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Ionic Conduction Enhancement in Nano-scale Thin Film Gadolinia-doped Ceria Electrolyte

Hong Huang, Yuji Saito, and Fritz Prinz
Rapid Prototyping Laboratory, Stanford University
440 Escondido Mall, Stanford, CA94305, USA

Lowering the operating temperature is one of the key issues for realizing solid oxide fuel cells as a practical power source. Ceramic electrolytes with sufficient oxygen ion conductivity at temperatures lower than 700°C are desirable. In comparison to the most widely used SOFC electrolyte material YSZ (Yttria Stabilized Zirconia), oxygen ion conductivity in doped ceria is reported to be 2-3 orders of magnitude higher at temperatures below 500°C. In addition, the ionic conduction domain in doped ceria is known to expand as the temperature decreases. For example at 500°C, the ionic transference number is larger than 0.9 [1]. Hence, doped ceria is an interesting electrolyte candidate for low temperature SOFC applications.

We have observed that ultra thin electrolyte membranes of doped ceria with thickness comparable to characteristic grain size possess higher oxygen ion conductivity compared to membranes with thickness above the grain size. We hypothesize that the elimination of cross grain boundaries leads to redistribution of space charge regions, which in turn may be accompanied by enhanced ionic conductivity [2].

In this paper we present methods to successfully measure the ionic conductivity of nano-scale films made from Gadolinia-Doped Ceria (GDC). GDC thin films were prepared by DC-sputtering of metallic components on silicon wafer followed by oxidation in air. Thickness variation from 50nm to 3μm could be achieved by controlling the sputtering time. In order to perform electrochemical measurements, GDC films were deposited onto 200nm thick sputtered platinum electrodes. A 10 nm Ti bond layer ensures adhesion of the bottom platinum electrode to the silicon wafer. A cross section of this multilayer structure is depicted in Fig. 1.

Composition and morphology of the films were characterized by XRD, XPS, and SEM. The GDC film is fully oxidized, showing homogeneous composition throughout its depth. The film is relatively dense, consisting of 30-50nm grains. Scanning Microscopy of representative cross sections indicates that film thickness is consistent with XPS depth profile measurements. Fig.2 shows an SEM cross section image of a 50nm GDC film.

AC impedance and dc polarization data were obtained with a Solartron 1287/1260 system. Microelectrodes were patterned on top of GDC film. Microprobes were used to establish electrical connection to the impedance unit. Impedance spectra were recorded in air between 100°C and 350°C. Impedance data were retrieved by fitting the spectra using Z-view software based on a non-linear least-squares method. Fig.3 (a) depicts conductivity of the GDC film as a function of temperature, Fig. 3 (b) shows activation energy of ion conduction as a function of film thickness. It is interesting to note that ionic conduction behaves differently in three thickness regimes.

(I) Films thicker than 1μm exhibit conventional impedance spectra with two arcs corresponding to bulk and cross grain boundary conductance with activation energy of 0.7 and 0.85eV, respectively. The cross grain boundary conductivity is two orders of magnitude lower than bulk conductivity indicating significant blocking.

(II) As the thickness decreases, the grain boundary conductivity approaches bulk conductivity level while the activation energy decreases to 0.5eV.

(III) Below 100nm only one arc is presented in the impedance spectrum. The conductivity is around one order of magnitude higher than bulk conductivity and the activation energy remains constant at 0.5eV. The enhancement of the conductance may be attributed to overlap of the bulk and grain boundary space charge regions, since 50nm is in the vicinity of the 4λ (Debye length) level, as discussed in ref. [2].

References

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2. N.Sata, K. Eberman, K.Eberl and J.Maier, Nature, 408(2000), 946-949.

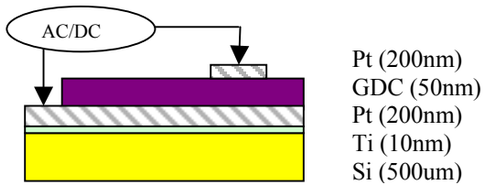

Fig.1 Configuration of the multilayer sample

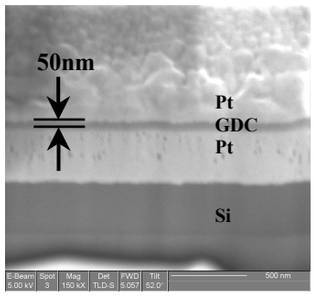

Fig.2 Cross section SEM image of the 50nm GDC film

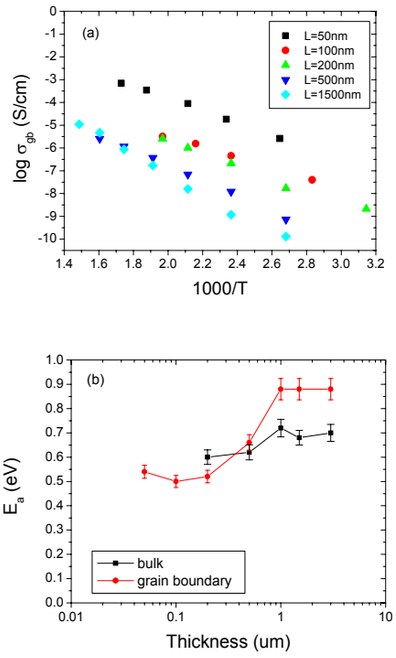

Fig. 3 (a) Conductivity vs. temperature
(b) Activation energy variation with thickness