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Electron Microscopy of Thin-Film Y_2O_3-Stabilized ZrO_2 and CeO_2 on MgO

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Yttria-stabilized zirconia (YSZ) and ceria thin films on <100> MgO substrates have been studied to provide insight in understanding the substantially enhanced ionic conductivities of nanocrystalline oxides that are potentially important for advanced electrochemical devices such as fuel cells and gas sensors. Single crystal films exclude grain-boundary effects but retain interface space-charge regions that are possibly highly conductive. Thin films of ZrO_2-10 mol% Y_2O_3 (10YSZ) and CeO_2 were grown by pulsed laser deposition (PLD) with a pulsed oxygen jet, at typically 0.05 to 0.1 nm/pulse, on substrates at 500°C, and then annealed for 1 h at 700°C in oxygen. Analytical electron microscopy (AEM) of ion-milled cross-sectioned specimens was performed with a Philips CM200FEG.

Although a 29-nm 10YSZ film showed a 10-fold increase in ionic conductivity at <650°C and 3-fold increase at >650°C, and a 15-nm film showed a 10-fold increase at 800°C and 150-fold increase at 400°C, all relative to 58-nm or thicker single crystal films, AEM characterization of cross-sectioned specimens of nominally 58, 29, and 15nm-thick films of YSZ on <100> MgO revealed the same general features in all specimens. The results for the nominally 29nm-thick YSZ film shown in Figure 1 are typical. The expected cube-on-cube orientation relationship was confirmed, but the ~22% lattice mismatch leads to large interface strains and to a mosaic spread of ~2°, but no threading dislocations, in the YSZ. X-ray energy-dispersive spectroscopy (EDS) confirmed the expected compositions (9.5±0.1 mol% Y_2O_3) and detected 0.5±0.1%Hf. High-resolution EDS and electron energy-loss spectroscopy (EELS) spectrum profiles failed to detect any segregated or depleted Y at substrate interfaces, but space charge regions arising from Y segregation at the surface and interface are still considered likely origins of the enhanced conductivity. A specimen of polycrystalline, thin-film YSZ was examined to help explain why its ionic conductivity properties were so poor. Extensive porosity (>20%) was observed and EDS revealed a grossly incorrect composition (21.5 mol % Y_2O_3). Selected area diffraction (SAD) yielded a lattice parameter of 0.515 nm, again consistent with high Y_2O_3 levels (0.5176 nm is expected for 21.5 mol% Y_2O_3). Future work employing spin coating and low-temperature anneals is expected to yield high-quality nano-structured polycrystalline oxide thin films.

A cross-sectioned specimen of a nominally 500-nm-thick film of CeO_2 grown by PLD on <100> MgO was also examined. Surprisingly, the expected single-crystal epitactic film was not observed. Instead, a polycrystalline film with columnar grains was present (Figure 2a). There were many defects and some residual stresses evident in the ceria grains, and cusps in the interface at grain-boundary intersections. The composition was confirmed by EDS and EELS. Figure 2b shows a $[010]_{MgO}$ SAD pattern with ceria reflections arising from four crystallographic variants. All four variants have $\langle 422 \rangle_{CeO2}//[001]_{MgO}$ (the surface normal); two twin-related variants have $\pm[111]_{CeO2}//[200]_{MgO}$, and the other two twin-related variants have $\pm[111]_{CeO2}//[020]_{MgO}$. The four variants were verified by dark-field imaging with ceria reflections. With <1% mismatch between CeO_2 d_{333} (= 0.104 nm) and MgO d_{400} (= 0.105 nm), and <10% mismatch between CeO_2 d_{220} (= 0.191 nm) and MgO d_{200} (= 0.210 nm), this orientation relationship has better matching of d-spacings in the plane of the interface than does a cube-on-cube orientation. Also, a possibly favorable <111> growth direction is nearly normal to the film. However, examination of other PLD ceria films on <100> MgO has revealed a cube-on-cube orientation, so the ~26% misfit is not too large to prevent epitaxy.

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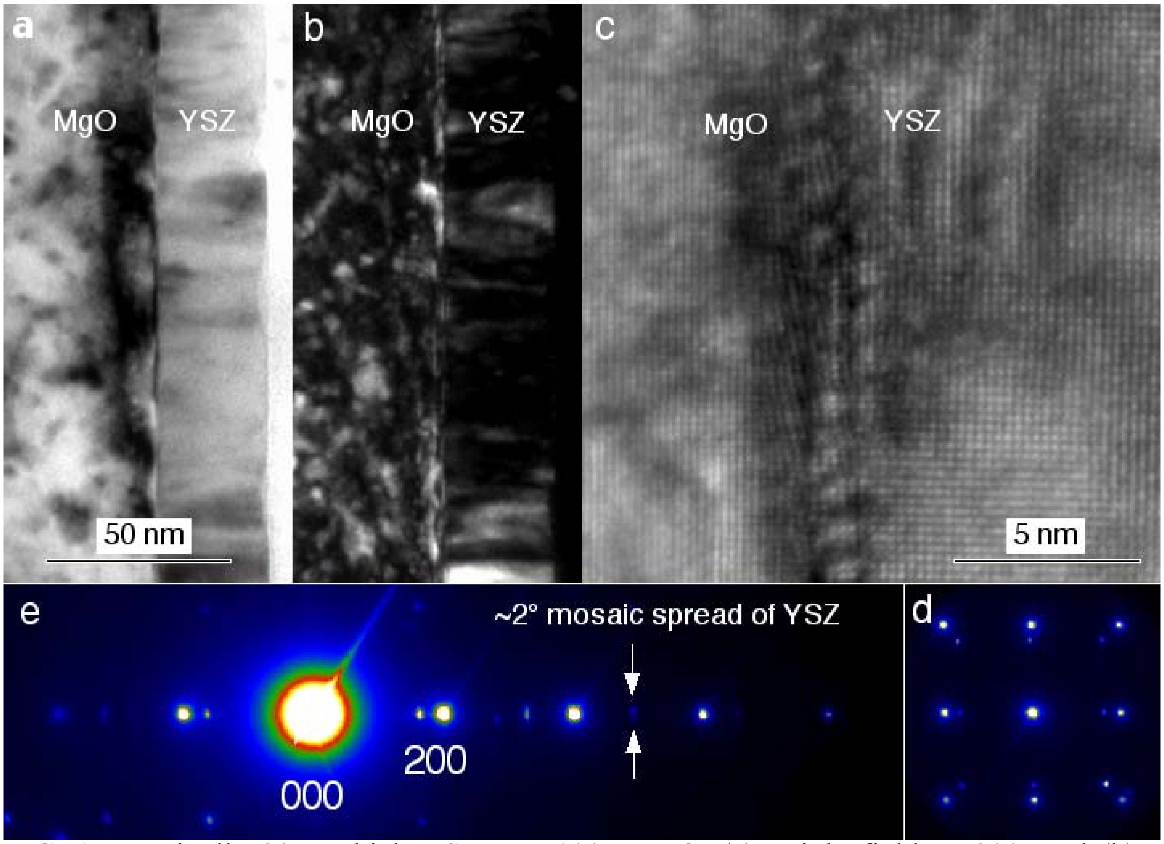

FIG. 1. Nominally 29nm-thick YSZ on <100> MgO. (a) Bright-field, g=200, and (b) g=200(800) weak-beam dark-field images showing highly strained YSZ . (c) High-resolution image of film-substrate interface showing periodic strain fields and slight misorientation between YSZ and MgO. (d) [001] SAD pattern showing cube-on-cube orientation relationship and 22% lattice mismatch. (e) 200 systematic-row SAD showing ~2° mosaic spread of YSZ.

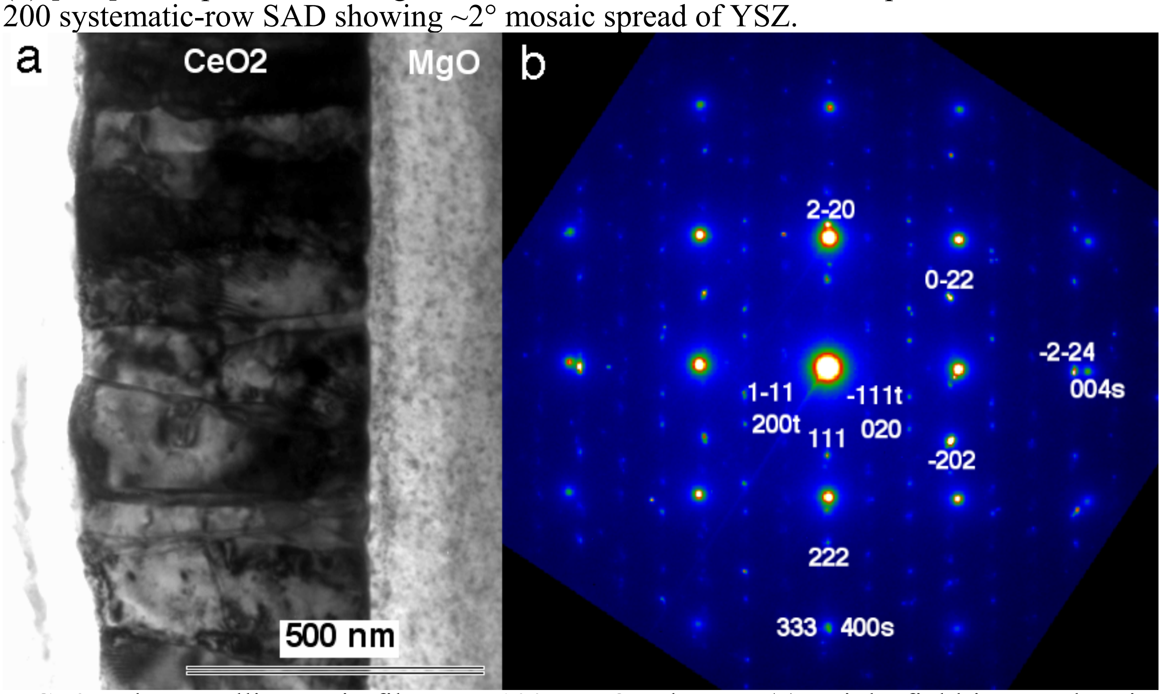

FIG. 2 Polycrystalline ceria film on <100>MgO substrate (a) Bright-field image showing columnar grains (b) Indexed SAD pattern, [010]MgO. Indices for ceria (t = twin), except s = MgO substrate.

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