Feasibility of a Stack Integrated SOFC Optical Chemical Sensor

UNIVERSITY AT ALBANY
State University of New York

George Sirinakis, Phillip H. Rogers, Rezina Siddique, Ian Manning, Michael A. Carpenter

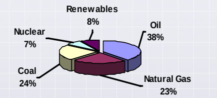
Abstract

Nanocomposite films consisting of Au nanoparticles embedded in a YSZ matrix were synthesized on sapphire substrates using a rf co-sputtering process in combination with a post-deposition annealing treatment at 1000 ˚C. The films exhibited an SPR absorption band centered at 600 nm which underwent a reversible change upon exposure to CO, H_2 and NO_2 in air at temperatures between 400 and 700 ˚C. The films responded to the presence of CO, H_2 and NO_2 in concentrations varying from 1000 to 10000 ppm in air, 1000 to 100,000 ppm in air and ~5 to 1000 ppm in air respectively. More specifically, we observe a blue shift along with a narrowing of the SPR band for films exposed to CO and H_2 and a red shift accompanied by a broadening of the SPR band for those exposed to NO_2. These findings indicate that this nanocomposite shows promise for an all-optical harsh environment gas sensor. The sensing mechanism has been investigated and will be discussed in further detail.

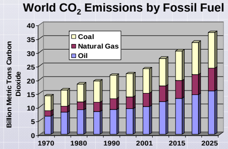
Fossil Fuels: Challenges & Alternatives

- Today, oil, coal, and natural gas account for ~ 90% of the world's commercial energy supply
- Fossil fuels are expected to remain a competitive energy source through the mid-21st century
- Carbon dioxide emissions are projected to increase from 23.9 in 2001 to 37.1 billion metric tons in 2025
- There is a growing scientific consensus that green house emissions are having a discernable effect on earth's climate

World Energy Consumption Shares by Fuel Type, 2001

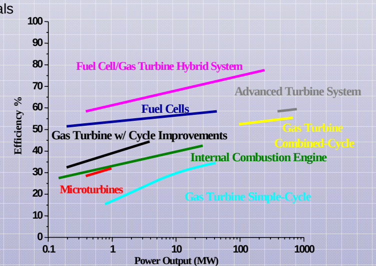


World CO_2 Emissions by Fossil Fuel



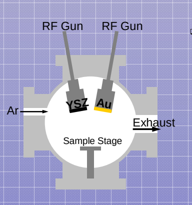
International Energy Outlook 2004
http://www.fossil.energy.gov/programs/powersystems/vision21

- **Department of Energy Vision 21 program: A new approach that builds on a portfolio of existing and developing technologies is expected to achieve the needed efficiency, environmental, and cost goals for the 21st century**
  - Develop new ceramic and alloy materials
  - Develop key enabling technologies
- **Paradigm: SOFC/Turbine hybrid system**
  - Efficiency far exceeding all other known fossil-fuel based power systems
  - Near-zero emissions
- **Sensor technology is a key element of this new approach**
  - Monitor and fine tune operations
  - Maximize efficiency
  - Reduce emissions
  - Lower operation cost



- **Existing sensing technologies cannot meet the needs of the Vision 21 research initiative**
- **All-optical sensing techniques offer a promising alternative to classical sensing technologies**
  - **Use the Surface Plasmon Resonance (SPR) band of Au nanoparticles as a signal transducer element for the detection of CO**

Synthesis of YSZ-Au nanocomposites

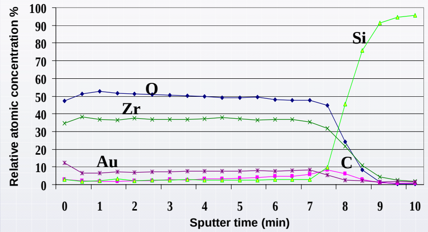


- Use a co-sputtering process in combination with a post-deposition annealing treatment to control the size & density of metal nanoparticles

Deposition Parameters	
Process Press.	5 mTorr
RF Power YSZ	200 Watts
RF Power Au	20 Watts
Deposition time	15 min
Substrate	Si
Base Pressure	~10^{-6}Torr

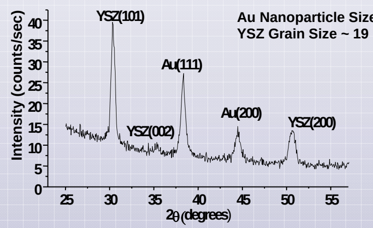
Annealing Parameters	
Ambient	Ar @ 760Torr
Temperature	1000 ˚C
Time	2h

Auger depth profile of a ~100nm thick Au-YSZ film

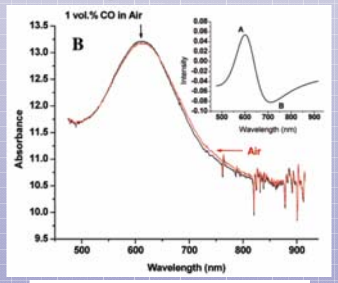


- Uniform composition throughout the film
- Low C contamination

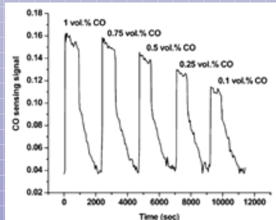
XRD spectra of ~30nm thick Au-YSZ films after annealing at 1000 ˚C



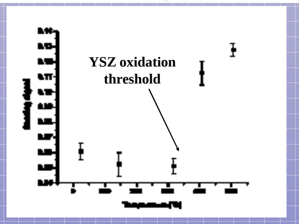
Quantification of CO Exposure



Absorbance spectra of Au-YSZ nanocomposite films in air and in the presence of 1 vol.% CO in air. The inset graph displays a curve indicative of the change in the absorption spectrum upon exposure to CO, obtained by subtracting the absorption spectrum in air from the one obtained in the presence of 1 vol.% CO.



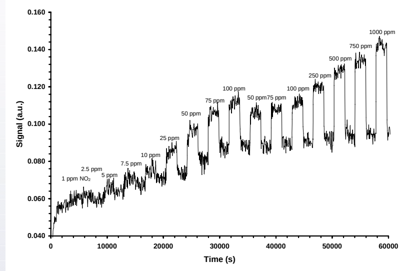
Response curve of the Au-YSZ nanocomposite film upon exposure to 1, 0.75, 0.5 and 0.25 vol.% CO in air at 500°C.



Nanocomposite film sensing signal as a function of temperature upon exposure to 1 vol.% CO in Air.

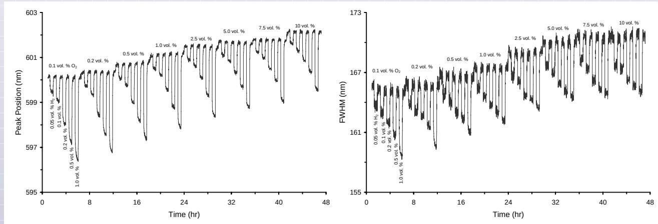
G. Sirinakis, R. Siddique, P. H. Rogers, I. Manning, M. A. Carpenter, Journal of Physical Chemistry B, 110 , 13508 (2006).

Signal Change Due to NO_2 Exposure



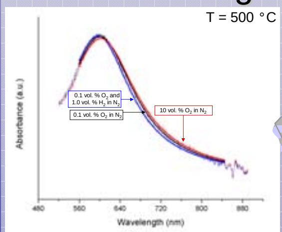
Raw exposure data for a Au-YSZ nanocomposite film in air and varied concentrations of NO_2. Exposures took place at 500 °C and were 30 min long per gas mixture.

H_2/O_2 Titration Exposures

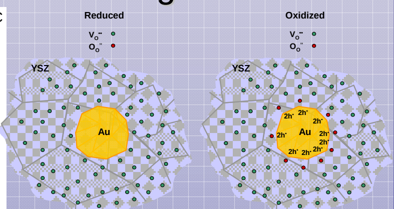


Raw exposure data for a Au-YSZ nanocomposite film undergoing exposures to different redox environments due to changes in O_2 and H_2 concentration in N_2. Exposures took place at 500 °C and were 30 min long per gas mixture.

Understanding the Sensing Mechanism



SPR Band for a Au-YSZ nanocomposite film undergoing exposures to different redox environments

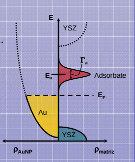


$$\sigma_{ext}(\omega) = \sigma_0 \frac{1}{(\omega-\omega_1)^2 + (\gamma/2)^2} \qquad \omega_1 = \sqrt{\frac{Ne^2}{m_e \alpha_{cl}}}$$

$$\gamma = \tau^{-1} = \sum_i \tau_i^{-1} = \tau_\infty^{-1} + \tau_{\text{size}}^{-1} + \tau_{\text{defects}}^{-1} + \tau_{\text{e-phonon}}^{-1} + \tau_{\text{e-e}}^{-1} + \ldots$$

$$\gamma = \gamma_\infty + A\frac{v_F}{R}$$

ω - photon frequency
τ - relaxation time
N - free electron number
m_e - electron mass
α_{cl} - polarizability



Future Directions

- Experiment with various analytical techniques to determine exact adsorbate energies
- Narrow gold nanoparticle size distribution by depositing colloidal gold monolayers between YSZ stacks
- AuNP size dependence study
- Coatings to increase selectivity

Acknowledgements

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