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Journal

Synthesis and Characterization of Nanostructured Cerium Dioxide Thin Films Deposited by Ultrasonic Spray Pyrolysis

Mario F. García-Sánchez,[†,‡] Armando Ortiz,[‡] Guillermo Santana,[‡] Monserrat Bizarro,[‡] Juan Peña,[‡] Francisco Cruz-Gandarilla,[§] Miguel A. Aguilar-Frutis,[¶] and Juan C. Alonso[‡]

[‡]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México; Ciudad Universitaria, Coyoacán 04510, México D.F., México

[§]Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional; Edif. 9, U.P.A.L.M. 07738, México D.F., México

[¶]Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Instituto Politécnico Nacional; Irrigación 11500, México D.F., México

Nanostructured thin films of cerium dioxide have been prepared on single-crystalline silicon substrates by ultrasonic spray pyrolysis using cerium acetylacetonate as a metal–organic precursor dissolved in anhydrous methanol and acetic acid as an additive. The morphology, structure, optical index, and electrical properties were studied by X-ray diffraction, scanning electron microscopy, atomic force microscopy, ellipsometry, and impedance spectroscopy. The use of additives is very important to obtain crack-free films. The substrate temperature and flow rate was optimized for obtaining smooth ($R_a < 0.4$ nm), dense ($n > 2$), and homogeneous nanocrystalline films with grain sizes as small as 10 nm. The influence of thermal annealing on the structural properties of films was studied. The low activation energy calculated for total conductivity (0.133 eV) is attributed to the nanometric size of the grains.

I. Introduction

Cerium dioxide (CeO_2) has been of great interest during the last years due to its multiple applications in several key areas of thin film technology. This material has a cubic fluorite-type crystal structure (lattice spacing 0.5411 nm) and combines a large bandgap (<3.5 eV) with a high dielectric constant ($\varepsilon \approx 26$), high ionic conductivity, and high-temperature stability.[1–8] Because of its chemical stability and close lattice parameter matching with silicon (0.35% lattice matching), CeO_2 has potential applicability in the area of optoelectronics: in silicon-on-insulator structures, stable capacitor devices for large-scale integration, photoelectrodes in dye-sensitized solar cells, and stable buffer layers between high-temperature superconducting materials and silicon substrates.[6–14] The high ionic conductivity has attracted great interest for applications such as gas sensors[15,16] and electrolyte or anode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC).[17–28]

Several physical and chemical processes have been used to prepare CeO_2 thin films, including flash evaporation,[3] electron-beam evaporation,[4,5,9,15] spin coating,[1,2,16,23] sputtering,[6,29] MOCVD,[30] laser ablation,[31–33], and spray pyrolysis in its three versions: electrostatic, pneumatic, and ultrasonic.[7,11–14,18–20,33,34] Among them, the spray pyrolysis techniques are very attractive for the industry, because they allow the deposition of a wide variety of ceramic films over large areas with a simple process at low costs. Each one of the spray pyrolysis versions has advantages and drawbacks in terms of complexity and quality of the deposit.[35,36] Electrostatic spray deposition (ESD) has been used for preparing YSZ- and CeO_2-based films.[14,18,20,36,37] This technique produces almost monodispersed and fine drops; however, the effect of preferential landing of the charged droplets can lead to porous and/or cracked films. In pressurized spray deposition, there is less control on the microstructure of the deposited films due to a higher dispersion of droplet sizes.[38] However, it is reported as a more adequate technique to deposit dense films compared with the ESD technique. Ultrasonic spray deposition (USD) allows a smaller and homogeneous droplet size than electrostatic or pressurized spray,[35] and it has been widely used to prepare YSZ thin films.[35,39–41] In contrast, CeO_2 thin films have been produced only by Wang *et al.*[13] using USD. Anyway, in the three cases, the selection of precursors and the process of parameters' optimization have a great influence in the final properties of the films.

Nanostructured materials are characterized by unique physico-chemical properties with important applications. One of the most rapidly growing areas of investigation is the IT-SOFC.[21–24,27,28,34,35,42,43] Recently, ultrasonic spray pyrolysis with optimized process conditions has been used for obtaining nanostructured YSZ thin films, improving their electrical properties,[35] but conductivities are still low. The efficiency of this material as an electrolyte in SOFC can be increased using multilayer systems with nanostructured ceria-based materials.[18,26,28] But there are no reports of nanostructured ceria thin films obtained by this technique.

In this work, ultrasonic spray pyrolysis was used to deposit dense CeO_2 thin films with nanometric grain size. A study of the influence of different deposition parameters and the thermal annealing in the morphology of the films was made. The electrical properties of the films obtained were measured and compared with previous reports.

II. Experimental Procedure

The experimental setup shown in García-Sánchez et al.[35] was used. The diameter of the nozzle was 16 mm and the distance nozzle-substrate was fixed to 20 mm. Films were deposited onto (100) n-type, 200 Ω · cm single crystalline silicon slices in order to perform electrical measurements at high temperatures. The substrates were ultrasonically cleaned, with trichloroethylene, acetone, methanol, and 5% HF solution in order to remove the native oxide. The spray solution was 0.025*M* of cerium (IV)

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[†]Author to whom correspondence should be addressed. e-mail: mf@iim.unam.mx