Freyhardt, T. Randall Lee, Allan J. Jacobson, Eduard Galstyan, Alexander Usoskin, and Alexander Rutt

***Abstract*—To reduce ac losses of coated conductors (CCs), microcontact printing was employed as an alternative technology for processing striated tapes. All CCs possessed the same basic cross-sectional architecture: stainless steel/ABAD-YSZ/CeO_2/PLD-YBCO. By magnetron sputtering, thin (100–300 nm) Au layers were deposited on bare (no cover layer on YBCO) tapes. Appropriate SAMs (self-assembled monolayers of alkanethiols) line patterns were printed with elastomeric stamps on the Au layer. A subsequent etching of Au, with ferri/ferrocyanide, and of YBCO, with phosphoric acid, was used to produce the desired filamentary structure. The sample performance was checked by angle-dependent measurements of the critical current density, J_c. Striating the CCs leads to a reduction of hysteretic ac losses of the HTS tapes, which according to E.H. Brandt's calculations depend on the width of the filaments. This was confirmed by AC SQUID measurements of the complex susceptibility and paves the way for long-length processing of low-loss CCs.**

***Index Terms*—AC losses, coated conductors, microcontact printing.**

I. Introduction

FOLLOWING ESSENTIALLY two different routes, YBCO or REBCO coated conductors (CCs) are now developed to a state where they can be applied favorably in devices for electrical and power engineering; with reduced size and weight and enhanced efficiency. Paving the way for green technology, they offer savings of energy and resources. However, if CCs are used, e.g., in motors, generators or transformers, the AC losses generated could considerably mitigate the benefit of these high-energy density CC cables. Consequently the AC losses must be reduced. There are two main sources of AC losses, hysteretic losses in the HTS (high temperature superconductor) wire and coupling losses between wires, tapes, or filaments [1]–[3]. While transposition or twisting diminishes coupling losses, the special architecture of the CC tapes requires a filamentization to reduce hysteretic losses, unless a novel method is utilized to reduce pinning losses [4]. To achieve this goal, various techniques have been employed, from simple scratching to laser scribing [5], [6] and photolithographical techniques [7], combined with dry-, wet-chemical or ion-beam etching, and even ink-jet printing [8], to mention only the most important ones. Irrespective of these attempts, a robust and reliable striation technology has not yet been developed. This technology would, amongst others, have to lead to (i) well defined filament cross-sections, (ii) a reduced deterioration of critical current densities J_c due to the filamentization procedure, (iii) non-bridged gaps, which are narrow enough in order not to "lose too much critical current". Because for microelectronic systems it could successfully be demonstrated that with large-area microcontact printing one can produce well-defined pattern on a micrometer scale, in a proof of principle, it was tried to investigate the possibilities of transferring this methodology the microstructure CCs.

In this contribution, therefore, microcontact printing was used to striate short-length CC tapes. All CC tapes [9], [10], which were manufactured by Bruker HTS [11], comprised the same cross-sectional architecture. A stainless-steel tape with an IBAD/ABAD-YSZ layer (Ion/Alternating Beam Assisted Deposition) and a CeO_2 cover layer served as textured substrate onto which the YBCO layer (which was characterized by TEM) was deposited with high-rate pulsed laser deposition (HR-PLD). Mainly 100–300 nm thick, smooth Au layers were deposited by magnetron sputtering on bare YBCO tapes, but also on Ag-covered tapes. An array of microscale lines of self-assembled monolayers (SAMs) of alkanethiols were printed on the Au. By subsequent etching of the patterned Au film and the YBCO below, the desired filamentary pattern was produced. The effect of different etchants was optimized and an alternative technique was tested, which used selective wetting. The potential of the patterning technology via microcontact printing [12] was then demonstrated by measurements of AC

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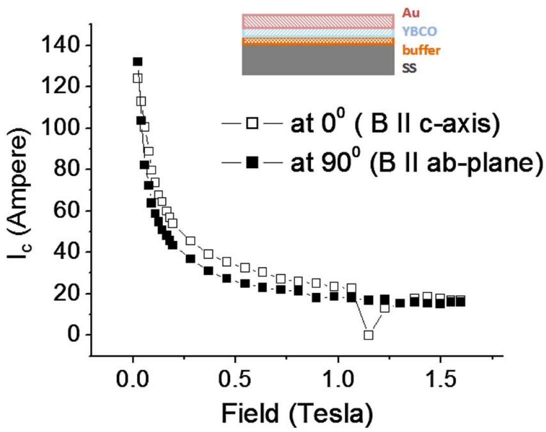

Fig. 1. Cross-section of the bare YBCO tapes covered with Au (inset) and typical critical currents for Bruker HTS tape (sample No. 880, 4 mm width, $I_c = 140$ A @ 77 K & self field) parallel and perpendicular to the (a,b)YBCO planes, which are parallel to the tape surface.

losses of striated CC samples, which were deduced from AC SQUID measurements of the complex susceptibility, and which were compared with theoretical predictions.

II. Sample Preparation and Filamentization Through Microcontact Printing

A. Samples

All high-performance tapes used in this application comprised 100 μm stainless steel tapes with a well-textured, about 1.5 μm thick IBAD/ABAD-YSZ layer, capped with a CeO_2 cover (see Fig. 1, which depicts the schematic tape cross-section as well typical critical current measurements for magnetic fields parallel and perpendicular to the tape surface). The high-rate pulsed laser deposited YBCO film generally possessed a thickness of about 1–1.5 μm. Different from the routine manufacturing process, the tapes had no protective Ag layer, nor a Cu envelope. They are called "bare" YBCO CC tapes in this paper. By magnetron sputtering, the bare YBCO tapes were covered with a layer of Au 100–300 nm thick. The Au was of homogeneous thickness, but contained voids and showed some roughness, which in part reflected some surface roughness of the PLD-YBCO. Later, also CC tapes with a 2 μm Ag cover layer on the YBCO were used, which, however, had to be polished before use.

B. Two Different Strategies for Pattern Generation by Microcontact Printing

From the beginning, several different filament patterns (i.e., with different filament separations and widths) were envisioned. As a proof of principle, however, a standard filamentary pattern was selected whereby the 4 mm wide CC tape was patterned to have 100 μm wide filaments, with 100 μm gaps between them.

For patterning, microcontact printing was selected as the most versatile soft lithographic patterning technology for a large variety of materials. The microcontact printing process is shown schematically in Fig. 2. An elastomeric stamp of

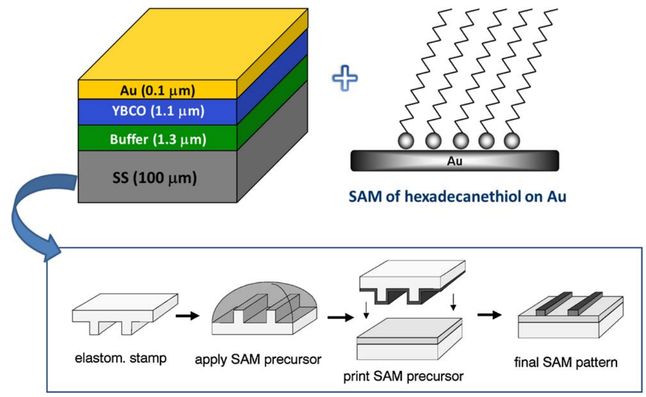

Fig. 2. Microcontact printing: Printing procedure of the self-assembled monolayer (SAM) of alkanethiols on Au-covered bare YBCO CC tapes (schematic processing steps).

polydimethylsiloxane (PDMS) was used to transfer the desired micropattern of the SAMs to the Au surface. The PDMS stamp was prepared by casting the elastomer against a master, which had the desired relief structure on its surface. This Si master, which was produced in the first step, was fabricated by a conventional photolithographic method, whereby a suitable photoresist was applied to a well-polished Si wafer and patterned by a mask with UV light radiation to obtain a submicrometer resolution.

Depending on the desired SAM pattern on the Au surface, a positive or negative photoresist was chosen to transfer the negative or positive line pattern of the mask, respectively. After peeling the PDMS stamp from the master, the stamp was "inked" with a 1 mM solution of 1-hexadecanethiol in ethanol as ink for the actual printing, whereby the ink formed a SAM on the surface. Thus, adsorbate molecules with thiol headgroups are spontaneously attached to the Au surface, which was then protected by the tailgroups of the adsorbate molecules.

Two different approaches were selected: (i) the thiol-based SAM acts as an etch resist, and the underlying Au-covered YBCO films were patterned by wet-chemical etching, as described below, and (ii) by employing n-hexadecanethiol, the printed SAM layers formed hydrophobic regions of low surface energy on the Au surface, whereas the uncovered bare Au remained hydrophilic. Subsequently, by dip-coating (in a PMMA resin, which was diluted to various degrees with anisole solvent), the hydrophilic regions or strips were covered with a film of polymethylmethacrylate (PMMA), which acted as an effective etch resist, while the hydrophobic regions remained free.

C. Pattern Etching

Reliable etching represents a particular challenge. It requires a complete removal of the Au layers in the unprotected areas and subsequently of the YBCO film right down to the underlying template oxide layers. No conductive bridges in the gap between the filaments should remain, which could potentially increase the AC losses via filament bridging. The etchant should not attack any region in the SAM covered (or PMMA protected) surface. Furthermore, the YBCO etchant should also lead to a well-defined rectangular cross-section of straight filaments,

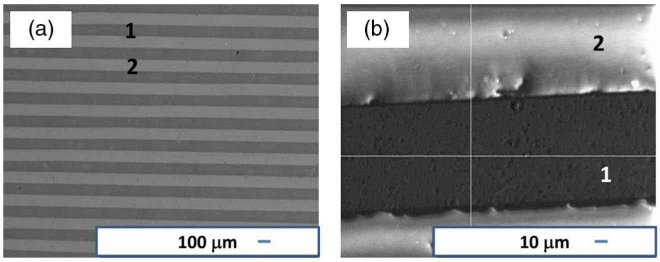

Fig. 3. Microcontact printing: 100 μm × 100 μm pattern. Etching of Au (with ferri/ferrocyanide) and YBCO (with phosphoric acid). SEM images. SAM-covered Au is marked by 1, and regions where Au & YBCO are removed by 2.

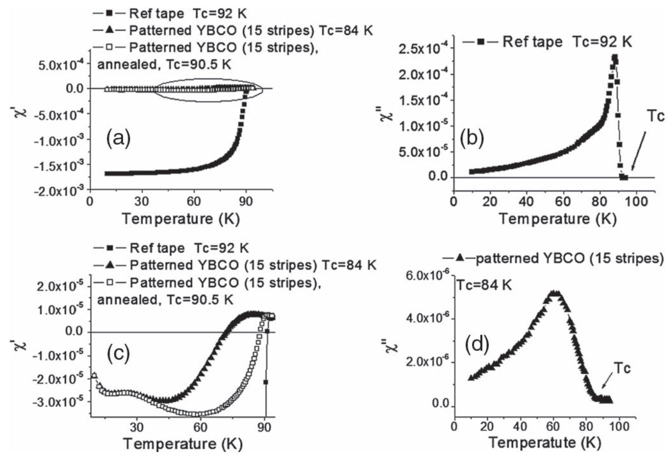

Fig. 4. Complex susceptibility $\chi = \chi' + i\chi''$ of unfilamentized (Ref tape) and patterned (100 μm × 100 μm) YBCO CC tapes. Annealing (1 h @ 400 °C) of the patterned CC almost completely recovers the original T_c [Fig. 4(c)].

without deteriorating the superconducting properties of the filament or filament edges. These expectations were complicated by the fact that the thin Au films were not always smooth on a submicron scale and might have been porous.

At first, a standard etchant was used for selective etching of the Au surface not covered with the SAM. The aqueous etching solution of KCN (0.1 mM) and KOH (1 mM) was stirred during etching and optimized etching times were selected. The Au etching was followed by YBCO etching in a 2% aqueous H_3PO_4 solution. Optical microscopy and SEM observations were employed to monitor the pattern-etching procedure and were complemented by SEM/EDX inspections for materials identification. Because the KCN etchant appeared to create defects in the SAM-covered region, thereby deteriorating the filament structure, it was successfully replaced by a ferri/ferrocyanide etching with an aqueous solution of $Na_2S_2O_3$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and KOH for the Au. The subsequent H_3PO_4 etching of YBCO resulted in a well-defined filamentary structure of the CC tape. SEM images of a 100 μm × 100 μm filament pattern are depicted in Fig. 3, which show some serration of the edges.

A promising alternative, however not yet fully developed, employed a selective wetting principle. The SAMs printed on the Au surface created hydrophobic stripes, whereas the uncovered Au regions remained hydrophilic. These hydrophilic regions were covered with PMMA (see above) as an etch resist during dip coating. To etch selectively the Au surface (including the thiol SAM layer), a KI/I_2 etching solution was used and again the HTS layer was removed with phosphoric acid. A dense PMMA cover (which unfortunately could not yet be obtained) should represent an ideal etch resist leading to well-defined filament pattern.

III. Superconducting Measurements: Results and Discussion

Critical transport currents, $I_c(B, \phi)$, versus magnetic field B and angle ϕ of the magnetic field relative to the tape normal were measured in a 4-probe measuring set up with a conventional (1.7 T) magnet. Results for the 4-mm-wide YBCO tapes used in this investigation are depicted in Fig. 1 and reveal their good quality. AC losses of striated and unstriated small (3 mm × 3 mm) samples were determined from measurements of the complex susceptibility $\chi(T) = \chi'(T) + i\chi''(T)$. χ'' yields a direct measure of the hysteretic loss, Q_h, per unit volume per cycle via the relation $Q_h = \chi'' \mu_o \pi H_o^2$ [13]. With a Magnetic Property Measurement System using a SQUID magnetometer, the temperature dependent $\chi(T)$ was determined between 10 K and 95 K for AC fields of 75 Hz and an amplitude H_o of 3 Oe applied perpendicular to the tape surface (i.e., parallel to c-axis of the YBCO) as shown in Fig. 4. Whereas the unpatterned tape reveals a sharp transition at $T_c = 92$ K, depicted by the sharp drop in χ' [Fig. 4(a)], the striated sample reveals a rather smeared transition that begins at a T_c of 84 K [Fig. 4(c)].

Apparently the etching caused a deterioration of T_c of the YBCO concomitant with a reduction in oxygen content. Consequently, an annealing of the sample in flowing O_2 at 400 °C for 1 hour could recover the sample and brought the T_c almost completely back to 90.5 K [Fig. 4(c)], nearly the original value. The origin of the small maximum in $\chi'(T)$ [Fig. 4(c)] at about 27 K is not yet clear, but can be attributed to a pick-up of trace amounts of Fe during the cyanide etching. A quantitative investigation will have to confirm this assumption.

χ'' is associated with the adsorptive or irreversible components, which arises from energy dissipation within the sample. For the unstriated reference sample, χ'' reveals a pronounced sharp peak below T_c [i.e., below 92 K in Fig. 4(b)], and the corresponding loss per unit volume $Q_h = \chi'' \mu_o \pi H_o^2$ is depicted in Fig. 5(a). These losses are connected with the absorptive and irreversible processes of fluxoid motion in the (well textured) YBCO layer. For the patterned sample, this peak in $\chi''(T)$ not only becomes much smaller, but is also shifted to lower temperatures around 60 K [Fig. 4(d)], which again reflects the broadening of the superconducting/normal transition, predominantly due to the above-mentioned oxygen loss during etching. The corresponding losses are decreased almost by a factor of 50 [Fig. 5(b)]. A recovering of the stoichiometry of the YBCO by the oxygen anneal at 400 °C shifts the maximum back to a position below a T_c of 90.5 K. Further experiments are needed to clarify whether the remaining low-temperature maximum [Fig. 5(b)] is caused by Fe possibly influencing current transfer through boundaries.

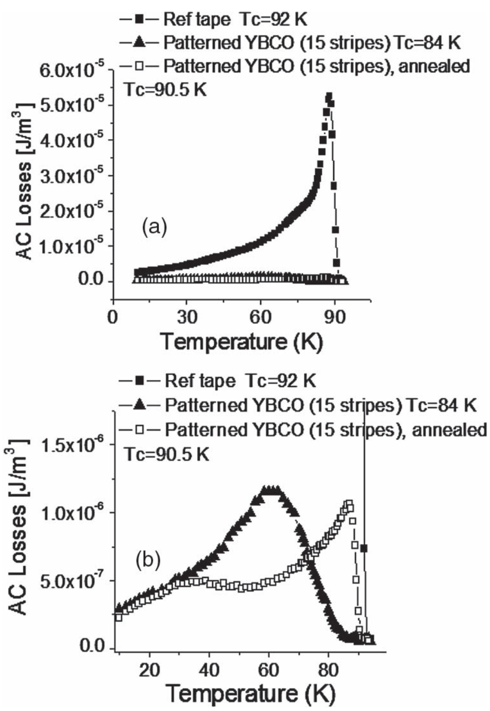

Fig. 5. AC losses of (a) unfilamentized YBCO CC tape, and (b) with 100 μm filaments separated by 100 μm gaps.

The results obtained for striated and unstriated CCs can be compared by using Brandt's [14] expression for hysteretic losses Q (area of the hysteresis loop times frequency) of a type-II superconducting tape (of width 2a and thickness d) in a perpendicular field: $Q = 4f\mu_o a^2 J_c H_o g(H_o/H_c)$, whereby $J_c = j_c d = I_c/2a$ is the current per unit length, $H_c = J_c/\pi$, H_o the amplitude of the oscillating magnet field with frequency f, and $g(x) = (2/x)\ln\cos h(x) - \tan h(x)$. Due to serrated filament edges introduced by the etching, a quantitative comparison of the AC loss reduction by filamentization is not possible. However, a good qualitative agreement was found.

IV. Conclusion

Microcontact printing was used as an alternative method to striate coated conductors, with PLD-YBCO layers deposited on IBAD-buffered stainless steel tapes. As proof of principle, a relatively coarse line pattern (100 μm YBCO filaments, separated by 100 μm gaps) was realized by printing 100 μm thiol SAM stripes on Au-covered YBCO tapes, where the SAM-covered stripes served as an etch resist. A ferri/ferrocyanide etching of the Au layer proved to be superior to a KCN etch, and the YBCO could successfully be removed by a conventional phosphoric-acid etch. While an apparent deterioration of the oxygen stoichiometry of the YBCO could be recovered by a suitable anneal, the reduction of the AC losses due to striation, as determined from AC SQUID measurements of the complex susceptibility, could be demonstrated and qualitatively explained with Brandt's model calculations. Imponderables of the method were addressed, and an alternative microcontact-printing method that employs PMMA on hydrophilic Au surfaces as the etch resist was briefly investigated.

Future experiments will seek to extend the microcontact-printing technology to the long-length processing of REBCO CC tapes.

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