INTERFACIAL EFFECTS AND IONIC TRANSPORT IN YSZ EPITAXIAL THIN FILMS*

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The enhanced ionic transport properties of nanocrystalline ceramics are attributed to the grain boundary and grain size-dependent defect equilibria, which become dominant when the grain size is < 100 nm. Surface and interfacial effects can have significant effects in such nanostructured materials. In the present experiments, we examined their influence by characterizing the effect of the thickness of epitaxial zirconia–10 mol. % yttria (YSZ) films on the ionic conductivity. In this geometry, the fraction of the atoms at the surface and substrate interfaces, versus that within the bulk, varies with the film thickness. The YSZ films were prepared by pulsed laser deposition on (001) MgO single crystal substrates at typical depositions of 0.5 to 1 Å per pulse. The electrical conductivity was measured using two-probe impedance with an electrode configuration to measure current flow parallel to the film and substrate surfaces. The temperature dependent conductivity was correlated with the thickness of the YSZ films, which was varied from < 50 nm to 2000 nm. For film thickness > 50 nm, the conductivity-temperature curves were essentially identical and mimicked those obtained with cubic YSZ single crystals. However, the conductivity increased by one to two orders-of-magnitude when the film thickness was < 50 nm. The associated activation energies below ~ 550°C averaged 1.13 eV for both single crystals and films of every thickness. Above 550°C, the activation energy for films < 50 nm was 0.6 eV as compared to 0.85 to 1 eV for single crystals and films thicker than 50 nm. These findings reveal that conductivity measurements on the thicker epitaxial films reproduce those for single crystals, and that conductivity enhancement similar to that observed for grain sizes < 50 nm can be achieved in epitaxial films of comparable thickness.

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*Research sponsored by the Laboratory Directed Research and Development Program and the DOE Office of Basic Energy Sciences' Division of Materials Sciences and Engineering, and conducted at Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-AC05-00OR22725.

Observation of *Superionic* Conductivity In Highly Oriented *Nanometer Scale* ZrO_2–10 mol % Y_2O_3 (10YSZ) Films

Research carried out by

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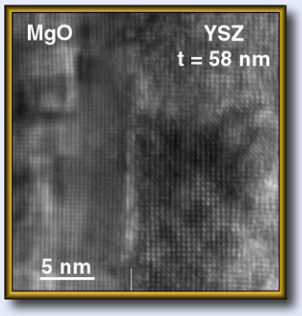
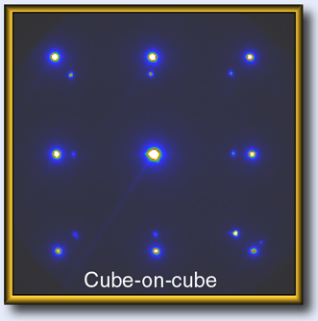
Research supported by

ORNL Laboratory Directed Research and Development Fund and Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U. S. Department of Energy

Exceptional Quality of Pulsed Laser Deposited Nanometer Scale, Oriented YSZ Films on (001) MgO

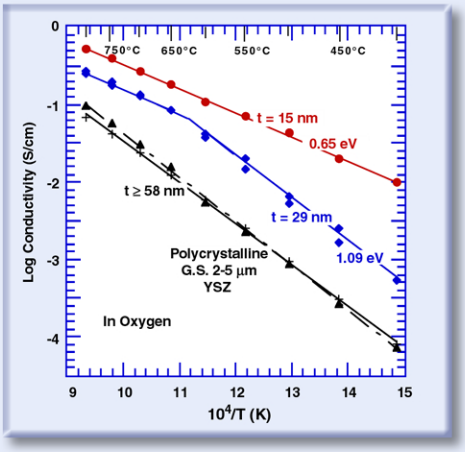
- Cube-on-Cube Orientation and Absence of Dislocation Arrays
- Optimum Y_2O_3 Content to Enhance Conductivity
  - Ionic conductivity reaches maximum value for 8 to 10 mol % Y_2O_3
  - EDS analysis confirms composition is ZrO2 – 9.5 mol % Y_2O_3
- Lattice imaging reveals YSZ films' high degree of crystalline perfection
- In-plane residual stress also present due to ~22% lattice mismatch





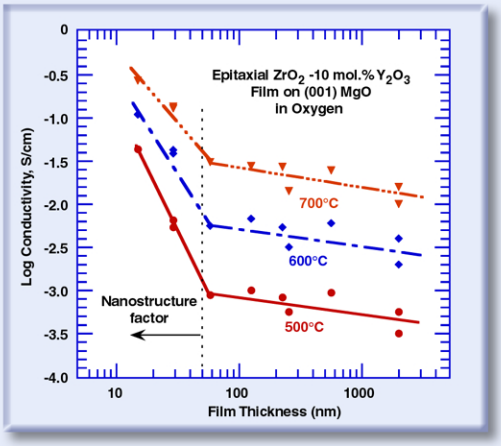
Nanometer Scale, Oriented 10YSZ Films Become *Super*ionic Conductors as Film Thickness Decreases

- 15-nm thick oriented 10YSZ film exhibits *highest ionic conductivity ever reported*
- ~140-fold greater than that of conventional zirconia electrolyte ceramics at 400°C!
- Conductivity at 550°C is equivalent to that of YSZ ceramics at 800°C.



Data for polycrystalline 8YSZ (+) from I. Kosacki et al., Solid State ionics 2000

Nanostructured Films are the Model for the Next Generation of Solid Oxide Fuel Cell (SOFC) Electrolytes



- Important scientific implication:
  Ionic conductivity is *dominated by interfacial and surface conduction mechanisms, which can be uniquely accessed due to film characteristics*
- Technological implications:
  Thickness–dependent interfacial and surface effects suggest using nanostructure and superlattice effects for variety of applications

ORNL 2001-04110/jcn