



Deposition of CeO₂ nanoparticle layer on Al₂O₃ (0001), LaAlO₃ (001), and Y₂O₃-stabilized ZrO₂ (001) substrates from colloidal toluene solution

Masakuni Ozawa^{1*}, Toshitaka Karai², and Takashi Hattori²

¹*Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-0005, Japan*

²*Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-0005, Japan*

*E-mail: ozawa@imass.nagoya-u.ac.jp

Received May 13, 2017; accepted October 10, 2017; published online December 21, 2017

CeO₂ nanoparticle (NP) layers on Al₂O₃ (0001), LaAlO₃ (001), and Y₂O₃-stabilized ZrO₂ (YSZ) (001) substrates were prepared from colloidal toluene solution. Atomic force microscopy (AFM) indicated that isolated CeO₂ NPs of less than ca. 40 nm diameter were formed on YSZ, and the thin CeO₂ NP layers maintained the granular surface morphology of CeO₂ even after heat treatment at 1000 °C. The surface charges (zeta potentials) of crystal substrates were evaluated and it was found that they depended on the kind of substrates before and after the deposition of CeO₂ NP layers. The experimental and theoretical results suggested that the control of thickness was determined by the surface potential of the substrate, when well-dispersed NP colloids in a nonpolar solution were used for film formation. © 2018 The Japan Society of Applied Physics

1. Introduction

Cerium dioxide (CeO₂) is a versatile material owing to its wide range of applications in, for example, electrolyte materials of solid oxide fuel cells, solar cells, and oxygen sensors, and for its catalytic properties in reactions including water-gas shift reactions and automotive catalytic.^{1–5} In all these cases, the use of nanostructured CeO₂-based materials is expected to result in improved properties in comparison to micron-size or bulk like materials. CeO₂-based materials are industrially used as polishing agents in semiconductor device processes, as better catalytic promoters in automotive three-way catalyst (TWCs), and as diesel particulate matter removal catalysts because of their high oxygen activator and storage capacity (OSC).^{6–11} Also, CeO₂ nanostructured films are useful for various electronic and optical applications, such as silicon-on-insulator structures, miniaturized stable capacitors, oxygen sensors, optical coatings, and buffer layers for superconducting metal oxides.^{12–14}

In a film formation process, solution methods allow novel candidate nanoparticles or nanocrystals to be used as precursors, leading to microstructural control by controlling the morphologies of deposits or films at the nanometer scale. In general, a CeO₂ film is prepared by dry processes in vacuum including the magnetron sputtering technique,^{15,16} pulsed laser deposition (PLD),^{17,18} and molecular beam epitaxy (MBE).^{19,20} Recently, researchers have reported several methods for the fabrication of CeO₂ nanocrystals of single-nanometer size, which can produce the dispersed nanocrystal (NC) in colloid solutions.^{20–23} We have examined a method of fabricating CeO₂ NP layers on α -Al₂O₃ (0001) using CeO₂ NCs dispersed in toluene solution, followed by heat treatment in an oxidizing or a reducing atmosphere.^{24,25} After heat treatment, the sintering and solid-state reaction resulted in good densification of CeO₂ films on (100)-oriented CeAlO₃ interlayers with less thicknesses of than 50 nm when Al₂O₃ was used as the substrate. In general, thin films are influenced by the kind of substrates and the crystal plane orientations. However, there are few studies on forming layers using NPs on different crystal substrates using solution processes, because the usage of completely dispersed colloidal solution has only recently been developed and applied to a CeO₂/substrate system.

In this work, we prepared CeO₂ NPs layers on three crystal substrates; α -Al₂O₃ (0001), LaAlO₃ (001) and 18 mol % Y₂O₃-stabilized ZrO₂ (YSZ) (001). Factors for controlling morphology and thickness were investigated, and the results showed that the isolated and layered CeO₂ NPs were maintained on each substrate even after heat treatment at 1000 °C in air. Also, we discuss the deposition mechanism regarding the interaction between substrates and CeO₂ NPs during the initial film formation process from a colloid solution.

2. Experimental methods

The starting CeO₂ NPs were prepared by the same method as described in previous papers.^{24–26} Briefly, diammonium cerium(IV) nitrate [(NH₄)₂Ce(NO₃)₆] and potassium oleate [C₁₇H₃₃COOK] were dissolved and mixed in distilled water by stirring, followed by the addition of ammonia aqueous solution. The solution was then sealed in a Teflon-lined stainless-steel autoclave (100 mL) and heated at 200 °C for 48 h, and the products were separated from the reaction solution by centrifugation at 3000 rpm for 30 min. The resulting CeO₂ precipitates were washed with distilled water three times and dried at 90 °C for 24 h in air, and then dispersed in toluene (C₆H₅CH₃), producing a stable colloid solution. The concentration of CeO₂ in a solution was set at 1.0 g L⁻¹.

For the deposition of CeO₂ NP layers, α -Al₂O₃ (0001), LaAlO₃ (001), and YSZ (001) crystal plates were used as substrates. The process included the following stages. The substrate was partially immersed in the CeO₂ solution at a constant speed of 10 mm s⁻¹, and fully immersed for a dwell time of 5 s. After CeO₂ NPs were deposited, the substrate was pulled upward at a constant speed of 10 mm s⁻¹. Excess liquid was drained from the surface, and evaporated by drying in atmosphere. Subsequently, CeO₂/substrate samples were heat-treated at 1000 °C for 3 h in air.

X-ray diffraction (XRD) patterns were collected using a MiniFlex II (Rigaku) diffractometer with Cu K α radiation at 15 kV and 30 mA. An X-ray diffractogram was recorded at a scanning rate of 1°/min with a 0.02° step size in the 2 θ range between 10 and 90°. Dynamic light scattering (DLS; Zetasizer ZS Malvern) was used to determine the particle size of CeO₂ isolated in colloid solution. The zeta potentials of