

**Hybrid Micro-Electro-Mechanical Systems for Highly Reliable and Selective
Characterization of Tank Waste (DE-FG07-01ER62718)**

**Annual Progress Report for the Period September 15, 2001 – September 14, 2002
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Significant progress was made in the tasks that were listed in the work plan for DOE EMSP project “Hybrid Micro-Electro-Mechanical Systems for Highly Reliable and Selective Characterization of Tank Waste.”

Research Objectives

Our multifaceted research program is aimed at the fundamental and practical development of hybrid micro-electro-mechanical-systems (MEMS) that integrates several elements of chemical selectivity and sensor function. We are developing MEMS sensors that combine chemi-mechanical transduction, and surface enhanced Raman spectroscopy (SERS) and radiation detection.

One of our goals is to develop highly effective methods of immobilizing a wide variety of molecular and ionic recognition phases onto micromechanical surfaces. We have introduced fundamentally new modes of adsorbate-induced surface stress through nano-structuring of microcantilever surfaces; the responsivity for has increased by over two-orders of magnitude over previously existing technological approaches. Noble metal nanostructures similar to those that enhance chemi-mechanical transduction exhibit substantial Raman enhancement factors.

Research Progress and Implications

During this years efforts we have developed arrays of microcantilevers (MCs), nanostructured on one side and configured in spatially-dense arrays, for the sensitive sensing of organic vapor mixtures. MCs singularly coated with seven different molecular recognition phases exhibit differential selectivity and response. The phases are films of nanodimensional thickness and have been structurally characterized post deposition. Analyte-induced bending of the MCs in arrays is monitored using beam displacements of vertical cavity surface emitting lasers using a time multiplexing scheme. The magnitudes and shapes of the array response profiles are unique to the analytes tested.

In this part of the work, we have demonstrated the analyte recognition performance of a MC array. The MC array consists of ten nanostructured silicon MCs functionalized by polymeric and GC phases and macrocyclic receptors as spatially-dense, differentially-responding sensing layers for the detection and quantitation of individual analyte(s) and their binary mixtures. In order to prepare a well-designed array, we used MRPs that span a fairly wide range in their distribution between typical modes of analyte-phase interactions. The binding constants are considerably smaller than with most bioaffinity systems (hence kinetics can be fast), but should span a couple orders of magnitude with respect to a given analyte to achieve adequate molecular recognition

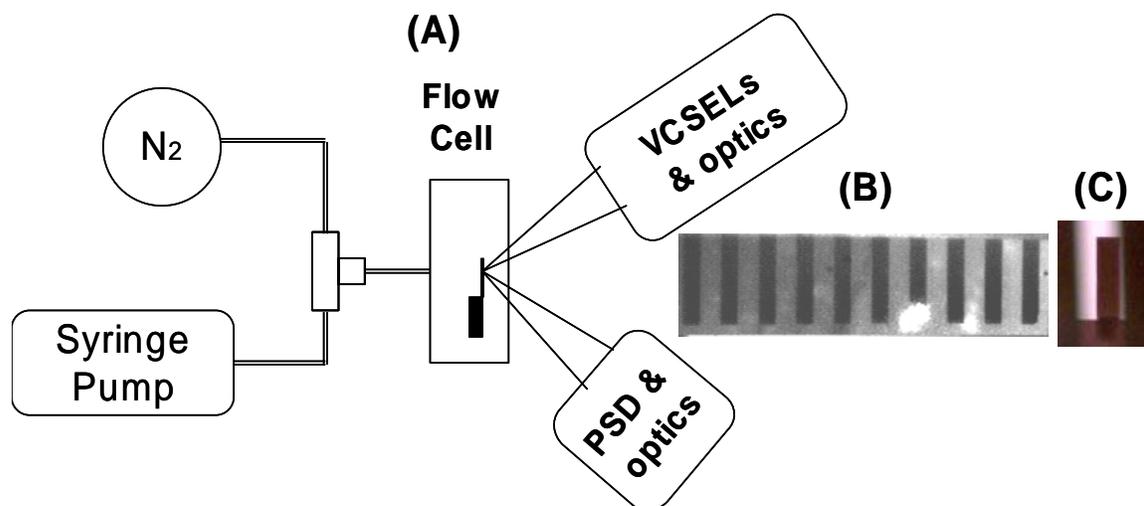


Figure 1. Schematic representation of the instrumental set-up with analyte delivery system (A), 10-MC linear array (VCSEL reflected off fourth from right) (B), and a mask with slit for coating individual MCs in arrays using PVD (C).

contrast. Interactions between the studied VOCs and the MRPs (cyclodextrins, Calix[n]arenes, polymeric phases) are shown to be reversible and give rise to characteristic response patterns. Optical detection techniques were used to probe the MCs motion in the array (see Figure 1).

Since the MRPs were coated onto the cantilever surfaces by physical vapor deposition (PVD), it was important to determine if the compound decomposed during the evaporation process. Although we have previously demonstrated that the synthetic CDs used herein can be vapor deposited intact, both GPC and FTIR spectroscopy were used to characterize the phases before and after vapor deposition. The FTIR spectra of a polymeric thin films, poly(diphenoxyphosphazene) (PDPP), before and after vapor deposition indicate that it deposits without substantial functional group chemical decomposition. Moreover, FTIR spectra of all the vapor deposited films show all the major bands of the native materials, although the FTIR data for the various MRPs shows very small shifts of few bands (within 4-10 cm⁻¹). Changes in the relative intensities of some bands may be attributed to the loss of an impurity during the vaporization process.

GPC studies showed that the molecular weight distribution of the polymer poly(isobutylene) (PIB) changed before and after vapor deposition. The polymer PIB, M_w over 200,000 decomposed to yield a number of volatile products with lower molecular weight. Also, the data from GPC studies of the three different polymers PIB, PDPP and poly(epichlorohydrin) (PECH) employed indicated that all polymers underwent PVD largely as very small oligomers.

Figure 2 shows a typical response pattern of the cantilever multisensor array specifically coated by several sensing films upon exposure of binary mixtures with different concentrations of trichloroethylene (TCE) and Ethanol (EtOH). The responses were rapid, reversible, reproducible among replicate exposures, and in all but one case (MC D that was coated with PIB) compressive in nature (positive bending response corresponding to swelling of the coating). These vapor phase analytes reversibly and differentially partition into sensing phases and this differential partitioning gives rise to the characteristic response patterns specific to the analytes. The magnitudes and shapes of the response profiles are unique to the analytes and to the coatings on MC in the multisensor array. As the composition varies from solely TCE to solely ethanol,

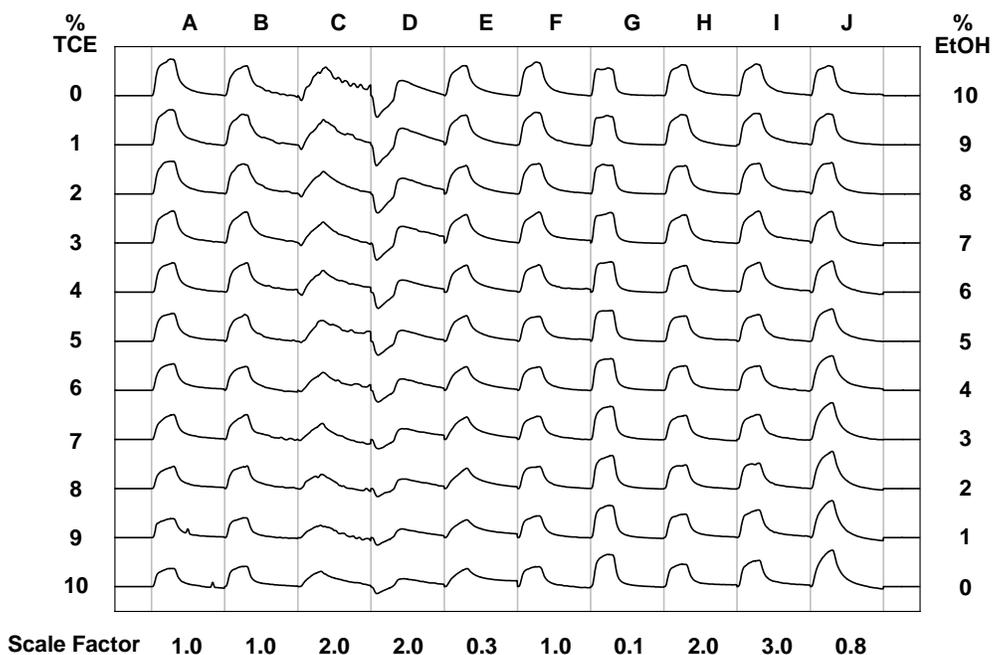


Figure 2. Response of the MC array to 10% (v/v) of TCE and Ethanol mixture diluted with nitrogen where TCE and Ethanol concentrations were varied within 0-10% of room temperature head space concentration in the mixture. Each grid corresponds to 200 second response of each phase among 10 different MRPs from A to J. Where A - propanethiol functionalized dealloyed; B - CD(350nm); C - PDPP(452nm); D-PIB(450nm); E – Cal-6(400nm); F - same as A; G – same as B(450nm); H - Squalane(450nm); I - PECH(450nm); J – Cal-4(400nm). Response scaling factors are shown near bottom of the figure.

the response patterns change in a simple monotonic fashion. Kinetic phenomena involving analyte diffusion into the MRP, the response of the phase and transmission of that phase's change to the underlying MC, all influence the shape of the response curve. Importantly, these phenomena are analyte and phase dependent. It is clear from Figure 2 that both equilibrium and kinetic behavior is present in the response profiles of the differentially coated MCs. The figure shows slower responses for PIB, PDPP, 4-tert-Butylcalix[6]arene (Cal-6) and 4-tert-Butylcalix[4]arene (Cal-4) coated MCs relative to other phases and the TCE relative to EtOH. The thickness dependence of the response profiles was demonstrated by Heptakis (6-O-tert-butyl dimethylsilyl-2,3-di- O-acetyl)- β -CD (CD) coated MC with different thicknesses (compare MCs B and G). MC coated with CD films exhibit larger responses to the analytes with increasing layer thickness. Unique to MC arrays, it should be possible to individually tune the sensitivity and the dynamic range of each MC by selectively adjusting MRPs thickness and thinning of the silicon MC itself.

For calibration, different descriptors (such as peak height, peak area, initial slope) from the responses are required that are most meaningful. Standard addition methods are particularly useful at compensating the effects of matrices on the responses of the measured analyte. However, the traditional standard addition method does not cope with additive responses, at least

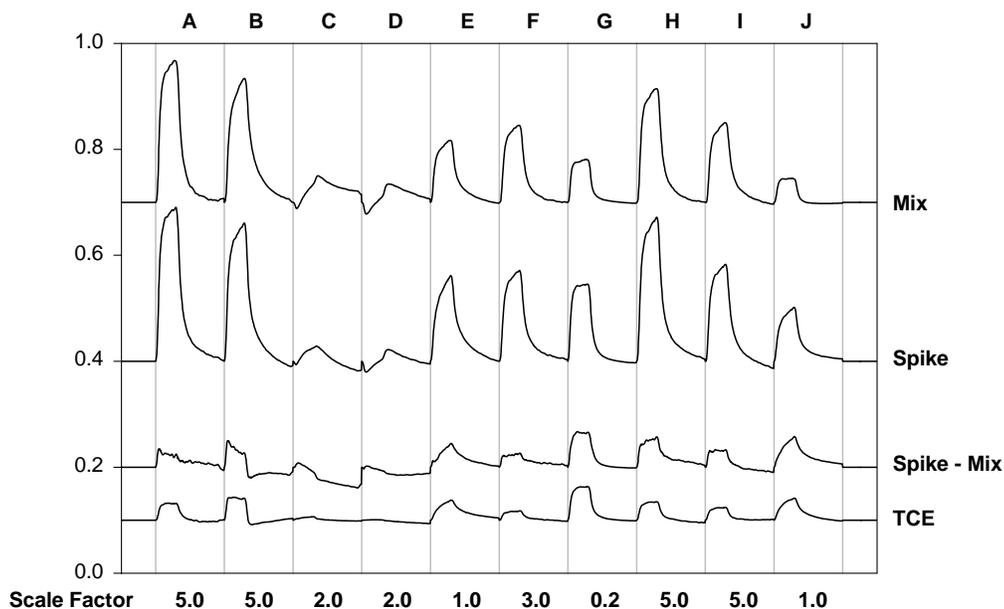


Figure 3. Response of the MC array to 10% (total v/v) for water, ethanol and methanol mixture diluted with room air (Mix) as well as to 10% (v/v) TCE diluted with mixture (Spike) along with the plots of Spike response-Mix response and 10% (v/v) TCE diluted with nitrogen. A to J is same as Figure 2.

without a great deal of training involving all possible interferences. In real sensing applications, the matrix effects will vary depending on chemical and physical conditions (e.g. temperature and humidity) in the sensing environment. If there are descriptors that respond linearly with analyte concentration but not to the sample, the traditional standard addition method may be effective. As seen in Figure 3, subtraction of the generated mixture matrix from the standard addition sample of TCE (see TCE Spike Test in Supporting Information for compositions of these samples) yielded an overall response profile that closely resembled a standard TCE sample of the same concentration, which bodes well for calibration by this approach.

Response profiles for the 10 different MC in the array are highly reproducible among replicate exposures on the same day. Additionally, Figure 4 shows a comparison of the response pattern of a MC array for TCE with an identical TCE response pattern obtained five weeks earlier on that array (numerous measurements were performed in the intervening period of time). It is clear in this figure that long term MC response reproducibility involving most of the phases is good. In this sense the worst sensor was PIB coated one. Array to array production was not particularly reproducible with regard to response patterns. Thus, each array would need to be uniquely calibrated. With certain modifications of our PVD systems to better control the deposition process we expect array production reproducibility to improve. Specifically, refinement in MC fabrication and the control over phase deposition will lead to improved reproducibility for similarly prepared MCs. By custom fabricating MC we hope to improve on the uniformity e.g., the MC- to- MC variation in the resonance frequency for the commercial MC arrays we have purchased often vary by 15% or more within a given batch.

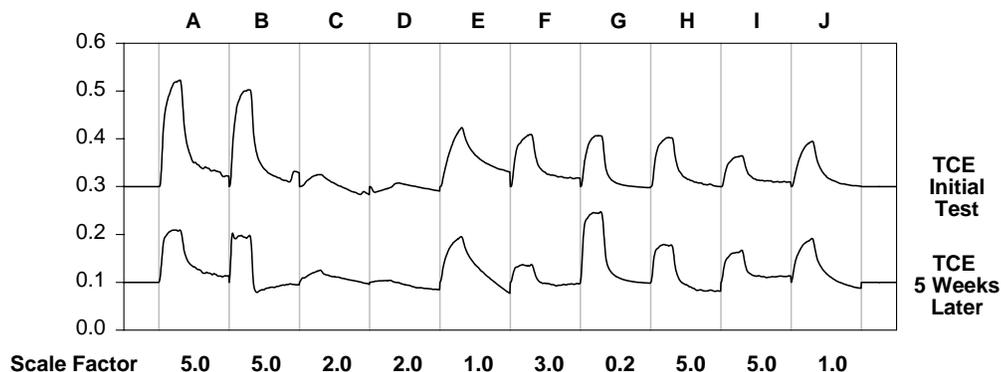


Figure 4. Comparison of the response of the MC array to 10% (v/v) TCE (diluted with nitrogen) with the response of an identical measurement obtained 5 weeks later after multiple measurements. A to J is same as Figure 2.

Plan Activities

We plan to construct an apparatus to serve as rugged and compact prototype for field testing. This includes: the integration of the sampling compartment containing the detector array, and associated analysis, readout, and interface electronics. The performance of the fieldable prototype detector/sensor will be demonstrated under realistic operating conditions

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