

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 $\mu\text{mol/mol}$ (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 TiO₂ and SnO₂ 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 interferents 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.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.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 $\mu\text{V}/\text{Pa}$, 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 SF₆ 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. 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). 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/m². 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 (TEDPs) 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

This presentation will describe the design of electronic polymers that have the ability to undergo self-amplified responses.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

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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 Semiconducting Polymers 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.

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