Metal−Organic Chemical Vapor Deposition of CeO_2 ⟨100⟩ Oriented Films on No-Rolled Hastelloy C276

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High-quality cerium dioxide (CeO_2) films are useful materials for several applications. CeO_2 represents an interesting candidate for various technologies because of its insulating properties,[1] its remarkable chemical stability,[2] and its interesting optical properties.[3] In addition, its lattice parameter closely matches those of both silicon[4] and high-T_c superconducting (HTS) materials.[5] In particular, CeO_2 represents a considerable challenge, among the most used buffer layers, to grow $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films on substrates suitable for industrial fabrication of prime interest second-generation conductors.[6] The deposition of the HTS films, mainly YBCO, is predominantly carried out on YSZ/CeO_2 or CeO_2/YSZ/CeO_2 buffer layers deposited on Ni tapes. As a matter of fact, the CeO_2 lattice constant (a = 5.411 Å) favors, because of the small lattice mismatch, YBCO film growth having crystallites 45° rotated in the $a-b$ plane, thus giving rise to epitaxial growth.[5]

CeO_2 buffers of different qualities and preferential orientations have been grown on conventional[7] and unconventional[8] substrates by different methods in the 700−900 °C temperature range. Developments have been focused on coating either polycrystalline or well-textured substrates using the ion-beam-assisted deposition (IBAD)[9] and rolling-assisted biaxially textured substrates (RABiTS) technique, respectively.[10] CeO_2 films have been grown on Hastelloy C276 at room temperature by IBAD.[11]

Recently, particular attention has been devoted to metal−organic chemical vapor deposition (MOCVD) processing of CeO_2.[12−16] In general terms, MOCVD is a promising technique for industrial applications because of the rather simple hardware, the large area deposition, the conformal step coverage, the lower deposition temperatures, and its adaptability to large-scale processing. Nevertheless, MOCVD of CeO_2 usually requires temperatures in the 680−800 °C range.[17,18] Lower deposition temperatures (≈500 °C) have been reported only in the case of CeO_2 films on single-crystal substrates.[19,20]

In this communication, we report on the deposition of ⟨100⟩ oriented CeO_2 films on a no-rolled, random Ni-based alloy, namely, Hastelloy C276, using the $Ce(hfa)_3\cdot$diglyme [H-hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, diglyme = $(CH_3O(CH_2CH_2O)_2CH_3)$] precursor. To our knowledge, these are the first data related to ⟨100⟩ oriented CeO_2 films obtained via MOCVD on a non-epitaxial substrate.

The MOCVD fabrication of CeO_2 films has already been attempted adopting first-generation precursors $Ce(thmd)_4$[21] and/or $Ce(fod)_3$.[22] They, however, have shown severe drawbacks because of the low deposition rates and the considerably high deposition temperatures required for epitaxial growth.

The higher volatility of the present second-generation $Ce(hfa)_3\cdot$diglyme precursor allows the use of a source temperature (120 °C), which is considerably lower compared with those reported for previously mentioned cerium first-generation sources. This property implies a real simplification of the MOCVD reactor. In addition, there is evidence that the present $Ce(hfa)_3\cdot$diglyme produces good quality CeO_2 thin films at deposition temperatures (450 °C) significantly lower than those usually required. This is an even more important issue because lower deposition temperatures are desirable for multilayer devices fabrication.

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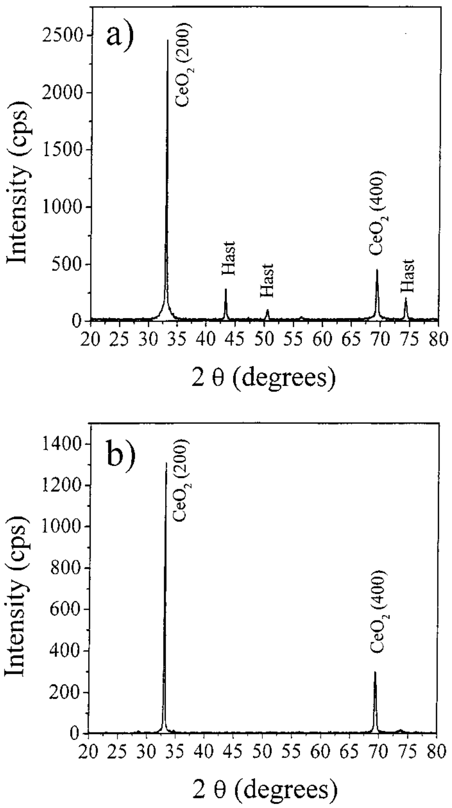

Figure 1. XRD patterns of CeO_2 films grown at 450 °C on (a) Hastelloy and (b) polycrystalline YSZ.

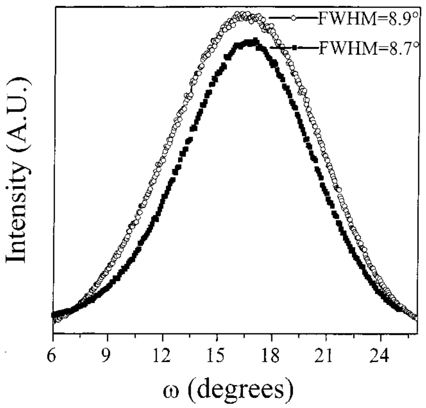

Figure 2. ω scan rocking curves of the (200) reflection of CeO_2 films deposited on Hastelloy (■) and polycrystalline YSZ (○) at 450 °C.

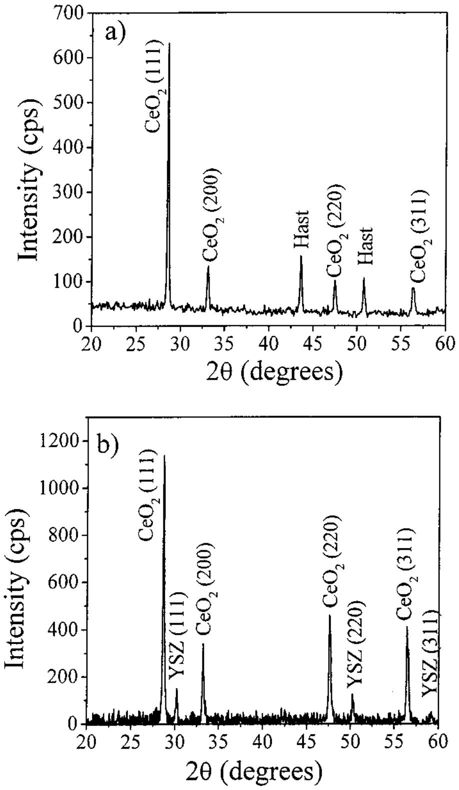

Figure 3. XRD patterns of CeO_2 films grown at 1000 °C on (a) Hastelloy and (b) polycrystalline YSZ.

In this context, CeO_2 films have been deposited directly onto Hastelloy in a horizontal cold wall MOCVD reactor, using the second-generation $Ce(hfa)_3$·diglyme precursor, prepared as reported elsewhere.[23] The choice of the Hastelloy substrate was motivated by several peculiarities: (i) it is oxidation resistant at high temperature, (ii) it has a thermal expansion coefficient very close to that of YBCO, and (iii) it is available in long mechanically robust thin tapes.

The Hastelloy substrates, presently adopted, were mechanically polished (with 0.25-μm diamond paste). The source sublimation temperature was kept constant at 120 °C in all experiments, and the substrate temperature was varied from 450 to 1000 °C. Deposition experiments were carried out for 90 min under Ar as the carrier gas (100 sccm). A water saturated (T_{bubbler} = 25 °C) oxygen flow (100 sccm) was added during the deposition as a reacting gas to hydrolyze the fluoride phases, which may arise from the precursor decomposition. The total pressure during depositions was 4 Torr. No particular hazards are related to the MOCVD deposition process, the carrier and reaction gases are innocuous, and even the precursor is harmless. The unique chemical product, which may give problems by inhalation, is the Hhfa ligand. Therefore, during the precursor synthesis, the Hhfa ligand should be carefully manipulated under a well-ventilated hood.

A typical $\theta-2\theta$ X-ray diffraction pattern (XRD) (Figure 1) of a CeO_2 thin film produced at 450 °C on Hastelloy shows only the CeO_2 (200) and (400) reflections. The rocking curve of the (200) reflection (Figure 2) has a full width at half-maximum (fwhm) of 8.7°, which implies a high degree of grains dispersion. Nevertheless, the observation of a rocking curve points to an effective $\langle 100\rangle$ CeO_2 fiber texturing on a non-epitaxial and no-rolled substrate. Similar $\langle 100\rangle$ textured films are obtained on both polished and as-received Hastelloy substrates.

Preliminary experiments at higher (>450 °C) deposition temperatures (keeping constant all the other parameters) point to the formation of randomly oriented films. The diffraction pattern (Figure 3) of films grown at 1000 °C on Hastelloy presents, in fact, all the reflections expected for a random CeO_2 film.[24]

Control experiments were, therefore, carried out on polycrystalline YSZ (yttria-stabilized zirconia) substrates to rule out any possible effect on the CeO_2 film

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orientation due to thermal instability of the Hastelloy substrates[25] (usually observed at temperatures >850 °C).

Cerium dioxide films deposited on polycrystalline YSZ at 450 °C show the same morphological and crystalline microstructure observed for the $\langle 100 \rangle$ oriented films grown on Hastelloy. The XRD pattern (Figure 1) indicates that films are $\langle 100 \rangle$ oriented also on polycrystalline YSZ substrates. Furthermore, the fwhm value (8.9°) of the rocking curve associated with the (200) reflection is also close to that obtained on the Hastelloy.

Similarly to films grown on Hastelloy, the fiber texturing on YSZ tends to disappear beyond 450 °C. Thus, a random orientation is observed at 1000 °C. This observation indicates that the fiber texturing of CeO_2 films on non-epitaxial substrates does not depend on the nature of the substrates. Rather, it is clearly influenced by the deposition temperature.

The chemical purity of the samples was determined by wavelength-dispersive X-ray (WDX) analyses. All the experiments on present films indicate negligible C and F contaminations (0.1 and 0.08%, respectively). The analyses were carried out at 15-kV accelerating voltage, 10-nA current, and 100-s acquisition time. A TAP (thallium acid phthalate) crystal was used as an X-ray selector.

Scanning electron microscopy (SEM) images of the CeO_2 films indicate that the surface consists of a well-defined crystalline structure with 100-nm-wide grains (Figure 4). The thickness, determined from cross-sectional SEM images, is about 1 μm. The cross-sectional image of films grown on Hastelloy at 450 °C (Figure 4) shows a highly columnar microstructure. This morphology can be rationalized on the basis of the Mochvan−Demchishin model[26,27] used for metallic and refractory films grown via physical vapor deposition (PVD).

The Mochvan and Demchishin zone model relies upon three different kinds of structures, depending on the homologous temperature, T_h ($T_h = T_{dep}/T_{melting}$, $T_{melting} = 2223$ K), for metallic, alloy, and refractory films grown on non-epitaxial substrates. Zone 1 shows a porous “cauliflower” structure caused by a low adatom mobility on the substrate surface at $T_h < 0.3$.

The columnar crystallites found in Zone 2 are due to the higher adatom mobility. In this case, the substrate homologous temperature range rises to 0.3−0.5. The columns’ lateral width is smaller than the film thickness.

Zone 3 shows equiaxial grains controlled by the highest adatom mobility. In this case the T_h must be higher than 0.5. Transition temperatures from zone 1 to zone 2 are 0.3 for metals and 0.22−0.26 for oxides, while from zone 2 to zone 3 they are 0.45 for both metals and oxides.

Interestingly enough, the observed columnary growth at 450 °C is typical of zone 2 and the related $T_h = 0.32$ falls exactly within the expected T_h limits for the second zone observed in PVD experiments.

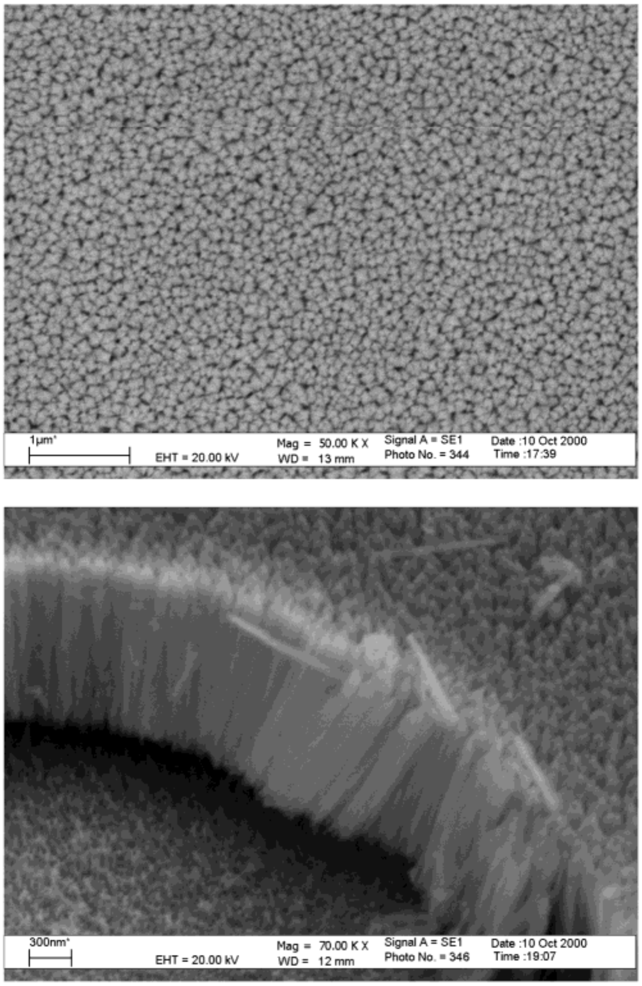

Figure 4. SEM micrographs of a CeO_2 film deposited on Hastelloy at 450 °C: (a) plane view and (b) cross-sectional image.

This is an indication of a possible extension of growth models used for PVD film deposition even to MOCVD processes.

In conclusion, CeO_2 $\langle 100 \rangle$ oriented thin films were deposited by an MOCVD process on a non-epitaxial industrial substrate, from the $Ce(hfa)_3 \cdot$diglyme second-generation precursor. The films obtained are well-crystalline and homogeneous and have promising texturing for the application to second-generation HTc tape conductors.

The formation of columnar microstructure crystallites at 450 °C is consistent with the homologous temperatures required for this morphology within the Mochvan and Demichishin model. Further studies are in progress to better understand the influence of all deposition parameters (sublimation temperature, O_2 and Ar gas flows, and deposition rate) on the CeO_2 film growth.

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