

CeO₂ epitaxial films by spray MOD

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Abstract

Dense films of CeO₂ have been epitaxially grown on bi-axially textured Ni tape from a spray MOD technique. Ce-2-ethylhexanoate in toluene solution has been used as a precursor. This carboxylic precursor is ultrasonically sprayed in a specially designed machine allowing the tape to be covered to move. After drying, the film is converted to the oxide above 600 °C in reducing atmosphere, avoiding oxidation of the Ni substrate. The ceramic film is densified at 900 °C (grain size 90 nm) and it grows epitaxially on the substrate. The thickness of the film is determined from IR reflectivity to be 87 nm in agreement with SEM. This continuous process could be easily scaled up.

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1. Introduction

CeO₂ has attracted much interest due to unique physical properties, such as lattice constant ($a = 5.41 \text{ \AA}$) similar to Si making it suitable for Si-device technology, a high refractive index (1.58–2.34 function of porosity) attractive for optical and dielectric applications. On the other hand, although insulating at room temperature (optical gap $E_g = 3 \text{ eV}$), CeO₂ is an anionic conductor at high temperature (>700 °C) and especially when it is doped with Gd that introduces oxygen vacancies in the anionic network. It has also exceptional catalytic activities for the treatment of exhaust gas from automobiles and for hydrogen storing. It is also used as corrosion resistant coating on metals like aluminum or stainless steel. Among these numerous applications, many are concerned with the potentialities of CeO₂ as a buffer layer in thin films devices and especially in coated conductors.

Coated conductors are one of the most regarded applications of superconductivity for high power applications. They are composed of a flexible metal substrate acting as a template to grow a bi-axially textured layer of high T_c superconductor YBa₂Cu₃O₇ (YBCO) on top. In sandwich is inserted buffer layers to avoid corrosion of the metal substrate, diffusion of the metal toward the YBCO layer and adaptation layers to match the crystallographic structure of YBCO to that of the metal substrate. The CeO₂ has attracted much attention as one of the best compatible oxide with YBCO.

Chemical solution deposition (CSD) has a great interest in film formation due to the flexibility of solution chemistry, high rate of film deposition, inexpensive investments, easy scalability for industrial applications as compared to physical deposition methods like pulse laser deposition or sputtering. This is even more critical for the long length materials necessitated in coated conductors. CSD offers several alternatives from inorganic polymerization to metal organic decomposition to cover surfaces. Alkoxydes have a great popularity due to their ability to form polymer network when reacted with humidity. However thick layers are often “mud cracked” because gels are often brittle. More plasticity is offered by

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some metal organic carboxylate, like 2-ethyl-hexanoate, a carboxylate with a long carbon chain that pyrolyses cleanly to metal oxide. Such precursor, soluble in toluene, have good wet ability and then is adequate for liquid film formation by conventional spin-coating¹ or dip-coating. Dip coating is appropriate for tape covering but on both faces. Very few attempts have been made to use spray to form liquid films, it is appropriate to cover on one face and present a rather easy way to control thickness.

In this communication we describe a machine built to deposit liquid films on a moving substrate by the spray MOD technique using Ce(III)2-ethylhexanoate precursor. After recalling some characteristics of the liquid precursor, the technique of spray is described and the conversion to the oxide discussed. The achievement of dense epitaxial nanoscale layers of CeO₂ layers on cube textured Ni is described.

2. Experimental

The solution is prepared by dissolution of dried Ce(III)2-ethylhexanoate (Aldrich) in toluene that delivers a transparent colorless viscous syrup after a few hours of mixing. The viscosity (Rheomat 180) was measured at 20 °C temperature versus time. The apparatus allow to check the Newtonian feature of the liquid. X-ray diffraction were recorded in θ - 2θ mode (Siemens D500) or in a four circle (Sieffert) apparatus equipped with a high flux source allowing measurements on films. Grazing angle X-ray diffraction has been made in an home made diffractometer using a PSD from Inel. SEM was made with a FEG environmental microscope (Philips).

3. Results and discussion

3.1. Ce ethylhexanoate

Ce-2-ethylhexanoate (Ce(EH)₃), EH≡CH₃(CH₂)₃CH(C₂H₅)CO₂, is soluble in toluene where it forms a viscous liquid that ages under air heating or under sun light where it become transparent yellow. Ageing decreases substantially the initial viscosity (from ~30 mPa s for a 0.05 M solution to ~2 mPa s after several 10th of hours at 60 °C). In the fresh product the viscosity is strain dependant, this non-Newtonian behaviour is lost after ageing. The non-Newtonian behaviour suggests some polymeric organisation in the solution linked to the carboxylic bidentate or bridging binding mode, also encountered in manganite-2-ethylhexanoate.² During ageing, the liquid is de-polymerised what is also evidenced by IR spectroscopy in the typical 1600–1400 cm⁻¹ frequency range. Having reproducible and known viscosity is an important aspect for ultrasonic spray that operates only for viscosity smaller than 2 mPa s (Fig. 1).

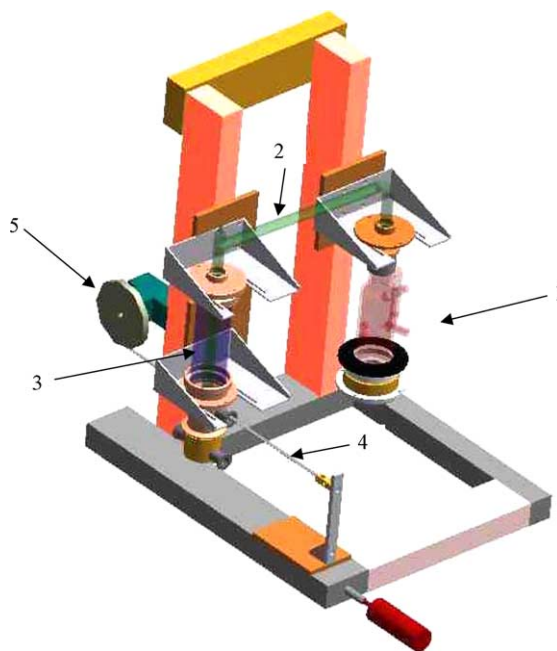


Fig. 1. Spray MOD on a moving tape.

3.2. Spray MOD

The spray unit is described elsewhere,³ it is composed of: a pulverisation pot (1); a transport zone (2); a deposition chamber (3); a moving (reel-to-reel (5)) substrate (4). The pulverisation pot contains the solution (typically 200 ml). It is submitted to ultrasonic waves (800 kHz) generated by a piezoelectric ceramic. This creates a mist of the Ce(EH)₃ solution that is carried through the vessel by a neutral gas (Ar or N₂). It arrives in the deposition chamber with a laminar flow. To avoid heating of the solution, the pulverisation pot is water-cooled (13–20 °C).

At the end of the transport zone (2), the droplets (initially ~10 μm) are feed with toluene vapour in order to compensate their depletion in toluene by evaporation, otherwise their viscosity rises too much and this prevent their spreading on the substrate to form a liquid film. When liquid height in (1) and ultrasonic power, temperature in (1), carrier gas speed, toluene vapour pressure, position of the tape with respect to the deposition chamber are adjusted correctly, a continuous liquid film can be formed on the substrate, either in static conditions or on a moving substrate. Fig. 2 shows such a film deposited on a (1 0 0) Si wafer (10 mm × 10 mm) in a static mode after being dried in air.

Drying takes a few minutes and is favored by air circulated on the freshly deposited film thanks to an adjustable gas extractor located at the bottom of the deposition chamber to trap waste aerosol and toluene vapor. The dried films are formed of a plastic polymer of Ce(EH)₃, not cracked, even when micrometers thick. This device was also used to deposit on a moving tape of Ni at a speed of 1 m/h. We chose bi-axially textured Ni tapes, alloyed with 0.1% Mo processed

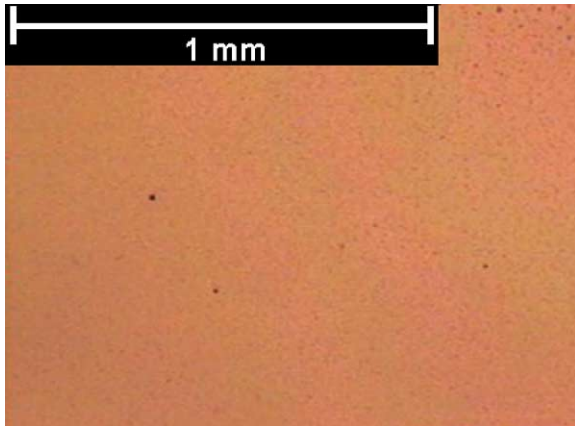


Fig. 2. Continuous film on Si after drying.

by cold rolling and re-crystallization.⁴ The texture consists of Ni cubes parallel to the surface of the tape and to its length.

3.3. Epitaxial dense CeO_2 film on Ni bi-axially textured

$\text{Ce}(\text{EH})_3$ decomposition is favored by the presence of H_2 and ends up under Ar–5% H_2 at 600°C by the formation CeO_2 , Fig. 3. The oxygen bounded in the carboxylate precursor is sufficient to synthesize CeO_2 directly on Ni without oxidation of the substrate. First nucleus of crystallized CeO_2 appears at 650°C in agreement with TGA but no indication of epitaxy can be seen up to 850°C for a film deposited on a moving bi axially textured substrate of Ni. The microstructure of such film, Fig. 4, present small grain size (40 nm (std 7 nm)) but large porosity preventing an epitaxial layer to grow from the interface to sufficient thickness to be detectable by X-ray diffraction.

When heat treated above 900°C , Fig. 5, the film become transparent with a blue color indicative of a thickness in the range of 50–100 nm. It reaches full density with a substantial grain growth (90 nm (std 20 nm)). Note that the imaged zone

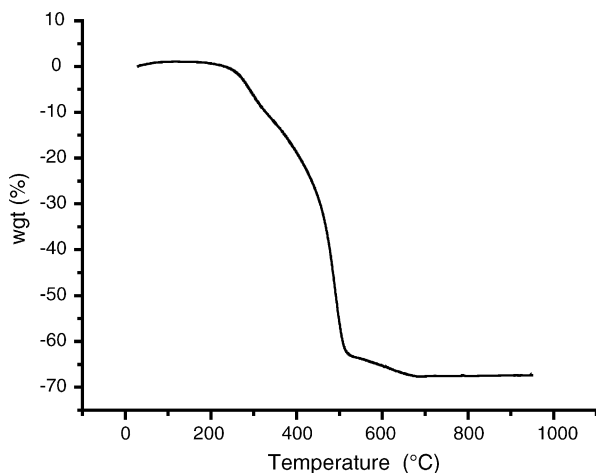


Fig. 3. TGA of $\text{Ce}(\text{EH})_3$ under Ar H_2 flow.

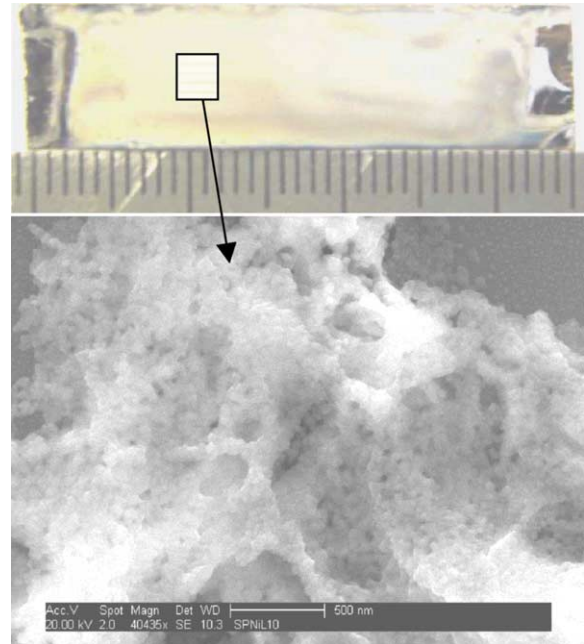


Fig. 4. Microstructure of a CeO_2 film deposited on Ni. Heat treated at 850°C .

is almost pore free, it is representative of the middle part of the sample.

The measurement of the thickness of the layers is not a trivial one. Making a step would be the most direct way, unfortunately this is not simple for CeO_2 that is a hard material. In the last decade, optical methods (ellipsometry, spectroscopy) have been more and more applied for production monitoring of thin films. They are non-destructive and offer a performing

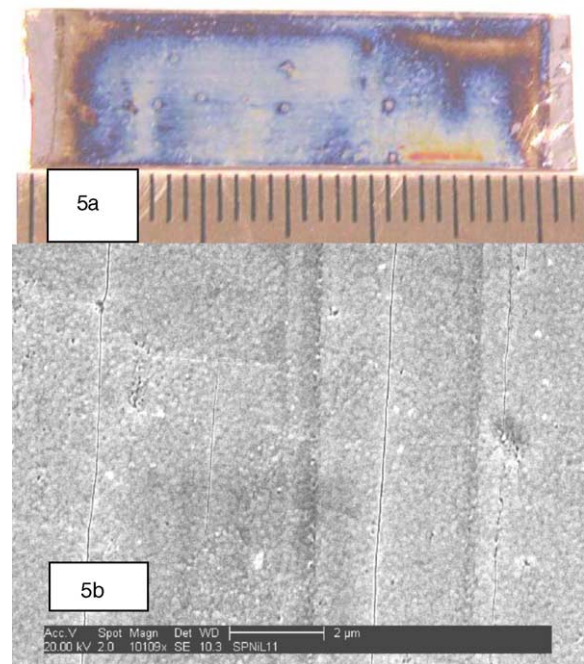


Fig. 5. (a) Typical macroscopic view for a film annealed at 900°C . (b) Typical microstructure for a film annealed at 950°C .

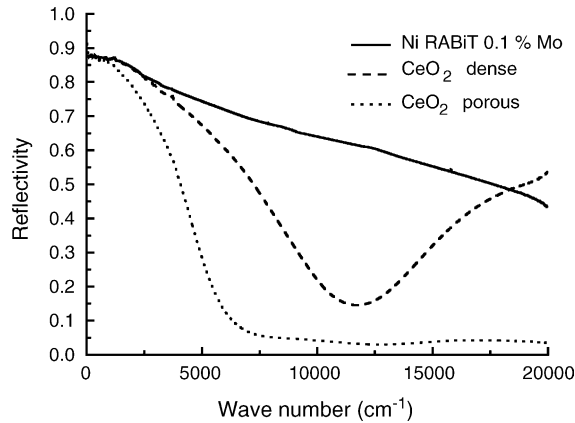


Fig. 6. Reflectivity spectra at room temperature of (straight line) Ni RABiT 0.1% Mo; (dash line) dense CeO₂ layer; (dot line) porous CeO₂ layer.

metrology approach, in particularly for thickness measurement. In the case of a dense dielectric layer deposited on an opaque metallic substrate, the optical response of the system is function of the thickness δ of the layer, of the complex dielectric function of the film, $\tilde{\epsilon}_{\text{CeO}_2}$, and of the complex dielectric function of the metallic substrate, $\tilde{\epsilon}_{\text{substrate}}$.⁵ Thereby we have measured the reflectivity spectra of both CeO₂ films (porous and dense) at room temperature in a very large spectral range (50–20,000 cm⁻¹), Fig. 6. We have also characterized the infrared reflectivity spectra, $R_{\text{substrate}}$ of a clean and optically polished Ni 0.1% Mo bare substrate to extract $\tilde{\epsilon}_{\text{substrate}}$ from $R_{\text{substrate}} = |\sqrt{\tilde{\epsilon}_{\text{substrate}}} - 1/\sqrt{\tilde{\epsilon}_{\text{substrate}}} + 1|^2$. Data have been acquired by the combination of two Fourier Transform spectrometers (Bruker IFS 113 V and Bruker IFS 88). It is obvious from Fig. 6 that the porous film behaves very differently than the dense one because of a strong diffusion of the light by heterogeneities (grains, pores). This impedes to determine the thickness of the porous film by simulation of the optical data as it is done next for the dense one. For the fully dense film, each dielectric function has been simulated with a dielectric function model based on the generalisation of the Lyddane–Sachs–Teller relationship.⁶ In the case of $\tilde{\epsilon}_{\text{CeO}_2}$ we have used previous data concerning a CeO₂ single crystal.⁷ We have reproduced the optical response of the dense deposited layer by adjusting, δ . The simulation provides a value of $\delta = 87$ nm in good agreement with what expected from SEM. It is to stress again, that this method is not valid for porous films especially when the characteristic length of the heterogeneities is in the range of magnitude of that of to the wavelength of the incident beam (Fig. 7).

The dense layer is also bi-axially textured. ϕ scans and pole figures⁸ show an epitaxial layer of CeO₂ on Ni, cube on cube, but rotated 45° with respect to Ni axis, with a mosaic spread smaller than 7° (for both in-plane and out of plane directions). This takes into account the structural mismatch (+8%) with respect to Ni substrate. As one can see on Fig. 5 the film is dense (almost no detectable porosity), but with several straight fractures. These fractures disappear when the film thickness is decreased to approximately <50 nm, in agree-

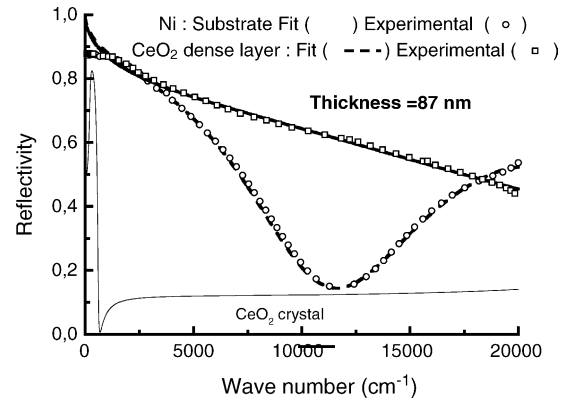


Fig. 7. Best fits of the experimental reflectivity spectra at room temperature of Ni RABiT 0.1% Mo, and dense CeO₂ layer.

ment with the critical thickness concept.⁹ Between 850 and 900 °C, the layer has substantially densified allowing the epitaxial layer to grow from the substrate as demonstrated some years ago for YSZ.⁹ Such dense and epitaxial packing probably needs narrow size distributed cubes of CeO₂ on cube of Ni. However, no detailed analysis of the interface has been made up to now.

We have tried to increase the thickness of the layer by multiple sequential deposition by spin coating followed by annealing steps. The CeO₂ texture is preserved in these treatments allowing good chance of success by the spray process. More studies are however needed to optimize the resulting layer (density, fractures). The surface characteristics (roughness, (1 1 1) faceting, random nucleated grains) have an important impact on the quality of the texture after multiple deposition. X-ray diffraction at grazing angle can be used successfully as a guide to search for better sample quality. Recent experiments on dense samples observed at 2° of incidence angle indicate that some grains have not the right orientation at the surface of our films, suggesting a range of improvement of the sample quality.

4. Conclusion

Dense films, 87 nm thick, of CeO₂ have been epitaxially grown on bi-axially textured Ni tapes. The films are deposited from a carboxylic precursor using a spray of liquid droplets on a moving tape, allowing a continuous process to be scaled up. Such film designed for coated conductors could have other utilization in several fields like solar absorbers.

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