

MOD approach for the growth of epitaxial CeO₂ buffer layers on biaxially textured Ni–W substrates for YBCO coated conductors

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Received 11 August 2003, in final form 15 September 2003

Published 17 October 2003

Online at stacks.iop.org/SUST/16/1305

Abstract

We have grown epitaxial CeO₂ buffer layers on biaxially textured Ni–W substrates for YBCO coated conductors using a newly developed metal organic decomposition (MOD) approach. Precursor solution of 0.25 M concentration was spin coated on short samples of Ni–3 at%W (Ni–W) substrates and heat-treated at 1100 °C in a gas mixture of Ar–4%H₂ for 15 min. Detailed x-ray studies indicate that CeO₂ films have good out-of-plane and in-plane textures with full-width-half-maximum values of 5.8° and 7.5°, respectively. High temperature *in situ* XRD studies show that the nucleation of CeO₂ films starts at 600 °C and the growth completes within 5 min when heated at 1100 °C. SEM and AFM investigations of CeO₂ films reveal a fairly dense microstructure without cracks and porosity. Highly textured YSZ barrier layers and CeO₂ cap layers were deposited on MOD CeO₂-buffered Ni–W substrates using rf-magnetron sputtering. Pulsed laser deposition (PLD) was used to grow YBCO films on these substrates. A critical current, J_c , of about 1.5 MA cm⁻² at 77 K and self-field was obtained on YBCO (PLD)/CeO₂ (sputtered)/YSZ (sputtered)/CeO₂ (spin-coated)/Ni–W.

1. Introduction

Chemical solution processing techniques have emerged as viable low-cost nonvacuum methods for producing ceramic oxide powders and films [1–3]. The most commonly used solution techniques are (i) sol–gel processes that use 2-methoxyethanol as a reactant and solvent; (ii) hybrid processes that use chelating agents such as acetylacetonate or diethanolamine to reduce alkoxide reactivity and (iii) metal organic decomposition (MOD) techniques that use high-molecular-weight precursors and water insensitive carboxylates, 2-ethylhexanoates, etc [4]. These processes offer many desirable aspects, such as precise control of metal oxide precursor stoichiometry and composition, ease of formation of epitaxial oxides, relatively easy scale-up of the film and low cost. In recent years various rare-earth oxides (RE₂O₃) and rare-earth zirconium oxide (RE₂Zr₂O₇) films have

been grown epitaxially on biaxially textured Ni and Ni–W substrates by solution based methods [5–7].

In the rolling-assisted biaxially textured substrates (RABiTS) approach, four-layer architecture of CeO₂/YSZ/Y₂O₃/Ni/Ni–W is used to fabricate long lengths of buffered tapes. The purpose of the buffer layers is to retard oxidation of Ni, to reduce the lattice mismatch between Ni and YBCO and also to prevent diffusion of Ni into YBCO. We have chosen cerium oxide, CeO₂ as a potential buffer layer for this study. CeO₂ has a fluorite CaF₂ structure with a lattice parameter of 5.41 Å and it gives better chemical compatibility with Ni–W substrates and also good lattice matching with YBCO. Thin films of CeO₂ have been grown by various vacuum [8–11] and nonvacuum [12] based deposition techniques on rolled-Ni substrates. In this paper, we describe our successful development of the growth of CeO₂ seed layer on rolled Ni–W substrates by MOD

technique which is different from reported chemical solution deposition techniques as in [12], where sol-gel CeO_2 solution buffers were grown on biaxially textured Ni substrates. By using CeO_2 seed layers, we have eliminated the need for Ni over-layers as mentioned above. The three-layer architecture of $\text{CeO}_2/\text{YSZ}/\text{CeO}_2/\text{Ni-W}$ is utilized to produce short prototype samples of YBCO coated conductor in the present study. The CeO_2 seed layer helps us to grow cube textured YSZ buffers on Ni-W substrates; otherwise it is difficult to grow YSZ directly on Ni or Ni-W substrates using our experimental conditions. Here, the CeO_2 seed layer was grown by a solution process. Both YSZ barrier and CeO_2 cap layers were grown by rf-magnetron sputtering and the YBCO films were grown by pulsed laser deposition (PLD) technique.

2. Experimental details

The MOD precursor solution was prepared in ambient atmosphere. The reagents cerium (III) acetylacetonate ($\text{Ce}(\text{acac})_3 \cdot x\text{H}_2\text{O}$), acetic acid and methanol were used as received from Alfa Aesar. $\text{Ce}(\text{acac})_3 \cdot x\text{H}_2\text{O}$ (2.1872 g, 5 mmol) was dissolved in acetic acid (15 ml) by heating in a hot plate at 60°C for 10 min with continuous stirring. Then 5 ml of methanol (25% in volume of the solution) was added, which helps us to stabilize the solution. The final volume of the solution was adjusted to 20 ml by adding methanol to obtain 0.25 M CeO_2 precursor solution. This solution was then spin coated onto short cube textured Ni-W substrates of $2\text{ cm} \times 1\text{ cm}$ in size at 5000 rpm for 30 s; followed by heat treatment at 1100°C for 15 min in a reducing forming gas atmosphere of Ar-4% H_2 . The samples were introduced into a pre-heated furnace kept at 1100°C after a 5 min purge with Ar-4% H_2 gas mixture at room temperature. After 15 min heat treatment at 1100°C , the samples were quenched to room temperature with the same atmosphere. The heating and cooling rates were in the range of $350\text{--}400^\circ\text{C min}^{-1}$.

The CeO_2 films were characterized by using x-ray diffraction (XRD) for phase purity and texture, high temperature XRD for nucleation and growth, scanning electron microscopy (SEM) for homogeneity and microstructure and atomic force microscopy (AFM) for surface roughness analysis. A Philips model XRG3100 diffractometer with $\text{CuK}\alpha$ radiation was used to record the θ - 2θ XRD patterns. The texture analysis was performed using a Picker 4-circle diffractometer. High temperature *in situ* XRD experiments were carried out in a flowing atmosphere of He-4% H_2 and heating ramp of $400^\circ\text{C min}^{-1}$ on a Scintag PAD X diffractometer with an mBraun linear position sensitive detector (PSD) covering a 8° range centred at $2\theta = 31^\circ$. The microstructure analyses of these samples were performed by using a Hitachi S-4100 field emission SEM and Digital Instruments nanoscope AFM in contact mode.

The superconducting quality of the CeO_2 seed layer was tested with a layer sequence of YBCO/ CeO_2 /YSZ/ CeO_2 /Ni-W. Using rf-magnetron sputtering, a 200 nm thick YSZ layer and a 10 nm thick CeO_2 cap layer were deposited on the CeO_2 seeded Ni-W substrates at 780°C in 10 mTorr of forming gas and 2×10^{-6} Torr pressure of water vapour. The YBCO deposition was done by PLD at 790°C in 120 mTorr oxygen with an average laser energy of 400–410 mJ using

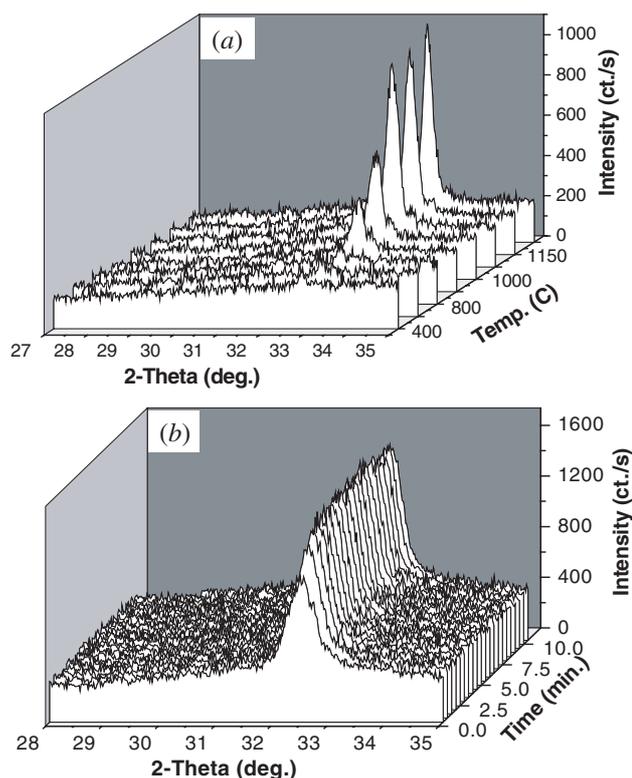


Figure 1. A typical θ - 2θ scan obtained for a 20 nm thick CeO_2 buffered Ni-W substrates in a high temperature *in situ* XRD heat-treated at (a) various temperatures and (b) at a constant temperature of 1100°C for various times. The CeO_2 film has a preferred *c*-axis orientation and the crystallization starts around 600°C (a) and crystallization is completed in 5 min (b).

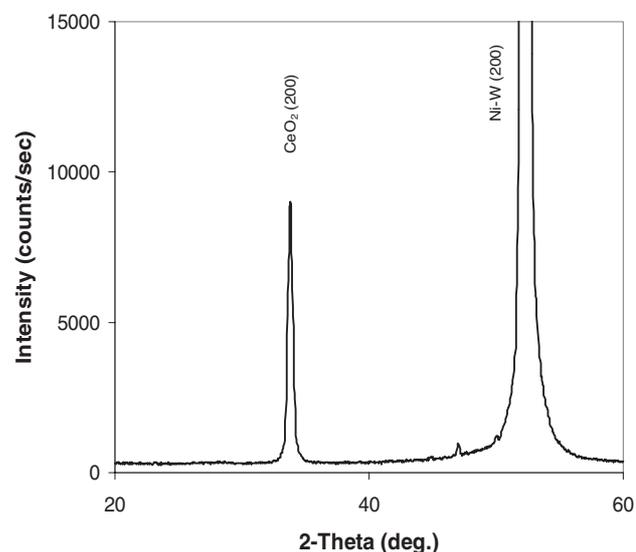


Figure 2. A typical room-temperature θ - 2θ scan obtained for a 20 nm thick CeO_2 buffered Ni-W substrates. The CeO_2 film has a preferred *c*-axis orientation.

a stoichiometric YBCO target, followed by annealing under 550 Torr oxygen during cool down. Details of the PLD process have been published elsewhere [13]. The samples were

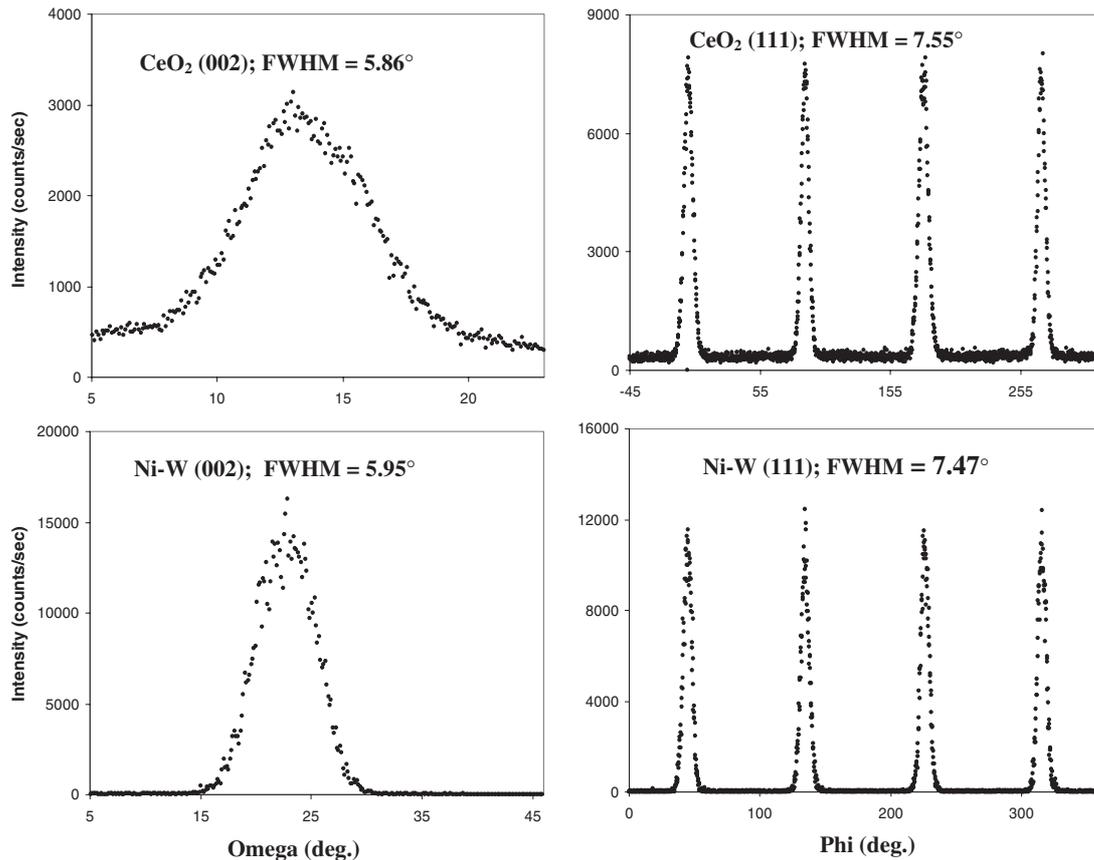


Figure 3. The ω and ϕ scans obtained for a 20 nm thick MOD CeO₂ film grown on textured Ni–W substrate. The FWHM values for each scan are shown inside the patterns.

prepared for electrical property measurements by depositing silver for current and voltage contacts, followed by oxygen annealing at 500 °C for 1 h. The transport critical current density, J_c , was measured using a standard four-point probe technique with an electric-field criterion of $1 \mu\text{V cm}^{-1}$. The J_c measurements were also performed with the applied magnetic field parallel to the substrate ($H//c$).

3. Results and discussion

3.1. Nucleation and growth analysis by *in situ* HTXRD

The sample was heated from room temperature to 1200 °C at a heating rate of 400 °C min^{-1} in a reducing atmosphere of He–4%H₂ and the θ – 2θ XRD patterns were recorded at 400, 600, 800, 900, 1000, 1100, 1150 and 1200 °C. For the growth test, a sample was heated to 1100 °C with the same heating ramp and atmosphere and then XRD patterns were recorded for every 30 s for 1 h. Plots for nucleation and growth characteristics of CeO₂ film on textured Ni–W substrates are shown in figures 1(a) and (b). The nucleation of CeO₂ starts at 600 °C and the growth of the film was completed within 5 min when heat-treated at 1100 °C.

3.2. Structure and texture analysis by XRD

A typical θ – 2θ XRD scan for a spin-coated CeO₂ film on the Ni–W substrate is shown in figure 2. The intense CeO₂

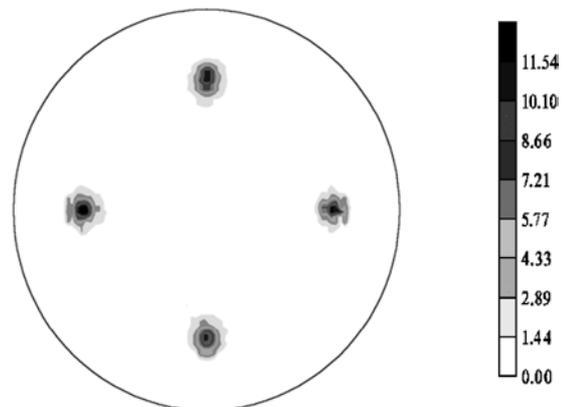


Figure 4. The typical CeO₂ (111) pole figure obtained for a 20 nm thick MOD CeO₂ film grown on the textured Ni–W substrate.

(200) peak reveals the presence of a c -axis-aligned film. The ω (out-of-plane) and ϕ (in-plane) scans of these films on the Ni–W substrates are shown in figure 3. The CeO₂ film has a good out-of-plane and in-plane texture with full-width-at-half-maximum (FWHM) of 5.86° and 7.55° , respectively. These values are well comparable to those of Ni–W substrates ($\Delta\omega = 5.95^\circ$, $\Delta\phi = 7.47^\circ$). The typical (111) pole figure for a CeO₂ film grown on the Ni–W substrate is shown in figure 4, which indicates the presence of a single cube-on-cube texture.

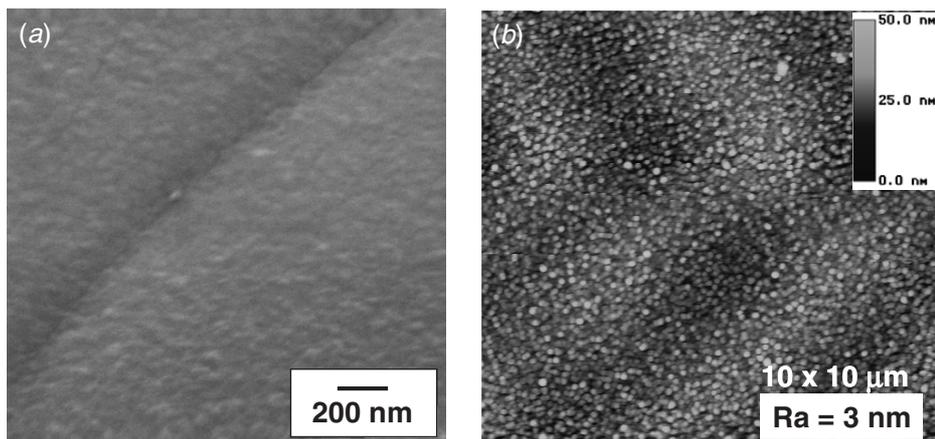


Figure 5. SEM micrograph (a) and AFM image (b) obtained on a 20 nm thick CeO₂ surface.

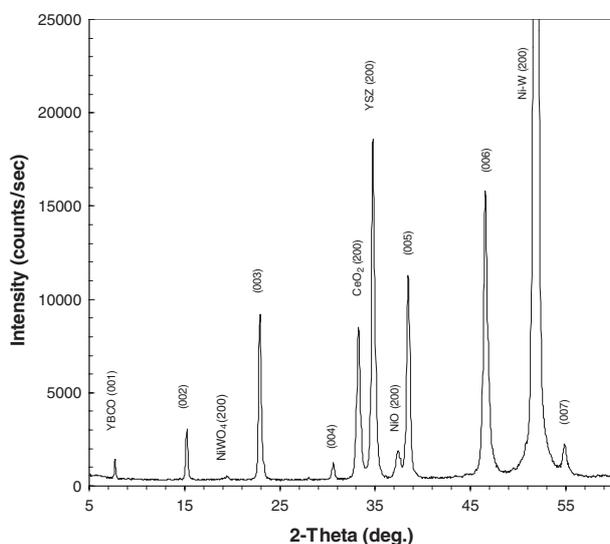


Figure 6. A typical room-temperature θ - 2θ scan obtained for a 200 nm thick PLD YBCO film on a CeO₂ (sputtered)/YSZ (sputtered)/CeO₂ (MOD)/Ni-W substrate. The YBCO film has a preferred *c*-axis orientation.

3.3. Microstructure analysis by SEM and AFM

SEM studies of the CeO₂ films exhibit a uniform, smooth and crack free surface morphology as can be observed from figure 5(a). An AFM image of the same sample is shown in figure 5(b). It reveals a root-mean-square roughness (*Ra*) of the CeO₂ films as 3 nm, which is comparable to that of the underlying alloy substrate (*Ra* = 1 nm). It should be mentioned that for lower concentration of CeO₂ solution (i.e. thinner film) there was a partial coverage of the substrate surface and for thicker CeO₂ films (i.e. higher concentration) crack formation was detected due to lattice mismatch and/or thermal expansion coefficient difference between the CeO₂ and the Ni-W substrate. Details of this observation need further investigation.

3.4. Superconducting test structure

The XRD pattern obtained from the YBCO/CeO₂/YSZ/CeO₂/Ni-W multilayer structure is shown in figure 6,

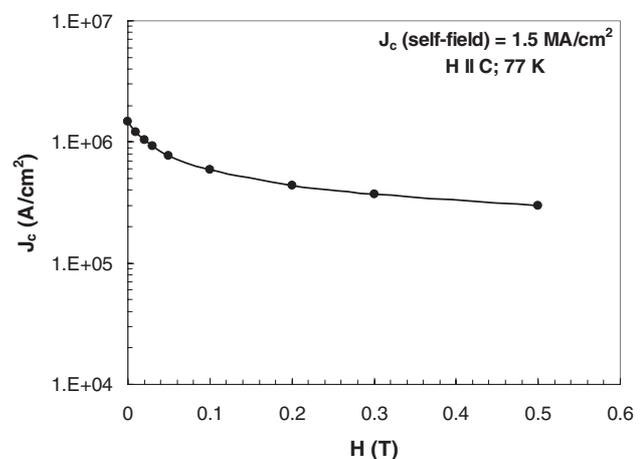


Figure 7. Field dependence of critical current density, J_c , for a 200 nm thick PLD YBCO film on a CeO₂ (sputtered)/YSZ (sputtered)/CeO₂ (MOD)/Ni-W substrate.

indicating that the YBCO film has a strong *c*-axis texture. It also reveals the presence of a small amount of NiO and NiWO₄ at the buffer-substrate interface. The magnetic field dependence of J_c (77 K) for a 0.2 μm thick YBCO film grown epitaxially on CeO₂/YSZ/CeO₂/Ni-W is shown in figure 7, where the magnetic field is applied parallel to the *c*-axis. The highest J_c obtained is about 1.5 MA cm⁻² for a 0.2 μm thick YBCO film in self-field. The J_c at 0.5 T was about 20% of the zero-field J_c , which resembles the field dependence of a typical YBCO coated conductor. Efforts are being made to optimize the growth of CeO₂ as a cap layer on suitable barrier layers.

4. Conclusions

We have successfully developed a new MOD process to grow epitaxial CeO₂ buffer layers on Ni-W (100) substrates. The spin-coated buffers on Ni-W substrates were smooth, crack free and dense. On spin-coated CeO₂ seed layers, having a total buffer layer sequence of CeO₂ (sputtered)/YSZ (sputtered)/CeO₂ (spin-coated)/Ni-W, high-quality YBCO films with J_c values around 1.5 MA cm⁻² at 77 K and self-field

were obtained. By this demonstration, we have eliminated the need for Ni over-layers.

Acknowledgments

Thanks are due to Lee Heatherly for annealing the substrates and Don Kroeger for useful discussions. This work was sponsored by the United States Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Distributed Energy and Electric Reliability—Superconductivity Program. This research was performed at the Oak Ridge National Laboratory, managed by UT-Battelle, LLC for the USDOE under contract DE-AC05-00OR22725. M S Bhuiyan would also like to acknowledge the help of AFOSR for providing financial support.

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