

# Atomic Layer Deposition of Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> Nanolaminates:

## A Route to Ultra-Thin Solid State Electrolyte Membranes

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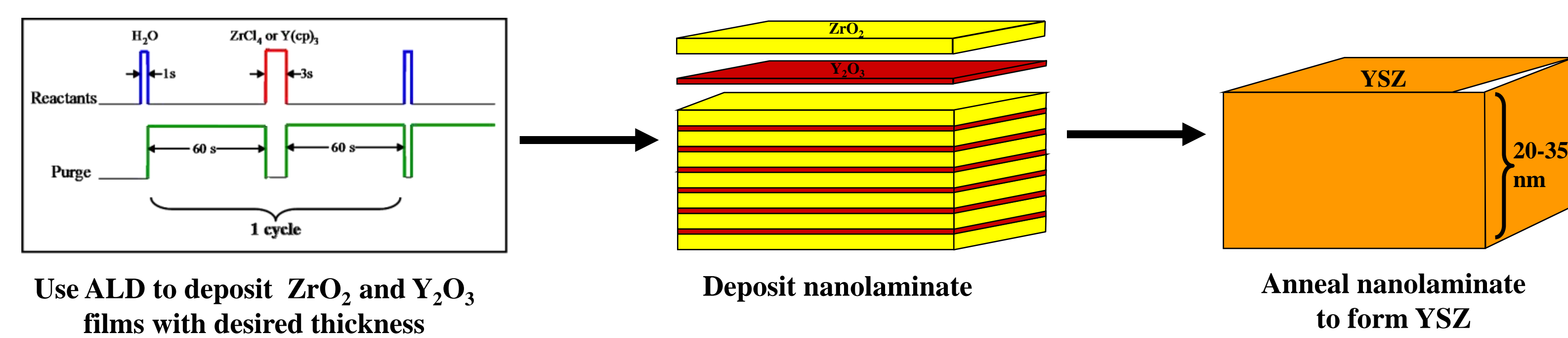
### Introduction

Solid oxide fuel cells (SOFCs) are interesting as an energy conversion technology with potential applications in transportation systems. A major disadvantage of current SOFC technology, however, is the relatively high operating temperatures (600–1000°C)<sup>1</sup>, limiting their range of practical use to large power systems. Reducing operating temperatures can be achieved by making the SOFC electrolyte membrane thinner, thereby making it easier for oxygen ions to move across the membrane at lower temperatures. Yttria-stabilized zirconia (YSZ) is the most widely used material for SOFC electrolytes and is a well-studied alloy, known for thermal stability, fast oxygen ion conduction, and electronic insulation<sup>2</sup>. The YSZ SOFC electrolyte is typically ≥ 40 μm in thickness, and reducing its thickness to the nanometer scale may lead to improved SOFC performance at lower operating temperatures. We report on the growth and electrochemical properties of nanoscale (20-35 nm) yttria/zirconia alloys synthesized using a laminate approach via atomic layer deposition (ALD).

1. Lashway, R. Fuel cells: The next evolution. *MRS Bulletin*, 30, 581-583 (2005).  
 2. Yokokawa, H. et al., Electrolytes for Solid-Oxide Fuel Cells. *MRS Bulletin*, 30, 591-595 (2005).  
 3. Singhal, S.C., Science and Technology of Solid Oxide Fuel Cells, *MRS Bulletin*, 25, 16-21 (2000).

### Technique

In order to synthesize ultra-thin yttria/zirconia alloy electrolytes, yttria/zirconia nanolaminates having either long (~ 10 nm) or short (~ 1 nm) bilayer periods and varying average compositions were deposited via atomic layer deposition (ALD), a film growth method noted for its efficacy in deposition of thin pin-hole-free metal oxide films. Different yttria contents were achieved by varying the number of Zr and Y precursor pulses during alloy film growth. Post-deposition annealing at 950 °C for 2.5 hours enabled layer interdiffusion in the nanolaminate structures.



The precursors zirconium tetrachloride (ZrCl<sub>4</sub>) and tris(cyclopentadienyl)yttrium [Y(cp)<sub>3</sub>] were used with water as an oxidant to deposit zirconia and yttria, respectively. Processing conditions for these nanolaminates are outlined below.

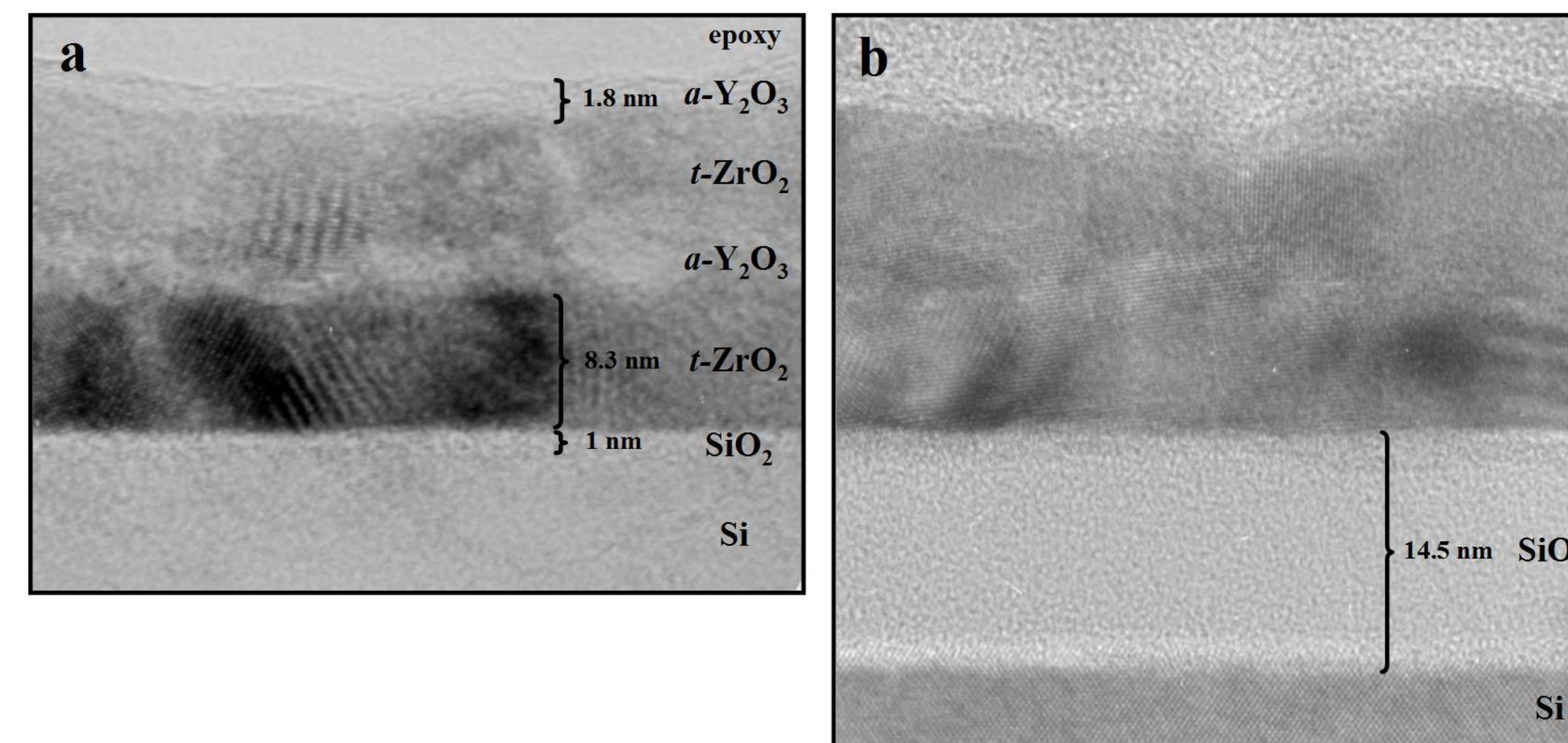
	ZrO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>
<b>Precursor (Temp.)</b>	ZrCl <sub>4</sub> (150°C)	Y(cp) <sub>3</sub> (185°C)
<b>Oxidant (Temp.)</b>	Water (25°C)	Water (25°C)
<b>Growth Per Cycle</b>	0.45-0.60 Å	0.45-0.60 Å
<b>Film Uniformity</b>	±2 Å (100%)	±2 Å (75%)
<b>Structure</b>	Tetragonal (<14 nm) <sup>3</sup>	Amorphous (<5 nm)
<b>Substrate Temperature</b>	300°C	

Processing conditions for ALD of ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>

<sup>3</sup>Kim, et al., Microstructural evolution of ZrO<sub>2</sub>-HfO<sub>2</sub> nanolaminate structures grown by atomic layer deposition. *J. of Mat. Res.*, 19, 643-650 (2004).

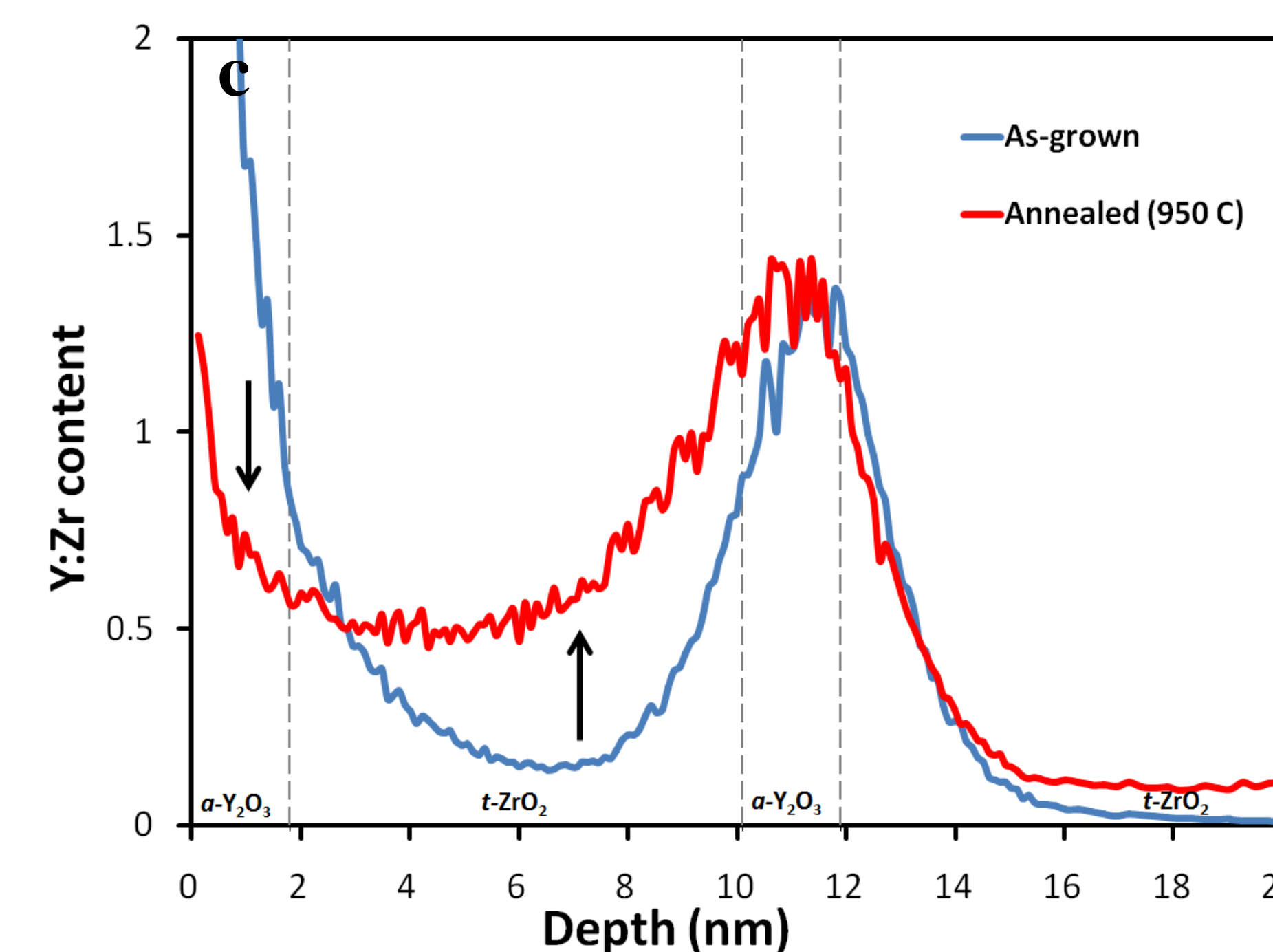
### Long-Period Nanolaminate

Initially, long-period (bilayer period ~10 nm) laminates were grown to observe interdiffusion of relatively thick yttria and zirconia layers upon annealing at 950 °C for 2.5 hours.



High resolution cross section TEM images of (a) as-grown and (b) annealed long-period Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanolaminate.

- 20 nm total film thickness
- ~8.3 nm-thick polycrystalline tetragonal ZrO<sub>2</sub> layers
- ~1.8 nm-thick amorphous Y<sub>2</sub>O<sub>3</sub> layers
- Total laminate thickness decreased from ~20.8 nm to ~19.7 nm
- Significant SiO<sub>2</sub> interfacial growth from ~1 nm to ~14.5 nm



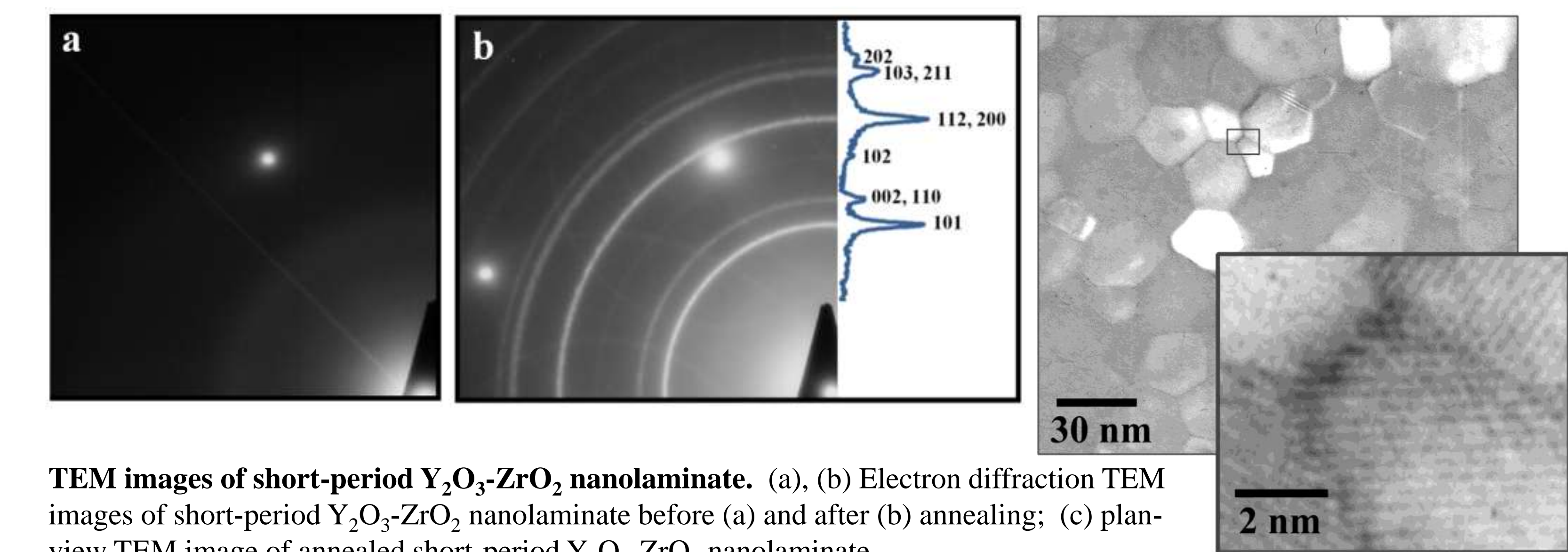
Y:Zr content depth profiles. Extracted from SIMS data for as-grown (in blue) and annealed (in red) long-period Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanolaminate.

Layer interdiffusion is evident by TEM and SIMS but the yttria layers remain discernible, suggesting incomplete intermixing. Cation diffusion calculations based on published Y, Zr, and YSZ diffusion studies<sup>4,5</sup> and Darken's flux equation suggested that post-deposition anneals at 950 °C for 2.5 hours would result in an effective diffusion distance of ~ 0.6 nm. This distance is similar to the bilayer periodicity of the short-period nanolaminates but quite small compared to that of the long-period laminates. Thus, our observation of partial layer interdiffusion in the long-period yttria/zirconia nanolaminates with SIMS analysis, an observation not possible for the short-period nanolaminates due to the limited depth resolution of this analytical technique, is consistent with the estimated diffusion length. These annealing experiments strongly suggest complete component interdiffusion may occur for thinner bilayers under same annealing conditions.

4. Kilo, M., et al, Cation self-diffusion of Ca-44, Y-88, and Zr-96 in single-crystalline calcia- and yttria-doped zirconia. *J Appl Phys* 94, (2003).  
 5. Lee, T., Navrotsky, A., Enthalpy of formation of cubic yttria-stabilized zirconia. *J. Mater. Res.* 18, 908-918 (2003).

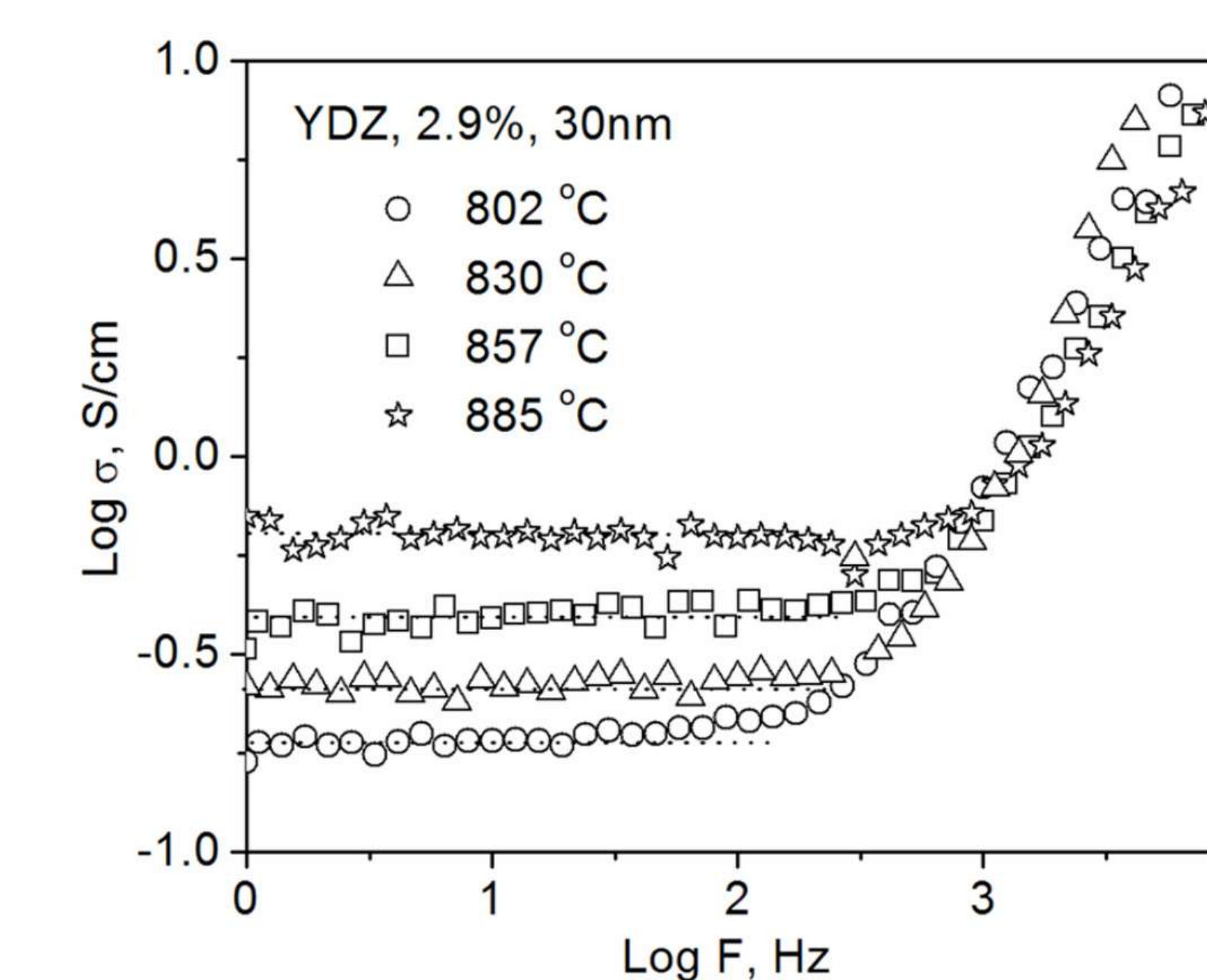
### Short-Period Nanolaminate

Subsequently, in order to promote thorough interdiffusion of homogeneous yttria-zirconia alloys, short-period (bilayer period < 1 nm) yttria/zirconia laminates were and annealed under the same conditions as the long-period laminates.

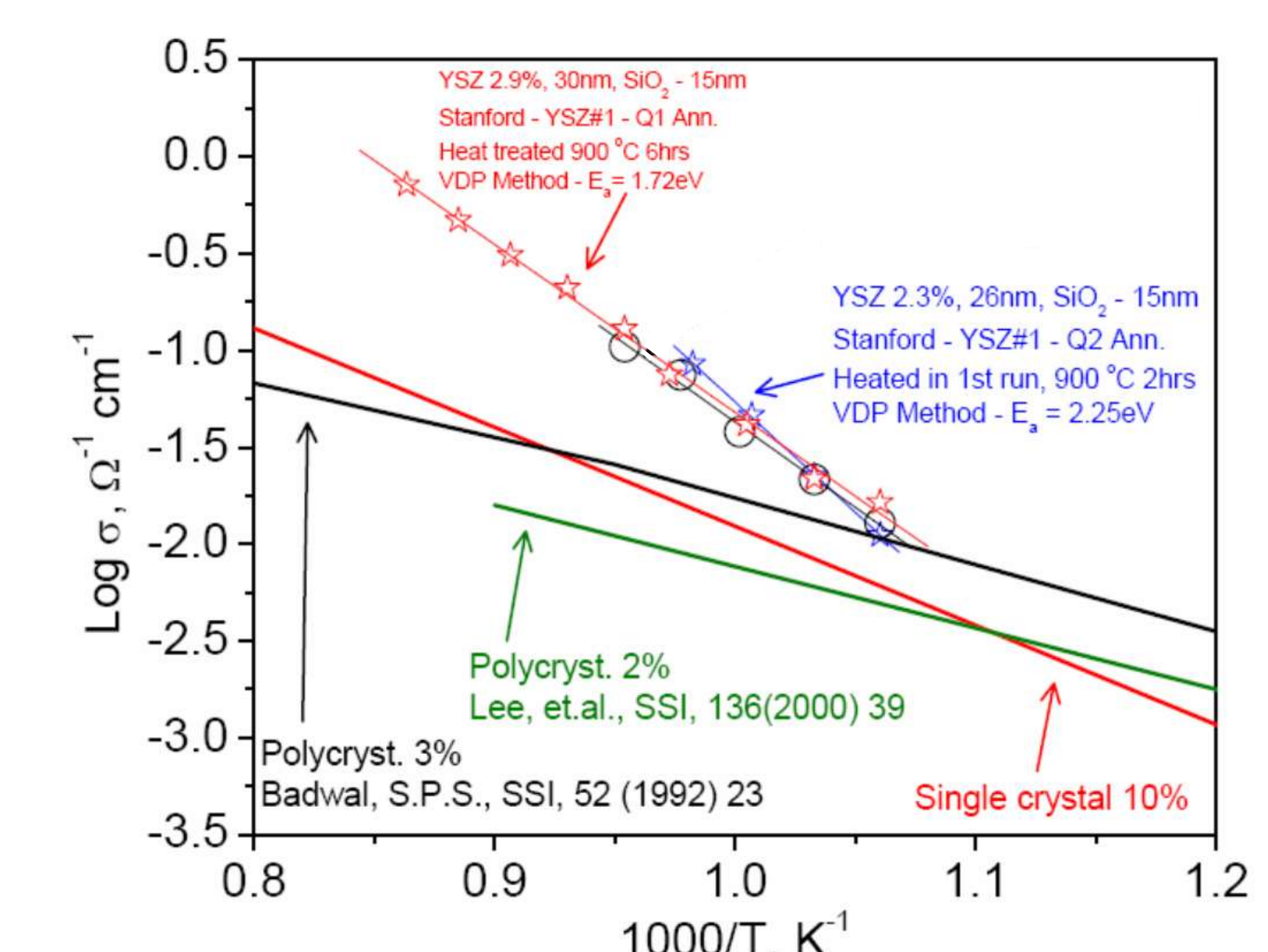


TEM images of short-period Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanolaminate. (a), (b) Electron diffraction TEM images of short-period Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanolaminate before (a) and after (b) annealing; (c) plan-view TEM image of annealed short-period Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanolaminate.

- 2-4 mol% YSZ films with thicknesses 20-35 nm
- As-deposited YSZ is amorphous; annealed is polycrystalline
- Annealed YSZ with 3 mol% yttria (3YSZ) is tetragonal, as expected from bulk phase diagram<sup>6</sup>
- Annealed short-period laminate exhibits columnar grain structure (~5-25 nm grain diameter) that spans entire film thickness
- XRR indicates density increase from 5.78 ± 0.29 g/cc to 6.13 ± 0.31 g/cc (commercial bulk 3YSZ, 6.05 g/cc), likely due to removal of excess H<sub>2</sub>O incorporated during ALD process and film crystallization
- Densification was accompanied by 2.8 (± 1.7) % reduction in film thickness



Frequency dependence of total conductivity of 2.9% yttria-doped zirconia film of 30 nm thickness at various temperatures



Temperature dependence of total conductivity of 2.9- and 2.3YSZ compared to reported bulk values for YSZ with varied yttria concentrations

Detailed electrical conductivity measurements were carried out on selected as-deposited and heat treated samples using the van der Pauw technique. Electrical characterization of ultrathin (25-35 nm thick) 3YSZ films indicated a **10 times enhancement** of the total electrical conductivity compared to bulk 3YSZ<sup>6</sup> and is about 15 times higher than that of bulk polycrystals with 2% yttria<sup>7</sup>. It is interesting to note that the films show very high total conductivity even with very low yttria content. Further investigation of yttria-doping effects and phase transformation kinetics are needed to understand the observed increase in electrical conductivity of these yttria-zirconia alloys.

6. Fevre, M., et al, Local order and thermal conductivity in yttria-stabilized zirconia. I. Microstructural investigations using neutron diffuse scattering and atomic-scale simulations. *Phys Rev B*, 72, 104-117 (2005).  
 7. Badwal, S., Zirconia-based solid electrolytes: microstructure, stability and ionic conductivity. *Solid State Ionics*, 52, 23-32 (1992).  
 8. Lee, et al, Electrical and microstructural characterization on nitrogen-stabilized zirconia. *Solid State Ionics*, 136, 39-44 (2000).

### Acknowledgements

The authors would like to thank EAG Labs (Sunnyvale, CA) for SIMS measurements, Dr. A. Vailionis for x-ray reflectivity measurements and Dr. A.F. Marshall for help with TEM.