Homeland Security
Room: C-209 - Session HS+SS+BI-WeA

Chemical and Biological Detection
Moderator: J.N. Russell, Jr., Naval Research Laboratory

2:00pm **HS+SS+BI-WeA1 Photonic Crystals Derived from Nanocrystalline Porous Si: Applications in Detection of Chemical Warfare Agents, Explosives, Pollutants, and Biochemicals**, ***M.J. Sailor***, University of California, San Diego **INVITED**

The optical properties of nanostructured porous silicon films are exploited for a variety of sensor applications. With appropriate modification of the electrochemical preparation conditions, multilayered structures can be generated that behave as photonic crystals. These structures can be encoded and used as remote sensors for chemicals. For example, small particles of nanoencoded microporous Si are used to detect chemicals by measurement of the intensity of reflected light from a remote laser probe. The particles contain a periodic porous nanostructure that defines the code. The periodic structure forms a Rugate reflector which displays sharp maxima in the optical reflectivity spectrum at wavelengths that are controlled by the etch parameters. The intensity and wavelength of reflected light is determined in part by the refractive index of the porous nanostructure, which can be modified by adsorption of vapors within the porous matrix. Using a 10 mW laser as an optical probe and telescope collection optics, detection of ethanol, acetone and toluene vapors has been achieved at a distance of 20 m. Control experiments using water vapor at comparable partial pressures show very little response, demonstrating selectivity towards the hydrocarbon analytes. Examples of irreversible detection and reversible sensing modes for explosives, nerve warfare agents, and various biochemicals will also be discussed. A catalyst can be incorporated into the nanomaterials to provide specificity for nerve warfare agents. For example, rapid detection of a fluorophosphonate is achieved by catalytic decomposition of the agent to HF and subsequent detection of the HF in the porous silicon interferometer. The catalyst system can be integrated on the silicon chip and consists of a TMEDA[Cu(II)] catalyst (TMEDA = tetramethylethylenediamine) encapsulated in cetyltrimethylammonium bromide (CTABr) micelles. An operational battery-powered unit has been constructed and tested on the live nerve warfare agent Sarin. These devices are all compatible with conventional Si microfabrication technologies.

2:40pm **HS+SS+BI-WeA3 Magnetic Labeling and Microarray Detection of Biomolecules**, ***L.J. Whitman***, Naval Research Laboratory **INVITED**

NRL is developing two novel biosensor systems using magnetic microbeads to probe for target biomolecules specifically bound to receptor-patterned surfaces, with an initial focus on detecting biological warfare agents.[1,2] The microbeads serve both as reporter labels and as force transducers to allow "force discrimination" - a technique developed at NRL that greatly reduces the background signal-enabling the identification of single biomolecular ligand-receptor interactions with high sensitivity and specificity. Assays using magnetic labeling and force discrimination have been developed for a variety of bacteria, viruses, and protein toxins (immuno-sandwich assays), and for oligonucleotide microarrays (hybridization assays). How the assays are incorporated into a practical sensor system depends on how the specifically bound beads are detected. We are currently perfecting two detection approaches, an optical system that images beads captured on a patterned nanoporous membrane, and a chip-based sensor system that directly detects beads using an array of giant magnetoresistive (GMR) magnetic field microsensors. The optical system has achieved sensitivities of 10 pg/ml for proteins, $10^{2.5}$ cfu/ml for bacteria, and 10^3 pfu/ml for viruses. Using a single GMR sensor, we have successfully detected 1 fM of DNA in a 30 µL sample with only 15 min of hybridization. I will discuss how the interplay between surface chemistry, sensor design, and microfluidics determines the overall performance of our biosensor systems. Supported by ONR, the DoD JSTPCBD, and DARPA.

[1] Lee et al., Anal. Biochem. 287, 261 (2000).

[2] M. M. Miller et al., J. Mag. and Mag. Mat. 225, 138 (2001).

3:20pm **HS+SS+BI-WeA5 Optical Microarrays for Chemical and Biological Detection**, ***D.R. Walt***, Tufts University **INVITED**

We have used coherent imaging fibers to make fiber-optic chemical sensors. Sensors can be made with spatially-discrete sensing sites for multianalyte determinations. We are investigating the limits of our ability to create high-density sensing arrays containing thousands of microsensors and nanosensors. Micrometer- and nanometer-sized sensors have been fabricated by etching the cores of the optical imaging fiber to create wells and loading them with micro and nanospheres. Such arrays can be employed for making genosensors for bio-agent detection. We have also created optical sensors based on principles derived from the olfactory system. A cross-reactive array of sensors is created such that specificity is distributed across the array's entire reactivity pattern rather than contained in a single recognition element. The ability to use such information-rich assemblies for broad-based chemical sensing will be discussed.

4:20pm **HS+SS+BI-WeA8 Real-time Detection of TNT Using Microcantilevers with Microcyclic Cavitand Coatings**[1], ***N.V. Lavrik***, *T. Thundat, G. Muralidharan, P.G. Datskos*, Oak Ridge National Laboratory

Real-time detection of nitroaromatic aromatic explosive compounds in various environments is a highly significant task in forensics, anti-terrorist activities and global de-mining projects. In particular, ability to detect trace levels of trinitrotoluene (TNT) in air and soil could greatly reduce continued fatalities from land mines among civilians and be a measure in tracking and locating explosive materials. In our work, we address this challenge of detecting TNT vapors in gaseous environment by using an innovative, highly sensitive microcantilever transducer combined with a chemically sensitive molecular coating based on the macrocyclic cavitand of a calixarene family. We measured responses to vapors of TNT and its analogs, 0-mononitrotoluene and 2,4-dinitrotoluene vapors in the range of temperatures of 298 K to 318 K. Our results were used in order to estimate the limits of detection (LODs) for these compounds and optimize the temperature regime of the designed detection system. In the case of TNT, the steady state responses were large, however, the response kinetics was significantly elongated, which is consistent with an analyte depletion model. As compared to more traditional surface acoustic wave sensors with a proven potential for detection of TNT, our approaches offer a simpler, low-cost alternative without sacrificing the performance. The reported results together with these advantages of microcantilever based gas detectors clearly indicate a viable technological approach to mass produced detectors of explosive materials.

[1] This work was supported by the U.S. Department of Energy and Micro Sensor Technologies, Inc. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by UT-Battelle under contract DE-AC05-96OR22464.

4:40pm **HS+SS+BI-WeA9 A New Nanoscale Platform for Gas Sensor Applications**, *A. Kolmakov, Y. Zhang, G. Cheng*, ***M. Moskovits***, University of California Santa Barbara

The application of metal and semiconductor nanowires as solid state gas sensors has been an area of tremendous promise currently limited by challenges related to nanowire growth and device fabrication. We present an approach for fabricating individual and arrays of nanowires of a variety of metals and metal oxides with tunable, uniform diameters and length in the range of 10-100 nm and 5-200 micrometers, respectively, configured for gas sensing application. The materials successfully employed include Pd, Ag, Cu, Pb, PbO, CuO and SnO$_2$. Arrays of nanowires were fabricated in hexagonal close-packed nanochannel alumina templates. Electrodes deposited on the surfaces of these nanostructures provides electrical contacts which with the incorporated heaters determines the device architecture. Based on this method we explored the electronic and structural properties of Pd and SnO$_2$ nanowires using HRTEM, XPS and Auger spectroscopy. Chemical reactivity and gas sensitivity toward hydrogen and carbon monoxide of individual and assemblies of ca 10^9 Pd and SnO$_2$ nanowires were assessed using conductivity measurements and TPD analysis. This approach constitutes a novel platform for micro- and nanosensor application.

5:00pm **HS+SS+BI-WeA10 Metal Phthalocyanine Thin Films as Gas Sensors**, ***L. Lozzi***, *S. Santucci*, INFM and University of L'Aquila, Italy, *C. Cantalini*, University of L'Aquila, Italy

Metal Phthalocyanine (MPc) thin films have shown interesting properties as gas sensor, in particular for NO2. The wide variety of different available molecules, changing both the central atom and/or the chemical structure of the outer benzene rings, allows a fine modulation of the film sensing properties. In this work we will present our result on the interaction between oxidating gases (O2 and NO2) and different MPc films. We have deposited thin films (about 50 nm thick) of Copper Phthalocyanine (CuPc) and Exadecafluoro-copper-phthalocyanine (F16CuPc) onto Si3N4 substrates, for the spectroscopic characterizations, and onto Pt interdigital circuits, for the gas sensing tests. These films have been analysed both as deposited and after different thermal annealing. The electrical sensing analyses have shown a sizeable decrease of the film resistivity during the film exposure to NO2, even at very low concentration (up to 100 ppb). We have studied the electronic structure by means of the X-ray and ultraviolet photoemission spectroscopies (XPS-UPS) after the exposure to NO2 and O2 both at room and at higher temperature, in order to investigate the surface reactivity of these samples and in particular the preferential adsorption sites.

Authors Index

Bold page numbers indicate the presenter