Feasibility of a Stack Integrated SOFC Optical Chemical Sensor

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Abstract

The work performed during the UCR Innovative Concepts phase I program was designed to demonstrate the chemical sensing capabilities of nano-cermet SPR bands at solid oxide fuel cell operating conditions. Key to this proposal is that the materials choice used a YSZ ceramic matrix which upon successful demonstration of this concept, will allow integration directly onto the SOFC stack. Under the Innovative Concepts Program the University at Albany Institute for Materials (UAIM)/UA Albany School of NanoSciences and NanoEngineering synthesized, analyzed and tested Pa, and Au doped YSZ nano-cermets as a function of operating temperature and target gas exposure (hydrogen, carbon monoxide and 1-dodecanethiol). During the aforementioned testing procedure the optical characteristics of the nano-cermets were monitored to determine the sensor selectivity and sensitivity.
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Executive Summary
The “Feasibility of a Stack Integrated SOFC Optical Chemical Sensor” DOE UCR Innovative Concepts program phase I award has been utilized towards the development of all-optical sensors for the detection of hydrogen, carbon monoxide and thiol compounds at operating temperatures up to 900°C. The sensing system is based on interpreting the optical properties of noble metal, gold and palladium, nanoparticles embedded in an yttrium stabilized zirconium oxide matrix (YSZ). The phase I award was leveraged for the design and implementation of two new experimental benches that include: 1) An RF magnetron sputtering system that has been used to deposit high quality films comprised of Au and Pd nanoparticles within a YSZ matrix, 2) A high temperature transmission gas cell has been designed and implemented for the in-situ monitoring of the nanocomposite film optical properties as a function of temperature and chemical exposure.

The nanocomposite films were characterized using SEM, TEM, Auger, AFM, ellipsometry and in-situ Uv-visible transmission spectroscopy. The Au based films show a strong and stable SPR band that has been used within specifically tailored films to sense either carbon monoxide or 1-dodecane thiol. We were able to demonstrate a signal response towards 100ppm of CO at an operating temperature of 700°C, and likewise an atto-molar sensitivity towards 1-dodecane thiol under ambient exposure conditions. Furthermore a PdO/YSZ nanocomposite has also been tailored for the detection of 1-3% hydrogen in air mixtures at an operating temperature of 650°C. The above results display a very promising set of individually tailored nanocomposite materials that have demonstrated with a high degree of specificity, the ability to detect the above target gases. Hydrogen and carbon monoxide were detected under conditions relevant to both SOFC and DOE Vision 21 research initiatives. While the nanocomposite film developed for hydrocarbon sulfur compounds requires further development for testing at elevated temperatures, it has shown a remarkable sensitivity under ambient conditions. Several publications are being drafted that outline the initial results of the phase I program and specifically include articles describing the optical, material and thermal stability properties of the Au/YSZ nanocomposites (submitting to Journal of Materials Research), along with an article describing in detail, the dielectric function of the nanocomposite as measured using ellipsometry and modeled using Maxwell-Garnett theory (Submitting to Journal of Applied Physics). Dr. Carpenter has also filed a New Technology Disclosure form so that patents can be filed which will outline and protect the sensing technology that is being developed through this DOE UCR Innovative Concepts Phase I program.

The broader impacts of these studies includes the support of a graduate student and an undergraduate research intern, nanotechnology graduate course development, and through the involvement of the UAlbany School of NanoSciences and NanoEngineering (SNN) summer intern program, the education of both undergraduate and high school students. Dr. Carpenter supervised the summer 2003 internship program which placed 23 interns within the SNN program, of which 5 were high school students. Dr Carpenter had 4 interns working in his lab in summer 2003 that included two undergraduates and one high school student working on projects related to the DOE-NETL Innovated Concepts phase I program. These internship activities will continue during 2004 and likewise we will be applying for DOE-NETL summer research internships upon acceptance of the Innovative concepts phase II proposal.
1. Introduction

We proposed to investigate the feasibility of an innovative chemical sensor based on monitoring the surface plasmon resonance (SPR) bands of metal nanoparticle doped Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ nano-cermets), as a function of fuel concentrations, impurities (CO and RS, R = hydrocarbon chain) and temperature (500-900°C). Since the SPRs of nano-cermets are directly correlated to the composition and shape of the metal particles, along with the composition of the surrounding matrix, the nano-cermets were tested and designed to provide real time sensory outputs for the chemicals of interest. The proposed sensor has a YSZ matrix, which is commonly used as both an electrolyte and, when doped with nickel, as an anode in SOFC, thus upon feasibility demonstration, integration directly into the SOFC will be possible. The development of an integrated SOFC chemical sensor will provide the following benefits: 1) In situ monitoring of the fuel cell chemical composition, linked to a feedback loop, will allow smart control of the SOFC, 2) Monitoring the chemical composition of a low temperature SOFC in real time will enable a more complete understanding of the catalytic and reaction mechanisms and thus lead to more efficient stack designs, 3) The development of sensors with operational specifications for simulated SOFC environments also meet the design specifications of chemical sensors for the Department of Energy Vision 21 Initiative.

The outcome of this proposal and its future phases will be the development of smart nano-cermet materials that have been tuned and tailored to display characteristic optical responses as a function of various sensing conditions. During the Innovative Concepts Phase I of this research program we have demonstrated tailor-designed nano-cermet materials with a given particle size,
composition and matrix host material, that has from the initial results shown the detection of hydrogen, and CO at 700°C and through ex-situ experiments the detection of 1-dodecane thiol.

The key to the continued success of this program is that correlations found between the nanocermet characteristics (material composition, particle size, particle density and particle shape) and the optical responses to the changing sensing environment will drive the development of theoretical models (further developed in phase II of this program). This cooperative effort will allow a complete understanding of the fundamental operating parameters of these unique films. The outcome of this work will be a library of materials with diverse physical characteristics, that produce a given change in the optical characteristics of the sample as a function of sensing environment. To increase the marketability of these nano-cermets into cost efficient chemical sensors, our synthetic techniques are compatible with the integrated circuit (IC) fabrication industries toolset.

The intellectual merit of these activities include, the development of a further understanding of nanoparticle based nanocomposites and their resulting SPR bands. Furthermore, this work will aid the development of harsh environment chemical sensors suitable for the sensitive, selective and reliable detection of the target compounds within SOFC, through the novel use of tailored nanomaterials and their intrinsically sensitive optical properties. The broader impacts of these studies includes the educational support of a graduate student and an undergraduate research intern, nanotechnology graduate course development, and through the involvement of the UAlbany School of NanoSciences and NanoEngineering (SNN) summer intern program the education of both undergraduate and high school students. Dr. Carpenter supervised the summer
2003 internship program which placed 23 interns within the SNN program, of which 5 were high school students. Dr Carpenter had 4 interns working in his lab in summer 2003 that included two undergraduates and one high school student, working on projects related to the DOE-NETL Innovated Concepts phase I program. These internship activities will continue during 2004 and likewise we will be applying for DOE-NETL summer research internships upon acceptance of the Innovative concepts phase II proposal.

Nanoparticle Surface Plasmon Resonances: Background

The work of Van Duyne and Schatz et al. have shown that SPR band tunability, of 100s of nm, can be achieved for a variety of nanoparticles (Ag and Au) through modification of the shape, size and composition of the nanoparticle via various nanosphere lithography schemes. The sensitivity of the SPR bands to the local environment is displayed by the reversible 100nm shifts in the SPR peak wavelength by using air, water, and methanol as the solvent material. The resulting SPR bands also showed a 3nm shift in peak wavelength per carbon atom for a variety of thiol compounds.

While the above work shows the feasibility of using nanoparticles and their SPR bands as chemical sensors, the material set is not ideal for the harsh conditions that we are interested in probing. Au and Ag thiol bonds have been shown to decompose and in many cases completely desorb at temperatures between 200 and 300°C and furthermore due to grain growth the nanoparticle size distribution will be unstable at elevated temperatures. Although it has been demonstrated that noble metal nanoparticles exhibit significant potential in optical sensing devices, embedding the nanoparticles in an appropriate matrix is believed to expand the sensing
range to more severe thermal, chemical, and environmental operational conditions. Most of the experimental work to date that has investigated the optical properties of embedded Au nanoparticles, has been focused on studying the non-linear optical properties of Au nanoparticles in binary oxide matrices, including aluminum oxide (Al₂O₃), titanium oxide (TiO₂), and silicon dioxide (SiO₂). While matrices with a large refractive index, like TiO₂, have more promising nonlinear optical characteristics, the SiO₂ based system has the advantage of being more easily integrated into future silicon-based optoelectronics devices.

While our immediate target application is focused on the detection of gas phase species within SOFC type environments or other harsh environments with temperatures between 500 and 900°C, future applications applied towards catalyst and fuel cell sulfur poisoning sensor indicators can also be realized. Sulfur poisoning of Ni doped SOFC anodes is presently a major problem with the development of reliable SOFC. Currently the only method of determining that there has been a S poisoning event is that upon a significant decrease in power output, the SOFC stack is taken apart and analyzed off-line. This is clearly an area where fundamental research involving the studies of harsh environment chemical sensors will lead to broader impacts in the SOFC research and development. Likewise, the development of the nano-cermet material set will further the materials and sensor expertise that will meet objectives set forth in the DOE Vision 21 research Initiative.
2. Experiment

Equipment Installation

Con-focal Sputtering Chamber

Depositions were carried out in a high-vacuum capable, custom-designed, sputtering system. The system consisted of a stainless steel chamber equipped with two confocally designed “MAK” type magnetron sputtering guns, manufactured by US Incorporated. The two guns were mounted on individually retractable, vacuum compatible feedthroughs. Each sputtering source was driven by a 13.56 MHz radio-frequency (rf) power supply model number AE RFX600, manufactured by Advanced Energy. The ZrO$_2$ and Au targets were, respectively, a 5.08 cm diameter disk of ZrO$_2$ stabilized with 5 w.t.% Y$_2$O$_3$ (99.9% purity), and a 5.08 cm diameter disk of Au (99.99% purity), both fabricated by Williams Inc. The sputtering chamber was also equipped with a shutter system that enabled complete isolation of the targets from the substrates during the initial stages of plasma formation and pre-deposition target clean-up.

Two types of substrates were employed: single crystal (100) silicon (Si) and optical quality sapphire provided by Edmund industrial Optics. In a typical deposition run, the silicon substrates were first ultrasonically cleaned prior to loading in the chamber for 5 minutes in ethanol and then in acetone to remove excess surface organic material, while the sapphire substrates were used as received. The substrates were then loaded in the sputtering chamber, and the latter was pumped down to a base pressure of ~5x10$^{-7}$ torr using a turbomolecular pump. The distance between the substrate and the YSZ and Au targets were set at, respectively 50 mm and 85 mm. Argon (99.999% purity) gas flow was then initiated at 5 sccm and co-sputtering was realized at an operating pressure of 5x10$^{-3}$ torr. Pre-deposition target clean up was performed by
sputtering with the shutters closed for 60 minutes at 200W rf power for the YSZ target and for 15 min at 20W rf power for the Au target. The as-deposited films were subsequently annealed ex-situ at 600, 700, 800, 900, and 1000°C for 2 hours in an Ar atmosphere. Typical sputtering and annealing conditions are summarized in Table 1. The silicon substrates were used for thickness measurements and Auger Electron Spectroscopy (AES) analysis, while the sapphire substrates were utilized to determine the optical properties and the microstructure of the resulting nanocomposite films.

In-Situ Sensor Testing Chamber

To enable the in-situ monitoring of the nanocomposite SPR absorption bands as a function of temperature and gas exposure, we have designed and implemented a high temperature optical cell as pictured in Figure 2. The oven allows for gas cell temperatures up to 1000°C and within its center sits the quartz cell, which has an overall length of 12” and an inner diameter of 2”, with an internal volume of 600ml. The cell is composed of two parts, linked via an o-ring sealed clamp, which allows for sample introduction. The nanocomposites are deposited on sapphire samples, 1cm in diameter, and are held on the centerline of the gas cell using a Macor sample holder. Currently we are using a Xe flash lamp as the light source, which is collimated and dispersed using a monochromator. The dispersed light is then collimated and passed through the high temperature cell and is then focused onto a silicon photodiode detector. With a pulse rate of 30Hz and allowing for signal averaging, a scan from 400nm to 800nm takes 8 minutes. Since the gas flow rate is 2000 sccm the purge time of the cell is approximately 30 seconds, thus our time resolution is limited by the acquisition time of the optical assembly. The background was
subtracted from the absorption spectrum by measuring the transmission properties of an as-
received sapphire substrate prior to each nanocomposite sample.

**Materials Analysis/Characterization Techniques**

The microstructure of the as-deposited and post-annealed YSZ-Au nanocomposite films was
examined by x-ray diffraction (XRD). The x-ray diffraction patterns were derived on a Scintag
XDS 2000 x-ray diffractometer using Cu K$_\alpha$ radiation. The XRD system was equipped with a
horizontal wide angle four axis goniometer with stepping motors which allowed independent or
coupled $\theta$/$2\theta$ axes motion. XRD spectra were collected in the standard $\theta$-$2\theta$ mode with $2\theta$
ranging from $25^\circ$ to $55^\circ$ in steps of 0.03$^\circ$. The collected XRD patterns were compared to the Cu
reference patterns from the standard Joint Committee for Powder Diffraction Standards (JCPDS)
powder diffraction files: PDF# 802187 for YSZ and PDF# 040784 for Au. The average
crystallite size $D$ was calculated from the Scherrer formula:

$$D = \frac{0.9\lambda}{B \cos \theta}$$

where $\lambda$ is the x-ray wavelength, $B$ is the FWHM of the appropriate elemental XRD peak and $\theta$
is the diffraction angle. The elemental XRD peak was fit using a Lorentzian curve.

Films with thicknesses of approximately 100nm were used. Film thickness measurements
employed a LEO 1550 scanning electron microscope (SEM) using a 5keV primary electron
beam. The Au content was found to be approximately 10 at.% measured using a Perkin-Elmer
PHI 600 Auger Electron Spectroscopy (AES) system employing a cylindrical mirror analyzer.
The primary electron beam energy was 10 keV, at 1 $\mu$A, yielding a spot size of approximately 1
$\mu$m. Relative compositional depth uniformity of the deposited YSZ-Au films can be determined
within 10\% relative experimental accuracy. Finally the spatial distribution of Au atoms as a function of film depth was measured by Rutherford backscattering spectroscopy (RBS) on a Dynamitron linear accelerator using a 3.0 MeV \(^4\)He\(^+\) primary ion beam.

3. Results and Discussion

Microstructure and Morphology as a Function of Annealing Temperature

Prior to the chemical exposure studies we have performed a detailed study on the material and optical properties of the Au SPR band as a function of the annealing temperature. Figure 3 displays typical XRD patterns for the evolution of the microstructure of YSZ-Au nanocomposite films as a function of the annealing temperature. The XRD patterns are plotted as diffraction peak intensity versus diffraction angle \(2\theta\) for the range from 25\(^\circ\) to 55\(^\circ\). Two polycrystalline phases were detected, one corresponding to the tetragonal YSZ phase, and the other to face centered cubic Au phase. As can be seen in Figure 3, the XRD peaks became sharper and more intense with higher annealing temperature, indicating an increase in the crystallinity of the YSZ matrix and a rise in the average grain size of the Au crystallites. These trends are expected and are attributed to the availability of a larger thermal energy at higher annealing temperature which drives grain coalescence, growth, and realignment.

The average Au crystallite size was calculated from the Scherrer formula\(^{11}\) using the Au XRD (111) reflection. The results of this analysis are displayed in Figure 4, which plots the average crystallite size for Au as a function of annealing temperature. In this respect, the average Au grain size exhibited a gradual rise with annealing temperature, from ~4.0 nm at 600\(^\circ\)C to ~9.5 nm at 900\(^\circ\)C. However, a marked increase of ~5.5 nm was observed as the annealing temperature
was increased from 900°C to 1000°C, indicating a potential change in the underlying mechanism that drives the coalescence and regrowth of the Au nanoparticles.

Figure 5 displays RBS data for the spatial distribution of Au atoms versus film depth within the YSZ matrix. The data is plotted as elemental RBS peak intensity versus RBS channel, with the width and the height of each peak determined by the spatial distribution and relative concentration of the corresponding element respectively. In this context, no significant change was observed in the height or FWHM of the Au RBS peak with respect to the Zr peak as a function of annealing temperature, indicating that the average concentration of Au atoms as a function of film depth is not affected by the annealing process. These findings, when coupled to the increase reported above in the average Au particle size with the rise in annealing temperature, imply that at temperatures below 900 °C, Au nanoparticles grow through a solid state diffusion mechanism of individual Au atoms through the YSZ matrix. Above 900 °C, the annealing temperature becomes quite close to the melting point of Au, which is 1064 °C for bulk Au, but has been shown to be significantly lower for Au in the nanoparticle form. In particular, a melting point of 900 °C was reported for 10nm silica-encapsulated Au particle. Therefore, above 900 °C, it is believed that the growth of Au nanoparticles is still governed by the diffusion of Au atoms through the YSZ matrix. However, in contrast to solid state diffusion of individual Au atoms observed below 900 °C, the marked increase in Au nanoparticle size above 900°C suggests the occurrence of Au nanoparticle growth via an Ostwald ripening process, wherein larger Au nanograins with lower interfacial curvature grow at the expense of their smaller counterparts with higher interfacial curvature, via the migration of individual Au atoms. This
suggestion is in agreement with previous studies on the growth mechanism of Au nanoparticles in a silica matrix.  

Optical Properties as a Function of Annealing Temperature

Figure 6 shows typical absorbance spectra of Au-YSZ nanocomposite films over the wavelength region from 300 nm to 800 nm. In particular, a band due to the surface plasmon resonance (SPR) of Au nanoparticles was observed around 600 nm. As the annealing temperature increased, the band maximum was observed to shift towards longer wavelengths and become sharper and more intense. Twice the half-width-at half-maximum (HWHM), calculated using the area under the absorbance intensity curve extending from the absorbance band maximum towards longer wavelengths, was used to determine the FWHM. This approach was necessitated by the fact that the Au 5d-6sp interband transitions, with an onset energy around 2.4 eV (517 nm), affects the shape of the absorption peak on the low wavelength side, resulting in an asymmetric peak profile.  

It should be noted that the Mie theoretical treatment provides a straightforward and effective tool to describe the optical properties of metal nanoparticles. In the Mie treatment, the interactions of electromagnetic radiation with a spherical physical system whose size is much smaller than the wavelength of the incident light are treated from first principles using Maxwell’s equations, while the optical properties of the system are introduced through appropriately chosen dielectric functions. This is especially important in the case of small particles where the bulk dielectric functions are expected to have limited applicability, either due to structural changes or finite size effects such as the reduced mean free path effect. In particular, for nanoparticles with sizes
smaller than or comparable to the bulk mean free path, the collisions of the conduction electron with the surface of the particle become increasingly important and result in an effective mean free path which is smaller than the bulk. For spherical particles, this reduced mean free path effect can be described by a modified Drude damping constant:

\[ \gamma(R) = \gamma_b + A \frac{\nu_F}{R} \]

where \( \gamma_b \) is the damping constant of the bulk conduction electrons, \( \nu_F \) is the Fermi velocity, \( R \) is the particle radius, and \( A \) is a coefficient which depends on the particular metal-particle/matrix system under investigation, with a value that is determined experimentally by comparison of the FWHM of the SPR band with the particle size. The magnitude of the coefficient \( A \), is directly correlated with the degree of interaction between the metal nanoparticles and the embedding medium and thus details the corresponding nature of the metal-matrix interface. It has been shown that for Ag clusters, the presence of a SiO\(_2\) matrix opens additional channels for the dissipation of the plasmon energy resulting in an \( A \) value higher than that of a free Ag cluster.\(^{25}\) This has been attributed to chemical interface damping\(^{26}\) i.e. the transfer of free electrons in unoccupied energy levels of the surrounding medium and back again, resulting in the dephasing of the collective motion of the excited free electrons. In the case where strong chemical interactions are present, chemical interface damping effects become more prominent and result in the broadening\(^{27}\) or quenching of the SPR band.\(^{28}\) It should be noted that for sensor development research initiatives, the characterization of the coefficient \( A \) is required for determining the sensing mechanism of a tailor designed nanocomposite material, as the target compound of interest can interact with either the embedded nanoparticle and/or with the surrounding matrix.
Figure 7 displays a plot of the Au-YSZ SPR band FWHM versus the inverse particle radius as determined from the XRD analysis. The data can be fit reasonably well using a linear regression, and the values $A=0.18$ and $\gamma_b=6.7\times10^{13} \text{ sec}^{-1}$ are obtained. The value of $\gamma_b$ extracted from the data is within a factor of two of the theoretical prediction for bulk Au ($3.3\times10^{13} \text{ sec}^{-1}$) indicating that the Au-YSZ system follows the $(1/R)$ dependence of the SPR band width. Although quantitative comparison of our experimental value with theoretical results can not be made, since that would require detailed information on the physical and chemical nature of the YSZ-Au interface, the experimental value of 0.18 indicates a weak interaction between the Au nanoparticles and the YSZ matrix. Also, there is good agreement with values reported for Au nanoparticles embedded in other oxide matrices i.e. 0.15 for the SiO$_2$ matrix.  

Figure 8 displays the peak position of the SPR band as a function of annealing temperature. As the annealing temperature increases there is a marked redshift in the position of the peak from ~550 nm to ~595 nm up to 800$^\circ$C. Upon further increase of the annealing temperature to 1000$^\circ$C the peak experiences a modest redshift to ~600 nm. It should be noted that by using bulk dielectric functions for Au, and dielectric functions for YSZ measured by spectroscopic ellipsometry, Mie theory predicts a 595nm peak position. In this context, the marked change in the SPR band redshift up to 800$^\circ$C, is an indication that the Au nanoparticles are undergoing a phase structural transition from a cluster to a bulk state. Recent work suggested that the critical size for this transition is at ~8 nm, which is in good agreement with our data. It should also be noted that the Au content in the current films is rather high (~35% in volume fraction) and interactions between neighboring particles are expected. The signature of these interactions on the optical spectra would result in both a red-shift and a broadening of the SPR band, while our
current work displays a redshift with a corresponding narrowing of the SPR band. The modest redshift of the SPR band at temperatures above 800°C may be attributed to interactions between neighboring particles, however these interactions appear to be weak since the SPR band continues to become narrower instead of broader.

Figure 9 portrays both an SEM cross section and a TEM micrograph of a typical film with 10at.% gold in YSZ and a film thickness of 100nm. The TEM micrographs allow for Au nanoparticle sizing and by measuring 50 particles the size distribution is 4.7nm ± 0.7nm after annealing this film to 500°C for two hours. Recently, during the 3rd quarter of this one year program, we have optimized the deposition and annealing treatments such that the SPR band has a narrower FWHM (85nm) as shown in Figure 10. This is a vital characteristic as the limiting FWHM for single nanoparticles is 50nm, a particle size distribution of this film set has not been measured with TEM, however we can conclude from the FWHM that our Au/YSZ nanocomposite has a nanoparticle size distribution that has decreased significantly. A narrow FWHM is vital for the chemical sensor design, as any shifts in wavelength or intensity are much more apparent and are a more sensitive parameter set if they mimic a single nanoparticle parameter set.

Chemical Exposure Studies

Carbon Monoxide

The exposure studies have started with the in-situ optical absorption studies of a 100nm thick Au(20at%)-YSZ film annealed to 700°C for 30 minutes and then exposed to 100ppm CO in nitrogen. As detailed in Figure 11, the SPR peak shows an immediate (within our 8min time resolution) decrease in the red “tail” of the spectrum and a subsequent blue shift in the peak by
approximately 25nm. We have had difficulty in achieving reproducible shifts in both the intensity and wavelength of the SPR band upon CO exposure, and these variations may be attributed to subtle differences in both the microstructure and composition of the nanocomposite films. Further studies are needed and will be completed during the DOE IC phase II part of the program to determine whether these signal variations are due to a change in the dielectric function of the material or are convoluted with a change in the chemical surroundings of the nanocomposite.

1-dodecane thiol

Previous studies by Van Duyne et al (ibid 5,6) have shown that the binding of sulfur to gold or silver nanoparticles does not tend to affect the overall intensity of the SPR band, however it does tend to shift the peak either to the red or blue depending on the reductive or oxidative power of the newly added ligand. These studies were performed to provide the necessary benchmark for comparison to the work of Van Duyne on gold and silver nanoparticles exposed to thiol compounds of varying chain length (6 – 12 methylene units long), prior to attempting to expose sulfur compounds at elevated temperatures to the nanocomposites. Their well-developed work has demonstrated a zepto-molar sensitivity to thiol and related compounds. The zepto-molar factor \(10^{-21}\) of Van Duyne arises from a mM liquid thiol sample exposed to Ag nanoparticles deposited on glass substrates, the exposed sample is rinsed thoroughly to remove any unbound thiol, and the number of molecules forming a monolayer of coverage is equivalent to approximately 60,000 molecules (or zepto-molar quantities). In summary, it was found that for alkane based thiol compounds the SPR band shifted to the red by 3nm/carbon unit, and it is
predicted that sulfur atoms, with their lone pair of electrons, will shift the SPR band to the blue by 10nm.

Our initial work with sulfur related compounds began with a simple ex-situ exposure of an optimized 80nm thick Au 10at%/YSZ nanocomposite to an 8mM solution of 1-dodecane thiol dissolved in ethanol. The results from this experiment showed no discernible change in the SPR peak position. In order to achieve sensitivity to the thiol compounds, which for dodecane thiol are 6nm in length, we were required to tailor design the nanocomposite material. We deposited a thin nanocomposite film, 10nm, which had a 40 at.% Au/YSZ composition and annealed this film to 700°C. The film is very stable as a function of subsequent increases in temperature, up to 700°C. The resulting particle size and its corresponding distribution are quite large, 40 ± 30nm, and many of the particles are not spherical but are a variety of 3-D shapes, these characteristics cause the SPR band to be shifted to 600nm with a resulting FWHM of 170nm. However, upon exposure to the 8mM dodecane thiol solution and a subsequent thorough rinse with ethanol to remove excess thiol, the SPR band is shifted to the blue by 10nm, as shown in Figure 12. At this point it is not understood why the SPR band is blue shifted and not red shifted, but it may be a result of the YSZ matrix being a participant in the binding of the sulfur compound, possibly breaking down the hydrocarbon chain, which causes the blue shift. Through a similar set of calculations and assumptions (packing density, monolayer formation, nanoparticle area available) as Van Duyne, we have been able to determine that our sensitivity towards dodecane thiol is on the order of 100,000 molecules, or atto-molar levels. These initial results are important as this demonstrates that a thermally stable Au/YSZ nanocomposite can provide very good sensitivity towards extremely low concentrations of hydrocarbon based thiol compounds.
The binding process is reversible, for just several exposure cycles, as the SPR peak shifts back to the starting position at 600nm upon heating the sample to 300°C, however at this point the sample does saturate after 3-4 cycles and the blue shifted SPR band is no longer reversible. Our current work is focused on the continued optimization of the film structure and composition and further experiments to determine the reversibility properties of this film. We are also in the process of modifying the gas delivery system for H₂S, SO₂ or hydrocarbon based thiols such that an in-situ exposure experiment can be performed at temperatures up to 900°C.

Hydrogen

We have tested the 80nm thick 10at. % Au/YSZ film as a function of both temperature and hydrogen concentration and have observed no change in the optical properties even at 900°C and 50% hydrogen and nitrogen gas mixtures. This is not surprising as hydrogen is not known to interact with gold nanoparticles. Therefore, we have tailor designed a palladium based YSZ nanocomposite film that is sensitive to hydrogen at elevated temperatures. While palladium nanoparticles do not have a SPR band, due to the d-d transition damping of the plasmon band, we are able to monitor the transmittance of these nanocomposite films. A 100nm thick 40at. % Pd/YSZ nanocomposite film was deposited on a sapphire substrate and then subsequently annealed to 900°C in an argon atmosphere. The film appears stable as a function of several thermal anneals, and more testing is in progress to determine the film stability.

Experiments were first completed on an experimental bench used for the development of hydrogen sensors for PEM based fuel cells. This bench uses a white light CW diode source coupled to a bifurcated optical fiber for the detection of transmission changes in Pd based films.
as a function of hydrogen concentration and temperature (up to 90°C). On this test bench we were able to measure an 8% signal increase upon exposure to 10% hydrogen in nitrogen. This experiment proved that the nanocomposite film, under ambient operating conditions produced a measurable signal change. Subsequent experiments were performed on the harsh environment testing bench at elevated temperatures, 300, 500, 700 and 900°C. No signal change was observed at temperatures below 500°C, however at both 700 and 900°C a 10% and 20% decrease, respectively, in transmission occurs upon exposure to a gas mixture of 10% hydrogen in nitrogen. A transmission decrease is the result of the film becoming more reflective and thus, most probably, metallic in nature. Upon further investigation it became apparent that at these temperatures and pressures (1 atm) the hydrogen solubility in Pd is very low, and the sensing mechanism is not the result of PdH formation, which would have caused an increase in transmission.

Subsequently we hypothesized that the sensing mechanism could be the result of a PdO → Pd transition, with PdO being formed at elevated temperatures, via oxidation processes involving the low partial pressure of oxygen in the background gases of the flow cell. The PdO ↔ Pd reduction/oxidation process in the presence of both methane and oxygen at temperatures ranging from 600 to 1000°C has been well studied for the development of novel catalytic materials. The interaction of either methane or hydrogen with PdO in the presence of oxygen leads to the rapid reduction of PdO to Pd, and subsequently the optical properties of the resulting film will be affected. PdO/YSZ films were formed by first co-sputtering 40 at% Pd in a 100nm thick YSZ film, followed by thermally assisted oxidation of the Pd for 9 hours at 650°C in dry, CO₂ free air. XRD analysis of these films before and after the annealing process are shown in Figure 13. It is
readily apparent that the oxidation process is fairly complete (Pd/PdO ratio = 5%) with a resulting PdO (101) grain size of 4.7 nm. SEM analysis of the surface microstructure prior to hydrogen exposure, as shown in Figure 14, reveals a seemingly featureless surface. Gas exposure experiments were performed for 1, 2 and 2.4% hydrogen in air mixtures at 650°C and are displayed in Figure 15. The inset of Figure 15 displays the signal change and response times at these hydrogen concentrations, with the response time being seemingly independent of the hydrogen concentration. These exposure experiments have now been performed for over 50 different exposure cycles over a 3 week time frame and the film response characteristics are still within the specified error limits for the average signal change and response times. After 20 cycles of hydrogen exposure we again analyzed the sample using both XRD and SEM, and determined that the grain size had increased to 10 nm and the Pd/PdO ratio had increased to 7%. An SEM micrograph of the 20 cycle exposed sample is displayed in Figure 16 and it is interesting to note that the PdO grains are now needle-like in structure, which would lead to a higher surface area available for reaction than if they were spheres. Further testing needs to be performed to determine the dynamics and kinetics of the PdO-YSZ nanocomposite sensing mechanism and how these coincide with the tailored material properties. However, these results are very promising as there are no other all-optical sensing techniques that are able to detect hydrogen at such elevated temperatures.

4. Educational Impacts

Dr. Carpenter has been actively involved in the UAlbany School of NanoSciences and NanoEngineering internship program aimed at exposing young students to high technology research programs and thus laying the seeds for a career in the sciences. During the summer of
2003 he led the summer intern research programs of four students, two high school level and two undergraduates. Besides research mentorship he coordinated the 2003 UAlbany School of NanoSciences and NanoEngineering summer internship program of 18 undergraduates and 5 high school students. Dr Carpenter had 4 interns working in his lab in the summer of 2003, with two undergraduates and one high school student working on projects related to the DOE-NETL Innovated Concepts phase I program. These internship activities will continue during 2004 and likewise we will be applying for DOE-NETL summer research internships upon acceptance of the Innovative concepts phase II proposal. A senior graduate student has been actively working on the IC phase I program and will continue to be supported during phase II, however it is likely that this work will be the majority of his Ph.D. thesis and he is slated to graduate in early 2005. Graduate students have actively participated in attending and presenting results from the above work at National conferences located on the East coast. Undergraduate and select high school interns will be encouraged to participate in the local American Chemical Society meetings and will attend the annual regional meetings to present their results. Dr. Carpenter has also developed a course that was taught in Fall 2003 in the UAlbany School of NanoSciences and NanoEngineering entitled, SNN 679 “Nanoparticles and Nanoparticle Interactions in Environmental Sensing.

5. Conclusions

In summary the DOE UCR Innovative Concepts program phase I award has been utilized towards the development of an RF magnetron sputtering system that has been used to deposit high quality nanocomposite films comprised of Au and Pd nanoparticles within a YSZ matrix. A high temperature transmission gas cell has been designed and implemented for the in-situ
monitoring of the nanocomposite film optical properties as a function of temperature and chemical exposure. The nanocomposite films were characterized using SEM, TEM, Auger, AFM, ellipsometry and Uv-visible spectroscopy. The Au based films show a strong and stable SPR band that has been used within specifically tailored films to sense either carbon monoxide at 100ppm levels and at 700°C or atto molar quantities of dodecane thiol under ambient exposure conditions. A tailored PdO/YSZ nanocomposite has demonstrated the detection of % levels of hydrogen in air mixtures at 650°C. The above results display a very promising set of individually tailored nanocomposite materials that have demonstrated with a high degree of specificity, the ability to detect the above target gases. Hydrogen and carbon monoxide were detected under conditions relevant to both SOFC and DOE Vision 21 research initiatives. While the nanocomposite developed for hydrocarbon sulfur compounds requires further development for testing at elevated temperatures, it has shown a remarkable sensitivity. Several publications are being drafted on the initial results of the phase I program, and specifically include articles outlining the optical, material and thermal stability properties of the Au/YSZ nanocomposites (Submitting to Journal of Materials Research), and an article describing in detail, the dielectric function of the nanocomposite as measured using ellipsometry and modeled using Maxwell-Garnett theory (Submitting to Journal of Applied Physics). Dr. Carpenter has also filed a New Technology Disclosure form so that patents can be filed which will outline and protect the sensing technology that is being developed through this DOE UCR Innovative Concepts Phase I program.
Table 1. Typical Sputtering and Post-Deposition Annealing Parameters.

<table>
<thead>
<tr>
<th>Sputtering Parameters</th>
<th>Annealing Parameters</th>
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<tbody>
<tr>
<td>Process pressure: 5 mTorr</td>
<td>Atmosphere: Ar at 760 Torr</td>
</tr>
<tr>
<td>R.F. power (YSZ): 200 W</td>
<td>Temperature: 600, 700, 800, 900, 1000°C</td>
</tr>
<tr>
<td>R.F. power (Au): 20 W</td>
<td>Time: 2 h</td>
</tr>
<tr>
<td>YSZ target-substrate distance: 50 mm</td>
<td></td>
</tr>
<tr>
<td>Au target-substrate distance: 85 mm</td>
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</table>
Figure 1A&B: Schematic and picture of the confocal sputtering chamber
Figure 2: Schematic of in-situ high temperature sensor testing bench: A) Xe flash lamp, B) Collimating optics, C) Uv-Vis monochromator, D) Exit port optics, E) Mass flow controllers, F) Light guide coupled collimating optics, G) High temperature oven with Quartz sampling cell, H) Si photodiode detector
Figure 3: X-ray diffraction patterns of YSZ-Au nanocomposite films as a function of annealing temperature.
Figure 4: Average Au crystallite size versus annealing temperature. The error bars were estimated by an error propagation analysis from the errors in the FWHM and the peak position resulting from a Lorentzian fit to the Au XRD (111) XRD reflection.
Figure 5: RBS spectra of YSZ-Au nanocomposite films as a function of annealing temperature.
Figure 6: Absorption spectra of YSZ-Au nanocomposite films as a function of annealing temperature. Dashed vertical line indicates the position of the SPR band as predicted from Mie theory using bulk dielectric functions for Au
Figure 7: FWHM of the surface plasmon resonance absorption band of YSZ-Au nanocomposite films versus inverse particle radius.
Figure 8: Peak position of the surface plasmon resonance absorption band of YSZ-Au nanocomposite films as a function of the annealing temperature.
Figure 9: SEM micrograph portraying the 100nm thick nanocomposite film and TEM micrograph displaying the embedded nanoparticles within the YSZ matrix.
Figure 10: Uv-vis absorption spectrum of optimized 80nm thick, 10at.% Au/YSZ film. FWHM is only 85nm
Figure 11: Absorption spectra of a 100nm thick Au(20at%)-YSZ film as a function of 100ppm CO in nitrogen exposure
Figure 12: Absorbance spectrum showing the SPR band of the Au/YSZ nanocomposite as a function of dodecane thiol exposure.
Figure 13: XRD spectra for resulting PdO-YSZ films with a resulting 5.6% Pd/PdO ratio after a total annealing time of 9 hours at 650°C. 

<table>
<thead>
<tr>
<th>YSZ-PdO/Pd</th>
<th>PdO (101)</th>
<th>Pd (111)</th>
<th>Area ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G.S. (nm)</td>
<td>G.S. (nm)</td>
<td>Pd/PdO</td>
</tr>
<tr>
<td>3h-oxidation</td>
<td>4.53</td>
<td>4.12</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>35.6</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>3h+6h oxidation</td>
<td>4.71</td>
<td>3.6</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>39.2</td>
<td>2.2</td>
<td></td>
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</table>
Figure 14: SEM micrograph of PdO-YSZ film after a 9h anneal in air at 650°C
Figure 15: 100nm thick PdO-YSZ optical response to hydrogen/air gas pulses at an operating temperature of 650°C
Figure 16: SEM image of the PdO whisker-like surface microstructure of PdO-YSZ film after exposure to 20 cycles of hydrogen (2%) in air
References

13. Private Communication with Lane Wilson (2003), DOE NETL University Coal Research Program Manager.
17. Personal communication with Scintag. A Lorentzian peak is more appropriate than a Gaussian profile when the broadening of the XRD peak is due to nanograins instead of stress or strain.