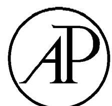
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Oxide films: low-temperature deposition and crystallization

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Abstract

Thin films of CeO_2 and $(Ce,Sm)O_2$ have been prepared by using the SILAR method of deposition in conjunction with hydrothermal and high-temperature annealing. Low-temperature, low-pressure hydrothermal annealing of amorphous $Mn{:}Zn_2GeO_4$ films has lead to the growth of grains having edge lengths near 1 μm. Thick films of crystalline Zn_2SiO_4 exhibiting limited cracking have been prepared by a doctor-blade method also in conjunction with hydrothermal dehydration and annealing.
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1. Introduction

We recently described a simple method [1] for the low-temperature deposition and crystallization of oxide films on the basis of a coupling of the successive-ionic-layer-adsorption-and-reaction (SILAR) deposition method [2,3] with low-pressure hydrothermal dehydration and annealing. The method extends the capabilities for deposition and crystallization of ceramic thin films at low temperatures [4], and it is of interest for realizing a general, low-cost, and environmentally benign manufacturing method for inorganic films in a variety of devices.

In this contribution, we present results on the use of this low-temperature method for production of undoped and doped CeO_2 thin films, and we extend its use by demonstrating crystallization and grain growth in amorphous $Mn{:}Zn_2GeO_4$ phosphor thin films and preparation of crystalline Zn_2SiO_4 thick films.

2. Experimental

2.1. $(Ce,Sm)O_2$ deposition and annealing

Films of CeO_2 and Sm-doped CeO_2 were produced on SiO_2/Si (oxidized Si) substrates by using the SILAR process. Aqueous solutions were prepared from $Ce(C_2H_3O_2)_3 \cdot 6H_2O$ (Alfa, 99.9%), $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa, 99.5%), $Sm(NO_3)_3 \cdot 6H_2O$ (Alfa, 99.9%), NaOH (Analytical Reagent), and 3–30% H_2O_2(aq). Solution concentrations were 0.06 M Ce^{3+}/Sm^{3+} (pH ~ 5) and 0.06 M OH^-/H_2O_2. Substrates were attached to the arm of a Gilson 223 XYZ robotic sample changer and successively immersed in the Ce^{3+}/Sm^{3+} solution, water, OH^-/H_2O_2 solution, and water for 10 s each; 200 cycles were used to develop a film thickness near 60 nm. The rinse-bath water was continuously circulated through a Millipore Milli-Q Academic ion-exchange system, and vigorous stirring was maintained near the substrate by using a magnetic stir bar. Following deposition, the wet film was transferred to a sealed Teflon-lined Parr reactor and heated at 378 K for 15 h or directly annealed in air at 878 K for 50 min.

X-ray diffraction measurements were done with a Siemens D-5000 diffractometer equipped with Cu*K*α radiation. Chemical analyses and scanning-electron-microscope (SEM) studies of the films were done in the Analytical Services Lab at Hewlett-Packard. X-ray photoelectron spectroscopic (XPS) measurements were made by using a PHI Quantum 2000 Scanning ESCA. The spectrometer is equipped with a monochromatic Al X-ray source with a photon energy of 1486.7 eV. The samples were analyzed as received, and the analysis was performed by using a 200-μm photon beam rastered over a 500 × 500-μm area. The data were charge corrected to C 1s at 284.8 eV. The samples were

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analyzed by secondary electron microscopy with a Phillips XL30S operating at 2.0 keV. The samples were fractured and mounted on a 60° stub. A 30° tilt was used to observe the top-layer structure and morphology, while a 90° tilt was used to observe the films in cross-section.

2.2. *Hydrothermal annealing of sputter-deposited Mn:Zn_2GeO_4*

Amorphous Mn:Zn_2GeO_4 films were deposited on glass by RF sputtering. The 3″-diameter target for this process was pressed from a combination of ZnO (99.99%, Alfa), SiO_2 (99.999%, Alfa), and $MnCO_3$ (99.9%, Alfa) and heated at 1473 K for 8 h. The as-deposited films were both hydrothermally and thermally annealed. For the hydrothermal treatment, the films were sealed in a Teflon-lined Parr reactor containing of a few drops of water and heated at 378 K for 30-min intervals up to 2 h. Corresponding high-temperature treatments were done in air at 928 K. The brightness of the green emission from the films was monitored with a low-pressure Hg lamp (254 nm), a band-pass filter, and a photomultiplier tube attached to a picoammeter. Film surface topography was examined with a NanoScope III atomic-force microscope (AFM).

2.3. *Zn_2SiO_4 thick film*

0.5 M $ZnSO_4 \cdot H_2O$ (Analytical Grade, Aldrich) and 0.5 M Na_4SiO_4 (Analytical Grade, Alfa) aqueous solutions were mixed to form an amorphous zinc silicate precipitate. The resulting gelatinous solid was filtered and heated on a hot plate to evaporate water and increase its viscosity to limit spreading during application to the substrate. The gel was applied to a nitrided silicon substrate through a template having a thickness of 50 μm; excess material was trimmed to the thickness of the template by using a doctor-blade method (excess material was simply trimmed by using a common razor blade). The template was lifted, and the film was either heated in air at 878 K for 1 h or placed in a Teflon-lined Parr reactor containing a few drops of water and heated at 478 K for 15 h.

3. Results and discussion

Because of technological interest for a variety of applications, several methods have been examined for the production of thin films of CeO_2 [5–8]. Tolstoy and Ehrlich have described [9] some results for the deposition of hydrated CeO_2 films on Si by using the SILAR process; characterization, however, was restricted to the use of ellipsometry to determine film thickness and Fourier-transform infrared measurements to examine dehydration. Typical scanning-electron micrographs for CeO_2 films deposited by our SILAR processing are given in Fig. 1. Following anneals under hydrothermal conditions, substrates are homogeneously coated with thin layers of nanoparticles having diameters near 20 nm. This result is similar to that observed with SILAR deposition and hydrothermal treatment of other binary oxide films [1]. Following a direct high-temperature thermal anneal, similar particles are observed, but coverage tends to be much less homogeneous, and extended regions of particle agglomerates are observed (Fig. 1).

Cross-sectional SEM views of several films revealed a thickness no greater than 60 nm, despite attempts to produce considerably thicker films by increasing the number of SILAR cycles and the pH of the Ce^{3+}(aq) solution. One of the challenges in using the SILAR method for preparation of oxides is preventing dissolution of the deposited hydroxide when the substrate is soaked in the cation solution. If the pH of this solution is too low, the precipitated hydroxide film will simply dissolve. For deposition of CeO_2, the low pH required for dissolution of Ce^{4+} necessitates the use of a Ce^{3+}(aq) solution. Even though the pH of the Ce^{3+}(aq) solution was increased as high as possible without precipitation, thicker film formation has not been observed. Dissolution of the hydroxide in the Ce^{3+}(aq) solution could still be occurring, or material could be washing away in the rinse bath. In contrast to previous applications of the SILAR process [2,3], we have used vigorous mechanical stirring to shorten soak times in the water bath. It is possible that this stirring is too aggressive for this system, limiting the overall film thickness. In any event, additional experiments are necessary to identify the factors limiting the growth, and many experimental variables are certainly available for

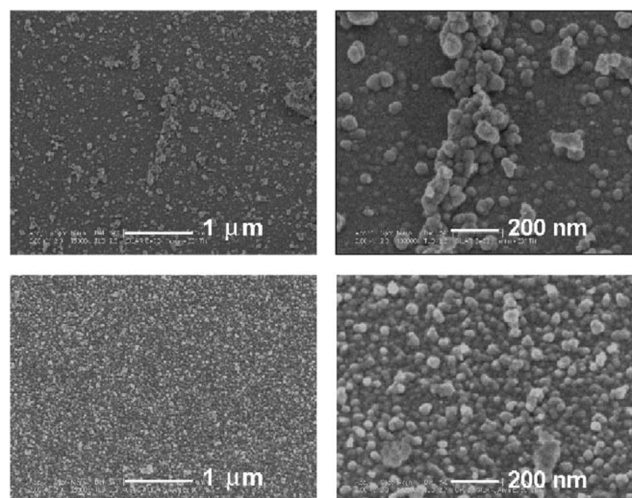

Fig. 1. Top: furnace annealed film of CeO_2. Bottom: hydrothermally treated film of CeO_2.

affecting the thickness and the growth rate of these films.

Examination of XPS spectra in the range of 880–910 eV for the Ce 3*d* levels clearly indicates that the predominant oxidation state for Ce in both the hydrothermally and thermally annealed films is +4. This result is consistent with hydrothermal and thermal annealing of bulk precipitates from the SILAR solutions, which lead to crystalline CeO_2, as determined by X-ray diffraction analysis. We should also note the presence of a small C 1 s band in the XPS spectrum near 289 eV, which is indicative of carbonate likely resulting from dissolution of CO_2 (g) in the basic H_2O_2/OH^-(aq) solution.

One of the primary goals of this work was to prepare Sm-doped CeO_2 films containing approximately 25 at% Sm. This was achieved by simply mixing Ce and Sm salts in the same solution for the SILAR deposition. Curiously, however, no Sm could be detected in the films when using acetate salts. When using only nitrates, Sm-doped films having compositions similar to the Ce/Sm solution could be prepared. For example, a solution containing a 4:1 Ce:Sm ratio resulted in films (as measured by XPS) having ratios in the range of 4–5:1.

As noted above, observation of porous layers of densely packed nanoparticles is a common feature of the films prepared by simple dehydration of hydroxides. For many applications, however, dense films having large grain sizes are required. To examine the prospects for achieving grain growth in oxide films under low-pressure hydrothermal conditions, we have examined annealing thin films of the luminescent, green-emitting material $Mn{:}Zn_2GeO_4$. Films of this material were initially sputtered onto glass substrates; they were found to be amorphous, exhibiting no X-ray diffraction peaks or Mn luminescence. As shown in Fig. 2, following a high-temperature furnace anneal at 873 K or a hydrothermal anneal at 398 K for 30 min, the standard green emission from Mn in the crystalline phosphor host is observed, i.e., a 30-min, low-pressure hydrothermal anneal at 398 K is equivalent to a 30-min furnace anneal at 873 K in terms of inducing crystallization for observation of Mn luminescence. For comparison, no luminescence is observed from an amorphous $Mn{:}Zn_2GeO_4$ film annealed in a furnace at 398 K for 30 min. As the annealing time is extended, the luminescence brightness of the film gradually increases (Fig. 2), but after 120 min, the hydrothermally annealed film is approximately four times brighter than the furnace-annealed film. The high brightness of the hydrothermally treated film is directly related to the large grains that are produced. As shown in the AFM image of Fig. 3, these grains extend the full thickness of the film, $\sim 1\,\mu m$. With such large grains, waveguide effects are limited and greater forward scattering of the emitted light is observed, effectively increasing the observed brightness. These results clearly demonstrate that low-temperature, low-pressure hydrothermal conditions can be used to promote grain growth. The effect is equivalent, for example, to those of high-temperature liquid-phase sintering of ceramics or grain-growth of phosphor particles by using small amounts of fluxing agents. The challenge now is to extend these results to other oxides that are only sparingly soluble in H_2O under these conditions.

As noted above (cf. Fig. 1), hydrothermal dehydration of hydroxide films generally limits film cracking, which results from the buildup of tensile stresses during elimination of water. This result could provide some advantages in low-temperature solution-based deposition of thick films, where cracking is a severe problem. A simple example of the results achieved in thick-film production with hydrothermal dehydration and annealing are shown in Fig. 4. Here, 50-μm thick films of zinc-silicate hydroxide slurry were applied through a template by a doctor-blade method. A furnace anneal

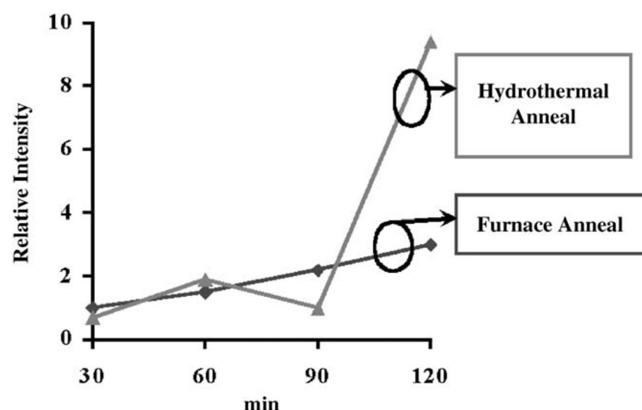

Fig. 2. Phosphor film brightness as a function of annealing conditions.

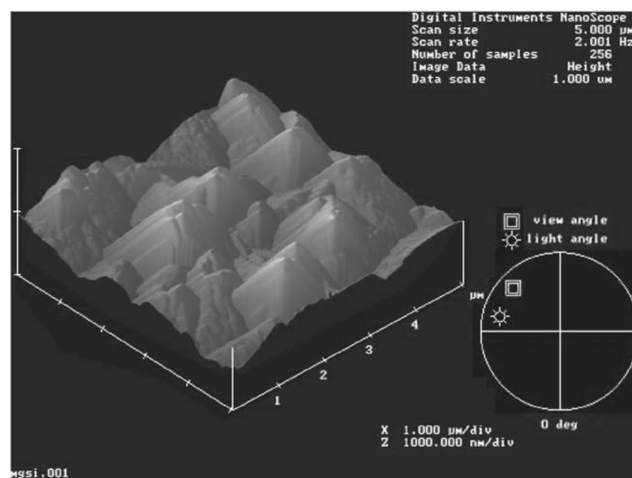

Fig. 3. AFM image of hydrothermally annealed $Mn{:}Zn_2GeO_4$ film on glass substrate.

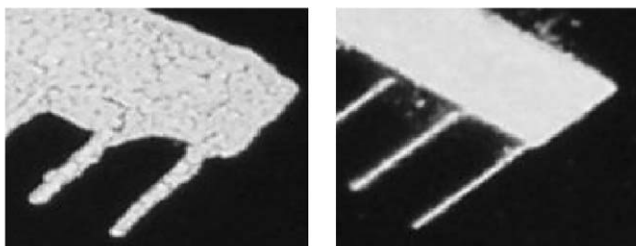

Fig. 4. Left: furnace annealed thick film of Zn_2SiO_4. Right: hydrothermally annealed thick film of Zn_2SiO_4.

of the film resulted in the typical cracking pattern for a solution-derived deposition; even drying the film at room temperature results in an extensive cracking pattern. For the hydrothermally derived film, however, a noticeable improvement in film quality is observed; in each case X-ray diffraction patterns typical for crystalline Zn_2SiO_4 were observed. We should note that no effort has been made to carefully control the water content and viscosity of the hydroxide gel prior to application; optimizing these properties may lead to the production of high-quality thick films.

4. Summary

Undoped CeO_2 films have been produced by using the SILAR deposition technique in conjunction with hydrothermal dehydration and annealing. By using nitrate solutions, the films can be readily doped with Sm. The application of low-pressure hydrothermal dehydration and annealing has been extended to realize grain growth and densification at low temperatures and to produce Zn_2SiO_4 crack-limited thick films. These hydrothermal processes represent a versatile tool in oxide film processing, independent of the deposition method.

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