Inkjet printing of multiple Ce$_{0.8}$Gd$_{0.2}$O$_2$ buffer layers on a Ni-5%W substrate

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Abstract. The successful inkjet printing of multiple cerium gadolinium oxide (Ce$_{0.8}$Gd$_{0.2}$O$_2$) layers on highly textured Ni-5%W is reported using a stable ink, developing a solid-liquid interface comparable with that arising from dip coating. Two different approaches were used for the deposition of CGO layers using a 16-nozzle piezoelectric drop-on-demand print head. Two overlapping square arrays of droplets with constant volume and spacing were printed, with and without an intermediate CGO crystallization. The shortest possible heat treatment of the deposited layers was applied, potentially suitable for continuous large scale production. The results from X-ray diffraction show that the single phase Ce$_{0.8}$Gd$_{0.2}$O$_2$ was obtained in all cases, but only the approach with intermediate CGO crystallization can produce a highly textured buffer layer. Optical micrographs and atomic force microscopy (AFM) also indicate the good quality of deposited films after heat treatment.

1. Introduction

No effort has been spared to find a simple multilayer architecture for 2nd generation Coated Conductors (CC) that could prevent oxidation of, and nickel interdiffusion with, nickel alloy substrates and impose heteroepitaxial growth of the subsequent layers. A promising early solution included CeO$_2$ buffer and cap layers, with intermediate Y$_2$O$_3$-stabilised ZrO$_2$ (YSZ) and/or Y$_2$O$_3$ layers [1; 2]. However, an alternative architecture consisting of La$_2$Zr$_2$O$_7$ (LZO) and CeO$_2$ [3; 4] is increasingly favoured, especially for the trifluoroacetate metal organic deposition approach (TFA-MOD). LZO buffer layers can be grown epitaxially on Ni substrates in a reducing atmosphere, and CeO$_2$ (a = 5.41 Å) reduces the lattice mismatch with YBCO, as well as preventing reaction between the LZO diffusion barrier and the growing YBCO layer in the TFA-MOD process.

Detailed studies of chemical solution deposition (CSD) CeO$_2$ thin films have revealed that, in a reducing atmosphere, carbon impurities from metal organic precursors remain trapped at grain
boundaries, inhibiting epitaxial growth [5]. However, an oxidizing atmosphere, which might avoid these impurities, is unsuitable where oxidation-sensitive substrates are used [6; 7]. Gd³⁺ doping of CeO₂ is effective at avoiding impurities including Ce₂C₃ in a reducing atmosphere, promoting epitaxial growth [8].

Using a metal-chelate gel route, we have developed a simple, all-CSD buffer layer architecture for YBCO CC consisting of two Ce₀.₈Gd₀.₂O₂ (CGO) layers. A stable precursor solution has been synthesized from Ce and Gd acetates in propionic acid, and a biaxially textured double coating has been produced by ink jet printing. This approach would be significantly more cost-effective than previous schemes, for example the CeO₂/YSZ/CeO₂/YBCO buffer layer architecture of early pulsed laser deposition (PLD) CC [1; 9].

2. Experimental Details

2.1. Preparation of CGO precursor solution
The organic Ce₀.₈Gd₀.₂O₂ precursor solution was prepared from cerium(III) acetate hydrate (Ce-Ac, Ce(CH₃COO)₃⋅1.02H₂O, 99.9% Sigma-Aldrich), gadolinium(III) acetate hydrate (Gd-Ac, Gd(CH₃COO)₃⋅4.17H₂O, 99% Sigma-Aldrich) and propionic acid (Et-COOH, CH₃CH₂COOH, 99.0% Fluka) as indicated in Figure 1 [10].

![Figure 1 Flow chart of CGO precursor solution preparation for inkjet printing](image)

2.2. Ni-5%W tape surface modification
The highly textured 80 µm thick Ni-5%W tape (Evico GmbH, Germany) was thermally cleaned at 800°C for 30 minutes under an Ar-5%H₂ reducing atmosphere in order to enhance wettability and improve cubic texture. It was then chemically cleaned for 10 minutes in acetone and then for a further 10 minutes in methanol. The substrates were stored in methanol in order to prevent degradation of the wettability and were used as soon as possible.

2.3. Inkjet printing procedure
A piezoelectric drop-on-demand inkjet printing system was used for the deposition of CGO layers on highly textured Ni-5%W tape. A Dimatix Materials Printer (DMP-2831) combining disposable cartridges, containing a 16-nozzle piezoelectric printhead with 21.5 µm orifice diameter, with an XY positioning system, was used to deposit 10 pL droplets of 0.5 M CGO solution (1.094 g/cm³) in a square lattice (Figure 2). A multi-segment waveform with peak voltages of +/-17 V, a slew rate of 35
V/μs and a total duration of 15.1 μs was used for all 16 nozzles. In order to facilitate comparison between droplets of different sizes and wetting behaviours, we express the droplet spacing relative to the droplet diameter. The normalized droplet spacing is $a_s/2r$, where $r$ is the droplet radius on the substrate, as shown in Figure 3. Based on our previous results the spacing between droplets ($a_s$) of the square pattern was fixed at 90 μm, or a normalized droplet spacing of 0.51 [10].

Two different approaches were investigated for the deposition of CGO multi-layers. In the first approach, a heat treatment resulting in full conversion of the CGO precursor solution into a highly textured oxide layer was performed after each layer was printed; CGO/CGO/Ni-5%W. In the second, layers of CGO precursor solution were printed in turn without intermediate annealing, and full conversion was performed with only one final heat treatment; 2CGO/Ni-5%W. Four samples with two CGO layers were produced using each approach to verify reproducibility, and characterization was performed after each heat treatment. In all cases inkjet printing was carried out at room temperature.

![Figure 2](image1.png)  
**Figure 2** a) Square pattern inkjet printed by a piezoelectric 16-nozzle head; $a_s$ indicates the spacing between droplets in the square array, and the numbers indicate the deposition sequence of 16 droplets in one vertical line; b) an optical image of 10 pL drops in flight shortly after ejection from the Dimatix Materials Printer cartridge.

![Figure 3](image2.png)  
**Figure 3** Different stages of droplet overlap in square pattern ($a_s/2r$ is the normalised droplet spacing, where $2r$ is the droplet diameter on the substrate)
2.4. Heat treatment
All printed samples were heated to 1000 °C at a heating rate 5 °C/min, preceded by oxygen removal from the furnace (at 60 °C for 2 h). After 30 min dwell time the furnace was allowed to cool to room temperature. A bespoke valve controller and Eurotherm PID controller were used under computer control to carry out the pyrolysis and sintering steps of CGO synthesis in an Ar-5%H2 reducing atmosphere inside a Carbolite tube furnace.

2.5. Characterisation techniques
Atomic Force Microscopy (AFM) in tapping mode was performed on thin film samples using a Veeco MultiMode Nanoscope III Scanning Probe Microscope (SPM). Digital images were analysed using WSxM software [11].

Optical microscopy in bright field mode was performed on thin film samples using a Zeiss Axiotech Reflected Light Microscope. Digital images were analysed using Image-Pro Plus software.

Thermogravimetry (TG) coupled with Fourier Transform Infrared (FT-IR) spectroscopy was performed using a TA Instruments TGA Q500 with a heating rate of 5 °C/min from room temperature to 1000°C under an Ar atmosphere (100 mL/min) in a platinum crucible and a Thermo Scientific Nicolet iS10, respectively.

X-ray Diffractometry (XRD) was performed on thin film samples using Philips X’Pert PW1730 and Bruker D8 diffractometers. The instruments used the Bragg-Brentano geometry and unfiltered CuKα radiation. 0/2θ scans were performed with 1/2° divergence and anti-scatter slits and a 0.2 mm receiving slit to minimize variations in measured intensity as a result of the finite sample area (typically 1 cm²). φ and ψ scans were performed with a graded mirror to give nearly parallel beam and pinholes to reduce beam size. The measurement range, counting time and step size were adjusted to give appropriate resolution and counting statistics for each sample type. The measured diffraction patterns were compared to standard patterns from the JSPDS database for phase identification using the Philips Highscore software package. The pole figures were measured and plotted using the DIFFRACplus XRD Commander software package.

3. Results and Discussion
The biggest advantages of the CGO precursor solution reported here are cost-effectiveness and high stability. It showed no sign of precipitation and an unchanged viscosity of 2.2 mPas at 25 °C after several months. Moreover, its formulation based on propionic acid resulted in excellent wetting on many substrates (γpropionic acid–air = 26.69 mN/m at 20 °C), and it was observed to spread evenly on a Ni-5%W tape suitable for YBCO coated conductors.

The results of thermogravimetric analysis (TG, Figure 4a) and the corresponding temperature derivatives (DTG, Figure 4b) clearly pinpoint the temperature range and the rate of mass loss occurring in 100 mL/min Ar flow at the 5 °C/min heating rate. For the 0.5 M CGO ink, there is rapid mass loss to 75 °C, corresponding to the evaporation of much of the propionic acid solvent together with acetic acid. Further mass loss occurs in a series of steps, and it is expected that the great majority of propionic acid and acetic acid are liberated below 200 °C.

The final weight loss is 91.81% for the 0.5 M CGO ink, of which 97.5% occurs below 365 °C. In comparison, mass loss is complete by 493 °C for Ce-Ac and 660 °C for Gd-Ac respectively. For these acetates, after water is evaporated the remaining mass loss is known to correspond to a multi-step decomposition process liberating CO and CO₂ [12]. A similar decomposition process is observed for the CGO ink, and FT-IR spectroscopy (Figure 5) confirms that CO₂ is liberated above 200 °C (after the majority of the solvents have evaporated). The magnitude of the CO₂ absorption peak falls to zero (100% transmittance) at approximately 565 °C; no other absorption peaks are observed above 565 °C, and the rate of mass loss is approximately zero (Figure 4), so it is likely that formation of the product oxide is largely complete at this temperature.
After decomposition, there might still be some residual substances such as carbon-rich impurities [8]. It should also be noted that the product oxide may initially be amorphous, and the TG and FT-IR analysis provides no information about the kinetics of formation of the textured crystalline layer. A previously reported nucleation and growth analysis for CeO₂ by in situ high temperature XRD analysis [13] suggests that growth of the product oxide crystals should be expected to take place from around 600 °C. The final weight loss of 0.5 M CGO ink, 91.81%, was used in thickness calculations (Figure 8).

Figure 4 a) TG curves indicating a shift towards lower values of the CGO ink decomposition temperature. The final weight loss (91.81%) was used in thickness calculations (Figure 9). b) Temperature derivatives from the TG analysis (offset for clarity) clearly pinpoint the temperature range of mass loss.
Figure 5 CO₂ absorption peaks from FT-IR spectra of the CGO ink exhaust gases: a) at different temperatures, indicating the end of pyrolysis at 565 °C, and b) transmittance at 2360 cm⁻¹ versus temperature, revealing the range of temperatures over which CO₂ is liberated.

A single 10 pL drop of 0.5 M CGO ink from the piezoelectric nozzle has a 175 μm diameter on the substrate and no shrinkage in area occurs after heat treatment (Figure 6a). Figure 6b and Figure 7a show the first CGO coating (CGO/Ni-5%W) and the second CGO coating (CGO/CGO/Ni-5%W), respectively, on the same substrate after heat treatment; whereas Figure 7b shows a double CGO coating (2CGO/Ni-5%W) after heat treatment. In all cases a 90 μm droplet spacing or 0.51 normalised droplet spacing was used (see Figure 3), giving a continuous and uniform layer in the CGO/CGO/Ni-5%W approach, but with visible variations in thickness in the 2CGO/Ni-5%W approach.

Figure 6 Optical micrograph of a) 10 pL single drops of CGO ink on Ni-5%W tape after heat treatment; the diameter of 175 μm remains unchanged; b) a single CGO ink layer deposited on Ni-5%W tape after heat treatment; CGO/Ni-5%W.
Figure 7 Optical micrograph of a) a single CGO ink layer deposited on CGO/Ni-5%W tape after heat treatment; CGO/CGO/Ni-5%W; b) a double CGO ink layer deposited on Ni-5%W tape after heat treatment; 2CGO/Ni-5%W; the colour variations indicate thickness variations.

Figure 8 shows the calculated dependence of layer thickness on normalized droplet spacing for the square deposition patterns. The volume of a single drop and its diameter on the substrate were assumed to be constant, 10 pL and 175 μm respectively. The wet layer thickness was calculated, assuming complete and uniform coverage, as the ratio of the total volume of ink dispensed (i.e. the product of the droplet volume, 10 pL, and the number of droplets printed) to the surface area of the substrate. The final dry layer thickness was then estimated using the total weight loss of the precursor solutions obtained from thermogravimetry (see Figure 4), and the difference between the theoretical density of the dry layer (7.65 g/cm³) assuming no porosity and the measured density of the wet layer (1.09 g/cm³). Using these values (Figure 8), the thickness of the CGO multilayers was estimated to be 35 nm.

Figure 8 Calculated layer thickness before and after heat treatment versus normalized droplet spacing for the single square pattern printed with the piezoelectric head (droplet volume 10 pL, droplet diameter on the surface 175 μm, spacing normalized against droplet diameter). Δd depends on the density difference between dry and wet layers as well as the total weight loss of precursor solutions.

XRD results are shown in Figure 9 - Figure 12 for one representative sample for each condition, i.e. CGO/Ni-5%W, CGO/CGO/Ni-5%W and 2CGO/Ni-5%W. Four samples were tested in each case and very consistent results were obtained. XRD patterns from θ-2θ scans (Cu Kα) of CGO layers deposited by the piezoelectric head (Figure 9) on (200) textured Ni-5%W tape clearly show better out-of-plane orientation for the CGO/CGO/Ni-5%W approach (i.e. including intermediate heat treatment) than for
2CGO/Ni-5%W, although a very small (111) reflection is recorded next to a dominant (200) peak in the former. As the degree of alignment was clearly so much worse for 2CGO/Ni-5%W, $\theta$, $\phi$, and $\psi$ scans were performed only for the other samples.

The full-width-at-half-maximum (FWHM) of CGO peaks in the $\theta$ scan for CGO/Ni-5%W and CGO/CGO/Ni-5%W is $4.62^\circ$ and $4.44^\circ$, respectively, only slightly higher than $4.22^\circ$, the FWHM of Ni-5%W substrate peaks (Figure 10). These results suggest only a small degree of out-of-plane grain misalignment, and hence a strong cubic texture and the occurrence of heteroepitaxial growth.

XRD scans in $\phi$ and $\psi$ were carried out to examine the in-plane orientation. The pole figures in Figure 11 and the scans in Figure 12 clearly confirm the formation of well-oriented heteroepitaxial CGO coatings on the Ni-5%W biaxially textured tape, both for a single layer (CGO/Ni-5%W) and for the CGO/CGO/Ni-5%W approach (including intermediate heat treatment). The pole figures of CGO (111) are rotated $45^\circ$ relative to those for Ni-5%W (111), confirming $45^\circ$ CGO grain rotation relative to the substrate tape grains for better lattice matching (Figure 11). The FWHM of CGO layer peaks in the $\phi$ scan (related to the degree of in-plane grain misalignment) for CGO/Ni-5%W and CGO/CGO/Ni-5%W are $5.81^\circ$ and $5.38^\circ$, respectively, only slightly higher than $5.33^\circ$, the FWHM of Ni-5%W substrate peaks (Figure 12).

![Figure 9 XRD $\theta$-2$\theta$ scans (Cu K$_\alpha$) of CGO buffer layers inkjet printed on textured Ni-5%W tape by different approaches, clearly showing the presence of cubic out-of-plane orientation in CGO/CGO/Ni-5%W approach.](image9.png)

![Figure 10 XRD $\theta$ scans (Cu K$_\alpha$) of a) CGO layer on Ni-5%W substrate (CGO/Ni-5%W) and b) CGO double layer on Ni-5%W substrate (CGO/CGO/Ni-5%W) at $\theta = 16.53^\circ$ (200) inkjet printed by the approach including intermediate heat treatment, indicating out-of-plane grain misalignments of 4.62$^\circ$ and 4.44$^\circ$, respectively.](image10.png)
Figure 11 XRD pole figures of a) Ni-5%W tape at 2θ = 43.68° (111), b) CGO layer on Ni-5%W substrate (CGO/Ni-5%W) and c) CGO double layer on Ni-5%W substrate (CGO/CGO/Ni-5%W) at 2θ = 28.53° (111) indicating the presence of in-plane orientation and 45° CGO grain rotation relative to the substrate grains for better lattice matching. d) Schematic representation of lattice matching between the Ni-5%W substrate and the coating.

Figure 12 XRD φ scans (Cu Kα) of a) CGO layer on Ni-5%W substrate (CGO/Ni-5%W) and b) CGO double layer on Ni-5%W substrate (CGO/CGO/Ni-5%W) at 2θ = 28.53° (111) inkjet printed by the approach including intermediate heat treatment, indicating in-plane grain misalignments of 5.81° and 5.38°, respectively.

Figure 13 AFM surface profiles of a) Ni-5%W tape, b) CGO layer on a Ni-5%W substrate (CGO/Ni-5%W) and c) CGO double layer on a Ni-5%W substrate (CGO/CGO/Ni-5%W). The rms roughness over these 1x1 μm areas is 0.3 nm, 2.2 nm and 2.6 nm, respectively.
The surface profiles shown in Figure 13 obtained from AFM reveal dense and crack-free CGO coatings, both for a single layer of CGO (CGO/Ni-5%W) and for double layer with intermediate heat treatment (CGO/CGO/Ni-5%W). The root mean square (rms) surface roughness over a 1×1 μm area is 2.2 nm and 2.6 nm, respectively. This is a sufficiently smooth coating for most applications, at less than 7.5% of the estimated film thickness in the case of double CGO layer.

4. Conclusions

We have successfully deposited by inkjet printing a cerium gadolinium oxide (Ce_{0.8}Gd_{0.2}O_{2}) bilayer on highly textured Ni-5%W using the stable precursor ink we have previously reported [10], developing a solid-liquid interface comparable with thin film formation by dip coating. The results from X-ray diffraction show that the single phase Ce_{0.8}Gd_{0.2}O_{2} was obtained in all cases, but only the approach with intermediate heat treatment between depositions produced a highly textured buffer layer. Most importantly we have proven the ability to deposit fully dense highly textured multiple buffer layers for YBCO coated conductors using inkjet printing, applying a simple and industrially-acceptable heat treatment. The extension of this approach to greater thicknesses and more layers is under investigation.

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