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Highly textured $La_2Zr_2O_7$ and CeO_2 buffer layers by ink jet printing for coated conductors

M. C. Cordero-Cabrera · T. Mouganie · B. A. Glowacki · M. Bäcker · M. Falter · B. Holzapfel · J. Engell

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Abstract The objective of this paper is to prove the possibility to produce single side buffered substrates for coated conductors. We report for the first time the production of highly textured NiW/$La_2Zr_2O_7$/CeO_2 system by all-chemical solution deposition means using an in-house built drop-on-demand ink-jet printer. Lanthanum zirconate precursor ink was produced using lanthanum acetate and zirconium n-propoxide modified with propionic and acetic acid, respectively, and diluted with methanol. Cerium oxide precursor ink was prepared using cerium acetylacetonate dissolved in acetylacetone and diluted in methanol. Optimized ink jet control parameters (inter-droplet distance, nozzle opening time and pressure in the chamber) allowed the deposition of homogeneous highly textured films with a thickness of approximately 150–200 nm at speeds as high as 27 cm/min. $La_2Zr_2O_7$ film showed in plane and out of plane misalignment of 6.6° and 7.4°, respectively, whereas values obtained for CeO_2 were 7.8° and 8.1°, respectively. This study represents a step forward in the production of reel-to-reel coated conductors in an efficient and economic way.

M. C. Cordero-Cabrera (✉) · T. Mouganie ·
B. A. Glowacki
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK
e-mail: mcorderouk@yahoo.com

M. Bäcker
Trithor Ltd, Heisenbergstr.16, 53359 Rheinbach, Germany

M. Falter · B. Holzapfel
Leibniz-Institut für Festkörper-und Werkstoffforschung (IFW), PF 27 01 16, 01171 Dresden, Germany

J. Engell
PF&U Mineral Development ApS, Kullinggade 31, Svendborg 5700, Denmark

Introduction

The production of long length and low cost Ni/Buffer/$YBa_2Cu_3O_{7-\delta}$ (YBCO) has been a target in the field of superconductivity for over a decade [1]. In this system, buffer layers have the role of avoiding Ni oxidation and diffusion to the superconducting layer, since it hinders its superconductive properties. Buffer layers also provide the crystallographic orientation needed to grow textured YBCO. Wide selections of materials have been studied for this purpose, most common being: RE_2O_3, $RETiO_3$, $REAlO_3$ and $REZrO_3$ (RE = rare earth) [2]. General disadvantages reported by these types of materials are their high forming temperature and their undesired transformation to monoclinic phases, which hinder their capability to transfer the texture to the upper layers [3].

Lanthanum zirconate $La_2Zr_2O_7$ (LZO) has proven to overcome such disadvantages and has become a widely used buffer due to the properties such as compatibility with the high critical current of YBCO, the small mismatch with YBCO *a* or *b* axis (~0.5% and 1.8%, respectively), the relatively low formation temperature (~900 °C), the high stability up to 1,500 °C, and its proven capabilities to grow textured on Ni tape [4–6], thus acting both as barrier for Ni diffusion and as a seeding for the upper layers. Cerium oxide has also attracted interest due to its excellent lattice and thermal coefficient match with YBCO and Ni [7], and is being intensely studied [7–9]. Advantages as a barrier buffer layer have also been reported [10].

Apart from the choice of materials for buffer layers, thin films deposition techniques also play a major role in defining the capability of a method to be scaled up to industrial applications. Vacuum deposition techniques are still widely used in research [11], however they have serious limitations for scaling up, such as the amount of sample to be prepared, long preparation times, ultra high vacuum needed and the high cost of required equipment to achieve it. Chemical solution deposition (CSD), on the other hand, is an effective and economic way to achieve these textured architectures [2–5, 12] as opposite to the more expensive and slow processes of vacuum deposition. Although these systems are regularly produced in laboratories in short lengths, the challenge now is to develop an industrial method that allows their production at large scale, a task in which CSD has also proven successful [5, 13].

Common CSD techniques used currently include spin coating [8] and dip coating [12]. It is clear however that spin coating cannot be used for the production of long lengths, especially when continuous production is required, something that dip coating is perfectly capable of [6]. Drawbacks presented by dip-coating include the coating of both sides of the tape, which represent a waste of sol and can potentially clog the pulleys used to transport the tape. Another important drawback is that the sol usually lays down in a tray open to the atmosphere, and therefore loss of solvent due to evaporation is likely to destabilize the sol and/or change its concentration and rheological properties, introducing undesired variations in the deposition process.

In this paper we report for the first time the use of ink jet printing as an alternative to dip coating in the production of single-sided highly textured buffered layers on coated conductors. A newly developed stable LZO sol is also reported, based on a modification of previously developed sols for piezoelectric applications (MC Cordero-Cabrera et al. in preparation). We are thus making the production of superconducting tapes in an economic way even more viable.

Experimental details

Sol preparation (inks)

The LZO ink was prepared using dried lanthanum acetate and zirconium n-propoxide as precursors. Lanthanum acetate was dissolved at ~90 °C in propionic acid using a 1:1 weight ratio. Zirconium n-propoxide 70% in propanol was modified with acetic acid using a molar ratio of 1:4. Modified zirconium sol was added to the cold lanthanum acetate solution, with continuous stirring, and the mixed sol was further diluted with methanol to produce a concentration of 0.05 mol/kg. Preliminary experiments showed this to be a suitable concentration to produce textured LZO. CeO_2 precursor was prepared dissolving cerium acetyl acetonate in acetyl acetone, followed by dilution with methanol to produce ink 0.05 mol/kg. Sols were characterized in density and viscosity using a Cannon-Fenske glass viscometer in order to assure its suitable as inks for the printing system.

Film deposition

An in-house built drop-on-demand ink-jet printer (Fig. 1) was used to produce the films. The printer consists of a single nozzle with an opening of 90 μm and a pressurized ink chamber. The opening in the nozzle is created from a piston lifted off the surface of the nozzle by an electromagnet. The printer program controls the number of droplets, opening time, inter-droplet distance and the pattern of deposition. Varying the open time of the nozzle and the pressure applied onto the chamber can control droplet size.

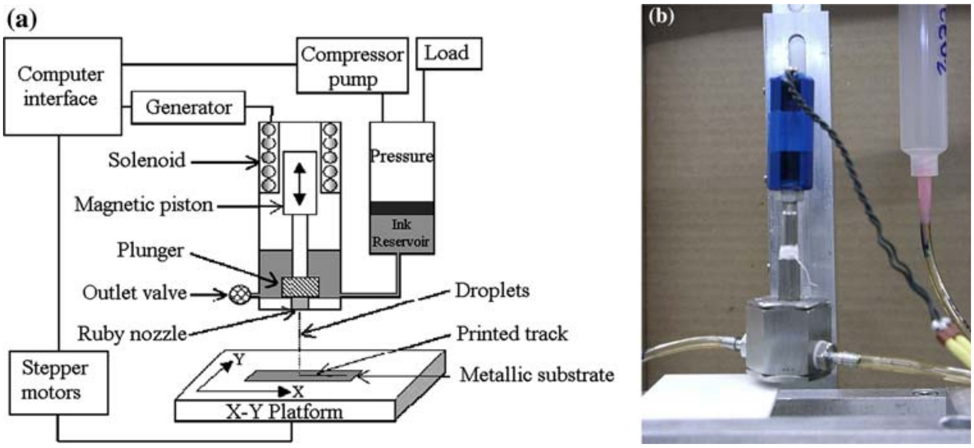

Fig. 1 In-house built drop-on-demand ink-jet printer used for film deposition: (**a**) Diagram of operation; (**b**) close view of a single nozzle printing

Substrates were washed three times with ethanol using a high power ultrasonic probe prior to deposition. LZO was deposited onto 4 mm wide textured NiW (200) tape with in plane misalignment of 5.1° carried out on Ni(111) and out of plane misalignment of 3.4° carried out on Ni(200). After LZO heat treatment, CeO_2 was deposited onto NiW/LZO. One single print line was used with an opening time of 500 µs, a pressure of 400 kPa and droplet spacing of 4.5 mm. $La_2Zr_2O_7$ and CeO_2 films were heated in Ar-5%H_2 at 12 °C/min up to 920 °C and 1,100 °C, respectively. Such temperatures were determined in preliminary experiments carried out in thermal analysis. In both cases 90 min annealing time was used.

Films were characterized in texture and phase composition using X-ray diffraction with Cu-K_α irradiation. Pole figures and in plane and out of plane misalignments were

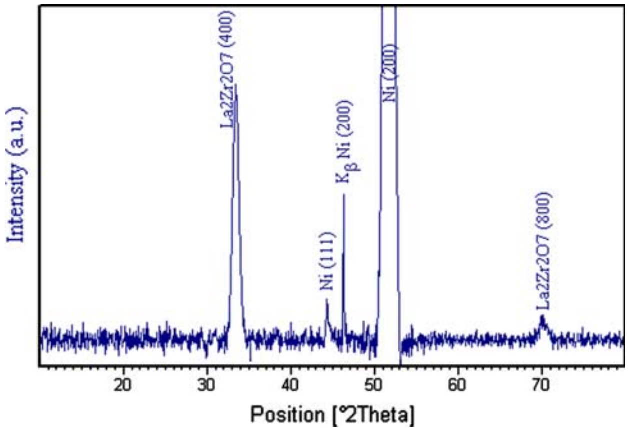

Fig. 2 θ-2θ scans (Cu K_α) of LZO buffer layer on Ni(200), clearly showing LZO (400) texture

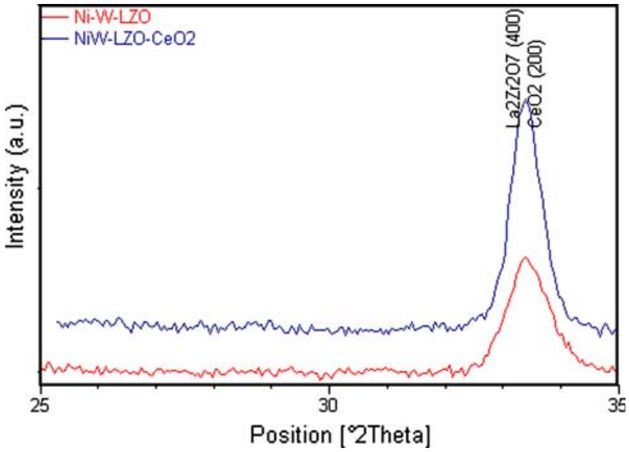

Fig. 3 θ-2θ scans (Cu K_α) of LZO–CeO_2 buffer layers on Ni(200), clearly showing LZO (400) and CeO_2 (200) textures

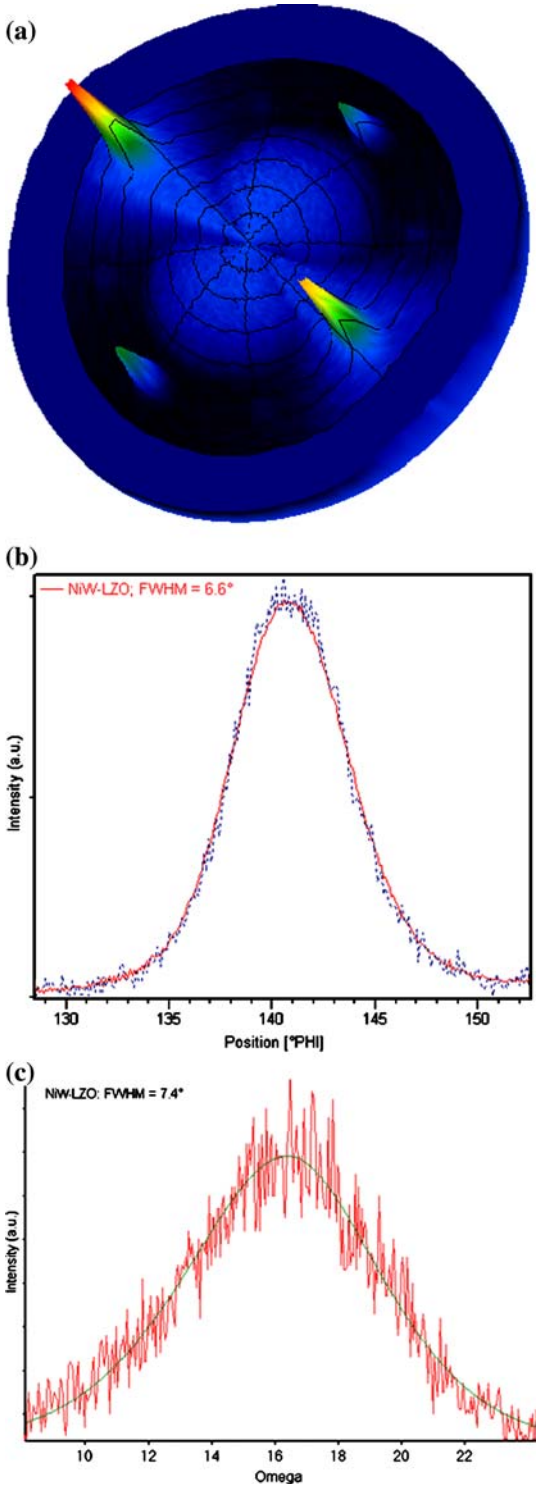

Fig. 4 Texture on NiW–LZO films: (**a**) Pole figure taken on LZO (222) at 2θ = 28.59°. Note that two of the peaks show weaker signal due to the narrow substrate (4 mm) used; (**b**) in-plane misalignment of 6.6°, taken on LZO (222); (**c**) out-of plane misalignment of 7.4° taken on LZO (400) at $\theta = \omega = 16.6°$

carried out in a four-circle X-ray diffractometer. Microstructure and thickness measurements were carried out using a FE-SEM. For thickness measurements, crossed sections of the films were mounted in epoxy, polished and analysed.

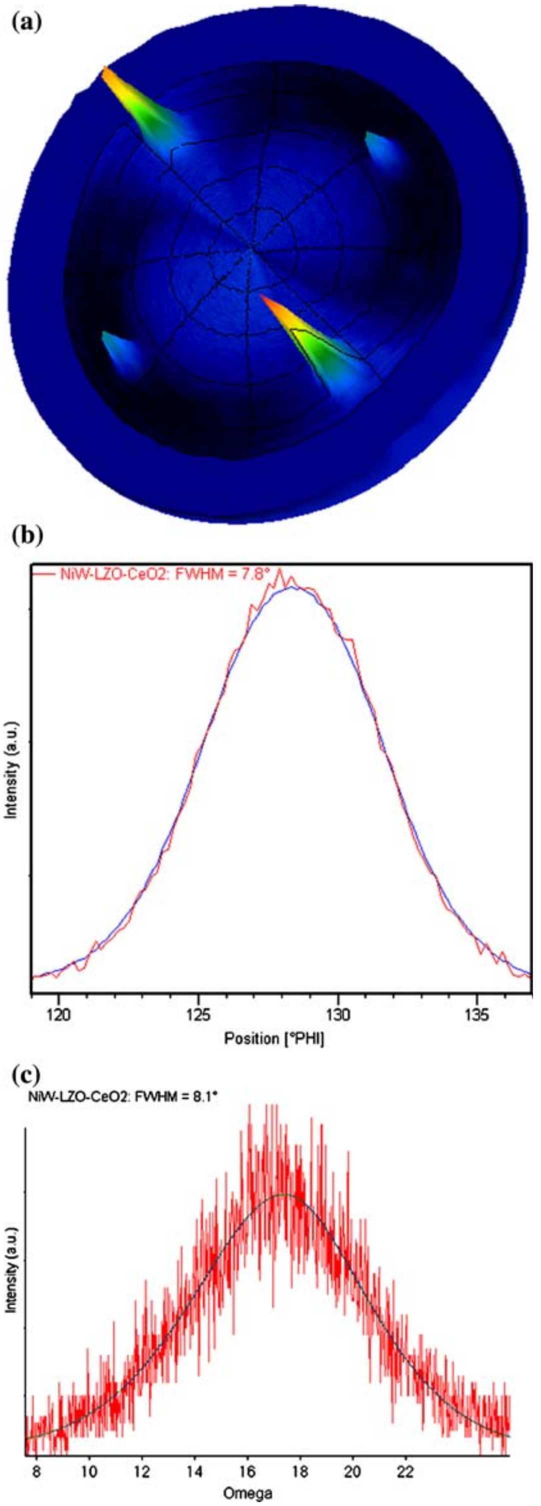

Fig. 5 Texture on NiW–LZO–CeO_2 films: (**a**) Pole figure taken on (111) at $2\theta = 28.54°$; (**b**) in-plane misalignment of 7.8°, taken on CeO_2 (111); (**c**) out-of plane misalignment of 8.1° taken on CeO_2 (200) at $\theta = \omega = 16.6°$

Results and discussions

Both LZO and CeO_2 inks show a viscosity of 0.6 mPas at 23 °C. Such values are well within the optimum ranges to be used in ink-jet printing, as described elsewhere (T Mouganie et al. in preparation). LZO sol shows an excellent stability with time, although CeO_2 ink stability only lasted for a few days. Both inks show an excellent wettability on the Ni substrate, spreading evenly and drying almost instantaneously after deposition. As deposited green films is stable and does not show any sign of hydration. Figures 2 and 3 show normal θ-2θ scans (Cu K_α) of LZO and LZO-CeO_2 buffer layers, respectively, on Ni(200). The LZO (400)/CeO_2 (200) texture is clear, as LZO (222) and CeO_2 (111) (both located approximately at $2\theta = 28.5°$) are absent.

Figure 4 shows pole figure and misalignment scans for the NiW–LZO system. It can be seen that in-plane and out-of-plane misalignments is 6.6° and 7.4°, respectively. Such

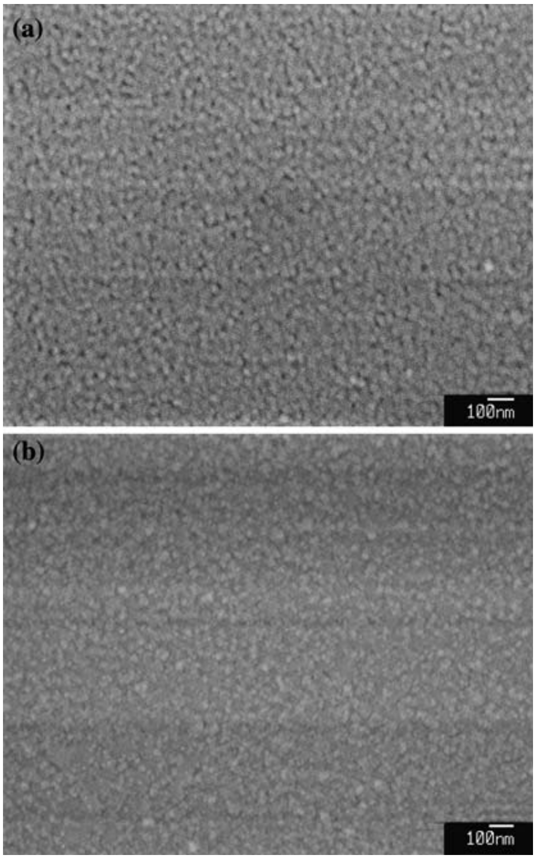

Fig. 6 FE-SEM images of: (**a**) NiW–LZO; (**b**) NiW–LZO–CeO_2

values are comparable to those reported previously in literature [13, 14] on films prepared by dip coating.

Figure 5 shows pole figure and misalignment scans for the NiW–LZO–CeO_2 system. For this case, in-plane and out-of-plane misalignment obtained was 7.8° and 8.1°, respectively. These values are slightly bigger than those reported in the literature [14, 15]. This may be due to the fact of the relatively instability of the CeO_2 sol.

Figure 6 shows microstructure of NiW–LZO and NiW–LZO–CeO_2. Both cases show a smooth surface comprised of grains in the range of 30–50 nm in size. CeO_2 particularly shows a fully dense structure suitable for its role as a barrier buffer layer.

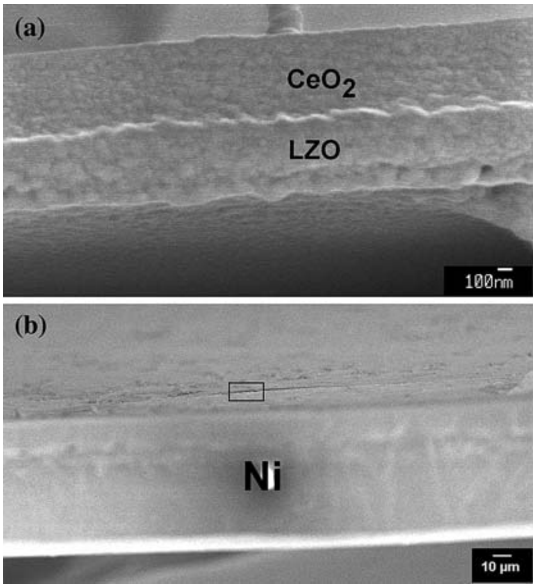

Fig. 7 (**a**) Magnification of the rectangular frame presented in Fig. 7b, showing fully dense films; (**b**) slightly tilted transversal image of a fractured sample showing the substrate. Note the differences in the length bars

Figure 7 shows a FE-SEM micrograph of a transversal section of the film, slightly tilted, therefore appearing thicker than they actually are. Thickness is estimated to be ~150–200 nm for each layer. Full density of the films seen in the microstructure can be confirmed with this transversal image. Finally, Fig. 8 is a micrograph of the NiW–LZO–CeO_2 system showing a smooth and full coverage of the NiW grain boundaries.

Conclusions

The possibility to produce single side buffered substrates for coated conductors using ink jet printing has been proved. In this paper we report the production of a new LZO sol having a wide margin to tailor viscosity and density properties. Most importantly we have proven the ability to produce fully dense highly textured buffered layers for YBCO coated conductors using ink jet printing. The possibility of printing long lengths on only one side of the conducting tape not only saves ink, but also eliminates the problems of clogging on wheels generated by conventional reel-to-reel processing techniques such as dip coating. For this case, printing speeds of up to 27 cm/min were achieved. Achieved results prove ink-jet printing an ideal technique for the preparation of buffered RABiT substrates for long length-coated conductors. On the other hand, inks (chemical precursors) are self-contained in syringes, therefore problems of evaporation or interaction with atmosphere are eliminated, and consequently the risk of sol instability is also avoided, which is vital for long length production of coated conductors at industrial scale.

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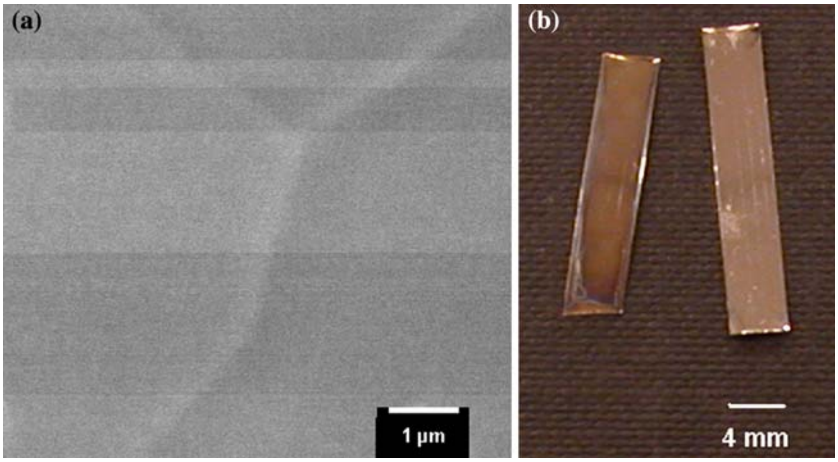
Fig. 8 (**a**) NiW–LZO–CeO_2 system showing a smooth coverage of the NiW grain boundaries; (**b**) substrate (coated and as received)



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