MICROELECTROMECHANICAL SYSTEM (MEMS) APPROACHES TO CHEMICAL SENSING FOR MARS EXPLORATION. R. C. Quinn[1], F. J. Grunthaner[2], R. E. Mielke[2], W. W. Chun[2], M. C. Lee[2], V.E. White[2], P. Ehrenfreund[3], A. J. Ricco[4], A. P. Zent[4] [1]SETI Institute (NASA Ames Research Center, Moffett Field CA 94035, Richard.C.Quinn@nasa.gov), [2]NASA JPL, [3]George Washington University, [4]NASA Ames Research Center.

Introduction: Chemical and biochemical sensors and sensor arrays offer some of the most promising measurement approaches for Mars exploration. Sensors arrays can provide high sensitivity with limited power, mass, and volume requirements making them an attractive cost effective alternative to traditional analytical instrument approaches. However, chemical and biochemical sensors frequently utilize detection mechanisms that rely on highly reactive chemical interfaces to measure target analytes. This active sensing interface is frequently a consumable material with a limited shelf life that is prone to performance degradation during extended space missions due to stress and aging. Compared to implementation on space missions, this problem is less of a restriction in ground-based laboratories, where new sensors can be made as needed, or in industrial settings where components can be replaced. In fact, in laboratory studies of chemical and biological systems on earth, sensor reagents or chemical interfaces are frequently synthesized or fabricated at the time of use to overcome their metastable nature.

We are addressing this problem through the development of microelectromechanical systems (MEMS) that are used to perform in situ chemical synthesis and nano-fabrication at the time- and point-of-use. Our lab-on-a-chip approach is based on the use of MEMS devices to perform thermal (e.g., sublimation), plasma, or chemical vapor, deposition of reactive materials in situ. These devices provide a solid-state chemical delivery method for the activation or fabrication of highly sensitive chemical interfaces. These time-of-use technologies expand the range of state-of-the-art methods of chemical extraction, detection, and measurement that can be used for Mars exploration.

Operating Principle: Figure 1 shows an example of a MEMS device designed for the solvent-free delivery of chemical reagents. Fabricated using micromachining technologies and packaged using industry standard methods, the array consists of 8 hermetically sealed chemical reaction cells (deposition devices). Once delivered to the planet's surface, a circuit on the inside of the chamber is used to deposit chemically sensitive reagents onto a target substrate (e.g., optical fiber, soil sample).

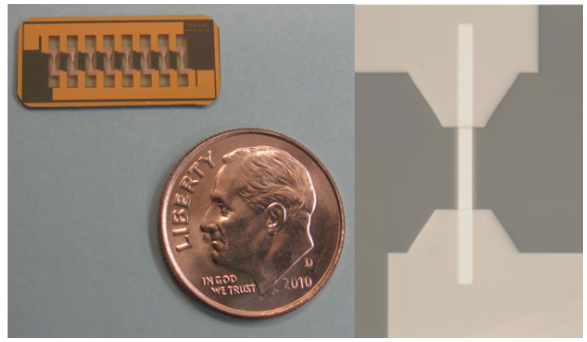

Fig. 1. MEMS chemical delivery device. This lab-on-chip-device contains an array of 8 hermetically sealed chemical reaction/deposition chambers with individually removable seals.

Mars Exploration Applications: MEMS deposition devices can be used as stand-alone chemical sensor arrays or as an enabling technology for fluorescence spectroscopy, surface enhanced Raman spectroscopy, and matrix assisted laser desorption instrument packages. These technologies can be used to directly address both near- and mid-term goals that fall under the Workshop Challenge Area 1: Instrument and Investigation Approaches including: light weight and low-cost instrumentation to identify high priority materials, the detection of trace-level organic matter in rock and dust and in situ assessment of sample/environment reactivity and toxicity.

Chemical Sensor Arrays. Highly reactive chemical thin films can be deposited directly onto sensor substrates (e.g., optical window/fibers, electrode arrays) using a circuit on the inside of the hermetically sealed chamber. The device membrane design allows for post deposition processing (e.g., annealing) and can be used to grow optically thin continuous or discontinuous

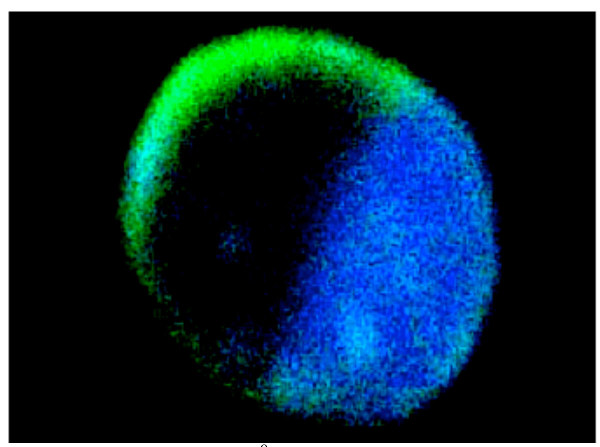

Fig. 2. Amino acid (10^{-8}g) detection (blue fluorescence) using a fluorescamine thin-film. The fluorescamine was coated only on the right-hand side of the substrate.

chemical sensing films in situ on Mars. After the deposition and processing is complete, a second circuit opens the device, exposing the sensor to the environment. Once deposited, the reaction of the target analytes with the thin-film sensors can be measured optically, via changes in fluorescence or absorbance, or electrochemically. Applications include the measurement of O_3, O•, H_2O_2, •OH and other reactive and hazardous species, as well as, trace levels of organics (Figure 2).

Surface Enhanced Raman Spectroscopy (SERS). In SERS, the surface electronic absorption band of a metal template is in resonance with a laser source, and generates enhanced Raman signals. The enhanced Raman scattering is a result of analyte adsorption on a SERS-active surface, normally nm-sized structures of silver, copper, or gold. For the portion of a molecule that is in contact with the surface, Raman signal enhancements of up to 10^8 may be obtained. SERS-active surfaces typically have short lifetimes, so the implementation of SERS for analysis on Mars is restricted by the requirement to generate SERS-active substrates in situ. By controlling operational parameters of the MEMS deposition device, the growth characteristics and morphology of deposited materials can be controlled and used to deposit discontinuous, nano-structured metal films in situ (Figure 3).

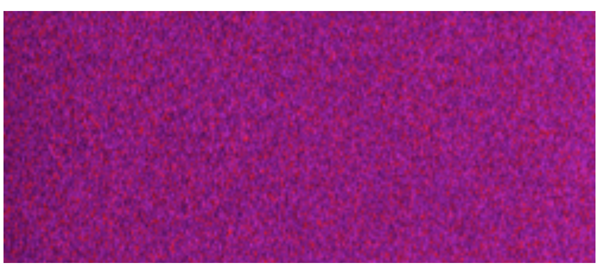

Fig. 3. Energy dispersive X-ray (EDX) map of a discontinuous nano-structured silver (red) template deposited on a SiO_2 substrate (blue) using the MEMS device shown in Figure 1.

Matrix-Assisted Laser Desorption. Laser desorption is a powerful method of trace-level organic matter extraction from rock and dust not requiring extensive in-situ sample processing. The technique, when coupled to a highly sensitive detection method (e.g., SERS, MS) presents one of the most promising approaches for the in-situ search for organics on Mars. However, the usefulness of laser desorption for the analysis of polymers, proteins and other heavy molecules, including possible organic components of sedimentary rocks on Mars (e.g., kerogen), is greatly enhanced by the use of an organic matrix (i.e., matrix-assisted laser desorption/ionization or MALDI). In the laboratory, for convenience, a matrix is most commonly applied to a sample from solution. However, sublimation can also be used as a method of matrix application [1]. Figure 4 shows a spectrum of 2,5-dihydroxybenzoic acid, a common MALDI organic matrix, that has been sublimed and deposited as a thin-film. Using MEMS deposition devices, organic materials, including MALDI matrices, can be readily applied directly to samples (or other substrates) in situ, thereby eliminating the need for fluidic systems to carry and deliver solvents.

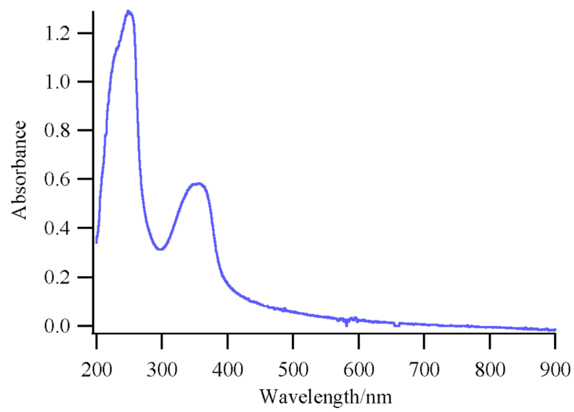

Fig. 4. Spectrum of a sublimed 2,5 dihydroxybenzoic acid (MADLI matrix) thin film. MADLI matrices can be applied in situ to soil and rock samples by sublimation without matrix decomposition.

Coupled with instrumentation under consideration for Mars exploration (e.g., Raman spectroscopy, mass spectroscopy, electrochemical detection methods), MEMS devices can provide low-mass and low-power methods to achieve required capabilities, including reagent mixing, synthesis, and delivery. MEMS devices also can provide, low-mass, low-power, and low-cost per unit capabilities that can be used as stand alone chemical sensing packages that address multiple Mars exploration goals and requirements. Examples include: 1) Sample identification including evaluation of sample organic content. 2) Monitoring, as a function of time, environmental conditions that may result in sample modification during sample collection, triage, and storage for MSR. 3) Inorganic and organic contamination monitoring of samples and collection sites. 4) Dust, soil, and environmental toxicity assessment.

References: [1] Hankin J. A. et al. (2007) J Am Soc Mass Spectrom, 18, 1646.

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