DEVELOPMENT OF CHEMICAL DEPOSITION METHODS FOR THE FABRICATION OF YBCO HIGH TEMPERATURE SUPERCONDUCTING COATED CONDUCTORS FOR HIGH-FIELD APPLICATIONS

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1. Introduction

Oxide thin films have a large range of applications in electronics, optics, catalysis, wear resistance, corrosion protection and superconductivity. The sol-gel processing route is particularly attractive for fabricating oxide thin films, since the liquid precursor can easily be applied on a substrate by dipping, spinning or spraying. The two principal gel-processing routes for oxide ceramics involve the gelation of either a sol by the removal of water, or the cross-linking of inorganic polymers by the hydrolysis of metal alkoxides in an alcoholic solvent. For both routes, the final conversion to oxides is accomplished by heat-treating the dried gel, resulting in either polycrystalline or oriented (epitaxial) thin films.

CeO_2, with a cubic fluorite structure (a = 5.411Å), has been widely investigated as a protective buffer layer for high temperature superconductors (HTS) in current-carrying applications, or as an insulating layer in multilayer electronic devices. Compared to yttria-stabilized zirconia (YSZ), for example, CeO_2 is a more attractive buffer layer for YBCO because of the smaller lattice mismatch and the similar thermal expansion coefficient, especially when biaxially textured Ni or Ni based alloys are used as substrates. Thus, so far, many growth techniques have been used for CeO_2 film growth including molecular beam epitaxy (MBE), pulsed laser deposition (PLD), sputtering and e-beam evaporation, metal-organic chemical vapor deposition (MOCVD). The so-called "chemical solution epitaxy" has emerged as a viable, versatile, non-vacuum process for fabricating oxide thin films on various substrates.

The trifloroacetates metalorganic deposition (TFA-MOD) of YBCO film is widely investigated because it requires no vacuum apparatus and ensures high deposition rates. Therefore, it is generally agreed that this might be one of the most adequate deposition methods for the scale up of long length superconducting tapes fabrication process. In the TFA-MOD method, a fluorine containing coating solution, namely a stoichiometric mixture of Y, Ba and Cu trifloroacetates obtained by the reaction of the corresponding acetates with trifluoroacetic acid, decompose to fluorides and finally to oxides by a thermal treatment in a humidified oxygen atmosphere. In order to obtain an epitaxial YBCO film, the as-prepared precursor film is treated at about 800 ^{o}C in pure oxygen.

2. Preparation of the coating solution for CeO_2 and YBCO deposition.

a) CeO_2 coating solution

All solution manipulations were carried out in an atmosphere of argon using standard Schlenk techniques for moisture sensitive compounds. The cerium methoxyethoxide solution in 2-methoxyethanol was prepared in two different ways.

First, by charging a flask with 1 g of cerium isoproxide 97%(Alfa) and 25ml of 2-methoxyethanol (Alfa). The content of the flask was refluxed for 1 hour and 15 ml of solvent (isopropanol and 2-methoxyethanol) was removed by distillation. The content was rediluted with 25 ml additional 2-methoxyethanol and the distillation/redilution cycle was repeated eight

more times to ensure the exchange of the isopropoxide ligand for the methoxyethoxide ligand as much as possible. Due to the intrinsic insolubility of cerium isoproxide in 2-methoxyethanol, a supplementary filtration was necessary to remove the unreacted solid. The final concentration was adjusted to about 0.15 molar. Difficulties have been also encountered in the preparation in house of cerium isoproxide from cerium metal and isopropanol in the presence of a mercury salt catalyst by the method of Brown and Mazidiyansi. The reaction is slow and hard to drive to completion.

Second, diluting the as-purchased 18-20 % wt. cerium (IV) methoxyethoxide in 2-methoxyethanol (Alfa) solution, it was brought to a concentration of 0.25 molar. For the partial hydrolysis, four parts of the as-obtained solutions were mixed with one part 1.0 molar H_2O in 2- methoxyethanol to produce the coating solution.

b) YBCO coating solution

We prepared the coating solution via a base-exchanging route in de-ionized water as a solvent. The starting materials are Y, Ba and Cu acetates and trifluoroacetic acid. First, the 1:2:3 stoichiometric amounts of acetates were dissolved in de-ionized water. The trifluoroacetic acid was added to the as-obtained solution of acetates, in stoichiometric amounts. The resulting aqueous solution was evaporated until a dark blue glassy residue was obtained. The glassy residue was dissolved in sufficient methanol and evaporated again. This procedure, which was repeated several times, is necessary to eliminate the water and the acetic acid from the coating solution. The final coating solution should contain only metal trifluoroacetates and methanol.

c) Deposition and thermal treatment of CeO_2 and YBCO precursor films

Prior to the deposition, the substrates, both single crystals ($SrTiO_3$, $LaAlO_3$, Al_2O_3, MgO,), pure Ni and NiV alloys, were ultrasonically cleaned with dry isopropanol. The spin coating technique was used to coat the substrates. 10mm by 10mm samples were flooded with the solution and the excess solution was thrown-off by spinning under different conditions (from 10 to 25 seconds and 2000 rpm to 6000 rpm). The coated substrates were placed in a quartz tube and some of the samples were purged for about 10 minutes at room temperature in $Ar+4\%H_2$. The tube was then placed in a tube furnace and thermally treated in $Ar+4\%H_2$ under different conditions (time, temperature, heating/cooling cycle). Coatings produced under these conditions were typically 50 nm. Thicker layers can be obtained by multiple coatings.

For the deposition of YBCO film the (100) $SrTiO_3$ was cleaned in the same way as for CeO_2 deposition. The TFA YBCO precursor film was deposited by spinning at 2000 rpm. The gel films were calcined at 400 ^{o}C in humidified oxygen for 18 h and further at 800 ^{o}C in pure oxygen. Finally, the film was cooled down at room temperature at a rate of 10 ^{o}C/min.

3. Structural and morphological characterization of CeO_2 film

The X-ray spectra of the dried Ce precursor states for its amorphous nature with a slight crystallization tendency at peaks corresponding to CeO_2 (111). The thermal analysis TG-DTA performed on the $Ce(OR)_x(OH)_y$ precursor evidenced the loss of weight with temperature and the endo- and exothermal effects, respectively. The total weight loss associated with the transformation of $Ce(OR)_x(OH)_y$ in CeO_2 in the temperature range 0-1200°C is 45,5% due to dehydration (0-200°C), decomposition of the organic rest (200-600°C). The exothermic effect can be attributed to the beginning of CeO_2 crystallization in agreement with the X-ray spectra.

SrTiO₃ /CeO₂ structures

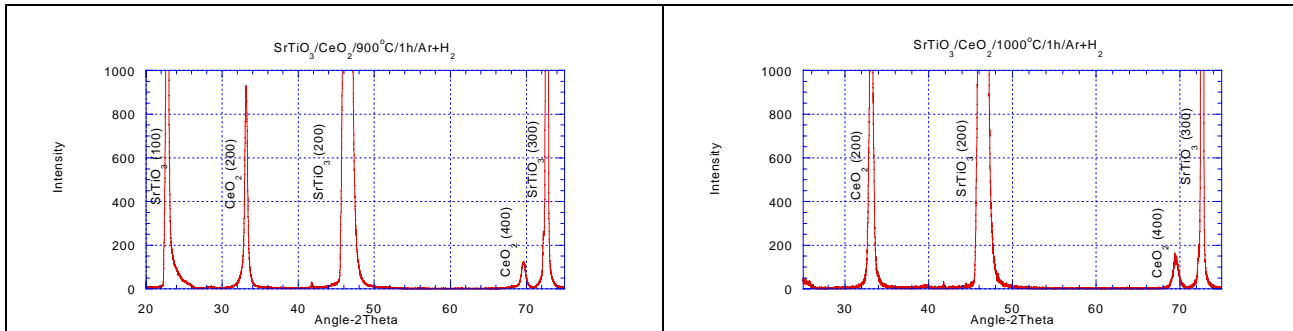Figure 1 shows the θ-2θ scans for the CeO₂ films grown at 900°C and at 1000°C for 1h in 4%H₂/96%Ar atmosphere.

Figure 1. XRD pattern of SrTiO₃-CeO₂ structures (a) 900°C, 1h; (b) 1000°C, 1h

The degree of crystal orientation of a CeO₂ film is defined as I(200)/I(111), where I(200) and I(111) are intensities of CeO₂(200) and CeO₂ (111) peaks in the θ-2θ scans, respectively. Apart from (200) and (400) CeO₂ peaks, no other CeO₂ reflections are detected. This demonstrates that the CeO₂ films are epitaxially grown with $[h00]//[h00]$ epitaxial relationship between the substrate and the film. The ω-scan of (200) CeO₂ peak has a Full-Width-Half-Maximum (FWHM) of 0.5° and 0.3° for the sample thermally treated at 900°C and 1000°C, respectively (Fig. 2).
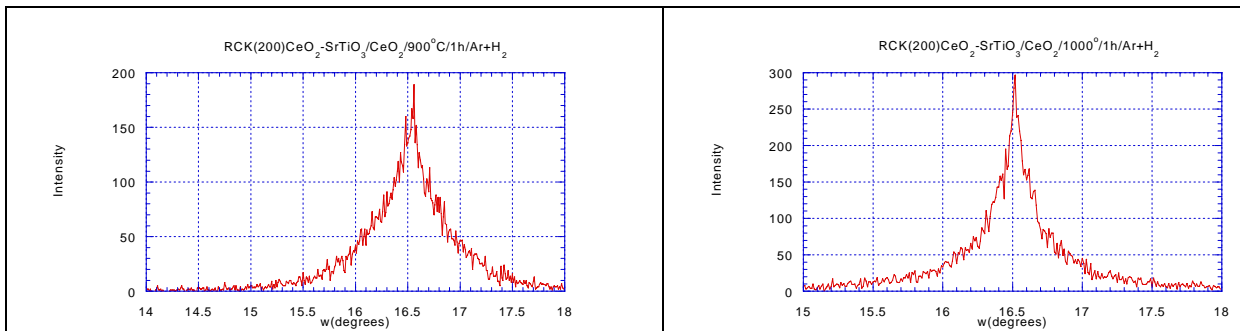

Figure 2. Rocking curves for the (200) peak of CeO₂ on SrTiO₃

The in-plane orientation was analysed by pole figures and ϕ scans Figure 3 presents the (200) and (111)CeO₂ pole figures. The in-plane crystallographic relationship between substrate and CeO₂ film is [100]SrTiO₃||[100]CeO₂. The FWHM of ϕ scans (Fig. 4) of (111)CeO₂ peak is of about 0.5° very close to those for the substrate, indicating a high degree of epitaxy for CeO₂. The FWHM of ϕ scans of (111)CeO₂ peak is of about 0.5° very close to those for the substrate, indicating a high degree of epitaxy for CeO₂.

In-plane aligned CeO₂ is considered to grow by solid-state epitaxy of an amorphous CeOₓ layer beginning at the film-substrate interface. It is believed that the difference of organic components (degree of hydrolysis) affects the grain size or local crystallinity of CeOₓ after the thermal treatment. In addition, a steep heating ramp in the crystallization step is considered to be essential for the growth of CeO₂ layers by CSD because it prevents the nucleation of randomly oriented polycrystalline CeO₂ grains inside the amorphous layer during the ramp.
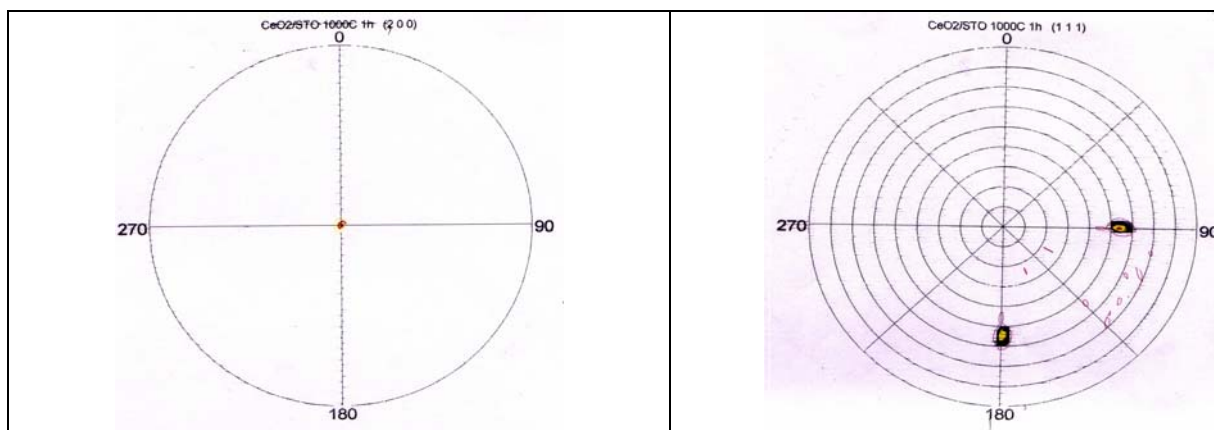
Figure 3. (200) and (111) CeO₂ pole figures

The FWHM of ϕ scans (Figure 4) of (111)CeO$_2$ peak is of about 0.5° very close to those for the substrate, indicating a high degree of epitaxy for CeO$_2$.

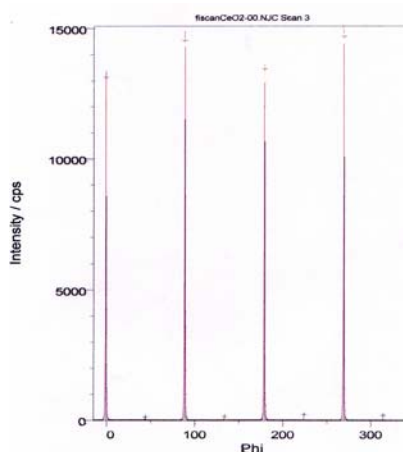*Figure 4. The X-ray phi-scans of (111) CeO₂ on STO*

The CeO$_2$ films grown on (100) LaAlO$_3$ (LAO) exhibit both (200) and (111) reflections, but the (200) is dominant and has a FWHM of about 0.8°. Thus, CeO$_2$ was epitaxially grown on LAO in spite of the difference in crystal structures of these materials which are the fluorite-and perovskite-types, respectively.

The deposition of CeO$_2$ on MgO(200), under the same conditions, emerge in a (111) orientation. Similarly, the (111) orientation relative to the sapphire (Al$_2$O$_3$) normal axis is the preferred growing mode of CeO$_2$.

Ni/CeO₂ and NiV/ CeO₂ structures

The deposition of CeO$_2$ on single crystals (STO, LAO, Al$_2$O$_3$, MgO) represents a preliminary step which precedes the deposition on biaxially textured metallic substrates. The CeO$_2$ films grown on biaxially textured Ni and Ni-V substrates exhibit both (200) and (111) reflections, but the (200) is dominant and has a FWHM of about 1,0° for the film heat treated at 900°C. In Figure 5 are presented the XRD patterns of Ni-CeO$_2$ structures heat treated at 900°C and 1000°C, respectively. Various thermal treatments schedules have been experimented in order to optimize the epitaxial growth of CeO$_2$. Due to the oxygen nonstoichiometry (CeO$_{2-x}$) occurring during the high temperature thermal treatments, a supplementary thermal treatment in oxygen is required in order to enable the epitaxial growth of CeO$_2$.
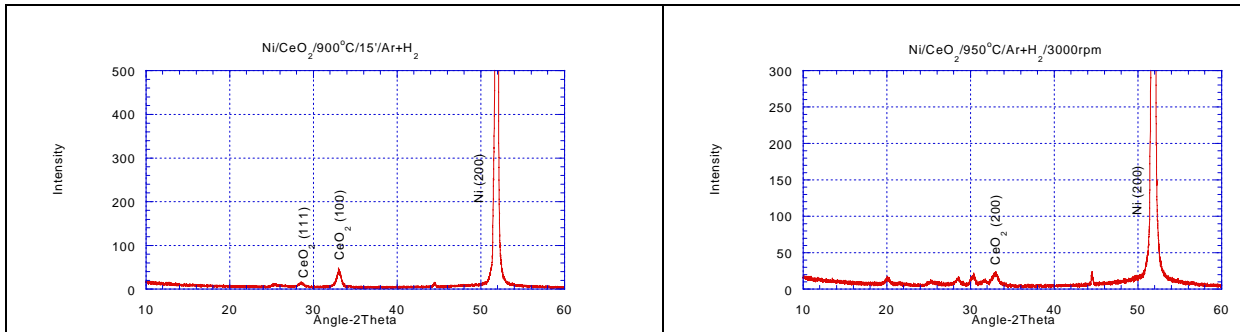
Figure 5. XRD pattern of Ni-CeO₂ structures heat treated at 900°C and at 1000°C, respectively

The CeO$_2$ films deposited on biaxially textured Ni-V alloys are polycrystalline. Moreover, the interaction with the substrate is evidenced, resulting in Ce-V-O compounds formation.

At low magnification scanning electron micrograph revealed a film morphology quite similar to that of the substrate: smooth, dense and continuous, free of cracks. Although this film was not produced in a dust-free environment, relatively few pinholes or defects are observed.

4. Structural and morphological characterization of the YBCO film

The X-ray diffraction of YBCO film on (100)SrTiO$_3$ substrate is presented in Figure 6. As can be seen, the $\theta-2\theta$ XRD spectrum mainly shows only the (h00) YBCO reflections, indicating that the YBCO film is epitaxially grown on (100)SrTiO$_3$ with a $[h00]//[h00]$ epitaxial relationship between the substrate and the film. The ω-scan of (500) CeO$_2$ peak has a Full-Width-Half-Maximum (FWHM) of 0.3°. The unidentified peak at 32.7° can be attributed to misoriented YBCO grains or/and unreacted CuO islands.

Figure 7 presents the SEM micrograph of YBCO film. At 35KX magnification the film morphology has a plate like aspect. It is to be noted that the coalescence of the film is quite good. Nevertheless, holes can be also observed. The high magnification (250 KX) image reveals that the grain size is of about 200 nm. The screw growing mechanism can be observed.

5. Superconducting properties of YBCO film on (100) SrTiO$_3$ substrate

Typical temperature dependence of resistance is shown in the Figure 8. The zero resistance critical temperature for the YBCO films is $\approx$ 88 K and the transition width is around 1 K. The films exhibited a linear behaviour of the normal state resistance with R(300)/R(100) ratio of about 2.6, which suggests a high *c-axis* oriented film.
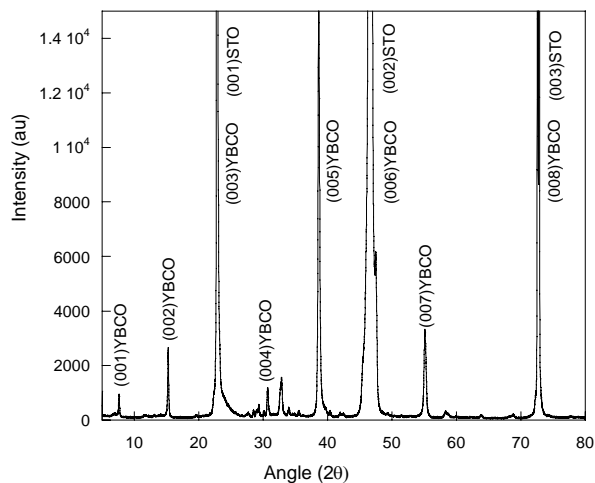
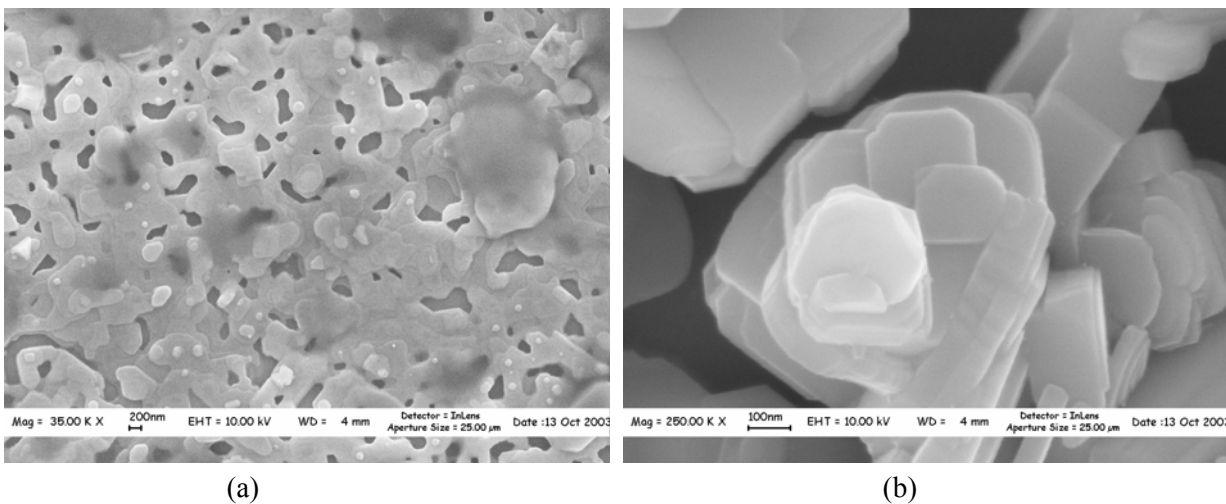*Figure 6. XRD spectrum of YBCO film on (100) SrTiO₃ substrate*

(a)

(b)

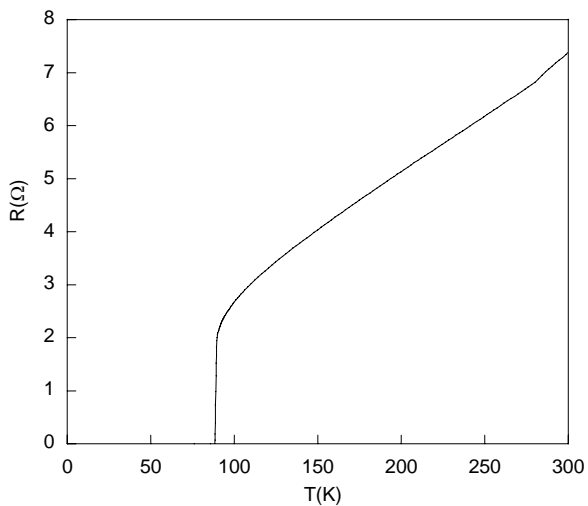*Figure 7 The SEM micrographs of the YBCO film grown on (100) SrTiO₃ substrate.*

Figure 8. Temperature dependence of the electrical resistance of YBCO film grown on (100) SrTiO₃

6. Conclusions

The research activity on **"***Development of Chemical Deposition Methods for the Fabrication of YBCO High Temperature*** Superconducting Coated Conductors for High-Field Applications"** was mainly focused on the development of coating solutions for the deposition of oxide buffer layers (such as CeO_2) and of superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) films.

The cerium methoxyethoxide solution in 2-methoxyethanol was prepared in two different ways: either by the reaction of cerium isoproxide 97%(Alfa) with 2-methoxyethanol (Alfa) or by diluting the as-purchased 18-20 % wt. cerium (IV) methoxyethoxide in 2-methoxyethanol (Alfa) solution, brought to a concentration of 0.25 molar. The trifluoroacetate based YBCO coating solutions we prepared via a base-exchanging route in de-ionized water as a solvent. The starting materials are Y, Ba and Cu acetates and trifluoroacetic acid.

Prior to the deposition on the biaxially metallic substrates, both coating solutions were experimented on (111) $SrTiO_3$ single crystal substrates. The as-deposited CeO_2 film exhibits a good epitaxy. The ω-scan of (200) CeO_2 peak has a Full-Width-Half-Maximum (FWHM) of 0.5° and 0.3° for the samples thermally treated at 900°C and 1000°C, respectively. This demonstrates that the chemical deposition method using alkoxides should be scaled up for long metallic tapes.

On the other hand, the YBCO film deposited on (111) $SrTiO_3$ single crystal substrates, using trifluoroacetate (TFA) method, exhibits good epitaxy with ω-scan of (500) YBCO peak of 0.3°. The zero resistance critical temperature for the YBCO films is ≈ 88 K and the transition width is of around 1 K. Nevertheless, the SEM analysis has revealed a YBCO film with an incomplete coalescence. From this reason, further experiments have to be carried out on the thermal treatment of the as deposited film.