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Project Title:
Chemically Functionalized Arrays Comprising Micro and Nano-Ectro-Mechanical Systems for Reliable and Selective Characterization of Tank Waste

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Significant progress was made in 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*. These tasks are listed below in modified form followed by the report on progress.

- Deposit chemically selective phases on model MEMS devices with nanostructured surface layers to identify optimal technological approaches.
- Monitor mechanical (deflection) and optical (SERS) responses of the created MEMS to organic and inorganic species in aqueous environments.
- Explore and compare different approaches to immobilization of selective phases on the thermal detectors.
- Demonstrate improvements in selectivity and sensitivity to model pollutants due to implemented technologies of nanostructuring and multi-mode read-out.
- Demonstrate detection of different analytes on a single hybrid MEMS
- Implement the use of differential pairs of cantilever sensors (coated and reference) with the associated detector electronics which is expected to have an enhanced sensitivity with a low-noise low-drift response.
- Development of methods to create differential arrays and test effectiveness at creating distinctive differential responses.

I. Disordered and Ordered Nanostructuring Technologies for Improved Microcantilever Transduction in the Liquid Phase

A. Significance

The use of microcantilevers (*MCs)* as chemical and biological sensors has increased in recent years. The need to make chemical and biological measurement in aqueous environments highlights a limitation of smooth surfaced *MCs*. The bending of a *MC* is caused by the creation of a differential surface stress between its two sides as described by the Stoney equation. The modulation of surface stress is related to the initial interfacial energy of the surface by the Shuttleworth equation;[1] consult Reference 1 for details. In aqueous environments the initial interfacial energy of a smooth surface is small and this limits the sensitivity of the *MC*. The interfacial energy is further reduced when an organic film is applied to the gold surface. Table 1 shows a comparison of interfacial energies of different interfaces with a gold surface.

Table 1. Interfacial Energies of Different Interfaces with a Gold Surface

Interface	**Interfacial Energy (mN/m)**
Au-Air	>1000
Au-Water	~150
Au-Organic-Water	~25

The use of chemically-selective thin film coatings has been shown to enhance both the chemical selectivity and sensitivity of *MC* chemical sensors. As an analyte absorbs into the coating, the coating can swell or contract causing an in-plane stress at the associated microcantilever surface. However, much of the stress upon absorption of an analyte may be lost through slippage of the chemical coatings on the *MC* surface, or through relaxation of the coating in a manner that minimizes stress to the cantilever. Both ordered and disordered structural modifications of *MC* chemical sensors can improve the stress transduction between the chemical receptor phase and the microcantilever, and increases the effective surface area, thus improving the sensitivity. We investigate the improvement of sensitivity of *MCs* using both disordered and ordered structural modifications to the *MC* surface.

B. Experimental Results

Microcantilever surfaces were modified in three manners. The first method involves the codeposition of gold and silver by physical vapor deposition, followed by a chemical etching step to remove the silver from the surface.[1-3] This "dealloyed" method produces a highly disordered nanostructured surface on one side of the *MC*. The nanostucturing process increased the available surface area and creates a quasi-3-D structure that is colloidal in nature (Figure 1A). This surface was then coated with different receptor phases as either a self-assembled monolayer (SAM) or a thin film of a vapor deposited phase. The phases were either commercially available calixarenes or newly synthesized cyclodextrin phases prepared as part of this project (see below). The responses of these *MCs* to 2,7-dihydroxynaphthalene is shown in Figure 1B. The dealloyed *MC* gives larger responses than smooth surface *MCs* and thicker films give the largest responses. It is important to note that the response for the 50 nm dealloyed film is to a 4-fold lower concentration than the response shown for the 18 nm film on dealloyed and smooth surfaces. In some instances the enahancement in response from nanostructuring exceeded 100-fold.[3]

While the dealloying process produces a highly disordered nanostructured surface, the second manner in which *MC* surfaces were modified involved creating an ordered nanostructured

surface by milling grooves across the width of the *MC* using a focused ion beam (FIB) mill.[7] An example of a milled lever is shown in Figure 2A. As seen in the figure the grooves are positioned approximately every 800 nm and are roughly 400 nm wide. Two different groove depths were milled, 200 and 400nm deep. The grooves covered the 100 μm nearest the base of the 200μm long *MCs*. The entire *MC* was not milled in order to leave an area to efficiently reflect a readout laser beam. The *MCs* were coated with a thin film of cyclodextrin phase by physical vapor deposition and responses to 2,3-dihydroxynaphthalene measured. As seen in Figure 2B the grooved MC outperformed the smooth one. The improvement is a combined effect of confining the receptor phase in the grooves and a reduced spring constant.

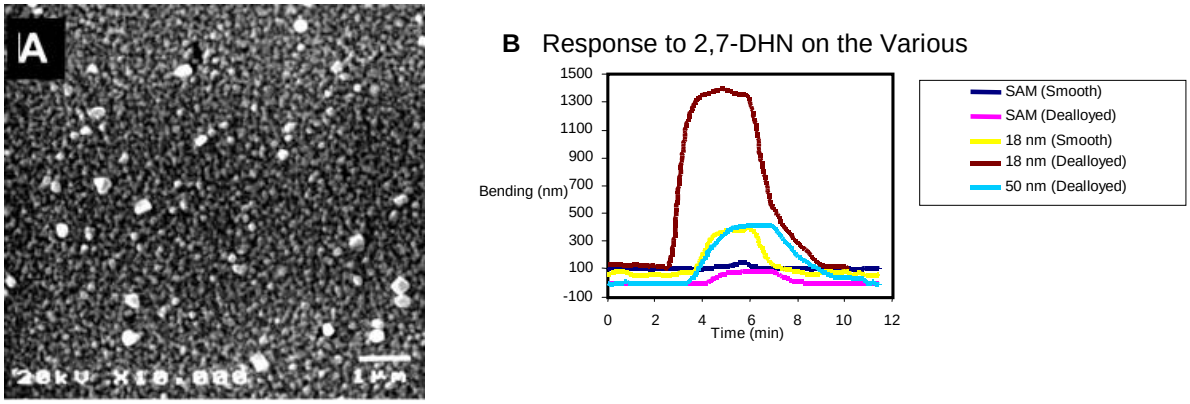

Figure 1. A) SEM image of dealloyed surface. **B)** Responses to 2,7-DHN

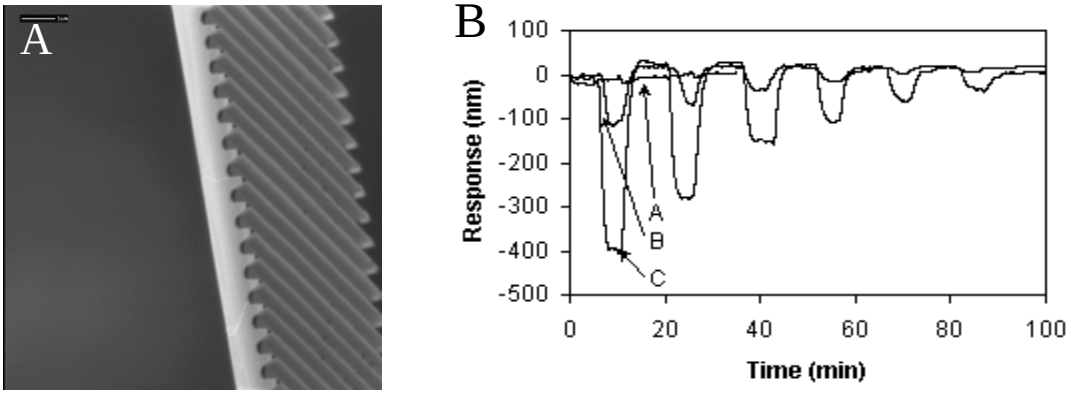

Figure 2. A) Grooved Microcantilever with 400nm deep grooves. **B)** Responses for surface modified microcantilevers to decreasing concentrations (left to right) of 2,3-DHN. (A) Ungrooved, (B) 200nm deep, (C) 400nm deep grooves.

The final method of preparing surface modified *MCs* produces ordered grooves similar to those produced by method 2. The method involves doping regions of the silicon *MCs* with

gallium ion using the FIB. The *MCs* are then etched in a 60% w/w KOH solution. The doped regions of silicon etch at a slower rate than the undoped regions producing V-shaped grooves. In addition to the unique shape of the regular surface structures the processing time is greatly diminished relative to the straight milling procedure. These structures are currently under investigation.

II. Exploring Microcantilever Compatible Surface Enhanced Raman Scattering (SERS) Substrates for Hybrid Sensors

A. Significance

Up to this point little work has been done with *MC*s to allow measurements in complex mixtures or to use *MCs* to acquire structural information. One technique that could be used to obtain structural information is Raman. Both *MC* measurements and Raman spectroscopy techniques use lasers to probe microscopic regions of a surface. In the case of *MCs* the laser is used to monitor the bending, while in Raman it is used to cause an excited state of the molecules absorbed to the surface. While Raman spectra offer a wealth of qualitative information the conventional Raman technique suffers from poor sensitivity. Fortunately, Raman sensitivity can be greatly enhanced by resonance and surface effects. In the latter case, it is found that chemical and electromagnetic enhancement effects produce large increases in Raman signals when analyte are adsorbed onto or very close to certain roughened metal surfaces.[3,4] Since roughened surfaces such as the dealloyed MCs discussed above provide for enhanced bending response, a goal of this work was to determine if these surfaces were also SERS active. The creation of a hybrid *MC-SERS* sensor would have specificity of receptor binding and be able to acquire vibrational signatures of the bound analytes on the surface of the *MC*.

B. Experimental Results

To produce a hybrid *MC-SERS* sensor a good SERS substrate needs to be found that can be used with *MCs*. We have explored several methods of preparing SERS active substrates on *MC* chips. The first SERS substrate investigated was the nanostructured, dealloyed film used previously to enhance *MC* bending. The dealloyed films gave responses that were as good as traditional silver island films on glass when used as SERS substrates. Figure 3 shows several spectra of thiolated compounds on a dealloyed gold surface.[3,4] Excitation was via the 633 nm output of a He-Ne laser. The same dealloyed surface showed significant improvement in SERS activity when a thin layer of silver (which better matches the laser wavelength) was coated over

the dealloyed surface. Another substrate used was a polydimethylsiloxane (PDMS) overcoated with a silver island film. This substrate shows even greater enhancement over the other types of substrates investigated.

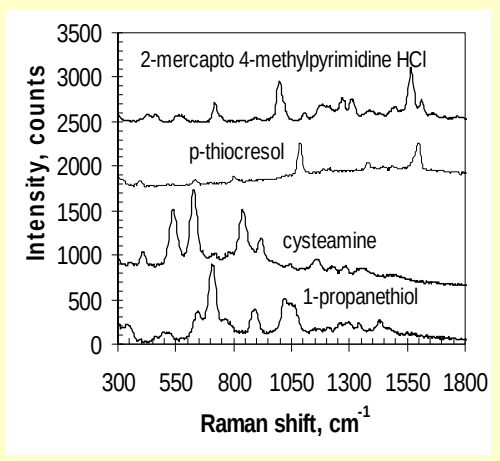

Figure 3. SERS spectra of several Thiolated compounds on a dealloyed Gold roughened surface

To date all of these substrates have shown drawbacks that include photodegradation of the SERS active substrate upon long exposure times and long desorption times of adsorbed molecules from the substrate. We discovered that the photodegredation problem can be overcome by very effectively rastering the laser spot onto new areas of the SERS substrate to prevent photodegredation without loss of signal.[8] The long desorption times of adsorbed molecules is a more complex problem that may require the development of thermal desorption methods. We have also recently demonstrate that metal-polymer nanocomposite SERS substrates out perform more traditional ones.[10]

III. Differential Microcantilever Readout for Improved Reliability and Robustness in Sensing Applications

A. Significance

The current trend in analytical sensing systems is to increase sensitivity and selectivity by employing array based devices. *MC*s are easily miniaturized and can be readily integrated into sensor arrays. These arrays achieve greater sensitivity and a higher degree of selectivity than using a single cantilever due to the reduction of background noise and the use of multiple chemically selective coatings, respectively. There are several key sources of noise that have plagued *MC* based sensing systems since their infancy. Temperature drifts, changes in refractive index, flow rate changes, and mechanical sources of noise are but a few. While some strides have

been made in the area of expanding the number of available selective coatings that can be employed using *MC* sensing systems, there are very few groups employing array based MC sensing systems. A goal of our work was to develop a simple, synchronous dual laser differential optical bending readout mode for *MC* sensing.

B. Experimental Results

The differential based system employs two lasers that are modulated between two adjacent *MC*s (see Figure 4). The reflected laser beams are then directed onto a position sensitive detector and *MC* bending is measured in an AC mode of operation using a lock in detector. This system was developed and compared to simple static bending measurements. Various factors that affect the performance of *MC* based chemical sensors have been studied using both systems. These effects were studied using non-chemically coated, nanostructured silicon array *MC*s so that there would be no chemical difference between the *MC*s that might lead to differences in response. The effect of these factors (i.e. temperature drift, refractive index, flow rate, ionic strength, mechanical noise, etc) has been minimized by using the differential based system. In most cases, the response caused by these factors in the simple static bending system has been decreased by a factor of 10 when using the differential system. Figures 5 shows the effects of sample flow rate on baseline stability with the differential and simple static bending modes of readout.[6]

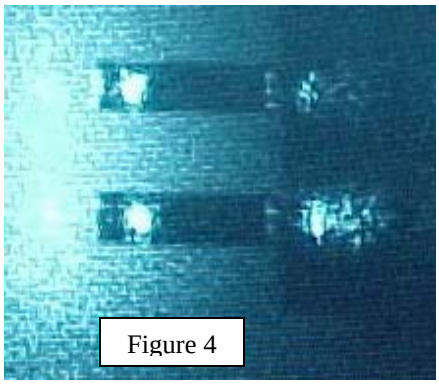
Figure 4

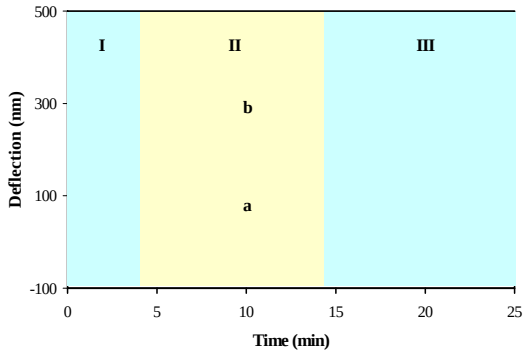

Figure 5. Illustration of the improvement in baseline stability when a simple single cantilever optical arrangement (DC output), **a**, is replaced by a differential (AC output) arrangement, **b**. Baselines were recorded under stagnant (region II) and flow at 1.0 mL/minute (regions I and III) conditions.

IV. Methods of Differentially Applying Novel Macrocycle Receptors to *MC* Surfaces for Selective Measurements of Mixtures

A. Significance

As stated above, *MC*s are well suited to be used as elements in sensor arrays. These arrays lead to a higher degree of selectivity than can be achieved using a single cantilever due to the use of multiple chemically selective layers. In order to impart selectivity when *MC*s are used in analytical sensing, these chemically selective receptor phases are immobilized on one of the sides of the cantilever. Limiting the phase to one side of the *MC* is important because differential modulation of the surface stress is achieved by using asymmetric *MC*s wherein one side of the cantilever preferentially interacts with the analyte via surface *ad*sorption or *ab*sorption into a thin chemical film on the *MC* surface. Ideally, this interaction of the analyte with the receptor phase is reversible and exhibits reasonable kinetics for sensing applications. While it is reasonably simple to coat all of the *MC*s in an array with the same receptor phase, it is quite challenging to coat an individual *MC* in an array with a receptor phase. Therefore, progress in developing simple and reliable methods of coating each *MC* in an array with a different receptor phase is vital to the application of these array-based sensors. Goals of this work include expanding the array of selective phases that are compatible with *MCs* and developing methods to differentially coat those phases onto *MC* array

B. Experimental Results

Since cyclodextrins have been shown to exhibit very good selectivity based on size, shape, and chemical properties we have development methods to functionalize them for use with MCs. The cyclodextrins are tea cup-shaped macrocycle sugars with two secondary hydroxyl groups on each sugar at the upper rim and one primary hydroxyl groups on each sugar at the bottom. We have functionalize the bottom with thio groups to bond to gold coated cantilevers.[1] In addition, the scheme shown in Figure 6 was used to functionalize both the primary and secondary hydroxyls to yield a structure that is thermally labile and stable.[9] The former are used as SAMs and the latter as thin films.

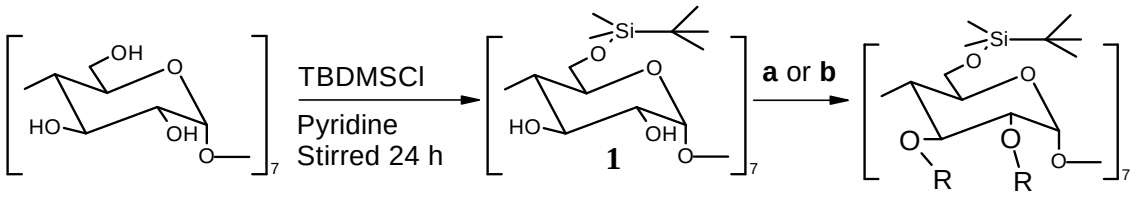

Figure 6. Synthetic scheme to create a cyclodextrin phase that can be vapor deposited onto *MCs*

We report herein two approaches aimed at selectively coating single *MC*s in an array. *MC*s have been coated with various calix[n]arene and functionalized cyclodextrin films using the vapor deposition through a mask procedure. Figure 7 shows the alignment of a *MC* over the slit used in this procedure. As can be seen in the figure, a single *MC* is clearly seen through the mask, while neither of the adjacent *MC*s is visible. This ensures that neither of the two adjacent *MC*s have been coated with the phase that has been applied to the MC shown. This coating approach has been applied to the measurement of a mixture of quinoxaline and 8-hydroxyquinoline in solution by coating two adjacent MCs with calix[6]arene and calix[8]arene, respectively. Calibration curves were obtained for each analyte independently using each phase and response factors were calculated using this data. An unknown mixture of the two analytes was then prepared and measured using the two calix[n]arene phases from above. Figure 8 shows calibration plots for the analysis of quinoxaline (quin) and 8-hydroxyquinoline (hq) on the two different types of *MC*s used, respectively. By using the data presented in Figure 8, the individual components in an unknown mixture could be quantified with associated errors of only 20.7% and 1.6% for the quantification of 8-hydroxyquinoline and quinoxaline, respectively.

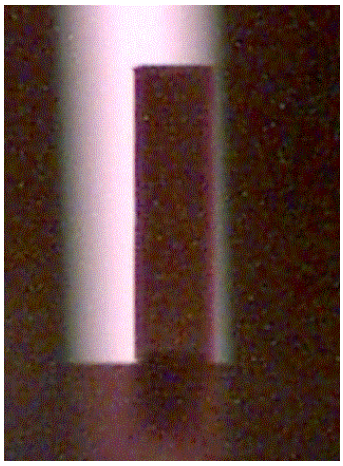

Figure 7. 100 μm wide *MC* from array seen through vapor deposition mask.

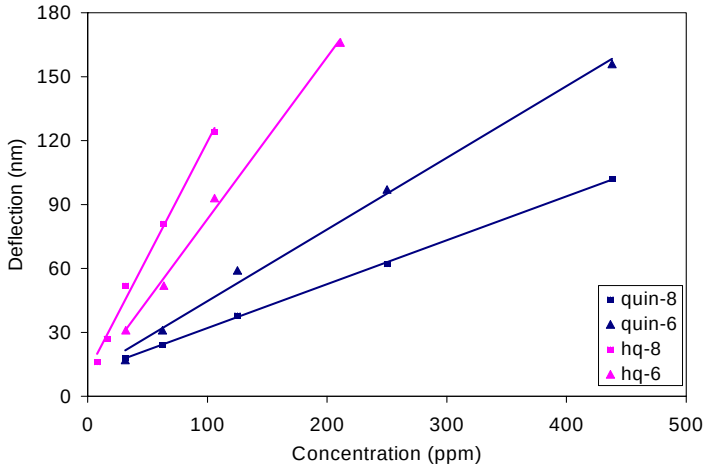

Figure 8. Calibration data for quinoxaline and 8-hydroxy-quinoline on two calix[n]arene phases.

*MC*s have also been coated with various phases utilizing liquid phase reactions with the surface. This approach utilizes a microcapillary filled with the phase to be reacted with the surface. The technique has been used to coat *MC*s with thiolated compounds and compounds of biological interest as well.

Most recently the vapor deposition approach was used to create *MC* arrays with ten different responsive phases in a single array.[12] The phases were a variety of polymers,

macrocyclic compounds, and GC phases. The gas phase responses to VOCs were then observed. This required the implementation of a multiplex vertical cavity surface emitting lasers in an array that matched that of the *MC* array. Details can be found in reference 12. Figure 9 shows the distinctive responses observed for tetrachloroethylene (TCE). The phases are labeled as A-J and the figure also demonstrates the long term stability of this system.

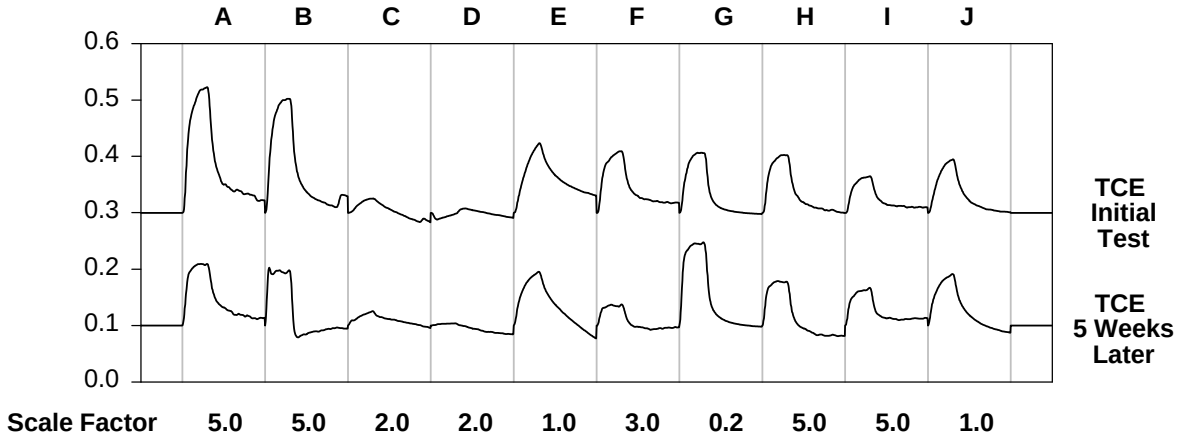

Figure 9. Comparison of the response of the MC array to 10% (v/v) TCE (diluted with nitrogen) with the response of an identical measurement obtained 5 weeks later after multiple measurements.

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