

Chemical approach to the deposition of textured CeO₂ buffer layers based on sol gel dip coating

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Abstract. The widespread use of vacuum techniques for the development of coated conductors, in which buffer and superconducting (REBa₂Cu₃O_{7-δ}) layers are deposited epitaxially on a substrate, is well established in the research environment. However, obtaining uninterrupted deposition at high speed, increasing flexibility in composition and in film thickness and attaining independence of geometric constraints are areas in which many vacuum techniques will need sustained development in order to answer industrial demands. This work describes the deposition of textured CeO₂ buffer layers based on sol gel dip coating under atmospheric environment and from aqueous precursor materials.

Research has been performed towards the deposition of CeO₂-buffer layers using the amorphous citrate method on sapphire substrates and Ni-W foils. Coating is performed using the dip-coating technique, which allows extension to a continuous system. The withdrawal speed and the thermal treatment have been optimised in order to obtain highly oriented (001) layers exhibiting a smooth and crack-free morphology both on ceramic and metallic substrates. From the results it was concluded that sintering atmosphere and sintering temperature play a crucial role in the growth mechanism.

This study describes the structural and morphological analysis of the thin layer with special attention to the difference between ceramic and metallic substrates.

Introduction

The development of high temperature superconductors, such as YBa₂Cu₃O_x (YBCO), has resulted in many applications in the fields of electronics, microwave and conductor technologies. For this reason, ceramic superconductors have been deposited as thin films by various methods (e.g. pulsed laser deposition, sputtering, electron beam co-evaporation...) on many substrates, including SrTiO₃, LaAlO₃, MgO, Al₂O₃ and flexible metallic substrates such as Ni and Ni alloys. These coated conductors are promising in the applications of transmission cables, motors, energy storage, magnets, fault current limiters, etc....

Excellent epitaxial relationships exist between YBCO and SrTiO₃ and LaAlO₃ [1-3]. These substrates however are expensive and are often only available in small sizes. For technical and industrially sized applications, the use of inexpensive and flexible metallic substrates becomes necessary. However, it has been shown that YBCO films deposited directly onto the latter substrates exhibit poor superconducting properties, because of chemical interactions and/or large structural mismatches [4]. In order to grow a good quality YBCO thin film, it is necessary to use buffer layers such as CeO₂ [5], Ytria-Stabilized Zirconia (YSZ) [6], MgO [7], SrTiO₃ [8], BaZrO₃ [9] etc.

Amongst these, CeO₂ is usually considered as a high quality material, because of the good lattice match of the (100) plane with the YBCO (001) plane, the comparable thermal expansion coefficient ($11.6 \times 10^{-6} \text{ K}^{-1}$ for CeO₂, $12-13 \times 10^{-6} \text{ K}^{-1}$ for YBCO), the oxidation

protection of metallic substrates and the chemical compatibility with YBCO and many substrate materials [10].

Thus far, many growth techniques including pulsed laser deposition [11], sputtering [12] and electron beam evaporation [13] have been used for CeO_2 film growth. The application of these physical vapour deposition methods is limited owing to the necessity of complex apparatus and slow deposition rate. Alternatively, the deposition of such coatings at atmospheric pressure from aqueous media presents many attractive features such as simplified apparatus, lower cost, upscalability, low process temperatures, control of purity of reagents, ability to coat complex shapes and the possibility to produce homogeneously mixed precursor powders on atomic scale with controlled stoichiometry.

In this paper, we report the successful epitaxial growth of CeO_2 buffer layers using a sol gel dip coating technique, based on a Cerium- nitrate precursor solution. This method provides some advantages compared to other sol-gel methods : it makes no use of expensive and difficult to handle metal alkoxides and the used solvent is water, which makes the method environmentally friendly.

Experimental procedure

Substrates. The substrates used were r-cut (1102) alumina and rolled and polished Ni-W alloys.

Prior to deposition, the alumina substrates were cleaned by a combination of degreasing in trichloroethylene, acetone and methanol, chemical cleaning in a hot mixture of sulfuric and phosphoric acid and ultrasonic cleaning in methanol. The combination of these cleaning methods leads to an almost complete wettability, shown by a contact angle of $< 14^\circ$ in the sessile drop contact angle measurement of figure 1.

For the Ni-tapes, the same procedure was followed, except for the second step, where the chemical cleaning was performed in a hot mixture of hydrogen peroxide and formic acid. This procedure leads to a contact angle of $< 8^\circ$ in the sessile drop method.

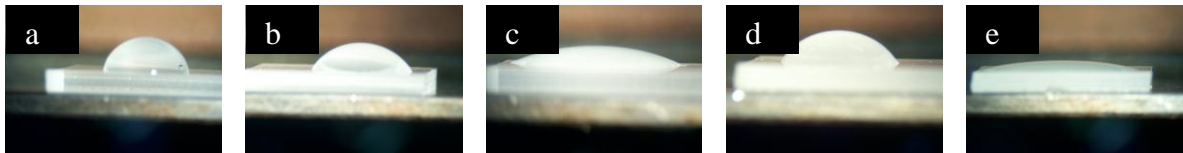


Figure 1 : Sessile drop contact angle measurement on alumina (a : untreated, 82° ; b : after degreasing, 50° ; c : after chemical cleaning, 30° ; d : after ultrasonic cleaning, 50° ; e : after combined treatment, 14°)

Sol gel precursor solution. The precursor gel was prepared using an amorphous citrate method. Here, $\text{Ce}(\text{NO}_3)_3$ is dissolved in deionised H_2O in a 1M concentration. Citric acid is employed to produce metal chelation. The pH is adjusted using NH_4OH . A series of mixtures varying in $\text{Ce}(\text{NO}_3)_3$ / citric acid ratio (1:1, 1:2, 1:3) and pH was produced to observe the effects on the properties of the coating solution. The solutions were stirred at 40°C for 30 minutes. After chelation was completed, the pH was changed by adding ammonia (25 wt% solution). Clear and stable gels could be obtained by drying a solution with a Ce: citric acid ratio of 1:3 and a pH between 5 and 7.

Coating procedure and thermal treatment. CeO_2 thin films were coated using a computer controlled dip coater (KSV Instruments) at speeds varying from 0.5 to 50 mm/min. The coated samples were dried at 60°C , for 15 min and then heat treated at 300°C for 60 min using a quartz tube furnace. After that, samples were subjected to different thermal treatments varying from 500°C to 1500°C for 10 to 360 min. For alumina substrates, the thermal process

was performed under air, for Ni/W substrates a 4%H₂/Ar atmosphere was used to avoid oxidation of the substrate.

Analysis. Thermal analysis (TGA-DTA Stanton Redcroft) was carried out at a temperature range between 25 °C and 700°C under air, at a heating rate of 10 °C/min. Powder diffraction patterns of the CeO₂ films were obtained using a Siemens D5000 diffractometer with CuK α radiation. Electron Back Scattering Diffraction (Link Analytical – OPAL) was used to determine out of plane and in plane orientations of the film. The out of plane alignment was measured by scanning the (100) plane of the film. The in plane alignment was determined by measuring the (111) plane. The thickness of the films was determined by variable angle spectroscopic ellipsometry. The surface morphology of the films was studied using optical microscopy (Leitz Laborlux) SEM (Philips 501) and AFM (Topometrix TMX 2010).

Results and discussion

Thermal treatment. Differential thermal analysis was performed to understand the thermal decomposition phenomena of the Ce-citrate precursor. In fig.2, the first weight loss can be observed at a temperature of 125°C, due to dehydration reactions. This is followed by a gradual weight loss until 300°C. The large weight loss between 300°C and 370°C, accompanied by a strong exothermic DTA signal, can be ascribed to decarboxylation of the precursor.

No thermal effects were observed above 370°C, which indicates that the citrate-gel method allows the synthesis of CeO₂ at low temperature.

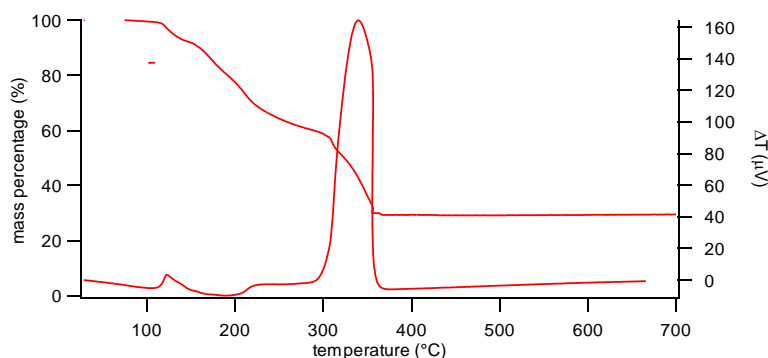


Fig. 2 : TGA-DTA curves obtained by heating the dried precursor gel in static air at a heating rate of 10°C/min.

Thickness. The thickness of the deposited films increases with increasing dip coat speed, according to the formula

$$h = 0.94 (\eta v)^{2/3} / \gamma^{1/6} (\rho g)^{1/2},$$

where h = thickness of the layer; v = dip coat speed; η = viscosity of the precursor solution; γ = surface tension of the precursor solution; ρ = density of the precursor solution and g = gravity constant.

For dip coat speeds of resp. 10mm/min, 1 mm/min and 0.5 mm/min, thicknesses of 60, 25 and 8 nm were obtained, as determined from variable angle spectroscopic ellipsometry.

Influence of dip coat speed on morphology. Fig. 3 shows the optical micrographs for CeO₂ layers dip coated at different speeds. For a dip coating speed > 10 mm/min, a bad morphology is obtained showing a high roughness and the presence of cracks. Homogeneous, smooth and crack free layers are obtained for dip coat speeds < 1 mm/min. Some inclusion are still visible, probably due to dust particles.

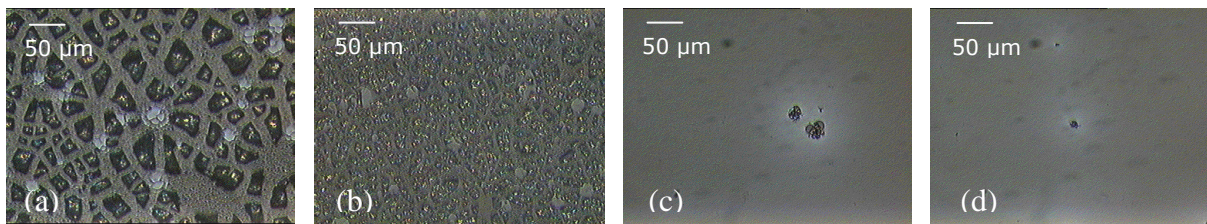


Fig. 3 : Optical micrographs of CeO_2 films dip coated at different speeds. (a) 50 mm/min; (b) 10 mm/min; (c) 1 mm/min; (d) 0.5 mm/min.

CeO_2 films on alumina. CeO_2 films coated at a dip coat speed of 1 mm/min. on alumina were heat treated between 500 and 1500°C in air, for 10 min to 360 min. The XRD pattern revealed a pure CeO_2 phase. In all the conditions, a mixture of (111) and (002), resp. at 2θ 28,64 and 33,18 is present. It was shown that the reflections are more intense as the temperature increases. Since all films were dip coated at the same speed and therefore have the same thickness, it can be concluded that raising the temperature improves crystallinity. In fig. 4, a remarkable increase from 20% to 85% for the relative fraction of (002) reflection (from 45% to 95% for the degree of orientation) is observed when the annealing temperature is increased from 1100°C to 1200°C. However, annealing at such high temperatures causes an increase in the roughness of the film, which can be clearly seen from SEM and AFM analysis in fig. 5.

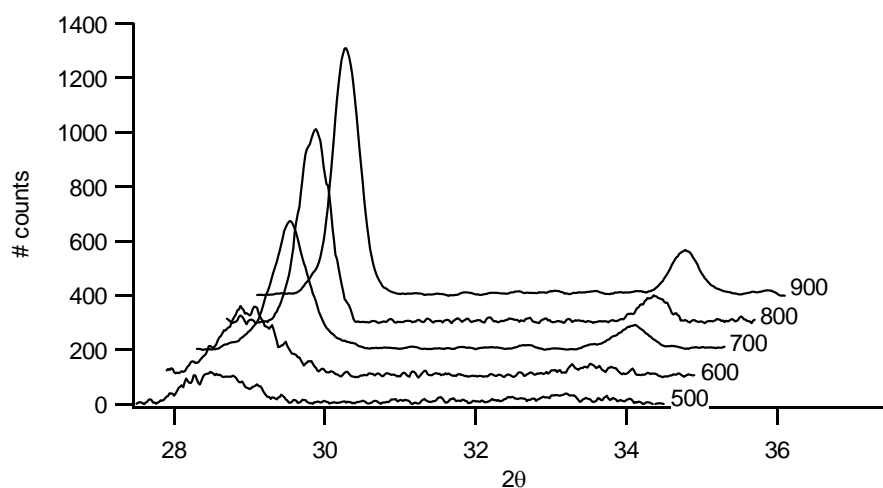
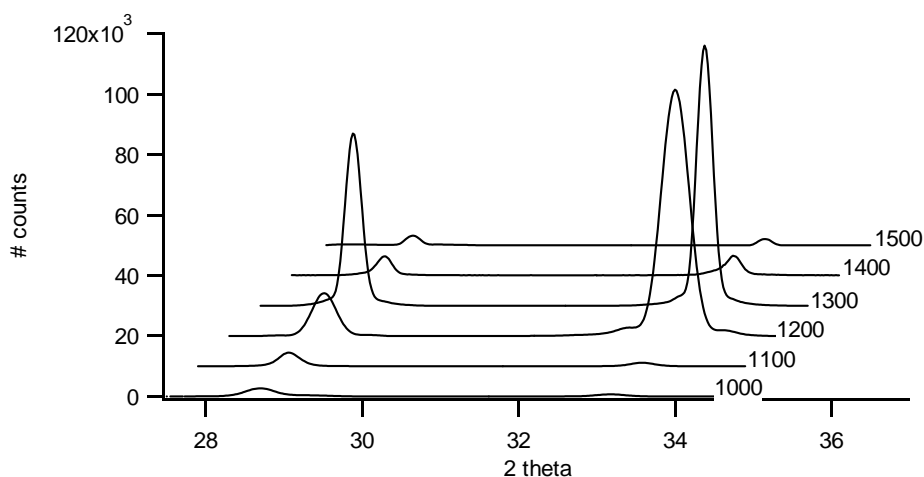


Fig.4 : XRD spectra for CeO_2 thin films on r-cut sapphire as a function of annealing temperature.



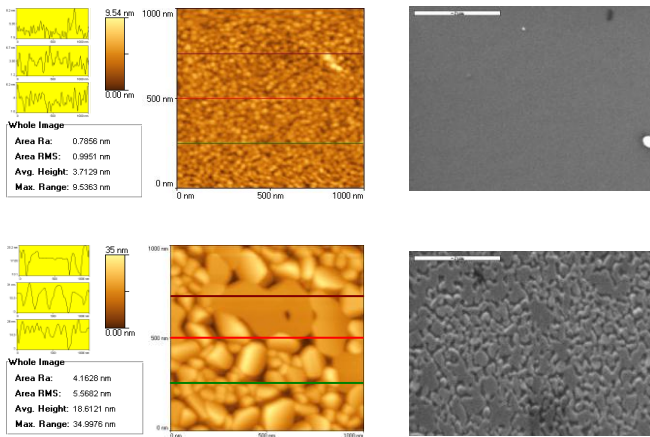


Fig. 5 : SEM and AFM graphs for CeO_2 films on r-cut sapphire annealed at (a) 800°C and (b) 1200°C .

CeO_2 films on Ni/W. Here, the annealing process was completed under reducing $4\% \text{H}_2/\text{Ar}$ atmosphere to prevent NiO formation. Textured annealing conditions were observed above 800°C . The X-ray diffraction pattern of fig. 6 shows only one peak at 33.6° from the CeO_2 (002) reflection, which indicates a good out-of-plane alignment.

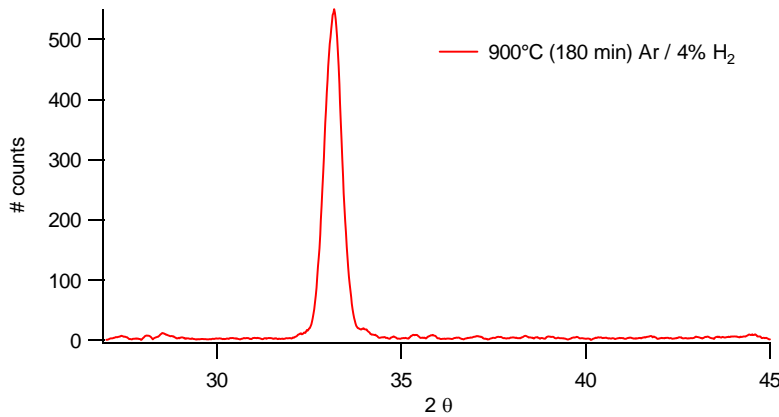


Fig. 6 : XRD spectrum of a CeO_2 film on a Ni/W substrate annealed at 900°C for 180 min.

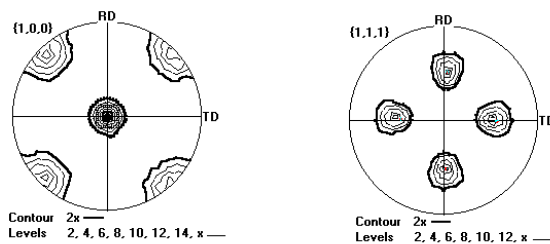


Fig. 7 shows a (100) and (111) EBSD-OPAL figure of the films annealed at 900°C . Four fold symmetry and cube biaxially texturing can be clearly seen.

Fig. 7 : (100) and (111) pole figures of CeO_2 annealed at 900°C .

Fig. 8 shows the morphology of textured CeO_2 films. The films are homogeneous, crack free and smooth. Since the CeO_2 films follow the morphology of the Ni/W substrate, grain boundaries are visible.

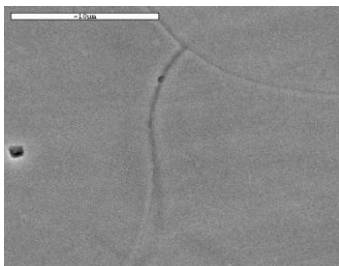


Fig. 8 : SEM micrograph of CeO_2 thin film on Ni/W substrate.

Conclusions

CeO₂ buffer layers were successfully grown on r-cut alumina and on textured Ni/W foil using a sol gel dip coating process. The precursor solution was prepared using Ce(NO₃)₃ and citric acid in an aqueous medium.

On alumina, CeO₂ films with a mixed (111) and (002) alignment were grown at temperatures from 500°C to 1500°C for 180min in air. The optimum condition for (002) orientation was 1200°C.

Fully (002) textured CeO₂ buffer layers were grown on Ni/W substrates at 900°C for 180 min in a 4% H₂/ Ar atmosphere. EBSD analysis revealed cube on cube biaxially textured growth. The CeO₂ buffer layers have a roughness ranging from 0.5 to 20 nm and are crack free.

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