SIGNIFICANCE OF MICROSTRUCTURE FOR A MOCVD-GROWN YSZ THIN FILM GAS SENSOR*

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November 1996

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Submitted to the Materials Research Society 1995 Fall Meeting, Symposium I: "Polycrystalline Thin Films II - Structure, Texture, Properties, and Applications," Boston, MA, November 27-December 1, 1995.

*Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under contract #W-31-109-ENG-38.

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ABSTRACT

We report the fabrication and characterization of a low temperature (200°C-400°C) thin film gas sensor constructed from a MOCVD-grown yttria-stabilized zirconia (YSZ) layer sandwiched between two platinum thin film electrodes. A reproducible gas-sensing response is produced by applying a cyclic voltage which generates voltammograms with gas-specific current peaks and shapes. Growth conditions are optimized for preparing YSZ films having dense microstructures, low leakage currents, and maximum ion conductivities. In particular, the effect of growth temperature on film morphology and texture is discussed and related to the electrical and gas-sensing properties of the thin film sensor device.

INTRODUCTION

Yttria-stabilized zirconia (YSZ), a well known oxygen ion conductor, is one of the many solid state ionic materials utilized in variety of electrochemical devices including fuel cells, oxygen pumps, and chemical gas sensors[1]. YSZ is the most common electrolyte found in sensors detecting oxygen and gases in equilibrium with oxygen [2]. Commercial YSZ sensors rely on traditional bulk ceramic fabrication and require temperatures above 600°C to achieve sufficient ionic conductivity[3]. Thin film structures with YSZ thicknesses on the order of several microns or less offer many advantages including compact dimensions with smaller power consumption, reduced ohmic losses, and often lower operating temperatures. While YSZ films have been prepared by many methods, we have chosen metal-organic chemical vapor deposition (MOCVD) since this technique provides superior conformal coverage, good thickness uniformity, and is readily scaled for high volume manufacturing. We fabricated sensor devices having a metal/YSZ/metal structure, a geometry which has been previously used in thin film sensors operated at a fixed or open potential [4,5]. However in this work, we adopted a cyclic potential method which has been successfully utilized for electrochemical analysis of solid electrolytes [6]. This approach provides current-voltage curves whose shapes and peaks are gas specific and can be read by pattern recognition methods. In order to create such a working device, the YSZ layer must be gas-tight, electrically insulating, and ionically conductive. The MOCVD YSZ film must therefore contain a minimum number of pinholes and voids to minimize electrical shorting between the bottom and top electrode. Hence, we focused our initial effort on the effect of growth conditions on the YSZ microstructure and texture and their relationship to sensor leakage current and gas-sensing response.

EXPERIMENTAL

Yttria-stabilized zirconia films (100 nm-2 μm thick) were grown in a low pressure cold wall horizontal quartz reactor. Commercially available $Y(TMHD)_3$ and $Zr(TMHD)_4$ solid precursors were employed. Source temperatures were chosen to give a final composition of 12-20% yttria as determined by energy dispersive x-ray analysis. We used UHP (99.9995%) O_2 and N_2 as the oxidizing and carrier gas respectively. Growth temperatures between 450°C and 800°C were investigated. Additional deposition conditions are listed in Table I. Films were grown on a variety of substrates, but for the current work we focus on results from films fabricated on (100) oriented Si (n-doped), sputter coated with a Pt (300 nm thick)/Ti (20 nm thick) bilayer. After film growth, a small region of the YSZ film was etched to expose platinum for use as a lower electrode. Electrical and gas-sensing tests were conducted on Pt/YSZ/Pt thin film structures fabricated by evaporating a Pt overlayer (10-50 nm thick) to provide an upper electrode which was exposed to an atmosphere of controlled composition.

Table I. Typical conditions for MOCVD growth of YSZ thin films

substrate	Pt/Ti/Si(100)
Growth temperature	450-800°C
Growth rate	0.1-0.6 μm/hr
Pressure	6-10 Torr
Zr source temperature	140-165°C
Y source temperature	115-125°C
Total flow rate	1 slm
Oxygen flow rate	300 sccm

RESULTS AND DISCUSSION

Film texture

The texture and morphology of YSZ films grown at temperatures between 450°C and 800°C were studied using x-ray diffraction (XRD) and scanning electron microscopy (SEM). In general crystal quality as judged by the intensity and sharpness of the x-ray film peaks is better for films grown at higher temperatures. All films grown above 500°C are 100% cubic phased, polycrystalline, and strongly (200) oriented. A typical Θ–2Θ x-ray pattern for a YSZ film grown at 600°C is shown in Figure 1.

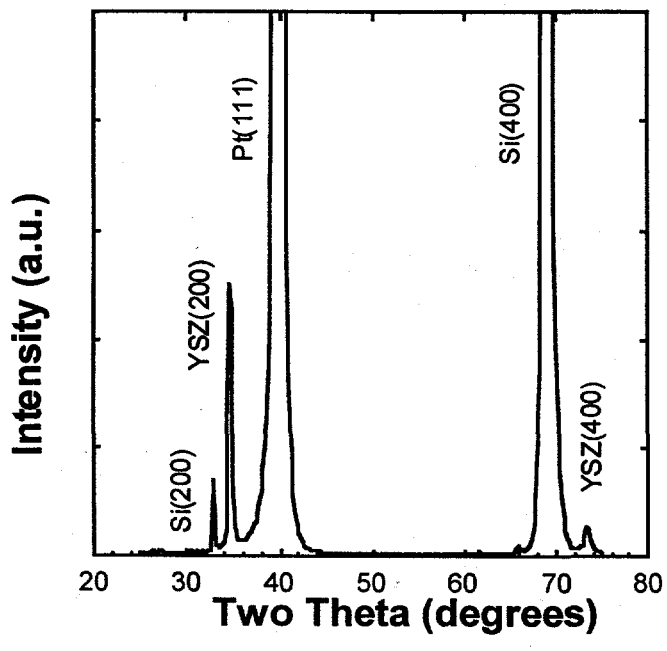

Fig. 1 Θ–2Θ X-ray diffraction scan for a (200) highly textured YSZ film

Although Pt and cubic YSZ have similar structures, they are not well lattice matched (24% average mismatch) and therefore epitaxial deposition is not expected. YSZ prepared below 500°C produced weak XRD peaks attributable only to Y_2O_3 suggesting this material is predominantly amorphous. Wavelength dispersive x-ray analysis indicated the films contain no detectable (<0.5%) carbon . Lack of crystallinity at these low temperatures may be due to unfavorable growth such as insufficient surface diffusion of oxygen or metal precursors.

Film Morphology

We found film morphology is also highly temperature dependent. While amorphous films contained no detectable microstructure, all crystalline YSZ films displayed a characteristic microstructure of columnar grains separated by a network of microvoids. Film porosity generally increased with increasing growth temperature. Sensors constructed using films grown above 600°C and having upper and lower platinum electrodes commonly became "short circuited" after heating the sensor to elevated (>100°C) temperatures. We attribute this shorting to platinum transported during MOCVD growth through open channels in the YSZ microstructure. Films grown at high temperatures were also susceptible to surface cracking and delamination at the silicon interface. The coefficients of thermal expansion in ppm/°K are approximately 10, 9, and 3 for YSZ, Pt, and Si respectively. Hence, YSZ films are under slight tension and crazing effects are expected especially in thick films grown at high temperatures. The fact that delamination occurs at the silicon and not the platinum interface suggest YSZ strongly adheres to the platinum surface. We did find YSZ layers (at least 0.6μm thick) having dense insulating microstructures could be fabricated at intermediate (500°C-600°C) temperatures. Figure 2 shows a cross-section SEM micrograph of a 1.5μm thick film grown at 525°C. Low growth temperatures may promote film density by increasing the initial density of nucleation sites, avoiding electrode diffusion, and/or reducing incorporation of large gas phase particles.

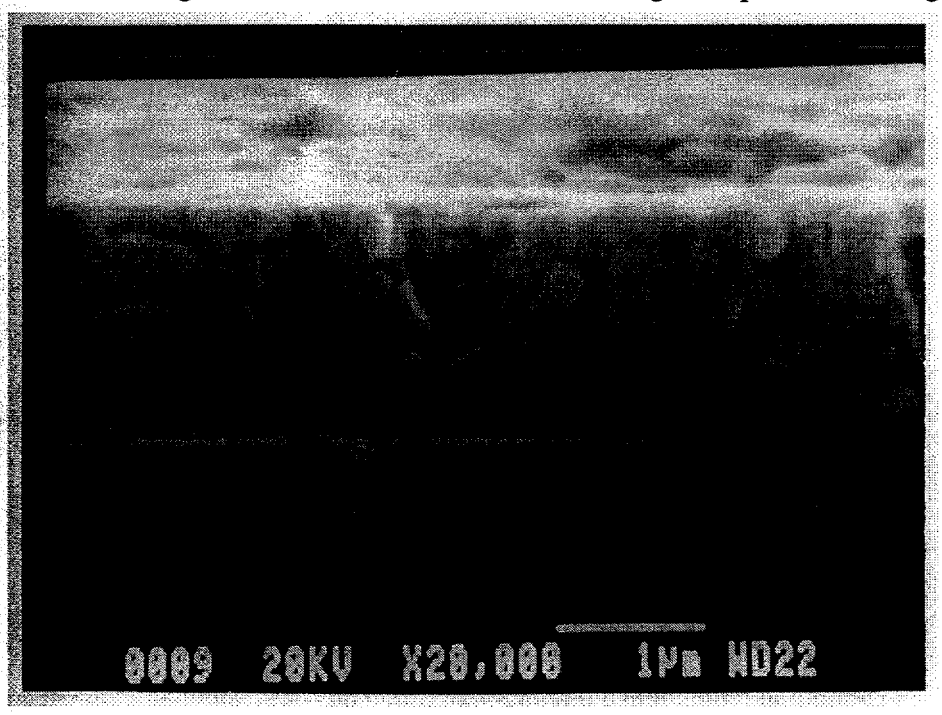

Fig. 2 Cross-sectional scanning electron micrograph of a YSZ film.

The surface of these films are crack-free and featureless in SEM. An atomic force microscope (AFM) image, reproduced in figure 3 of the same film reveals the films contain grains on average 100 nm in diameter and an rms surface roughness of 20-25 nm.

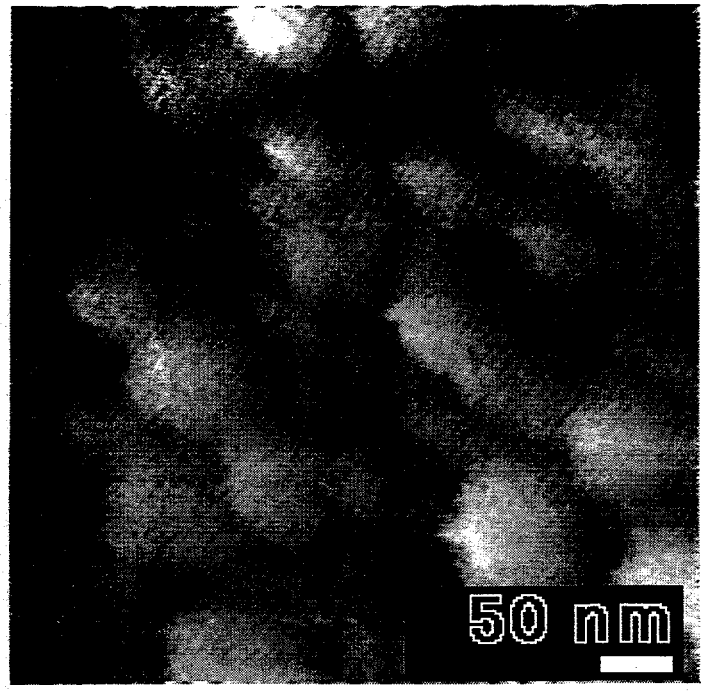

Fig. 3 Atomic force image of YSZ film surface

Electrical and Gas-Sensing Properties

A gas-sensing device was completed by evaporating an upper Pt film (20 nm thick) as a porous electrode to support and catalyze gas reactions at gas/Pt/YSZ contact points. An optical micrograph of a completed sensor is displayed in Figure 4. Devices were screened for shorting by recording the leakage current after applying a 1V dc potential across the electrodes. As shown in Figure 5, device structures suitable as sensors displayed an initially large current which decayed in several seconds to a nominal leakage current on the order of 0.5 μA, which corresponds to a current density of about 10^{-10}A/mm^2. The data is mosly closely fited to a power law dependence with an exponent of -2.1. The relatively slow decay and power law dependence is in agreement with a space-charge type polarization, which is expected since oxygen ions mobile in the YSZ layer should be blocked at the YSZ/Pt interface[7]. The gas-sensing response was evaluated by applying a cyclic dc voltage across the electrodes and measuring the transient current, which was

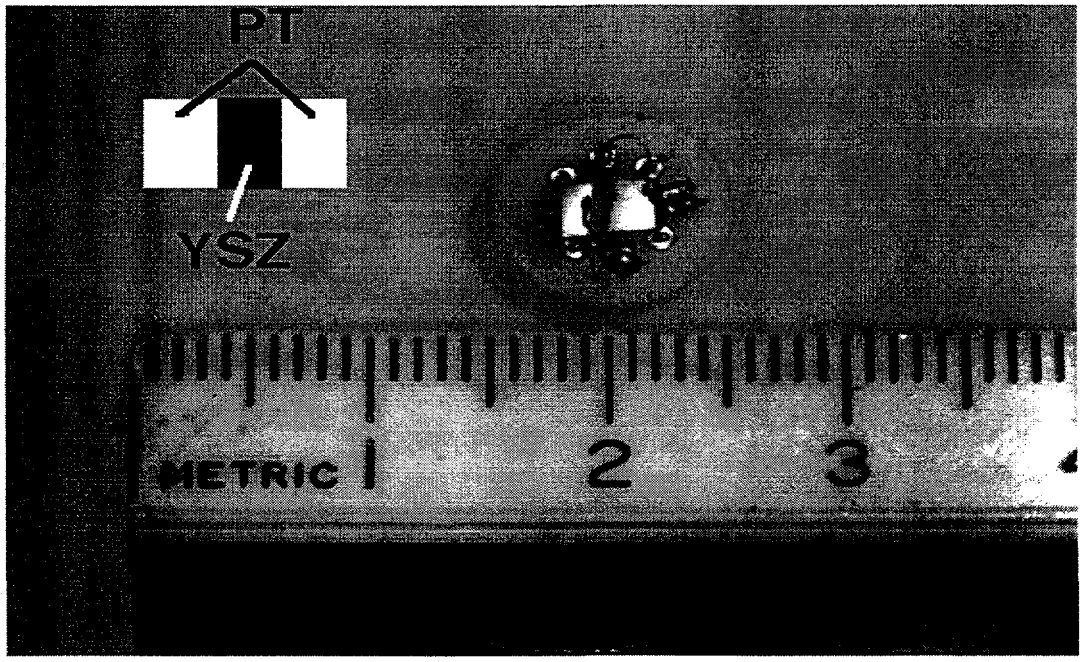

Fig. 4 Optical micrograph of a completed Pt/YSZ/Pt sensor on a silicon substrate

typically several orders of magnitude larger than the dc leakage current. A typical voltammogram is shown in Fig. 6 for a sensor heated to 280°C in flowing synthetic air (20% O_2) and UHP N_2 (<10ppm O_2). Reproducible current peaks of significant magnitude (especially at cathodic voltages) are seen in the air spectrum while no peaks above the baseline are evident in the N_2 test. Assuming the current peaks are electrochemical in nature, the current peaks may be

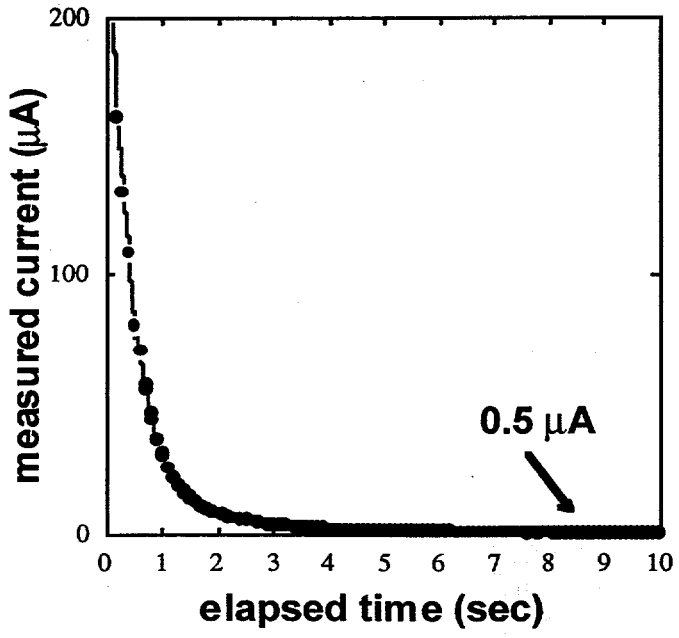

Fig. 5 Leakage current as a function of time after applying a 1V dc potential.

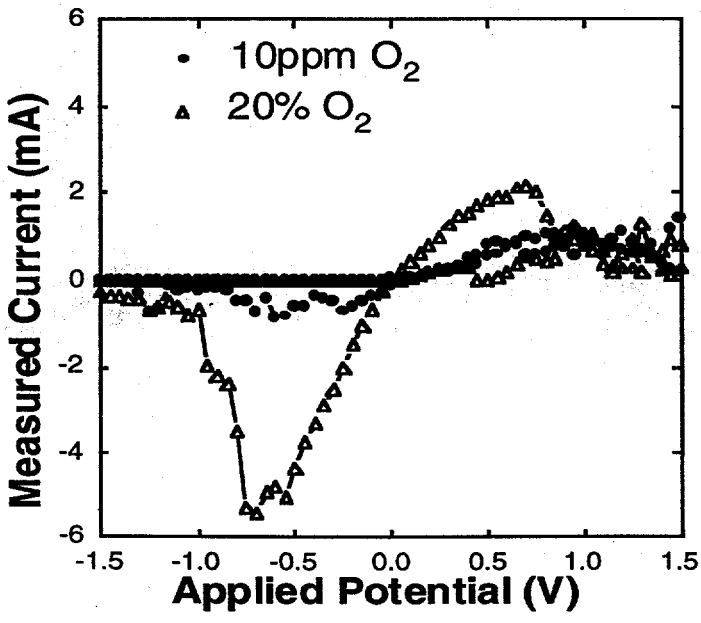

Fig. 6 Cyclic voltammogram gas-sensing response.

associated with redox type reactions between oxygen ions in YSZ and adsorbed gases so that a wide variety of gases may be detected via this unique sensor design.

CONCLUSIONS

YSZ films were deposited by MOCVD on platinum-coated silicon and found to have a characteristic columnar microstructure and (200) preferred crystal orientation. The smoothest and densest films were prepared between 500°C and 600°C and displayed electronic properties ideal for gas sensing. These films were coated with a porous Pt overlayer to form a thin film sensor having a Pt/YSZ/Pt structure. The device heated to near 300°C showed low leakage currents (10^{-10} A/mm^2) and a large current response to synthetic air but not to nitrogen demonstrating the high sensitivity and promising potential of the thin film sensor.

ACKNOWLEDGMENTS

This work was supported by Argonne National Lab, CCST LDRD contract 95200-00-200.

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