



## Chemicapacitive microsensors for chemical warfare agent and toxic industrial chemical detection

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### Abstract

Detection of chemical warfare agents and toxic industrial chemicals using Microfabrication and microelectromechanical systems (MEMS) chemicapacitive sensors is described. Our sensor chips consist of 10 parallel plates or interdigitated capacitors with an absorbant dielectric material to measure the dielectric constant of an array of selectively absorbing materials. The dielectric permittivity of these polymer filled chemicapacitors changes upon adsorption and desorption of the chemical vapors. Gaseous analytes including chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) have been exposed to our sensors with the results being displayed and discussed below. Sensor performance was characterized through exposure to various CWAs and TICs over a range of concentrations. The limits of detection (LOD) were determined for several chemicals. © 2006 Published by Elsevier B.V.

**Keywords:** Chemical warfare agent; Toxic industrial chemical; MEMS; Capacitance; Permittivity; Polymer; Sensor; Array

### 1. Introduction

The threat of attack from rogue nations and terrorist groups using chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) is on the rise. Thus, there exists an urgent need for reliable detectors for these classes of chemicals. Continuing concerns about utilization of chemical agents in warfare scenarios, as well as past attacks against civilian populations serve as reminders of the existing threats. Proliferation of chemical threats is facilitated by the fact that access to chemicals used to produce dangerous mixes is relatively easy. Many of these chemicals, especially toxic industrial chemicals, are used in legitimate civil applications and are, consequently, readily available.

Toxic industrial chemicals [1] are defined as materials produced in quantities of greater than 30 tonnes in a single facility with toxicity (LC<sub>50</sub> inhalation) of less than 100,000 mg/min/m<sup>3</sup> and an appreciable vapor pressure. TICs are emerging as likely threats because they are readily available, easier to handle than traditional chemical warfare agents and yet

still very toxic. TIC lists are extensive and can be delivered by a wide array of methods in a host of varied environments. Thus, the likelihood of chemical exposures of US citizens, both civilian and military, to this class of toxic chemicals is increasing.

The chemical agent detectors currently fielded are relatively large and expensive. These shortcomings preclude their employment for widespread pervasive deployment. Several of the most important chemical agent detectors are described in Table 1. Note that all of these systems weigh at least 1.7 kg, occupy a volume of at least 2.5 l, and cost at least \$6000. The size and weight of these systems is a significant logistical burden during their deployment. The relatively high cost limits the number of systems that will be deployed. For example, a system that costs several thousands of dollars would likely be deployed at the platoon or team levels leaving individual soldiers or first responders unprotected. The sensor elements described in this paper have been used to produce small, low-power, and lightweight sensor systems (Fig. 1) that could be deployed with individuals, allowing for better protection and faster response in emergency situations.

Microfabrication and microelectromechanical systems (MEMS) technology developed during the past few years has the potential to dramatically reduce the size and weight of chemical agent detectors [8–12]. Seacoast Science's MEMS

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Table 1  
Characteristics of key chemical agent detectors and monitors [2–7]

System	Weight (kg)	Size (cm)	Approximate cost (\$)	Technology	Manufacturer
M43A1	3.4	16 × 14 × 28	6,000	IMS	General Dynamics
M22 ACADA	6.4	17 × 18 × 36	9,000	IMS	Smiths
CAM	1.7	39 × 8 × 14	6,400	IMS	Graseby Dynamics
AP2C	2.2	38.5 × 9 × 14	18,200	Flame photospectrometer	Proengin
Sabre 4000	3.2	36 × 11 × 13	26,000	IMS	Smiths
APD2000	3	10 × 9 × 28	9,600	IMS	Smiths

chemicapacitors can be produced in high volume at reduced cost by simultaneously fabricating multiple sensor elements on silicon in a manner similar to that used to manufacture modern electronics. In this paper we describe the sensitivity and selectivity characteristics of these micromachined chemicapacitors when exposed to CWAs and TICs.

## 2. Experimental

### 2.1. Sensor elements

We have developed two micromachined chemicapacitors; the first has a parallel-plate structure (Fig. 2) that, unlike previous parallel-plate chemicapacitors, has a fixed gap width that makes it possible to construct an array of different capacitors on a single chip. The second type of chemicapacitor used in this study employs elevated interdigitated (IDT) electrodes (Fig. 3). The

sensor chips used in the present studies were fabricated with various geometries and combinations of IDT and parallel-plate capacitors on the same chip using the Multi-User MEMS Process (MUMPs) at MEMSCAP, Durham, NC. These IDT devices are different than the traditional planar metal on insulator structures or even the partially elevated structure described by Hierlemann et al. [13]. Taking advantage of the vertical nature of the polycrystalline silicon fabrication process and the fact that sacrificial layers could be etched from below conductive layers, a set of



Fig. 1. Seacoast Science's SC100 Badge-Size Chemical Warfare Agent detector prototype. Dimensions: 3.3 in. × 2.7 in. × 1 in.; weight: ~8 ounces (220 g) with battery.

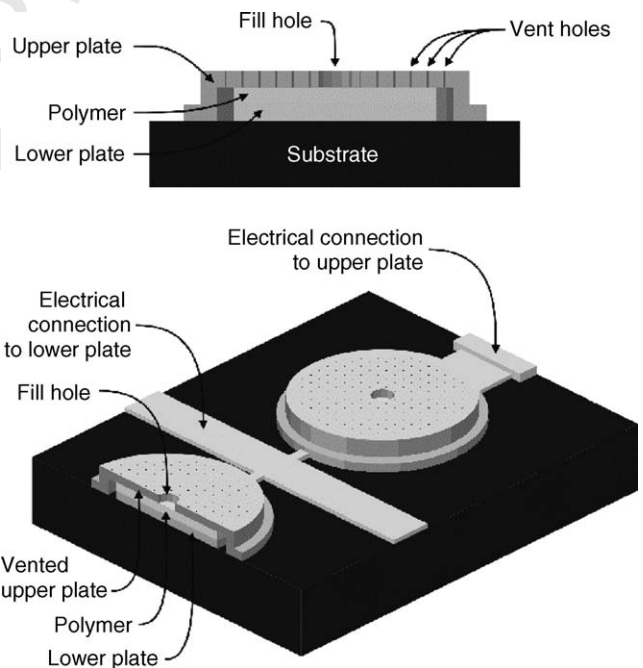


Fig. 2. Cross-sectional diagram of a Seacoast Science parallel plate sensor element.

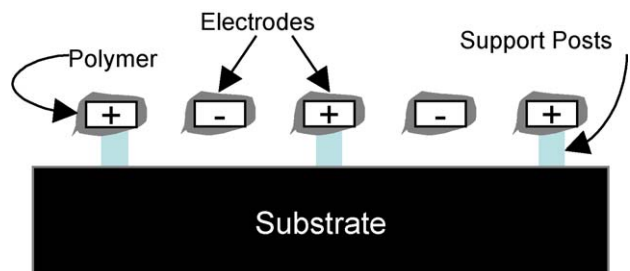


Fig. 3. Cross-section of the IDT design.

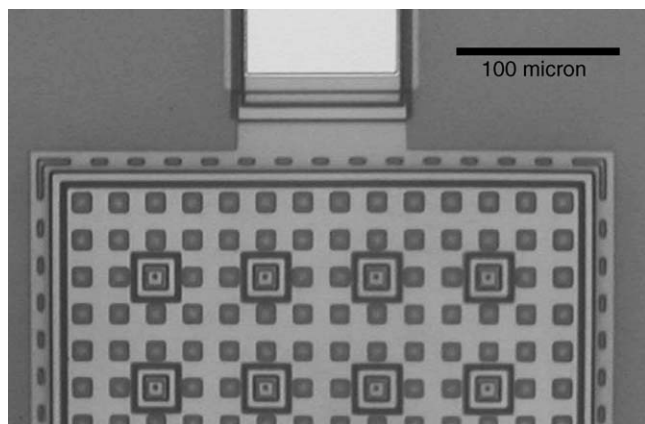


Fig. 4. Close up photo of the parallel-plate capacitor with high “void” density for easy vapor access.

84 elevated beams with periodic support posts or “anchors” were  
 85 constructed to form alternating and interdigitated electrodes.  
 86 The interdigital design provides the greatest amount of vapor  
 87 access to the polymer.

88 The detection and control electronics used to obtain the  
 89 present measurements on all sensor types have been described  
 90 previously [14–17]. In the past we have studied parallel-plate  
 91 chemicapacitors with two different gap spacings, 2 and 0.75  $\mu\text{m}$   
 92 [16]. The 0.75- $\mu\text{m}$  sensors were found to be more sensitive to  
 93 chemicals than the 2- $\mu\text{m}$  sensors. We have since further refined  
 94 the parallel-plate structures by increasing both the number and  
 95 size of openings in the top-plate to provide faster vapor access  
 96 to the sensors. In this study we present data from the 0.75  $\mu\text{m}$   
 97 parallel-plate chemicapacitors (Fig. 4) and the IDT structures  
 98 (Fig. 5).

99 The chips measured 5 mm  $\times$  2 mm and contained 10 chemi-  
 100 capacitors averaging 300  $\mu\text{m}$  in diameter with a 0.75  $\mu\text{m}$  gap.  
 101 Fig. 6 shows the various geometries and relative size of the  
 102 chemicapacitive sensors and 10-sensor chips. Each capacitor is  
 103 coated or filled with a different polymer or other dielectric mate-  
 104 rial using an inkjet.

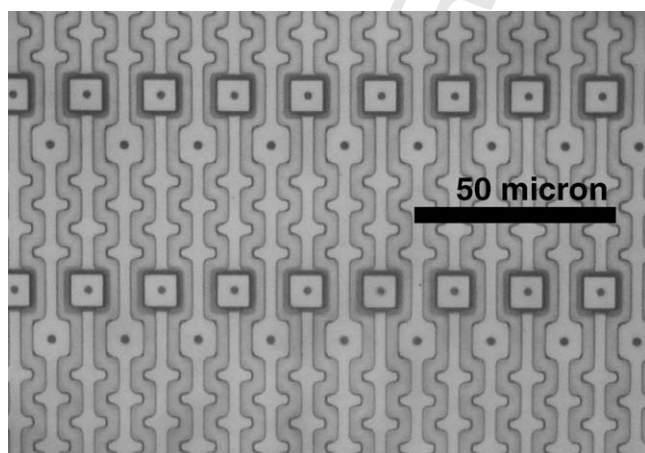


Fig. 5. Close up view of the elevated IDT design.

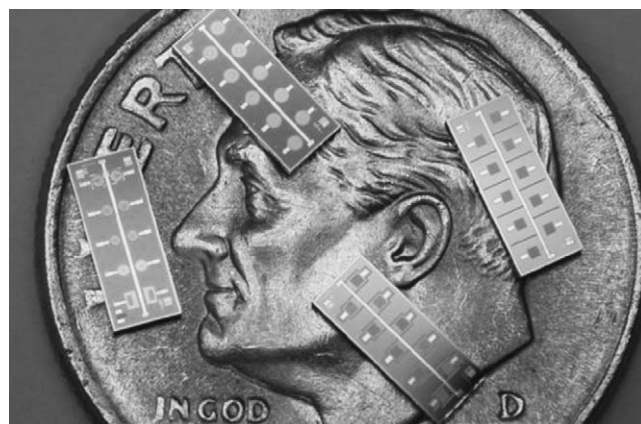


Fig. 6. Photograph of four Seacoast Science MEMS capacitive microsensors on a dime. Each chip contains 10 sensors for 40 total sensors.

## 2.2. Chemosensitive material deposition

105 The chemoselective materials (Table 3) were mixed with  
 106 a suitable solvent (typically 0.1 wt.% in chloroform) and then  
 107 deposited onto the sensors with a manually positioned piezoce-  
 108 ramic inkjet head (Microfab Technologies MJ-AB01-030 30- or  
 109 80- $\mu\text{m}$  dispenser with CT-M3-01 inkjet controller). The inkjet  
 110 head deposits individual droplets from 30  $\mu\text{m}$  to 100  $\mu\text{m}$  diame-  
 111 ter depending on the magnitude and waveform of the applied  
 112 voltage. The solvent evaporates in approximately 0.4 s leav-  
 113 ing the chemoselective material coating on the sensor. Typi-  
 114 cally 20–200 drops are needed to coat a sensor. The sensors  
 115 capacitance was monitored during deposition to ensure  
 116 coating reproducibility. The sensors were subsequently cured  
 117 in an oven at 110  $^{\circ}\text{C}$  for 30–60 min to completely remove  
 118 the solvent. Coatings were typically applied to seven “sig-  
 119 nal” capacitors, leaving one uncoated “reference” capacitor and  
 120 two unused, unconnected capacitors. Coating PAPPs requires  
 121 a slightly different process where a final rinse step follows  
 122 curing.

## 2.3. Readout electronics

123 The readout electronics have been previously described  
 124 [14–17]. In brief, a charge/discharge readout circuit (Fig. 7) on  
 125 an application specific integrated circuit (ASIC) is used, in a  
 126 multiplexed fashion, to measure the capacitance of each sensor  
 127 on the array. The ASIC produces an output voltage  $V_{\text{out}}$  that is  
 128 proportional to the capacitance of each sensor:  
 129

$$V_{\text{out}} = V_{\text{mid}} + \Delta V_{\text{osc}} \times \frac{C_{\text{sensor}}}{C_{\text{feedback}}} \quad (1)$$

130 where  $V_{\text{mid}}$  is a virtual ground voltage,  $\Delta V_{\text{osc}}$  is the ampli-  
 131 tude of the oscillator drive voltage,  $C_{\text{sensor}}$  is the capacitance of  
 132 the capacitive sensor, and  $C_{\text{feedback}}$  is the feedback capacitance  
 133 [14–17]. The sensor and readout ASIC chips were packaged in  
 134 a custom-made dual in-line package (DIP) with the readout chip  
 135 in a hermetically-sealed cavity and the sensor chip in a second,  
 136 exposed cavity.

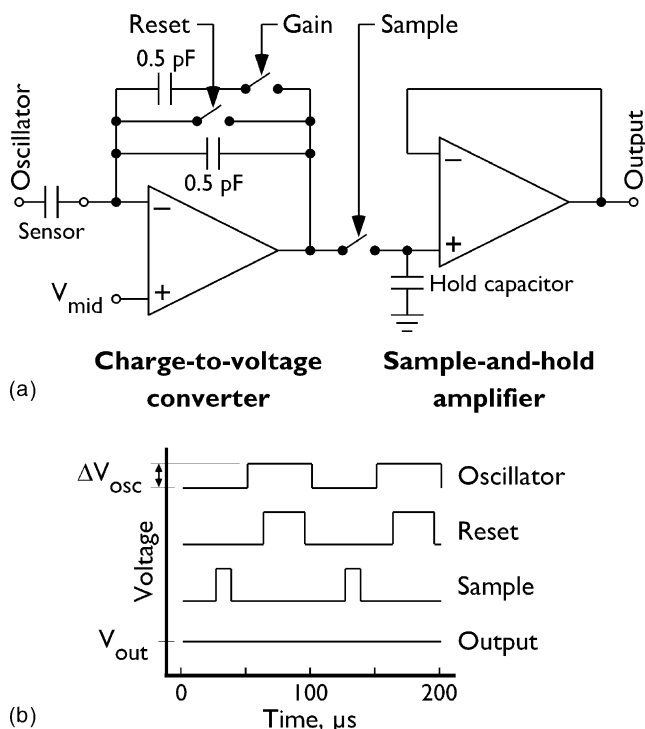


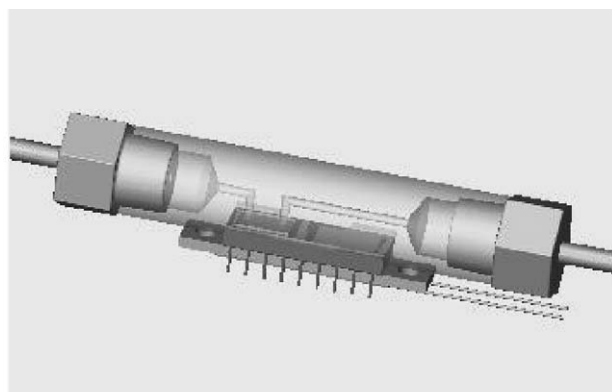
Fig. 7. (a) Diagram of the charge/discharge readout circuit. Opening or closing the “Gain” switch sets the feedback capacitance,  $C_{\text{feedback}}$ , to 0.5 or 1.0 pF, respectively; (b) control and output waveforms for the readout circuit.

#### 2.4. Seacoast sensor test system/analytes

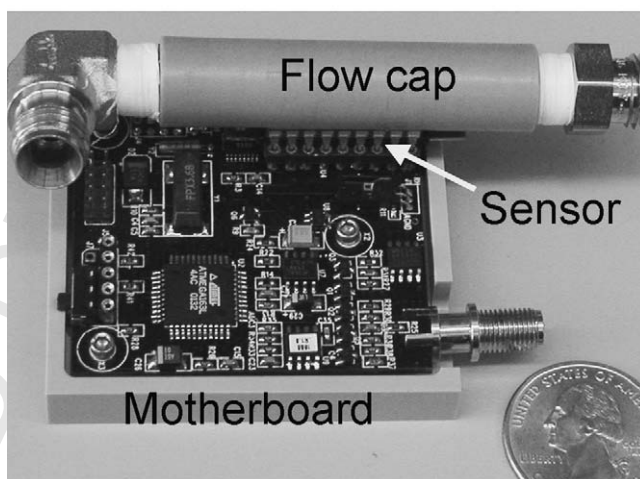
##### 2.4.1. Toxic industrial chemical testing

A vapor delivery system was designed and assembled specifically for accurate delivery of TICS. The toxic chemical vapor delivery/test system features an air-tight heated flow path with a chemical scrubber for safe operation. It is constructed of chemically-resistant materials and with computer control can accurately deliver compressed gasses, volatile and semivolatiles over five orders of magnitude of analyte concentration. Analyte and flow path temperature can be controlled from ambient to 150 °C. The chemical flow path length is approximately 15 cm with 1/16th in. (0.16 cm) inner diameter tubing. The sensor chamber (Fig. 8) volume is approximately 0.05 ml.

Table 2 contains a list of chemicals tested as part of this study. All chemicals (except the chemical warfare agents) were purchased commercially (Sigma–Aldrich Chemical Co., St. Louis, MO, Alfa Aesar, Ward Hill, MA, Fisher Scientific Inc., or VWR International Inc., West Chester, PA) and used as received. Chemical vapors were generated by bubbling nitrogen or air through gas-washing bottles (bubblers) containing liquid chemicals. Solid analytes delivered by placing these materials inside the bubblers and passing air over the headspace. To control the chemical concentration, the glass bubblers were immersed in a water bath; the temperature of the bath could be adjusted to vary the vapor pressure of the chemical. Furthermore, the output of the bubblers was diluted with air or nitrogen metered by mass-flow controllers (MKS Instruments, Andover, MA). A recirculating chiller that pumped water through water-jackets around the chamber regulated the temperature to  $\pm 0.1$  °C of



(a)



(b)

Fig. 8. (a) Transparent SolidWorks drawing of airtight cap fitting for vapor testing. Shows vapor path; (b) picture of machined cap/sensor flow cell: an integral component in the testing of TICS.

setpoint. The chiller had a closed-loop temperature control system regulated by a 4-wire RTD inside the chamber. Humidity inside the chamber was monitored with a Honeywell HIH-3602-C humidity sensor (Honeywell Inc., Freeport, IL).

##### 2.4.2. Chemical warfare agent testing

Chemical warfare agent tests were conducted at the Army’s Edgewood Chemical Biological Center (ECBC) in Edgewood Maryland. Four live agents were used including HD, GB, GA and GD at a concentration range from 0.046 mg/m<sup>3</sup> to 40 mg/m<sup>3</sup>. Two 8-sensor chips were tested simultaneously in a Seacoast Science designed test chamber. The test chamber was connected to the ECBC agent flow system by a 1/4 in. swagelok connector. It formed a tight seal so that all of the gas flowed out the other end of the chamber through a 1/4 in. swagelok connector. The vapor delivery system was contained inside of a large temperature controlled environmental chamber and operated by ECBC personnel.

#### 2.5. Polymers

The sensitivity and selectivity of the chemicapacitor sensors depends on the type and quality of the chemoselec-

Table 2  
TICS and CWAS tested in this study

Chemical name	Chemical class	Formula/molecular weight	Vapor pressure <sup>a</sup> (mmHg) at ambient temperature
Sulfur Mustard (HD)	Mustard Agent	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> S 159.1	0.11
Sarin (GB)	Nerve Agent	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> PF 140.1	2.9
Soman (GD)	Nerve Agent	C <sub>7</sub> H <sub>16</sub> O <sub>2</sub> PF 182.2	0.3
Tabun (GA)	Nerve Agent	C <sub>5</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> P 162.1	0.07
Hydrogen Cyanide (AC)	Blood Agent	HCN 27	Gas
Dinitrotoulene	Explosive	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub> /182.12	1.1 × 10 <sup>-4</sup>
Carbaryl	Pesticide	C <sub>12</sub> H <sub>11</sub> NO <sub>2</sub> /201.2	1.2 × 10 <sup>-6</sup>
Nitrobenzene <sup>a</sup>	Nitro	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> /123.11	1.5 × 10 <sup>-1</sup>
DIMP <sup>a</sup>	Phosphonate	C <sub>7</sub> H <sub>17</sub> O <sub>3</sub> P/180.21	5.9 × 10 <sup>-1</sup>
DMMP	Phosphonate	C <sub>3</sub> H <sub>9</sub> O <sub>3</sub> /P124.08	8.4 × 10 <sup>-1</sup>
Ammonium Hydroxide	Inorganic Base	NH <sub>4</sub> OH/35.04	42.91
Nitric Acid	Inorganic Acid	HNO <sub>3</sub> /63.01	2.7 × 10 <sup>-1</sup>
Allyl Alcohol	TIC	C <sub>3</sub> H <sub>6</sub> O/58.08	21.47
Carbon Disulphide	TIC	CS <sub>2</sub> /76.14	297.57
Phenol	VOC	C <sub>6</sub> H <sub>6</sub> O/94.11	2.2 × 10 <sup>-1</sup>
Methyl Benzoate	VOC	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> /136.15	4.1 × 10 <sup>-1</sup>
Styrene Oxide	VOC	C <sub>8</sub> H <sub>8</sub> O/120.15	3 × 10 <sup>-1</sup>
Acetophenone	VOC	C <sub>8</sub> H <sub>8</sub> O/120.15	2.1 × 10 <sup>-1</sup>
Hydrazine	Rocket Fuel	H <sub>4</sub> N <sub>2</sub> /32.05	10.55
Monomethyl Hydrazine	Rocket Fuel	CH <sub>6</sub> N <sub>2</sub> /46.07	37.49
Dimethyl Hydrazine	Rocket Fuel	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> /60.10	123.03

<sup>a</sup> For most of chemicals we used National Institute of Standards and Technology (NIST) Chemistry WebBook to calculate vapor pressure.

187 tive polymers applied to the sensor [18–27]. These materi-  
188 als have been designed and synthesized specifically to aid  
189 in the detection of the chemicals listed in Table 2. Chemos-  
190 elective materials were synthesized in our chemistry labo-  
191 ratory {propylaminopropyl polysiloxane (PAPPS), siloxane-  
192 fluoroalcohol (SXFA), fluoroalcohol coated gold nanospheres  
193 (AuHFA)} or acquired from Eric Houser [28,29] (HC, Adiol)  
194 at the US Naval Research Laboratory (NRL) or purchased from  
195 commercial sources {polyethylene oxide (PEO), polyepichloro-

hydrin (PECH), polyethyleneimine (PEI), OV225} see Fig. 9 for  
structures of the materials.

Important properties for polymers used with the chemicapac-  
itive sensors include:

- Solubility (products or reactants) in suitable solvents for easy coating of sensors.
- High density of functional groups for best sensitivity.
- Specific functional groups for improved selectivity.

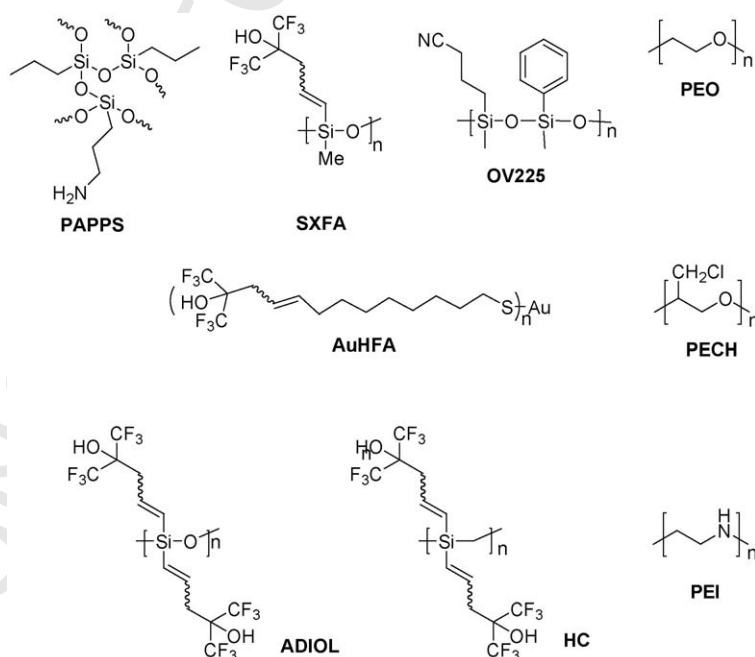


Fig. 9. Structures of chemoselective materials used in this study.

Table 3  
TICS limit of detection

Analyte	Lowest detected concentration (ppm)	S:N	LOD (ppm)	Chemoselective material
Nitrobenzene	0.4	6	0.2	AuHFA
2,6-DNT	0.02	40	0.002	SXFA
Carbaryl	0.0003	15	0.0006	OV225
DIMP	0.62	125	0.015	Adiol
Allyl alcohol	86	6.25	41.0	SXFA
Carbon disulphide	1600	6.7	720	PECH
Phenol	1.85	490	0.01	PEO
Methyl benzoate	3.7	55	0.2	HC
Styrene oxide	2.8	19	0.44	HC
Acetophenone	1.8	45	0.12	SXFA
Hydrazine	140	22	19	PEI
Monomethyl Hydrazine	50*	36.7	4.1	PEI, PAPPS
Dimethyl hydrazine	38	62.5	1.8	PEI, PAPPS
Hydrogen cyanide	100	12	25	PAPPS
Ammonia	884	25	110	AuHFA

- Reversible analyte binding so that sensor can be used for multiple exposures.
- High viscosity liquid or rubbery solid is the best physical property for vapor sorption.
- High thermal and chemical stability for long-term use.
- Stable interfaces with substrate for reduced sensor drift.
- Ability to selectively form weak reversible chemical interactions (hydrogen bonds, van der Waals bonds, and dipole-dipole interactions) with a particular analyte.

Polymers and synthesis precursors were purchased from Polysciences Inc. (Warrington, PA), Scientific Polymers Inc. (Ontario, NY) or Sigma–Aldrich Chemical Co. (St. Louis, MO).

### 3. Results and discussion

#### 3.1. Response characteristics

Chemicapacitors can exhibit a linear response, particularly when detecting chemicals at low concentrations and when used to measure humidity [30–32] but often their response is nonlinear. McGill et al. [20] have suggested that the response is nonlinear because as the films absorb an analyte, its ability to bind more analyte is reduced. Another contributing factor to the nonlinear response may be that as the polymer swells, the reduced polymer density between the parallel plates and IDT fingers causes a decrease in permittivity. This swelling effect counters the effect of adding a polar analyte and the resulting combination of factors may not be linear with concentration.

The chemicapacitor sensitivity to volatile organic compounds is generally comparable to that of other polymer-based VOC sensors. We have observed that the chemicapacitors typically have sufficient sensitivity to detect common industrial solvents below 100 parts per million (ppm) [33]. However, the chemicapacitor is compatible with a wider range of chemoselective coatings thus, expanding the range of detection to include other

classes of chemicals including many toxic industrial chemicals and inorganic gases.

#### 3.2. Toxic industrial chemicals

Table 3 shows the lowest concentration of several toxic industrial chemicals that we have detected with polymer-filled capacitors. Many of the values in Table 3 reflect the lowest concentration that our test system can deliver, rather than the lowest concentration the sensor can detect. Theoretical limits of detection (LOD) have been calculated using a signal to noise limit of 3:1.

Calibration curves were generated for four of the toxic industrial chemicals tested (Fig. 10). These curves can be used to set response levels on the prototypes. As an example of the data from which Fig. 10 was generated, Figs. 11 and 12 show the sensor responses to various concentrations of dinitrotoluene and ammonia. The concentrations are approximated from literature vapor pressure values [34].

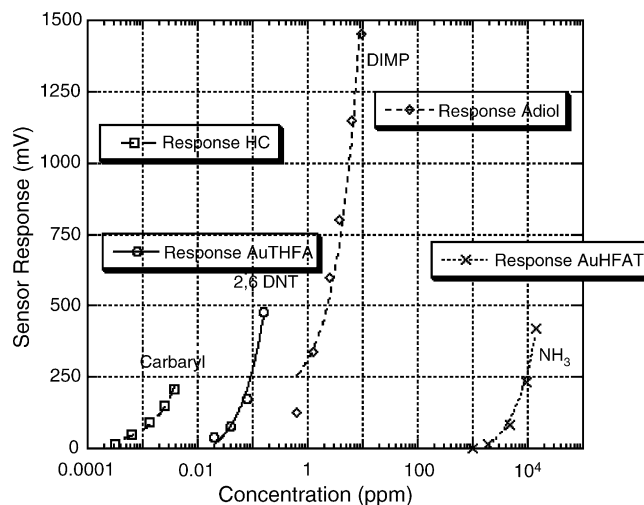


Fig. 10. Calibration curves indicating sensor response magnitude for dinitrotoluene (DNT), ammonia (NH<sub>3</sub>), carbaryl and diisopropylmethylphosphonate (DIMP).

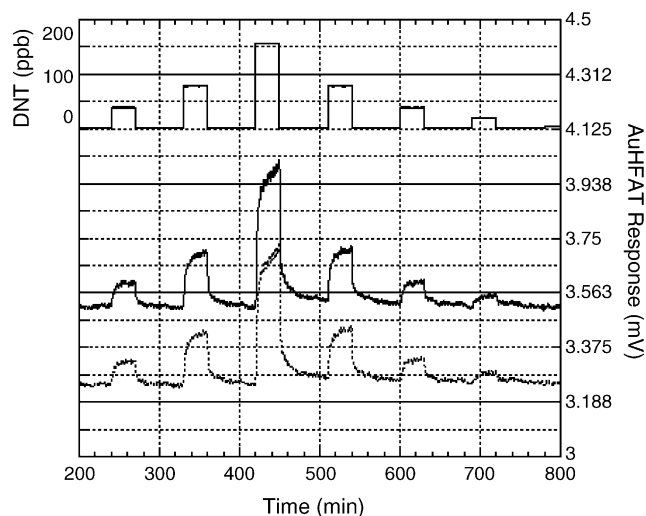


Fig. 11. Response of an AuHFAT coated capacitor to increasing and decreasing concentrations of DNT in a background of dry nitrogen. The sensor was at 20 °C and the peak-to-peak noise level was 1.0 mV.

### 3.3. Chemical warfare agents

The polymer filled chemicapacitors displayed reversible responses to all exposures of chemical warfare agents tested at ECBC, and calibration curves were generated for each of the four chemical warfare agents tested (Fig. 13, Table 4). Hydrogen cyanide (HCN) was exposed to PAPPS films resulting in a measureable capacitance shift, however, unlike the “G” and “H” agents detected by the polymer films, the PAPPS coatings require heating to show any appreciable response to HCN. We speculate that an acid/base interaction is the cause of the reversible change in capacitance (see Fig. 14). The optimal temperature for detection with this coating appears to be 90 °C (Table 5). The sensors were then exposed to three different concentrations of HCN for 10 min at four different temperatures.

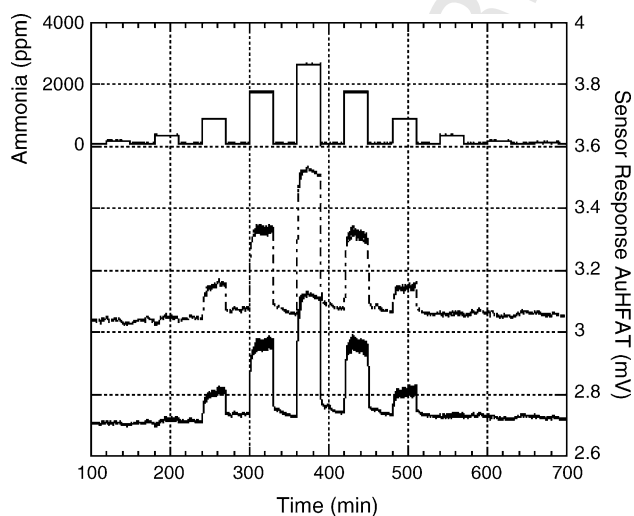


Fig. 12. Response of two AuHFAT coated capacitor to increasing and decreasing concentrations of ammonia in a background of dry nitrogen. The sensor was at 20 °C and the peak-to-peak noise level was 1.0 mV.

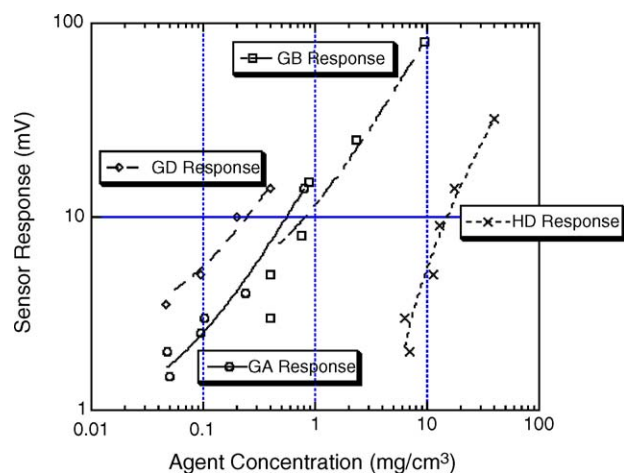


Fig. 13. Calibration curves indicating sensor response magnitude for Sarin (GB), Soman (GD), Tabun (GA) and Sulfur Mustard (HD).

Table 4  
Limit of detection for chemical warfare agent exposures

CWA	LOD <sup>a</sup> (mg/m <sup>3</sup> )	LCt 50 <sup>b</sup> (mg min/m <sup>3</sup> )	Polymer	S:N <sup>c</sup>
HD <sup>a</sup>	6.3	1500	SXFA	155:1
GA	0.048	400	Adiol	20:1
GB	0.4	100	HC	10:1
GD <sup>a</sup>	0.047	50	SXFA	5:1
AC	100 ppm	2500	PAPPS	20:1

<sup>a</sup> Limit of detection.

<sup>b</sup> Vapor or aerosol exposure necessary to cause death in 50% of the population.

<sup>c</sup> Signal to noise.

### 3.4. Response times

As mentioned in Section 2, we are using an optimized parallel-plate structure with a larger number and size of top-plate openings than in previous work [16], the result is both easier filling of the structure, and faster equilibration with the ambient environment, due to shorter diffusion distances, allowing for faster sensor responses. To further increase response speeds, the elevated interdigital electrode design was created, providing the

Table 5  
PAPPS coated sensor response (mV) at various temperatures

Temperature (°C)	Concentration HCN (ppm)	Sensor response (mV)
30	100	0
	500	15
	1000	25
50	100	0
	500	17
	1000	35
70	100	2
	500	15
	1000	20
90	100	12
	500	23
	1000	40

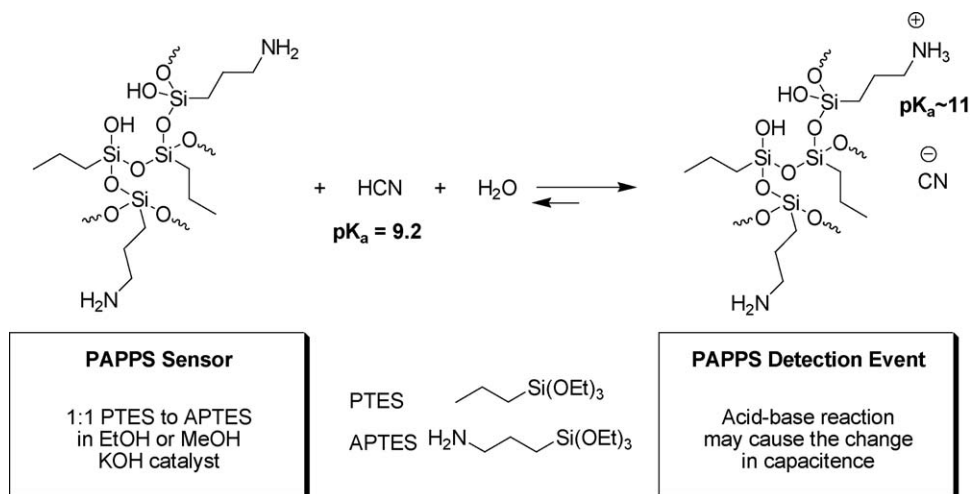


Fig. 14. The reversible reaction between PAPPS and HCN.

greatest amount of vapor access to the polymer. Fig. 15 shows a comparison of the responses of the two sensor designs, parallel-plate and IDT coated with the same chemoselective polymer and exposed simultaneously to the same concentrations of diisopropyl methyl phosphonate (DIMP). From these results we can determine that the new IDT sensors are slightly less sensitive but respond much faster than the parallel plate sensors.

Initial tests were performed using a very faster vapor delivery system. These tests were aimed at characterizing the lower limits of time of response as well as general sensor response to various common solvents and target analytes. The chemicapacitor sensor package was fitted with a small volume PEAK sensor enclosure (approximately 0.1 ml). The PEAK enclosed sensors were operated at temperatures up to 100 °C. Using Helium as a carrier gas, flow rates were set and recorded (typically from 25 cc to 100 cc). Detection and clearout takes less than 3 s for most volatile and semivolatile chemicals. Fig. 16 shows full scale

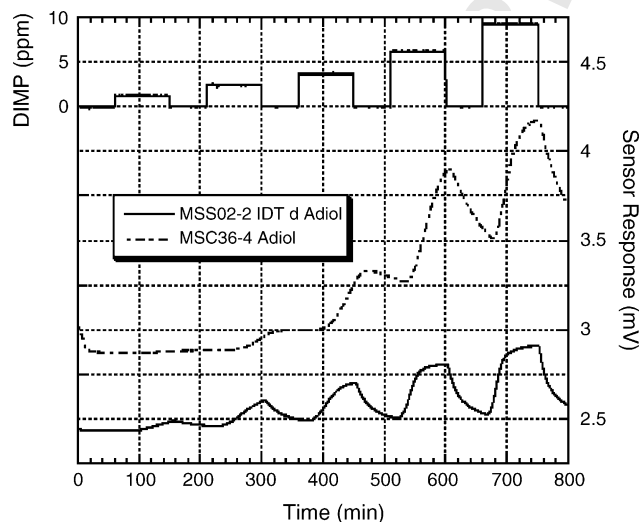


Fig. 15. Comparing sensor response of two MEMS capacitor sensors both coated with Adiol. The IDT sensor response much faster than the 2  $\mu$ m gap parallel plate sensor.

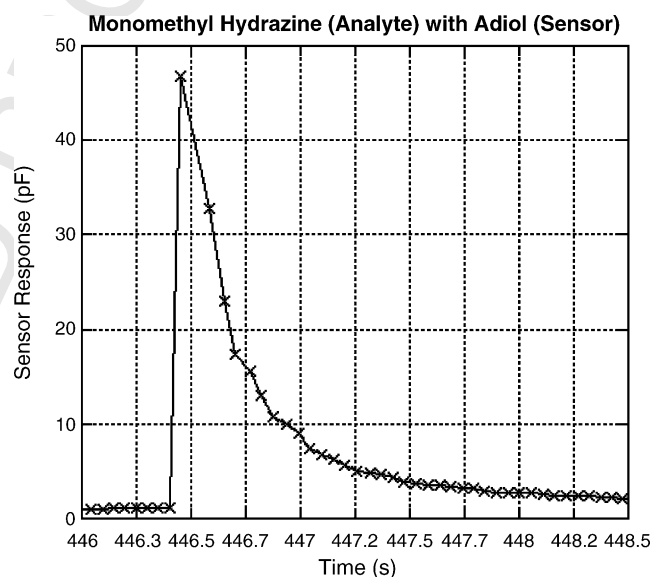


Fig. 16. Adiol coated IDT sensor response to a pulse of Monomethyl Hydrazine. Full scale sensor response takes place in approximately 50 ms. Complete desorption requires approximately 2 s.

response of our sensors to a monomethylhydrazine exposure in less than 50 ms.

Testing of the IDT devices demonstrates improved response times but lower sensitivity when compared to the parallel-plate devices for some chemoselective materials. This is due to the fact that the IDT geometry results in a lower fraction of electric field lines passing through the polymer [35]. Conversely, parallel-plate capacitors are more complex to manufacture, and they have a longer response time because the polymer is partially covered with the capacitor plate, reducing the surface area available for vapor exchange [35,32].

#### 4. Conclusions

We have established the viability of Seacoast Science's capacitive sensors by demonstrating detection of three classes of

chemical warfare agents and several toxic industrial chemicals. We accomplished this through the preparation of new sensor designs and the fabrications and testing of new chemoselective materials.

We have shown that micromachined, parallel-plate capacitors can be filled with polymers and used to detect chemical warfare agent and toxic industrial chemicals. Chemicapacitors are uniquely selective among polymer-based VOC sensors in that they offer selectivity due to the characteristic electrical properties of the analyte in addition, to the selective sorption due to the polymer/analyte interactions. This unique sensitivity of chemicapacitors to analyte permittivity can potentially lead to sensor systems with improved selectivity. In addition, smaller gaps lead to thinner polymer films and therefore faster response. Thus, the ideal gap dimension is the smallest that can be filled with polymer. We have successfully filled capacitors with 0.75  $\mu\text{m}$  gaps, which is the narrowest gap achievable with the MUMPs process. Over a testing period of several months, we have not observed differences in the stability of capacitors with a 0.75  $\mu\text{m}$  or 2  $\mu\text{m}$  gap.

The output of a chemicapacitor reflects the permittivity of its selectively absorbing dielectric. The sensor responds to chemicals when the dielectric absorbs an analyte, causing its permittivity to change. Hierlemann et al. [13] have previously hypothesized that a complex combination of response phenomena occurs and that the degree of change depends on four factors: (1) dielectric chemical structure modification from reversible weak interactions (hydrogen, dipole, van der Waals) with the analyte; (2) the amount of swelling that the dielectric undergoes upon absorbing the analyte (swelling reduces the density of dipole moments within the polymer, and therefore the permittivity of the polymer); (3) the permittivity of the analyte being absorbed; and (4) the amount of analyte that absorbs into the dielectric.

For some chemoselective material/analyte combinations, swelling dominates the sensor response, and the overall capacitance decreases, while with other combinations, with a higher permittivity analyte, the capacitance increases. This effect has been observed in several polymers with a variety of permittivity values [16], resulting in a relative sensitivity pattern that shifts direction depending upon the polarity of the polymer and analyte and on the polymer's ability to swell.

Following vapor absorption and polymer swelling the electric field will then pass through a polymer with lower density than in its neat state. Therefore, swelling alone would cause the capacitance to decrease. In contrast, the absorption of any analyte without concurrent swelling, whether it has a higher or lower dielectric constant than the polymer will increase the capacitance of the device, because it is an additive effect. The capacitance of the device upon vapor exposure can thus, either increase or decrease, depending upon whether the swelling or chemical absorption dominates.

In general, high-permittivity analytes produce larger responses than low-permittivity analytes. Also it has been observed, that low-permittivity analytes are more difficult to sense because they only produce small responses when they are absorbed. This can impart some difficulties when discrimi-

nating between a low concentration of a high-permittivity analyte and a high concentration of a low-permittivity analyte when using a single sensor. For applications where discrimination of multiple possible analytes is necessary, it is possible to compare the responses of several sensors using advanced response classification techniques to identify an unknown analyte.

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