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Feature article

Low thermal conductivity of atomic layer deposition yttria-stabilized zirconia (YSZ) thin films for thermal insulation applications

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A B S T R A C T

Thermal insulation applications have long required materials with low thermal conductivity, and one example is yttria (Y_2O_3)-stabilized zirconia (ZrO_2) (YSZ) as thermal barrier coatings used in gas turbine engines. Although porosity has been a route to the low thermal conductivity of YSZ coatings, nonporous and conformal coating of YSZ thin films with low thermal conductivity may find a great impact on various thermal insulation applications in nanostructured materials and nanoscale devices. Here, we report on measurements of the thermal conductivity of atomic layer deposition-grown, nonporous YSZ thin films of thickness down to 35 nm using time-domain thermoreflectance. We find that the measured thermal conductivities are 1.35–1.5 $W m^{-1} K^{-1}$ and do not strongly vary with film thickness. Without any reduction in thermal conductivity associated with porosity, the conductivities we report approach the minimum, amorphous limit, 1.25 $W m^{-1} K^{-1}$, predicted by the minimum thermal conductivity model.

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1. Introduction

Yttria (Y_2O_3)-stabilized zirconia (ZrO_2) (YSZ) is a widely used material in a variety of applications due to their range of properties, such as low thermal conductivity (similar to that of a glass), high chemical stability, and high ionic conductivity [1–4]. One popular example is the use of YSZ ceramics as thermal barrier coatings, which are primarily targeted to insulate and protect turbine and combustor engine components from combusting flows and thereby enhance the performance and durability of these engines [1,2]. Because low thermal conductivity is critical in thermal insulation applications, numerous efforts have focused on reducing the thermal conductivity of YSZ coatings [1,2,5–8]. These coatings are typically 100 μm to 2 mm thick and contain a large volume fraction of porosity [1,2,8].

Of recent interest are nonporous YSZ thin films with thicknesses on the order of 100 nm, grown by radio-frequency (RF) sputtering, atomic layer deposition (ALD) and other fabrication techniques, as solid-state electrolytes for solid oxide fuel cells operating at low temperatures (~300 °C) [3,4]. Compared to other fabrication techniques, ALD can offer uniform and conformal coating of the surface of three-dimensional structured micro- and nanoscale devices [3]. Many attempts have been made to grow YSZ electrolyte films by ALD and characterize their microstructural features and electrochemical performance [3,4]. But less is known about the thermal properties of these films.

In this work, we measure the thermal conductivity of ALD-grown, nonporous YSZ thin films with three different thicknesses (35, 61, and 138 nm) using time-domain thermoreflectance (TDTR) at room temperature. We find that the measured thermal conductivities are 1.35–1.5 $W m^{-1} K^{-1}$ and do not significantly depend on film thickness. The thermal conductivities we observe here are higher than the lowest reported for highly porous YSZ ceramics—0.06 $W m^{-1} K^{-1}$ with 77% porosity [8]—but are still low in the sense that they approach the minimum, amorphous limit, 1.25 $W m^{-1} K^{-1}$, predicted by the minimum thermal conductivity model [9] without any effects associated with porosity. To the best of our knowledge, the thermal conductivities measured here are the lowest ever reported for nonporous YSZ. Considering that ALD is particularly useful for uniform and conformal coating of the surface of three-dimensional nanostructures, the findings presented here may point to the possibility of using ALD YSZ for various thermal insulation applications in nanostructured materials and nanoscale electronic and energy conversion devices.

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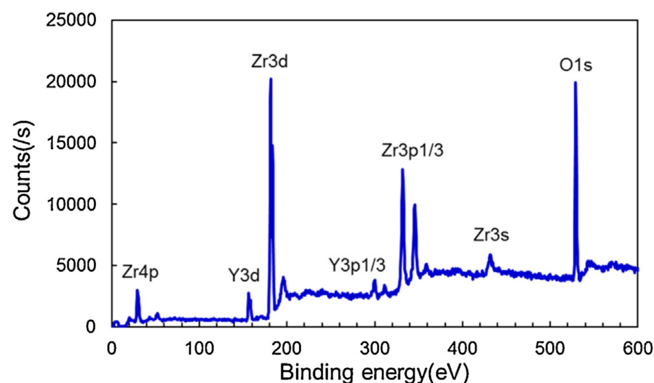

Fig. 1. XPS spectra of ALD YSZ films used in this study.

2. Material and methods

Three YSZ films of thickness 35, 61, and 138 nm are grown on p-doped Si substrates using ALD at a deposition temperature of 250 °C. The precursors used for ALD fabrication of YSZ are tetrakis-(dimethylamido) zirconium ($Zr(NMe_2)_4$) (Sigma Aldrich) for depositing zirconia and tris-(methylcyclopentadienyl) yttrium ($Y(MeCp)_3$) (Strem Chemical) for yttria. Water is used as the oxidant for both precursors. Seven zirconia deposition cycles and one yttria cycle constitute one super cycle, whose growth rate is ∼9–10 Å/supercycle. The number of supercycles for 35, 61, and 138 nm films are 35, 70, and 140, respectively. A 53–56 nm Al film that is typically referred to as a transducer layer for thermoreflectance measurements is electron-beam evaporated on the surface of the three YSZ films after an extended air break.

Prior to the deposition of the Al transducer layer, the stoichiometry of the ALD YSZ films is analyzed by X-ray photoelectron spectroscopy (XPS) in a SSI S-probe monochromatized XPS spectrometer with Al KR radiation (1486 eV) (Fig. 1). The composition of the ALD YSZ films is Zr 30.0%, Y 5.5%, and O 64.5%; the doping level, i.e., x in $(Y_2O_3)_x(ZrO_2)_{1-x}$, is therefore 8.4 mol%. The possible impurities, *i.e.*, C and N, in the films were not detectible, which means their concentrations are less than 0.1 at.% (detection limit of XPS).

The crystalline phase and quality as well as the thicknesses of the ALD YSZ films are analyzed by transmission electron microscopy (TEM). The film thicknesses are measured to be 35, 61, and 138 nm. TEM images show that our films are mostly polycrystalline with nanoscale grains, i.e., nanocrystalline, with some portion of an amorphous matrix. The average grain size is ∼10 nm in width (Fig. 2(a)–(f)). Lattice fringe measurement, as well as the selective area diffraction (SAD) pattern (Fig. 2(g)), confirms that our films are polycrystalline. The crystal structure of our films is dominantly tetragonal. A previous study reported that a mixture of tetragonal and cubic phases exists in 8 mol% ALD YSZ films deposited at 400 °C [10]. The relatively low deposition temperature of our films (250 °C) could be the reason why the metastable tetragonal phase is dominant in our films, although the cubic phase is the most stable phase in heavily-doped YSZ (7–10 mol%) [11]. We observe no significant change in crystallinity of films with increasing film thickness.

The thermal conductivities of the three ALD YSZ films are measured at room temperature using TDTR, an ultrafast, optical pump-probe technique based on thermoreflectance [12–14]. The output of a mode-locked Nd:YVO_4 laser (λ = 1064 nm and t = 9.2 ps optical pulses at a repetition rate of 82 MHz) is split into the pump (heater) and probe (thermometer) beams, which are concentrically focused on the sample surface using a 20× microscope objective lens. The frequency-doubled 532 nm pump beam, modulated at 6 MHz using an electro-optic modulator for lock-in detection, locally heats the sample. The time-delayed, unmodulated 1064 nm probe beam measures the time-evolution of the surface temperature through the temperature-induced changes in the reflectivity of Al. The topmost Al transducer layer acts as the pump absorber and probe reflector; i.e., it absorbs and converts the electromagnetic energy of the pump pulses into heat, and it reflects the probe pulses and generates the measurable transient surface temperature decay signal via its large coefficient of thermoreflectance at the probe wavelength. The temperature-induced changes in the reflected probe intensity are recorded by a radio-frequency lock-in amplifier at the pump modulation frequency as a function of delay time between the pump and probe beams. The $1/e^2$ diameters of the focused pump and probe beams are ∼10.2 and ∼6.2 µm, respectively, at the sample surface.

We utilize the amplitude $\sqrt{{V_{in}}^2 + {V_{out}}^2}$ of the in-phase $V_{in}(t)$ and out-of-phase $V_{out}(t)$ components of the thermoreflectance signal detected by the lock-in amplifier, which is essentially the amplitude of the surface temperature response (i.e., steady periodic temperature oscillations at the sample surface) to the pump heating, to monitor the surface temperature decay over the delay time from 0 to 3.5 ns. The time dependence of the measured amplitude data is compared with that of an analytical solution to the three-dimensional radial-symmetric heat diffusion equation for a multilayer stack of materials to determine unknown thermal parameters [12]. A nonlinear least-squares curve-fitting routine is employed to extract the unknown parameters by minimizing the deviations between the data and the model prediction. We validated the accuracy of our TDTR system with SiO_2 and single crystalline Si reference samples and found values (1.39 ± 0.4 W m^{-1} K^{-1} for SiO_2 and 145 ± 15 W m^{-1} K^{-1} for Si) that are within 2% of literature values for both materials. Further details of the TDTR setup that is used in this study can be found in Refs. [15] and [16]. For more general and detailed descriptions of the TDTR methodology and data analysis, including advantages and limitations of the methodology, see Refs. [12–14].

The multilayer thermal diffusion model contains many parameters, including the thicknesses, thermal conductivities, and volumetric heat capacities of the Al and YSZ layers and the thermal conductivity and volumetric heat capacity of the Si substrate, along with the thermal boundary resistances across the Al/YSZ and YSZ/Si interfaces. For each sample, we determine the Al and YSZ layer thicknesses from cross-sectional TEMs (Fig. 1). The uncertainty in the thickness measurement is estimated to be less than 5%. The thermal conductivity of the Al layer is estimated to be 123 ± 14 W m^{-1} K^{-1} from four-probe measurements of the in-plane electrical resistivity and the use of the Wiedemann-Franz law. The volumetric heat capacity of the Al layer is taken from literature to be 2.43 MJ m^{-3} K^{-1} [17], while that of the YSZ layer is estimated to be 2.55 ± 0.07 MJ m^{-3} K^{-1} from the product of the measured density (5.4–5.7 g cm^{-3}) [3] and the specific heat (0.45976 J g^{-1} K^{-1}) taken form the literature [18]. The thermal conductivity of the (p-doped) Si substrate is measured separately to be 110 ± 12 W m^{-1} K^{-1} using TDTR on the (p-doped) Si substrate coated with a 54-nm-thick Al film. The volumetric heat capacity of the Si substrate is taken from literature to be 1.65 MJ m^{-3} K^{-1} [19,20]. We thus have three unknown parameters in the multilayer thermal diffusion model: (i) the thermal boundary resistance across the Al/YSZ interface (TBR_{Al-YSZ}), (ii) the thermal conductivity of the YSZ layer (k_{YSZ}), and (iii) the thermal boundary resistance across the YSZ/Si interface (TBR_{YSZ-Si}). Here, we extract TBR_{Al-YSZ} and k_{YSZ} by performing a two-parameter fit of the multilayer thermal model to the measured data, while assuming a range of values from 0 to 15 m^2 K GW^{-1} for TBR_{YSZ-Si}. As we discuss in the next section, sensitivity analysis shows that our measurements are most sensitive

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