Wednesday Morning, November 5, 2003

Homeland Security Topical Conference
Room 309 - Session HS-WeM

Plenary Session on Homeland Security

Moderators: R.J. Colton, Naval Research Laboratory, J.N. Russell, Naval Research Laboratory

9:00am **HS-WeM3 The DoD Chemical Biological Defense Program: Technical Base*, R.A. Mackay,*** SBCCOM **INVITED**

The DoD Chemical Biological Defense Program (CBDP) is a joint service program, with oversight and management through the Office of the Secretary of Defense for CB. The technical base portion of the CBDP, basic and applied research and concept development, is managed by the Defense Threat Reduction Agency (DTRA). Participants in the program include the services, industry and academia, and the projects are executed principally through the service laboratories. Each service is assigned responsibility by DTRA for monitoring supporting SBIR/STTR projects with industry, and DTRA is also responsible for ensuring coordination with other federal agencies and organizations. While the principal function of the CBDP is to support the warfighter, it also supports dual-use technology, which may be applied to homeland security. Some examples of relevant technology will be presented.

9:40am **HS-WeM5 Framework for Technology in Homeland Security*, S. Hallowell,*** Transportation Security Administration **INVITED**

As an element of the Border and Transportation Security (BTS) under the Department of Homeland Security (DHS), the Transportation Security Administration is responsible for providing security solutions for rail, maritime, transit, pipeline, aviation and highway modalities. The Office of Security Technologies will develop and implement the best security technology solutions to protect the nation's transportation systems, ensuring freedom of movement for people and commerce. The provision of security against the safety, privacy, and surface of the traveling public is a challenging balance. The Transportation Security Laboratory is responsible for research development, and test and evaluation of next generation security procedures, processes and equipment. Our current security R&D program is addressing measures that can be taken to protect people, cargo, conveyances, and facilities against explosives, weapons, unauthorized access, and chemical/biological/radiological/ and nuclear agents. Many novel technologies are being developed and assessed in our laboratory in order to meet these challenges, including walk-through portals that detect explosive residues, explosive detection systems (EDS), nuclear quadrupole resonance, X-ray diffraction, and neutron and gamma ray systems. Other areas of R&D include enabling technologies such as biometrics, vehicle tracking and intrusion surveillance. The scope of the need is large, and the threat is real, but layered elements of technology and procedures suggest a blueprint for future security.

10:20am **HS-WeM7 The Role of the Science and Technology Directorate in Homeland Security*, A. Fainberg,*** Department of Homeland Security **INVITED**

The Science and Technology (S&T) Directorate is one of four directorates in the newly formed Department of Homeland Security (DHS). Its Office of Research and Development includes National and Federal Labs, University programs, and activities focused on standards, test & evaluations, and bio-countermeasures. The Plans, Programs and Budget Office will determine broad lines of R&D that will be carried out by the Office of Research and Development and the Homeland Security Advanced Reaerch Projects Agency. While DHS is not fundamentally a basic research agency/funder, the S&T Directorate will engage in both applied research and rapid prototyping of near-ready products. Longer-term exploratory research will be conducted by University programs or through the Homeland Security Advanced Projects Agency, a new component of the S&T Directorate.

Homeland Security Topical Conference
Room Hall A-C - Session HS-WeP

Poster Session on Science & Technology for Homeland Security

HS-WeP1 Testing Air Jets as Trace Explosive Particle Removers*, **R.A. Fletcher**, J.G. Gillen, E.S. Windsor, G.A. Klouda,* National Institute of Standards and Technology

Detection of trace explosive particles is vital to airport security. One of the key steps in detecting explosive particles is the removal of the particles from the surface that they reside. This can be accomplished by swiping the surface or by energetic disruption such as an air jet that will provide enough force to overcome the particle attachment due to van der Waals forces. Our initial experiments are following the experiments of Phares et al.@footnote 1@ and Smedley et al.@footnote 2@ for polystyrene latex spheres on smooth surfaces. We are utilizing fluorescence tagged spheres of various diameters that we can image through an optical fluorescence microscope. Images of fluorescent particles are captured and recorded before an air jet interrogates the sample. Particle removal is seen in live time; the particles that are not removed from the surface are captured in a subsequent image. Image processing allows us to quickly determine the size distribution the particles that have been removed and the ones that remain. By using polydisperse spheres, we can detect the particle release threshold for a given jet condition in terms of particle diameter. A second study is under way to examine the efficiency of removal for actual high explosives from characteristic surfaces like clothing and luggage. A test substrate is mounted in a small vertically oriented laminar flow wind tunnel. The airflow in the tunnel is hepa filtered to remove all particles greater than 0.3 um diameter. An air jet is used to remove particles from the test surface. The size distribution of the removed particles is determined in real time using a particle detector mounted down stream that works on the basis of measuring particle impact energy. Results from both experiments will be presented.@FootnoteText@@footnote 1@Phares, D.J. et al. J. Forensic Sci. 2000:45;(4) 774-784. 2. Smedley, G.T. et al. Exper. In Fluids 1999:26, 324-334.

HS-WeP2 Temperature-Dependent micro-Raman Study of Some High Explosives*, **E.S. Etz**, S.V. Roberson, G. Gillen,* National Institute of Standards and Technology

In collaboration with the Transportation Security Agency, NIST has initiated a chemical metrology program that will support the nationwide operational deployment and utilization of trace explosives detection devices. The project critically examines the analytical methodology whereby collections of micrometer-sized high explosives (HE) particles undergo thermal vaporization at the front-end of an ion-mobility spectrometer (IMS), leading to sample detection and identification. We have started to examine this front-end process in detail with a focus on particle transport and HE thermalization-vaporization for the IMS detection system. Of interest here is the temperature behavior and the thermochemistry of the analyte HEs in the temperature regime leading to the melting point, and beyond to the vapor phase. To understand the fragmentation and decomposition of HEs, we are using Raman microspectroscopy to study the particle spectra of relevant HEs heated to their melting temperature, and beyond, on a microscope hot-stage. The spectra are examined for (i) shifts in the peak frequency of Raman bands, (ii) temperature-induced changes in the spectral halfwidth and asymmetry of bands, (iii) changes in the relative intensities of bands and (iv) the presence of decomposition products. The spectra are acquired with a commercial Raman microprobe utilizing 514.5, 532, and 785 nm excitation. Discussed are the results obtained for the explosives TNT (m.p. 80.7 °C), PETN (m.p. 141.3 °C), RDX (m.p. 204 °C), and the plastic binary composites Semtex and C-4. The spectra show considerable changes as the sample is ramped up to the higher temperatures. These changes take on various forms, including substantial peak shifts to lower frequencies, band broadening with lowering of symmetry, and pronounced relative intensity changes. These spectral manifestations are correlated with the structural and compositional changes of these organic samples.

HS-WeP4 Vapor Preconcentration during Explosive Detection: Study of Variables in a NIST Standard Test System*, **R.M. Verkouteren,* National Institute of Standards and Technology

The reliable detection of ever-decreasing levels of explosives constantly challenges the public safety and analytical communities. The total absence of false negative responses is required while minimizing the rate of false positive responses. While much progress has been achieved, further significant improvements in methods may be enabled by the systematic study of the total measurement process, especially near the limits of detection. Fundamental data from such studies are needed by system designers, instrument manufacturers, and public safety officials in improving the sensitivity and specificity of portal screening systems, while balancing the human dimensions that include ease of use, speed of analysis, detection risk tolerance, personal invasiveness, and profiling decisions. Described will be a NIST standard test system and preliminary flash desorption experiments, designed to investigate variables affecting the efficiency of one segment of explosive detection: the preconcentration stage. The standard test system was built to enable robust monitoring and control over static and dynamic temperature regimes and gas flow, and was designed to allow modifications in the configuration of components. We intend that this system be used to compare reliably the relative performances of materials, configurations, and methods, and to provide a benchmarking reference to enable measured improvements to technology. In the NIST system, a known quantity of sample is introduced onto a metal felt collector, which is then desorbed into a gas stream by resistive heating and monitored by IR thermography. The vapors released are then trapped on a second metal felt collector, the temperature of which is controlled by a thermoelectric cooler. The amount of trapped sample is determined by off-line quantitative methods. Factorial experimental design will be discussed as an effective tool to investigate a large number of variables in a limited number of experimental runs.

HS-WeP5 Chemical-Biological Nanosensors*, N.L. Jarvis,* Edgewood Chemical Biological Center*; A.W. Snow,* Naval Research Laboratory*; H. Wohltjen,* Microsensor Systems, Inc.*; **R.R. Smardzewski**,* Edgewood Chemical Biological Center

A new class of nanometer-scale, low power, solid-state devices is being investigated for the detection of hazardous vapors. These chemical vapor sensors are comprised of nanometer-sized gold particles encapsulated by monomolecular layers of alkanethiol surfactant deposited as thin films on interdigitated microelectrodes. These new, alkylthiol-stabilized, gold nanocluster materials are appropriately categorized as metal-insulator-metal ensembles (MIME). When chemical (agent, hazmat) vapors reversibly absorb into these thin MIME films, a large modulation of the electrical conductivity of the film is observed. The measured tunneling current between gold clusters is extremely sensitive to very small amounts of monolayer swelling or dielectric alteration caused by absorption of vapor molecules. For chemical agent simulants, a large dynamic range (5-logs) of sensitivities is observed and extends down to well below sub-ppm vapor concentrations. Tailored selectivities of the sensors are accomplished by incorporation of chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure. Current research efforts are focused on examining the molecular mechanism(s) of conduction and mapping the selectivity and sensitivity of sensor elements. Targeted applications include: low-cost, low-power CB agent sensors, filter residual life indicators and orthogonal detector applications.

HS-WeP6 A Portable GC with a Nanosensor Array Detector*, **A.W. Snow**,* Naval Research Laboratory*; H. Wohltjen,* Microsensor Systems, Inc.*; N.L. Jarvis,* U.S. Army Edgewood Chemical and Biological Center

Development of portable rapid-screening analytical methods/instrumentation for the detection of chemicals identified by the Chemical Weapons Convention (CWC) as associated with the production and use of agents is an activity of interest to homeland security as well as to CWC inspection capabilities. The instrument described in this presentation consists of a temperature programmable gas chromatograph combined with a novel detector array based on gold nanocluster chemresistors.@footnote 1,2@ In this configuration peaks eluting from the GC are "fingerprinted" by the detector array using an on-board pattern recognition computer and an on-board library look-up. The thermoelectrically cooled array detector is very compact, works with any carrier gas, and uses minimal power. The array detector consists of four interdigital microelectrodes coated with different gold nanocluster materials. This device structure is called a "MIME" device (a pneumonic for Metal-Insulator-Metal Ensemble which reflects the electron transport through the organic monolayer shells encapsulating the metal cores of adjacent nanoclusters). Absorption of vapors into the insulating ligand shell surrounding the core produces a change in conductivity that is interpreted as a GC detector signal. The vapor sensitivity, selectivity and response time of each MIME device in the array are dependent on the composition, molecular structure and thickness of the ligand shell resulting in the array detector having a unique pattern for a particular analyte or interferent. Numerous candidate materials were evaluated for their effectiveness in the detection of organophosphorus compounds and other chemicals associated with the production of chemical weapons. @FootnoteText@ @footnote 1@ H. Wohltjen and A.W. Snow, "Colloidal Metal-Insulator-Metal Ensemble Chemiresistor Sensor", Anal. Chem. 1998, 70, 2856.@footnote 2@ A.W. Snow, H. Wohltjen, N.L. Jarvis, "MIME Chemical Vapor Microsensors", NRL Review, 2002, 45.

HS-WeP7 A Rapid Optical Assay for the Detection of Bioterriorism Agents Using Thin-Film Technology*, **S.C. Francesconi,*** Nova Research, Inc.*; A.M. Churilla,* Naval Research Laboratory

Rapid, field analysis of environmental samples for the presence of biological agents is important in both military and civilian law enforcement and public health applications. Development of assay formats, useful in these settings must be easy to operate and interpret. Additionally, the assay must be highly sensitive yet yield a low rate of false positive results. To this end, we have modified a commercially available, thin-film format to develop an assay capable of detecting multiple biological agents, simultaneously. The current assay is capable of simultaneously detecting ricin, botulinum toxin and anthrax, plus negative and positive controls, simultaneously in less than 30 minutes. The assay is performed on disposable silicon nitride wafers spotted with capture antibody specific to target agents. Samples, mixed with enzyme-coupled detector antibody are exposed to the capture antibody-spotted wafers. Exposure of the wafer to enzyme substrate results in a thin-film. Final detection of agents, therefore, is creation of a change in refractive properties of the wafer spots yielding a visible color change proportional to the amount of antigen originally present in the sample. The assays perform well using a number of sample matrixes including tap water, sea water or oily water. Further, the assay can be expanded to include additional target agent detection capability.

HS-WeP8 Detection of Nucleic Acid Hybridization by Infrared Absorption Spectroscopy*, **K. Miyamoto**, Y. Kimura, H. Ishii, M. Niwano,* Tohoku University, Japan

Biotechnology and medical diagnostics are currently in need of devices able to quickly and selectively detect biological molecules. DNA chip technology has gained considerable interest because of its importance to disease diagnostics, mutation detection, gene discovery, and so on. DNA chips facilitate the detection of specific DNA fragments (target DNA) by hybridization with a complementary strand (probe DNA). In conventional DNA chips, probe DNA that is immobilized on a solid substrate such as glass, are hybridized with fluorescently-labeled target probes, and the hybridization is measured with a laser scanner. However, if hybridization were in-situ monitored by spectroscopic tools, fluorescent label would be unnecessary. We propose an alternative method of monitoring hybridization of nucleic acids using infrared absorption spectroscopy in the multiple internal reflection geometry (MIR-IRAS). Since hydrogen bonding plays an important role in the hybridization of nucleic acids, we have investigated how hybridization induces spectral changes in the C=O and N-H stretching vibration regions of DNA. Results of ab-initio calculations demonstrate that changes in vibration frequency of the C=O stretching and N-H scissors modes are induced due to the base pairing of Guanine and Cytosine. We show the possibility of high-sensitive detection of DNA hybridization using MIR-IRAS.

Homeland Security Topical Conference
Room 309 - Session HS+MM-WeA

Detection of Explosives and Other Chemicals for Homeland Security

Moderators: R. Cavanagh, National Institute of Standards and Technology, R.T. Lareau, Transportation Security Administration

2:00pm **HS+MM-WeA1 MEMS Chemical Sensors for Homeland Security***, **D.C. Meier**,* National Institute of Standards and Technology*; C.J. Taylor,* Pomona College*; R.E. Cavicchi, Z. Boger, S. Semancik,* National Institute of Standards and Technology

Chemical sensors capable of accurate detection of trace quantities of chemical warfare (CW) agents would provide a potent tool for perimeter security, treaty verification, and battlefield threat detection. Ideally, such sensors would be highly sensitive, selective, compact, and require low power. Since many CW agents are lethal at µmol/mol (ppm) concentrations, reliable trace detection is the critical prerequisite to the employment of life-saving countermeasures. In order to meet these goals, microsensors consisting of CVD TiO@sub 2@ and SnO@sub 2@ sensing films on MEMS array platforms have been fabricated. Their response measurements to the CW agents GA (tabun), GB (sarin), and HD (sulfur mustard) in dry air at concentrations between 5 and 200 nmol/mol (ppb), as well as to CW agent simulants CES (chloroethyl ethyl sulfide) and DFP (diisopropyl fluorophosphate) between 250 and 3000 ppb are reported. The devices yield both excellent signal-to-noise and good reproducibility for similar devices. Detection in backgrounds of common battlefield interferants is also discussed. The temperature of each sensor element is independently controlled by embedded microhotplate structures that drive both the CVD process (375 °C) and sensor operation at elevated temperatures (325 to 475 °C). The concentration-dependent analyte response magnitude is sensitive to sensing film growth conditions. Long-term stability studies verify stable sensor responses to GB and HD for 14 hours of agent exposure. Use of fast (200 ms) temperature programmed sensing (TPS) over a broad range (20 to 480 °C) enhances analyte selectivity, since the resulting signal trace patterns include only kinetic data that are unique for each agent tested. Recursive training of an artificial neural network (ANN) assembles the set of most relevant inputs from the TPS data; subsequent validation of the trained ANN verifies positive agent and simulant identification and quantification.

2:20pm **HS+MM-WeA2 Development of a Piezoelectric Microphone for Trace Gas Detection***, **R.G. Polcawich**, P. Pellegrino,* U.S. Army Research Laboratory

Escalating environmental awareness has led to more restrictive regulations on air quality in both the workplace and the environment in general. As a result, there is an increasing desire to have portable trace gas analyzers especially for chemical and biological agent detection. To meet these goals, a gas detection system must be miniaturized allowing large scale production of affordable small sensing systems. Initial examination of the scaling principles associated with photoacoustic spectroscopy (PAS) in respect to microelectromechanical system (MEMS) dimensions indicate the photoacoustic signals would remain at similar or greater sensitivities commonly found in macro-scale devices.@footnote 1@ Several other issues including: increased stability, noise avoidance, small source-to-detector distances and monolithic sensor construction support the idea that a MEMS photoacoustic chemical sensor can be realized.@footnote 2@ Our current research efforts have focused on fabrication of a piezoelectric microphone for trace gas sensing using a MEMS PAS. Using lead zirconate titanate (PZT) thin films as the piezoelectric sensor, 500 to 2000 micrometer diameter acoustic sensors have been fabricated and have an unamplified sensitivity of 0.1 to 1.0 µmV/Pa, depending on geometry. Using a limit of detection determined from the noise floor of the PZT microphone, it is anticipated that a PZT based acoustic sensor should detect SF@sub 6@ at slightly less than 1 ppb. Our presentation will cover the fabrication, packaging, and testing of a piezoelectric microphone for use in a MEMS based PAS detector. @FootnoteText@ @footnote 1@ S.L. Firebaugh, K.F. Jensen, and M.A. Schmidt, Miniaturization and integration of photoacoustic detection, J. Appl. Phys., vol 92, pp.1555-1563 (2002).@footnote 2@ P. Pellegrino and R. Polcawich, Evaluation of a MEMS Photoacoustic Sensor, submitted to 2002 Joint Service Scientific Conference Chemical Biological Defense Research, Hunt Valley.

2:40pm **HS+MM-WeA3 Fabrication, Packaging and Testing of Micronozzles for Gas Sensing Applications***, **S. Li**,* University of Maryland, College Park*; C.B. Freidhoff, R.M. Young,* Northrop Grumman Electronic Systems Inc.*; R. Ghodssi,* University of Maryland, College Park

There has been recent, rapid development of MEMS-based gaseous microfluidic devices (GMDs) working under standard atmospheric conditions. One of the applications considered for the GMD is for a frontend of a miniature chemical sensor to improve its sensitivity. We report a fabrication technology for developing linear converging-diverging micronozzles using low temperature wafer-level adhesive bonding with SU-8. The process is quick, repeatable and relatively insensitive to presence of particles on the wafers to be bonded. A selection of wafer bonding tests with SU-8 as the intermediate bonding material has been performed to investigate the influence of different parameters on the bonding of structured wafers. A crack-opening method is used to evaluate the surface energy of bonded wafers to be in the range of 0.42-0.56 J/m@super 2@. Based on the results of wafer bonding test with SU-8, sealed micronozzles with throat widths as small as 3.6 µm are fabricated successfully. For the purpose of comparison, micronozzles of same geometries and dimensions are also fabricated using deep reactive ion etching (DRIE) and silicon-glass anodic bonding techniques. The micronozzles are packaged to interface with a gas flow test setup using capillary needles, O-rings and flexible tubing. Gas flow rates and pressure distributions in the micronozzles are measured and compared with those predicted from the one-dimensional isentropic flow model, which demonstrate that these developed techniques may extend the flexibility of fabricating and packaging microfluidic devices for gas sensing applications. The detailed fabrication process and testing results will be presented.

3:00pm **HS+MM-WeA4 Characterization of Portal-Based Trace Explosive Detection Systems***, **G. Gillen**, R.A. Fletcher, S.V. Roberson, C. Zeissler, E.S. Etz, J. Verkouteren, M. Verkouteren, E.S. Windsor, G.A. Klouda,* National Institute of Standards and Technology*; R.T. Lareau,* Transportation Security Administration

In collaboration with the Transportation Security Agency's (TSA) Trace Explosive Detection Group, the NIST Chemical Science and Technology Laboratory (CSTL) has been working to build a chemical metrology program to help support the widespread operational deployment and effective utilization of trace explosives detection devices throughout the United States. A second objective is to develop at NIST the specialized measurement expertise that will be needed to support the next generation of explosive detection equipment. Of particular interest for this work is the characterization of walk-through trace explosive detection portal (TEDPâ€™s) systems currently under evaluation by the TSA. The low volatility of most high explosives makes direct analysis of vapors impractical. Therefore, many detection systems are based on either airborne or surface swipe collection of micrometer-sized explosive particles with subsequent thermal vaporization of the particles into an ion mobility spectrometer for identification. The effective collection and thermal desorption of the explosive particles is the critical front-end process for the successful and reproducible detection of explosives. In order to understand this process in detail we are employing a number of microanalytical techniques including: SIMS and TOF-SIMS, SEM, Raman, Optical and Fluorescence Microscopy, Infrared Thermometry and Optical Particle Counting. These techniques are being used to study, at the single particle level, the collection and removal of individual explosive particles from surfaces and the chemical and morphological changes that occur during sampling. This presentation will review the NIST-TSA project and will present our recent findings with an emphasis on chemical characterization of individual explosive particles.

3:20pm **HS+MM-WeA5 Polymer Electronics for Ultra-Sensitive Chemical and Biological Sensors***, **T.M. Swager**,* Massachusetts Institute of Technology **INVITED**

This presentation will describe the design of electronic polymers that have the ability to undergo self-amplified responses.@footnote 1@ Optimal energy and charge transport properties are key to the amplifying ability of these materials. Design principles have been developed that can be used to improve the mobility and lifetime of excitons will be presented. To elicit a selective sensor response different molecular recognition principles have been integrated into the polymers. Effective implementation of recognition elements requires effective transduction events that are compatible with the amplifying ability of the polymers. Designs based upon energy transfer, quenching, and excimer formation will be presented for the detection of DNA, Proteins, Chemical Warfare Agents, Explosives, and Ions. I will also discuss our continuing efforts in the design of sensory materials that utilize molecular recognition events to product changes in conductivity. In many cases we use transition metal ions are redox active elements in these materials and I will outline the design principles for producing conducting polymers that utilize the metal ions as part of the conducting pathway. These materials have allowed us to produce new sensors for nitric oxide, a signaling agent in biological systems. @FootnoteText@ @footnote 1@ (a) Swager, T. M. "The Molecular Wire Approach to Sensory Signal Amplification" Accts. Chem. Res. 1998, 31, 201-7. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. "Conjugated Polymer Sensory Materials" Chem. Rev. 2000, 100, 2537-2574. (c) Self-Amplifying SemiconductingPolymers for Chemical Sensors Swager, T. M.; Wosnick, J. H. MRS Bulletin, 2002, June, 446. (d) J.H. Wosnick and T.M. Swager, "Molecular Photonic and Electronic Circuitry for Ultra-Sensitive Chemical Sensors" Curr. Opin. Chem. Biol. 4 (2000) p. 711.

4:00pm **HS+MM-WeA7 DIOS-MS and LC-DIOS-MS for Chemical Analysis***, Z. Shen, C. Fish,* University of California, San Diego*; G. Siuzdak, M.G. Finn,* The Scripps Research Institute*; **J.E. Crowell**,* University of California, San Diego

Desorption/Ionization On Silicon Mass Spectrometry (DIOS-MS) is a new mass spectrometry strategy based on pulsed laser desorption/ionization from a porous silicon surface. DIOS-MS is similar to matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS) in that it utilizes the same instrument; however, in DIOS-MS, porous silicon is used to trap analytes deposited on the surface and laser radiation is used to vaporize and ionize these molecules, without the presence of any matrix material. We have shown that DIOS-MS can be used for a wide range of biomolecules, organic molecules, and metal-containing compounds at the femtomole and attomole level with little or no fragmentation. DIOS-MS offers many unique advantages including good sensitivity, low background ion interference, and high salt tolerance. We will discuss the coupling of liquid chromatography separation with DIOS-MS for protein identification and peptide sequencing, and the use of chemical and surface modification for tailored analysis.

4:20pm **HS+MM-WeA8 A Novel Chemical Detector Using Cermet Sensors and Pattern Recognition Methods***, **S.L. Rose-Pehrsson**,* Naval Research Laboratory*; J. Ziegler,* General Atomics*; M.H. Hammond,* Naval Research Laboratory*; D. Gary, K. Caudy,* General Atomics

Smart microsensor arrays are being developed by combining cermet electrochemical sensors, intelligent firmware and software to drive the sensors and analyze the data. The chemical microsensors offer a small size, light weight, low power and low cost alternative to conventional electrochemical sensors. The chemical microsensor architecture may be modified for detection selectivity of a variety of chemical species including chemical agents and combustible or corrosive gases. The microsensor arrays have potential application for monitoring hazardous chemicals in the part-per-million to part-per-billion range in a variety of internal and external environments. The arrays sense analytes using pattern recognition techniques to determine the presence of vapors of interest. General Atomics and the Naval Research Laboratory are developing this technology for the detection of chemical warfare agents and toxic industrial compounds (TICs). A test demonstrator has been developed with a three-sensor array, readout electronics, and system control software. The three-sensor array was exposed to 15 test vapors. The 15-analyte sources, including 2 blood agents, 10 TICs and 3 simulants were generated at 5 different concentrations in humid air. The cermet sensor array provided unique responses for the various analytes tested. Similar analyte types produced similar results. The sensitivity is sufficient to detect all the analytes at their respective exposure limits. Two different pattern recognition methods were developed to identify the analytes.

4:40pm **HS+MM-WeA9 Chemical Warfare Agent Detection Using Random Networks of Single-Wall Carbon Nanotubes***, **E.S. Snow**, J.P. Novak, E.J. Houser,* Naval Research Laboratory

Single-wall carbon nanotubes (SWCNT) are unique structures in that they are composed entirely of surface atoms while exhibiting transport properties superior to single crystalline Si. These features make them an ideal candidate for a new class of molecular sensors. We report the use of random networks of SWCNTs as a sensor for chemical warfare agents. Random networks of SWCNTs are used to provide high-yield sensor fabrication using conventional microlithographic techniques. Molecular adsorption of chemical agents onto the nanotube networks results in a charge transfer that manifests itself as a change in the network conductance. In such devices sub-part-per-billion sensitivity to agent simulants is easily achieved. We discuss these results and our approach to functionalizing the networks to provide additional sensitivity, selectivity against potential interferents, and a high degree of chemical specificity. Arrays of such functionalized devices should provide highly sensitive and specific electronic detection of a wide range of chemical warfare agents and other toxic chemicals.

5:00pm **HS+MM-WeA10 Carbon Nanotubes for Molecular Sensors and Electronic Circuit Elements***, **M.J. Bronikowski**, D.S. Choi, M.E. Hoenk, B.D. Hunt, R.S. Kowalczyk, E.W. Wong, A.M. Fisher,* Jet Propulsion Laboratory/California Institute of Technology*; B. Rogers, J.D. Adams,* University of Nevada, Reno*; J. Xu,* Brown University*; J.F. Davis, L.W. Epp, D.J. Hoppe,* Jet Propulsion Laboratory/California Institute of Technology

This talk will focus on recent efforts at JPL's Microdevices Laboratory in developing several different types of nano-scale electronic devices based on carbon nanotubes (CNT). CNT exhibit a coupling between electronic structure and mechanical deformations: mechanical stress or deformation can result in charge injection into the nanotube, or likewise, charging of a nanotube can result in mechanical deformations. This electromechanical coupling can form the basis for nanotube-based oscillators, signal processors, and RF rectifiers. Nanotube electronic properties, specifically their resistance and current-voltage characteristic, can also change when various molecules bind to their surfaces. This property can form the basis for CNT-based chemical and molecular sensors. For both types of device, CNT are grown directly on silicon substrates in pre-patterned device structures: nanotubes grow by CVD from patterned arrays of particles of catalytic metals, with the pattern of the catalyst determining the pattern of CNT. Of key importance to producing devices by this means is controlled placement of catalyst on the substrate: several methods for generating catalyst patterns on surfaces and devices will be demonstrated and discussed.

Thursday Morning, November 6, 2003

Homeland Security Topical Conference
Room 309 - Session HS-ThM

Detection of Biological Agents and Self-Cleaning of Contaminated Surfaces

Moderators: L.J. Buckley, Defense Sciences Office, DARPA, D.W. Grainger, Colorado State University

8:20am **HS-ThM1 Direct Electrical Detection of Specific Protein Binding at Surfaces***, **T.L. Lasseter**, W. Cai, W. Yang, R.J. Hamers,* University of Wisconsin, Madison

Most biological analyses ultimately rely on optical methods of detection. Here, we show that the binding of proteins to surfaces can be detected electrically in a completely label-free manner using electrochemical impedance spectroscopy. Experiments have been conducted on several different substrates including gold, glassy carbon, and silicon. In each case, we covalently linked biotin to the surface, and then investigated the changes in electrical impedance when the surface was exposed to avidin over the frequency range from 5 mHz to 1 MHz. The changes in impedance are most apparent at low frequencies, < 1 Hz. By using fluorescently-labeled avidin, we also correlated the magnitude of the observed electrical changes with the intensity of the observed fluorescence from the surface. Measurements of the impedance changes as a function of avidin concentration show that the detection limit from these electrical measurements is comparable to or even better than the detection limit observed from fluorescence spectroscopy. Finally, circuit modeling of the interface is being use to relate the electrical changes observed to the physical structure of the interface.

9:00am **HS-ThM3 Autonomous DNA Testing for Bio-Detection***, **K. Petersen**,* Cepheid **INVITED**

After 18 months of extensive testing and evaluation, the US Postal Service has made a decision to deploy automatic bio-threat detection systems in mail sorting facilities throughout the United States. A team, including Northrop Grumman, Cepheid, Smiths Detection, and Sceptor has developed this system called BDS (Bio Detection System). The BDS system will be the first and only automated, nationwide bio-threat detection system approved through rigorous testing of stringent systems requirements. The highest possible detection sensitivity is achieved by using the polymerase chain reaction (PCR), which is increasingly becoming the "gold standard" for biological detection and identification; oftentimes better than culturing. The lowest possible false positivity rate is achieved by extensive internal controls and assay validation procedures. Some aspects of the performance of the BDS system actually exceeds that of the US blood banking system for pathogen detection. Yet, all of this sophisticated, state-of-the-art biological processing is performed completely automatically, in a dusty, industrial environment in about 30 minutes. This presentation will describe the advanced fluidic, biological, chemical, and engineering aspects of this revolutionary technology. We will also discuss how a key sub-system of the BDS, the GeneXpert, is being applied to many other biomedical applications such as the detection of infectious diseases and cancer.

9:40am **HS-ThM5 Magnetically Based Microarray Platform for Rapid Handheld Bioassays***, **M.C. Tondra**,* NVE Corp.

Biochemically functionalized magnetic beads are being used as labels in the development of rugged, handheld bioassays. These magnetic labels can be adapted for use in both protein and DNA assays. A palm-sized magnetic excitation module has been fabricated and demonstrated with integrated Giant Magnetoresistive (GMR) detector arrays. The arrays have 20 sites, each of which is a GMR magnetic sensor underneath a 200 micron diameter functionalizable assay surface. The sites are functionalized by attaching a reference protein or oligonucleotide to the surface. The assay is typically a sandwich-type assay, though other techniques are possible. The sensitivity of the assay is quite good, with reports of better than 1 femtoMolar detection limits. The integrated detectors can detect a single immobilized magnetic label, and has a dynamic range of better than 10^3. The ultimate performance of a given assay is dependent on microfluidics and sample handling. The magnetic detection scheme has several advantages over common optically based techniques. The excitation device and detector array are both solid state devices and are inherently rugged. Both are amenable to low cost mass- manufacturing techniques. And it is possible, with sophisticated sample handling, that PCR amplification may be unnecessary due the ability to detect a single label. Magnetic forces may also be used to enhance reaction rates and improve specificity. This presentation will address issues related to fabrication and surface modification of the GMR sensor array chip. The most common assay surfaces include silicon nitride, silicon dioxide, aluminum dioxide, and gold. In all cases, the surface quality must be very high to achieve predictable and desirable assay results. With continued development, this magnetic bioassay platform should prove to be ideal for applications where high speed multiplexed sandwich-type assays are done on a disposable platform.

10:00am **HS-ThM6 Microfluidic Approaches to Improving Biosensor Performance***, **J.C. Rife**, P.E. Sheehan, L.J. Whitman,* Naval Research Laboratory

The sensitivity of a microarray biosensor depends on many factors other than the sensor performance, including sensor area, analyte diffusion, and non-specific binding of target and/or label. However, when the detection system is sensitive enough to detect single labels, the performance will be limited by these factors. We are confronting such limitations in the development of two systems for biowarfare pathogen detection. The Bead ARray Counter (BARC) and the Force Discrimination Biosensor (FDB) systems use biomolecular recognition to bind magnetic microbeads to either a solid or porous substrate. At our current detection limits, we are labeling one analyte molecule per detectable microbead. Under these conditions, the BARC system can detect DNA concentrations as low as 1 fM (10@super 5@ molecules/ml) and FDB can sense protein toxins at concentrations <0.5 pg/ml (10@super 6@ molecules/ml). Further gains in system performance will depend on careful design of the fluidics systems. We will present analytical and finite element calculations aimed at understanding and optimizing the microfluidic delivery of assay reagents to the sensor surfaces. The role of flow profile, fluidic forces, and sensor geometry in maximizing the assay performance will be discussed.

10:20am **HS-ThM7 Comparison of Bioassay Surface Chemistries on Gold and Alumina Films***, **S.P. Mulvaney**, C.L. Cole, J.C. Rife, K.A. Wahowski, L.J. Whitman,* Naval Research Laboratory

The surface bioaffinity coating is arguably the most critical component of any biosensor based on ligand-receptor capture on a solid substrate. The characteristics of this interface have profound effects on the overall performance of the sensor, affecting the assay sensitivity and selectivity (including background due to non-specific binding), and signal transduction. The physical properties of the sensor surface must be compatible with the detection method employed and chemically suitable for functionalizing with receptor biomolecules such as antibodies or oligonucleotides. The utility of gold films for electrochemical and optical detection schemes has made it one of the most commonly used sensor surfaces. One common approach to functionalizing gold is to first conjugate the desired biomolecules to a mercaptan functional group which can then immobilized on the surface via a Au-S bond. Alternatively, thiolated self-assembled monolayers (SAMs) can be used as a base for subsequent conjugation with biomolecules. SAM-based films, while effective, often lack the reproducibility required for reliable, quantitative assays. Therefore, we are exploring alternate surfaces and surface chemistries. We have developed and characterized multilayer, biocompatible polymer films on alumina surfaces and found them to be more reproducible than similar films on gold. The effects on assay performance for various chemistries on top of gold and alumina films will be compared and contrasted as used in the Bead Array Counter (BARC),@footnote 1@ a biosensor system that uses paramagnetic beads. CL Cole and KA Wahowski are employees of Nova Research, Inc., Alexandria, VA. @FootnoteText@ @footnote 1@Edelstein et. al., Biosens. Bioelectron. 2000, 14, 805-813.

10:40am **HS-ThM8 Biocatalytic Nanocomposites as Self-Cleaning Surface Coatings***, **J.S. Dordick**,* Rensselaer Polytechnic Institute **INVITED**

The interface of biology and materials science has led to the development of new materials, with unique structural and functional properties, and new process technologies complete with the ability to produce, from "bottoms up", a wide range of biomimetic structures. These materials and their designs have broad application as catalysts, sensors, and devices for use in synthesis, cell and tissue engineering, bioanalysis and screening, and nanoelectronics. We have focused on the generation of nanostructures that are functionalized with and in some cases constructed from biological molecules, complete with tailored selectivities and biocatalytic activities at the molecular and nanoscales.@footnote 1,2@ In one example, we have incorporated enzymes attached to carbon nanotubes and further embedded into polymeric films, coatings, and paints to form biocatalytically active surfaces. These materials are capable of degrading proteins, fats, polysaccharides, and other organic and biological molecules. Furthermore, in some cases, these materials can prevent the microbial fouling often associated with surface coatings, and this may have significant impact in medical devices and in battlefield and homeland defense. This presentation will be focused on the preparation, characterization, and use of different enzyme-nanomaterial-polymer composites and potential broad-based applications arising from this technology. @FootnoteText@ @footnote 1@K. Rege, N.R. Raravikar, D.-Y. Kim, L. S. Schadler, P.M. Ajayan, and J.S. Dordick (2003), "Enzyme-Polymer-Single Walled Carbon Nanotube Composites as Biocatalytic Films", Nano Letters (submitted).@footnote 2@ P. Wang, M. V. Sergeeva, L. Lim, and J. S. Dordick (1997), "Biocatalytic Plastics as Active and Stable Materials for Biotransformations", Nature: Biotechnology 15, 789-793.

11:20am **HS-ThM10 Novel Surface-Segregating Materials for Chem-Bio Applications***, **J.A. Orlicki**, M.S. Bratcher, R.E. Jensen, C.A. Winston, S.H. McKnight,* Army Research Laboratory, AMSRL-WM-MA

Macromolecular surfactants based upon hyperbranched polymer scaffolds have been employed to deliver functional groups to the surface of a substrate. Careful selection of end group chemistry allows the control of thermodynamic phase segregation, leading to an increased loading of additive at a substrate surface relative to the bulk concentration. The high number of end groups of a hyperbranched polymer permits the covalent attachment of additional moieties for added functionality (e.g. solubility control, reactive groups, ligand binding sites). Employing these molecules as additive to bulk polymer systems will provide a method to impart chemical or biological resistance upon delicate materials (electronics packaging, clothing) at minimal cost. We have developed polymers capable of chelating metal centers (polyoxometalates), and have shown their ability to transport the metals to a substrate surface. Contact angle and XPS analysis indicated the segregation of metals to the surface only when interacting with the macromolecular surfactant. These results will be discussed, along with the accompanying synthetic techniques to spur the development of novel active groups for surface functionalization.

11:40am **HS-ThM11 Opportunities in Materials Chemistry at DARPA***, **L.J. Buckley**,* Defense Sciences Office, DARPA

Materials chemistry at the surface impacts many areas of science and engineering. As one approaches nanometer dimensions, the surface properties will dominate the material behavior. The Defense Advanced Research Projects Agency (DARPA) has many opportunities for the application of materials chemistry for the general modification of surface behavior. A summary of these opportunities will be presented.

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