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High temperature optical sensing of gas and temperature using Au-nanoparticle incorporated oxides

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ABSTRACT

Au-nanoparticle incorporated metal oxide based sensing layers show significant promise for high temperature optical sensing applications at temperatures approaching 800 °C or even higher depending upon the base oxide material. Several Au-nanoparticle incorporated oxide systems were synthesized and investigated here, namely TiO_2, ZrO_2, and Yttria-Stabilized Zirconia (YSZ). Gas (CO, H_2, and O_2) and temperature sensing responses were observed at wavelengths near the localized surface plasmon resonance (LSPR) absorption peak of the Au nanoparticles and addition of 1% O_2 content to a N_2 baseline gas stream resulted in significantly enhanced recovery kinetics for H_2 sensing. TiO_2 films with a relatively small bandgap as compared to ZrO_2 and YSZ enabled band-edge monitoring yielding a strong temperature sensing response with minimal cross-correlation to changes in gas composition. Testing of the films in high H_2-level gas streams demonstrated that monotonic responses to H_2 up to 98% H_2 by volume in 2% O_2 balance N_2 gas streams could be achieved by interrogation at wavelengths shorter than the transmittance minimum associated with the Au LSPR absorption peak. These results collectively demonstrate the importance of careful wavelength selection or broadband wavelength interrogation to minimize cross-correlation between composition and temperature and to optimize the gas sensing response in high temperature gas streams. Although the tested films were stable in the presence of simple gas mixtures (N_2, H_2, CO, O_2) used for gas and temperature sensing experiments, a preliminary study of film stability in a contaminated (H_2S-containing) high temperature fuel gas stream relevant for solid oxide fuel cell applications was also carried out and yielded two important conclusions deserving further investigation: (1) enhanced microstructural stability of Au nanoparticle incorporated TiO_2 due to grain boundary pinning and (2) significant mass loss of Au with an associated reduction in LSPR absorption.

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1. Introduction

Sensors capable of operating at elevated temperatures and in extreme environments could enable real-time monitoring of important process parameters for a wide range of industries including fossil and nuclear based power generation, aviation/aerospace, and industrial manufacturing. For example, higher efficiency and lower emission fossil-based power generation technologies including fuel cells, combustion turbines, and steam turbines all involve high temperatures (800 °C or higher) and harsh conditions (highly oxidizing or reducing, erosive, corrosive) making successful development of embedded sensors extremely challenging [1–4].

Development of a stable sensing layer with a suitable response to a particular quantity of interest can be an enabling technology for successful development of a harsh environment sensing platform. Optical based sensing platforms are of increasing interest for harsh environment sensing due to inherent advantages that include the elimination of electrically conductive wires as well as broadband wavelength interrogation. The number of known optical-based functional sensing material candidates is limited and fundamental mechanisms of observed optical responses are not as well understood as chemi-resistive based sensing responses, particularly for high temperature sensing applications above approximately 500 °C [5–8]. A clear need exists for additional research and development in this area.

Recent investigations on Au-nanoparticle incorporated plasmonic oxides such as Au/TiO_2, Au/Yttria-Stabilized ZrO_2 (YSZ), Au/CeO_2 and others have shown that these systems exhibit attractive properties for extreme temperature optical gas sensing

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Table 1
Chemical constituents of sol–gel precursors for preparing deposited thin films. Base oxide films were also prepared without addition of $HAuCl_4$.

Ti Isopropoxide	Zr Propoxide	Y Isopropoxide	Glacial acetic acid	Isopropanol	$HAuCl_4$	Sample
0.2 mL	–	–	0.32 mL	1.5 mL	16 mg	Au/TiO_2
–	0.3 mL	–	0.1 mL	1.5 mL	15 mg	Au/ZrO_2
–	0.3 mL	18 mg	0.1 mL	1.5 mL	18 mg	Au/YSZ

applications [7,9–18]. Recent work has demonstrated that sensing layers with Au nanoparticles embedded in wide band-gap oxides such as SiO_2 and Al_2O_3 can also show useful gas sensing responses at sufficiently high temperatures even though such oxides are typically considered "inert" [19,20]. Here we present new results for a series of Au-nanoparticle incorporated oxide thin films, including TiO_2, ZrO_2, and YSZ which further demonstrate the potential for simultaneous gas and temperature sensing at elevated temperatures expanding on our prior work originally reported for fabricated sensors based upon the Au/SiO_2 system [20]. We also explore long term stability of Au-nanoparticle incorporated oxides in a contamined (H_2S-containing) fuel gas stream relevant for solid oxide fuel cell applications.

2. Experimental procedure

Thin films were synthesized through sol–gel techniques using the recipes in Table 1 below. Two layer spin-coated films were deposited on 1″ (2.54 cm) diameter fused silica substrates using 100 μL of precursor solution with a 1.5 kRPM spin off for 5 s to remove excess precursor followed by a 2.5 kRPM spin cycle for 30 s to attain film uniformity. Films were cured at 100 °C for 10 min on a hot-plate between deposited layers and calcined at a temperature of 950 °C for 2 h with a 10 h constant heating rate ramp and a 3 h cool down to room temperature to stabilize the film for subsequent sensing tests.

Simulated optical sensing tests were performed using a custom testing system described in previous publications enabling transmission monitoring while temperature and gas atmosphere were varied [6,7]. Simulated gas sensing tests were performed at temperatures of 400–800 °C by exposing films to a flowing gas stream at 100 sccm consisting of varying O_2, CO, or H_2 levels in an ultra-high purity N_2 background after pretreatment at 900 °C for 1 h in 20% O_2 balance N_2. A 20% O_2 balance N_2 mixture was also used during the 30 min heating steps between sensing temperatures and for 30 min at each temperature before beginning the analyte exposure series. Due to safety considerations, flammable species during sensor tests are typically kept below the lower explosive limits (e.g. ~4% for H_2 at room temperature). However, fuel gas streams for motivating applications of interest often involve significantly higher levels of flammable gas species than the lower explosive limits and it is well known that gas sensing responses can undergo saturation behavior. A preliminary series of tests were therefore performed to explore the saturation behavior of the materials under study at high H_2 levels as discussed below. More extensive testing in high flammable gas species containing fuel gases and realistic complex multicomponent gas streams will ultimately be required and will be the subject of future investigations. Films were characterized with a Quanta FEG environmental scanning electron microscope and a Philips Elvis X-ray diffractometer. Optical transmission (T) and reflection (R) spectroscopy were performed in the UV/visible range/near-IR range from approximately 300–850 nm using a Lambda 1050 spectrophotometer equipped with an integrating sphere. Optical absorptance (A) for each film was calculated as $A = 100\% - (T + R)$ using measured transmittance and reflectance spectra. Stability of Au incorporated oxide sensing layers in contaminated fuel gas streams was investigated by exposing films to a simulated fuel gas stream representative of coal gasification containing a significant H_2S content at a temperature of 800 °C for 168 h after completion of gas sensing tests. Heat up and cool down were performed in flowing N_2 with a heating rate of 300 °C/h and a power off cool down. The simulated fuel gas mixture composition entered into the reactor was selected to be representative of a contaminated solid oxide fuel cell (SOFC) anode stream: 29.1% H_2, 28.6% CO, 27.1% H_2O, 12.0% CO_2, 3.2% N_2, 0.003% (30 ppm) H_2S, and flowed past the specimens at a rate of 87 mm/min. Gases were passed by a Pt catalyst at temperature prior to reaching the sample to help reach equilibrium. Equilibrium gas composition at 800 °C was calculated [21] to be 34.0% H_2, 23.6% CO, 22.2% H_2O, 17.0% CO_2, 3.2% N_2, 0.026% CH_4, and 0.0029% (29 ppm) H_2S. After exposure, all films were subsequently characterized to determine the stability of the microstructure as well as the optical properties of the films.

3. Experimental results and discussion

3.1. Film characterization

Scanning electron microscopy and x-ray diffraction results are presented in Fig. 1 for the Au/TiO_2, Au/ZrO_2, and Au/YSZ films with Au nanoparticle sizes ranging from ~10 to 30 nm in diameter. The Au nanoparticle size and the grain size of the TiO_2 matrix are relatively large in Au/TiO_2 as compared to Au/ZrO_2 and Au/YSZ. XRD results confirm the dominant phase of the oxide matrix for each case, namely anatase TiO_2, monoclinic ZrO_2, and cubic YSZ.

Optical transmittance and absorptance of films were characterized for an interrogated wavelength range of approximately 300–850 nm (Fig. 2). A minimum in film transmittance was observed in the vicinity of the Au localized surface plasmon resonance (LSPR) optical absorption peak for all films and the band-edge of the TiO_2 matrix phase can be resolved. Film thicknesses and effective refractive indices (n) for each of the base oxide films without Au nanoparticles were estimated as presented in Fig. 2c based on measured optical spectra not presented here [7]. Estimated values of n are consistent with differences in wavelengths of the Au LSPR absorption peak between the matrix phases as higher values of n in the matrix phase will shift the LSPR absorption peak to longer wavelengths.

3.2. High temperature optical sensing

It is well known that elevated temperature exposures to reducing or oxidizing gases cause a shift of the Au LSPR absorption peak to shorter or longer wavelengths, respectively. A characteristic temperature dependence of the Au LSPR absorption peak was also demonstrated in fixed gas atmospheres, which is potentially useful for temperature sensing. These effects are illustrated by measured transmittance spectra for Au/TiO_2 films in Fig. 3 for (a) two different measurement temperatures in a fixed gas atmosphere and (b) two different gas atmospheres at a fixed measurement temperature of 600 °C. A shift of the band-edge to longer wavelengths and a broadening/shifting of the LSPR absorption peak of Au with increasing temperatures resulted in the observed modifications to the transmittance spectra. In contrast, a shift in the band-edge cannot be resolved at this temperature for a change in gas stream composition from highly oxidizing (20% O_2/N_2) to highly reducing (4% H_2/N_2), and the primary modification to the Au LSPR absorption