

# 2000 R&D 100 Award Entry Form

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- f. **Affirmation:** I affirm that all information submitted as a part of, or supplemental to, this entry is a fair and accurate representation of this product.
- Submitter's signature \_\_\_\_\_

2. **Joint submitter:**

N/A

3. **Product name:**

Adaptive Photomechanical Chemical Sensor (APCS)

4. **Product description:**

The Adaptive Photomechanical Chemical Sensor (APCS) is a miniature device that can sense extremely small amounts of chemicals. It uses photons to enhance mechanical stresses in chemical microsensors induced by molecular adsorption.

5. **Eligibility**

**This product was first marketed/available for order:**

APCS first became available for licensing in 1999.

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6. **Inventor or principal investigator**

See the attached list.

7. **Product price:**

\$500

8. **Patent information**

a. **Patents held**

Yes \_\_\_\_\_ No  X

b. **Patents pending**

Yes  X  No \_\_\_\_\_

c. **Patents held by others**

Yes \_\_\_\_\_ No \_\_\_\_\_

“Detection of Chemicals Using Photo-induced and Thermal Bending in MEMS Sensors,” ERID 0624, March 1999.

“Uncooled Infrared Photon Detector and Multicolor Infrared Detection Using Microoptomechanical,” U.S. Patent 05977544 (1999).

“Chemical Detection Using Calorimetric Spectroscopy,” U.S. Patent 05923421 (1999).

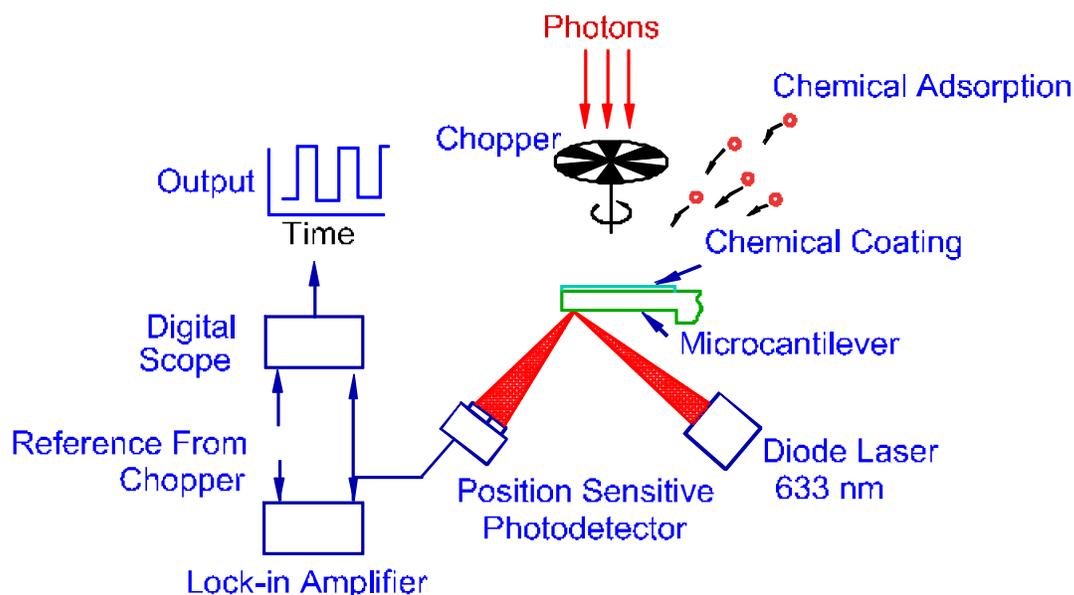
9. **Function**

The Adaptive Photomechanical Chemical Sensor (APCS) is a device that can sense extremely small amounts of chemicals. APCS is a gravimetric-based device that uses photons to enhance (or simply change) molecular adsorption and/or molecular-adsorption-induced mechanical stresses in microsensors. **The heart of the APCS device is a semiconductor microstructure that responds to optically modulated molecular adsorption.** Gravimetric-based micromechanical chemical sensors respond to chemical stimuli by undergoing changes in their bending and resonance frequency even when a small number of molecules are adsorbed on their surfaces.

When molecules adsorb on the surface of a microstructure they introduce a differential surface stress. These mechanical stresses depend on molecular adsorption and on whether photons are impinging on the semiconductor microdevice. The response of such a microstructure to chemicals (and photons) is depicted schematically in Fig. 1. Surface stresses  $s_1$  and  $s_2$  are balanced at equilibrium. These stresses become unequal upon exposure to chemicals, producing a bending force,  $F_z$ , that displaces the tip of the microstructure.

For this method of chemical detection we need accurate measurements in positional changes of the microdevice. Positional changes can be readily determined with extremely high sensitivity by a number of methods, including optical, capacitive, piezoresistive, and electron tunneling [1]. Although optical-based detection means (see Fig. 2) possess high sensitivity, piezoresistive readout schemes can be readily implemented in large arrays of APCS devices. However, this requires the APCS

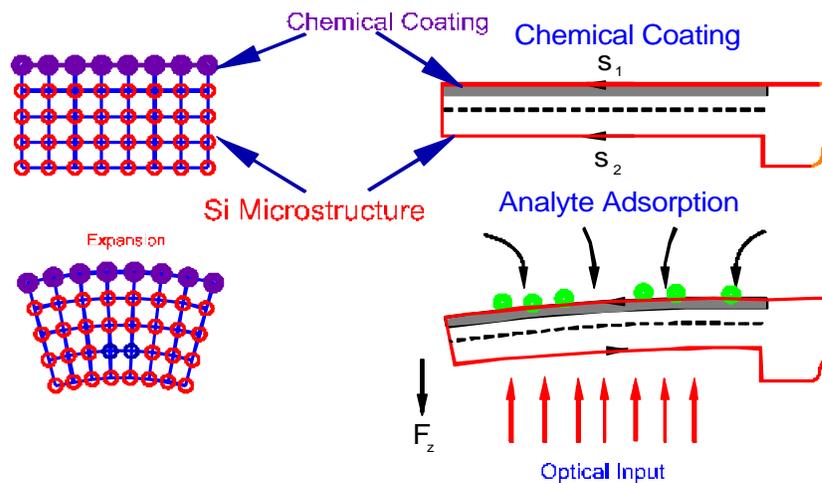
devices to be piezoresistive. In Fig. 3, we show an example of piezoresistive devices that can be used to implement large arrays of APCS devices.



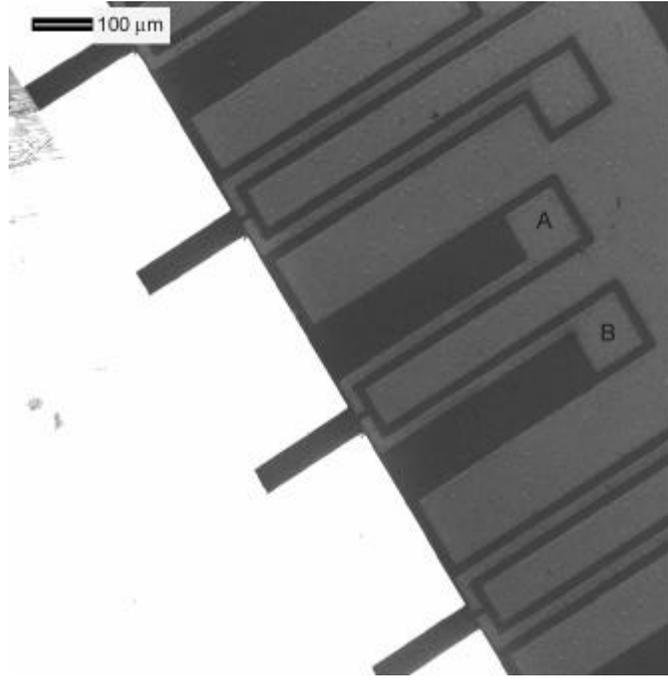
**Fig. 1. Schematic diagram depicting the bending response of a microstructure to chemical adsorption and photon irradiation. Surface stresses  $s_1$  and  $s_2$  are balanced at equilibrium but become unequal and cause bending upon adsorption of analyte molecules. A force along the z-direction is induced due to the differential surface stress, which causes the microstructure to change its radius of curvature. Optical input can be used to enhance (or simply change) molecular adsorption or adsorption-induced stresses.**

Traditional gravimetric chemical sensors achieve specificity with the use of chemically selective coatings. Selective coatings have been used in many different types of gravimetric sensors to sorb various gaseous analytes. **The APCS utilizes photons to produce changes in the chemical coating layer prior to (or during) chemical exposure.** Microstructures that have undergone photo-induced bending will adsorb molecules on their surfaces differently, mainly because of the preexisting surface stress generated by the photons. However, microstructures that have adsorbed molecules will undergo photo-induced bending that depends on the number of absorbed molecules on the surface. Depending on the photon wavelength and microstructure material, the microstructure can be made to bend by either expanding or contracting. This is important in cases where the photo-induced stresses can be used to counter any adsorption-induced stresses and increase the dynamic range. Although coating the surface of the microstructure with different materials can provide chemical specificity, by choosing appropriate photon wavelengths we can alter the chemical selectivity due to a differentiated photo-enhanced response.

Microstructures will also undergo bending by absorbing photons [2,3]. The photo-induced bending is caused by the differential surface stress developed between the top (side exposed to photons) and the bottom (unexposed side) of the microstructure. For the same number of photons absorbed, the photo-induced bending will differ for microstructures that have adsorbed different amounts of chemicals on their surfaces. This is a consequence of the fact that adsorbed molecules introduce surface stresses themselves. Therefore, microstructures that have adsorbed molecules on their surfaces will undergo photo-induced bending that depends on the amount of analyte present on their surface. When the photo-induced bending is used as the detection method, the chemically selective coating does not have to be restricted to only one surface, as is traditionally the case for other gravimetric chemical sensors [4–8]. Coating both sides with a chemically sensitive layer will essentially increase (double) the effective area available for adsorption of analytes. Since these microstructures are also very sensitive temperature sensors, care should be taken to account for bending due to heat dissipation. One approach would be to employ reference cantilevers that are not exposed to analytes and to perform differential measurements.



**Fig. 2.** Schematic of the setup that will be used to determine the photo-induced bending of microstructures exposed to analytes. In this arrangement the diode laser with  $\lambda=790$  nm (or 1400 nm) is used for photo-enhanced bending due to molecular adsorption-induced stress. The diode laser with  $\lambda=633$  nm is used to measure the deflection of the microstructure.



**Fig. 3. A small array (4 × 1) of piezoresistive Si microstructures with a thin layer of Al. In these devices, electrical resistance changes when they undergo bending. Each microsensors can be addressed by electrically connecting to its pads (indicated for one of them by A and B).**

In a semiconductor microstructure, the generation of “free” charge carriers (electrons and holes) via photon irradiation results in the development of a local mechanical strain [2,3]. This additional strain adds to other strains resulting from temperature changes of the semiconductor. In a semiconductor structure of thickness  $t$  and energy bandgap  $g_g$ , the change in total surface stress,  $\Delta s$ , due to photogenerated excess charge carriers,  $\Delta n$ , and changes in temperature,  $\Delta T$ , will be the sum of the additional photo-induced stress,  $\Delta s_{pi}$ , and thermal stress,  $\Delta s_{th}$ , viz. [2,3]

$$\Delta s = \Delta s_{pi} + \Delta s_{th} = \left( \frac{1}{3} \frac{dg_g}{dP} \Delta n \right) E + \alpha \Delta T E \quad (1)$$

where,  $dg_g/dP$  is the pressure dependence of the energy bandgap,  $\alpha$  is the coefficient of thermal expansion, and  $E$  is the Young’s modulus. When  $dg_g/dP$  is negative the photo-induced stress is of opposite sign than that of the thermal stress and will tend to make the semiconductor crystal contract. It is the photo-induced stress that can modulate molecular absorption or absorption-induced stress.

For a rectangular bar (Figs. 1 and 3) of length  $l$ , width  $w$ , and total thickness  $t$ , the maximum displacement  $z_{max}$  of the microstructure is given by [2,5, 9–11]

$$z_{\max} = \frac{l^2}{t_1+t_2} \left( \frac{1+(t_1/t_2)^2}{3(1+t_1/t_2)^2 + (1+t_1E_1/t_2E_2)(t_1^2/t_2^2 + t_2E_2/t_1E_1)} \right) \frac{E_1}{E^*} \left( \frac{d\varepsilon_g}{dP} \Delta n + \alpha \Delta T \right) \quad (2)$$

where,  $t_1$  and  $t_2$  are, respectively, the thicknesses of the substrate and the coating,  $E_1$  and  $E_2$  are the Young's moduli of the substrate and the coating. The first term inside of Eq. (2) is due to photo-induced surface stress and the second term is due to thermal stress caused by temperature changes.

Assuming that an incident radiant power,  $M_e$ , in a semiconductor microstructure generates a number density of excess charge carriers,  $n$ , we get

$$\Delta n = \eta \frac{\lambda}{hc} \frac{\tau_L}{lwt} \Phi_s \quad (3)$$

where  $\eta$  is the quantum efficiency,  $h$  ( $=6.625 \times 10^{-34}$  J s) is Planck's constant,  $c$  ( $=3 \times 10^8$  m s<sup>-1</sup>) is the speed of light, and  $\tau_L$  is the lifetime of the carriers in the semiconductor. Then the maximum displacement  $z_{\max}$  can be rewritten as

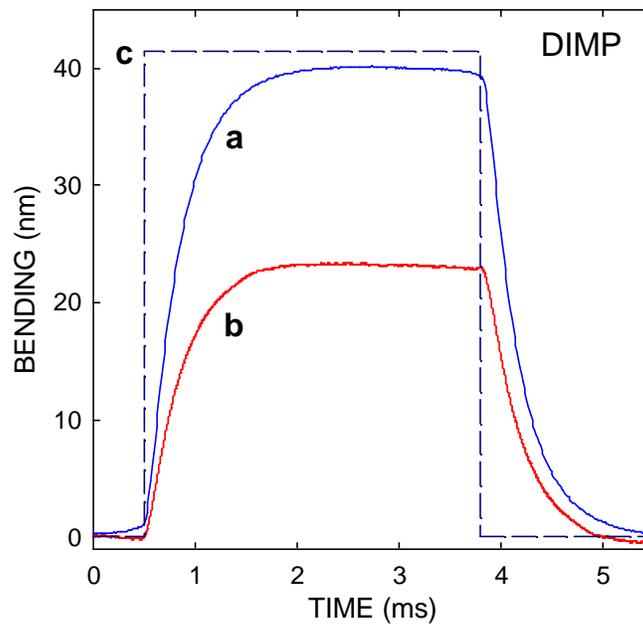
$$z_{\max} = \frac{l^2}{t_1+t_2} \left( \frac{1+(t_1/t_2)^2}{3(1+t_1/t_2)^2 + (1+t_1E_1/t_2E_2)(t_1^2/t_2^2 + t_2E_2/t_1E_1)} \right) \times \frac{E_1}{E^*} \left( \eta \frac{d\varepsilon_g}{dP} \frac{\lambda}{hc} \frac{\tau_L}{lwt} \Phi_s + \alpha \Delta T \right) \quad (4)$$

When this is applied to chemical sensing, the approach provides a fast and efficient method to detect the presence of target molecules as they adsorb on a microstructure surface.

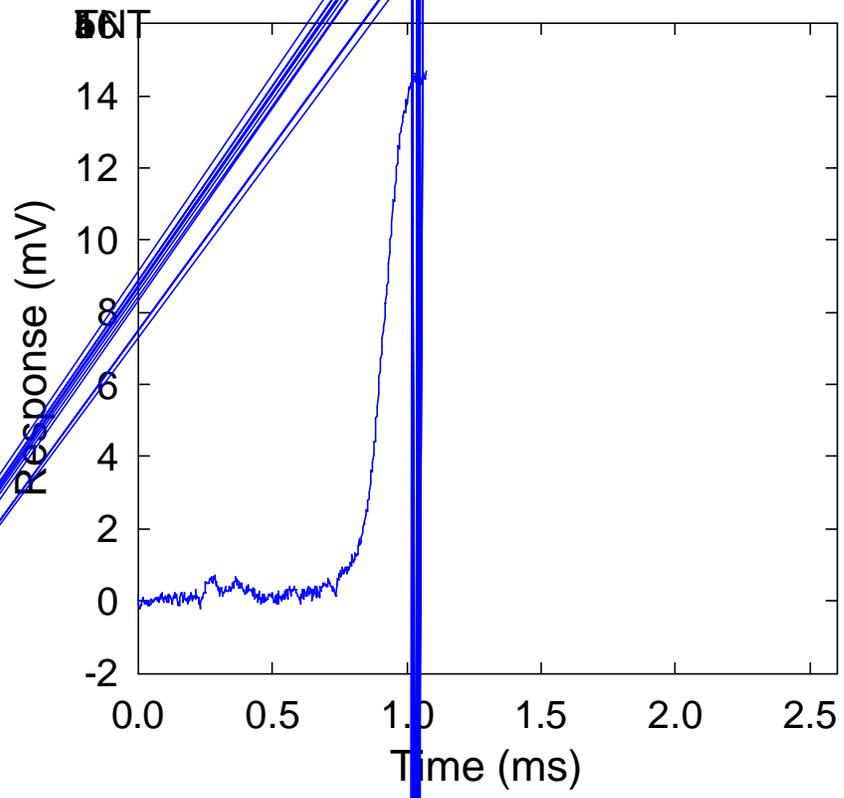
We used gold-coated Si microstructures to detect diisopropyl methylphosphonate (DIMP) and trinitrotoluene (TNT) employing the photo-enhanced bending effect. Depending on the photon wavelength and microstructure material, the bending can be in either direction. During the exposure of the microstructure to DIMP we did not detect any changes in the resonance frequency ( $< 0.1$  Hz) of the microstructure and put a limit on the adsorbed mass of less than  $1 \times 10^{-9}$  g/cm<sup>2</sup>. In Figure 4 we plotted the photo-enhanced response of the microstructure before and after exposure to DIMP vapor.

Because of the very low vapor pressure, adsorption-induced stress will be very small for TNT since only a small number of molecules will be adsorbed on the surface. We measured the photo-enhanced stress both before and after exposure to TNT using a 10 mW diode laser. In Fig. 5 we plotted the photo-enhanced response of the microstructure before and after exposure to TNT vapor. As it can be seen from Fig. 5, the photo-induced bending depends on the presence of TNT molecules on the surface. We found that the photo-induced bending decreases as more TNT molecules adsorb on the surface of our detector. In order to get an estimate of the number of TNT molecules actually adsorbed on the gold-coated microstructure surface, we measured the resonance frequency of the microstructure before and after it was exposed to TNT molecules. We estimated an upper limit on the adsorbed mass of TNT of less than  $10^{-16}$  g or fewer than  $3 \times 10^7$  adsorbed molecules.

Both the selectivity and sensitivity can be tailored using the photo-enhanced stress in semiconductors and we believe that this limit can be extended to well below parts per trillion.



**Fig. 4. Photo-enhanced bending of a gold coated microstructure (a) with no analytes adsorbed and (b) exposed to DIMP. The dashed curve (c) shows the amount of time the microcantilever was exposed to photons that caused the observed photo-induced bending. During the exposure time no measurable change in the resonance frequency was observed.**



- [7] T. Thundat, E. A. Wachter, S. L. Sharp, and R. J. Warmack, "Detection of Mercury Using Resonating Microcantilevers," *Appl. Phys. Lett.* **66** (1995).
- [8] J. Janata, *Principles of Chemical Sensors* (Plenum, New York, 1989).
- [9] F. J. von Preissig, "Applicability of the Classical Curvature-stress Relation for Thin Films on Plate Substrates," *J. Appl. Phys.* **66**, 4262 (1989).
- [10] S. Tomishenko, *Theory of Plates and Shells* (McGraw-Hill, 1940).
- [11] G. G. Stoney, "The Tension of Metallic Films deposited by Electrolysis," *Proc. Royal Soc. London A* **82**, 172 (1909).

## 10A. The competition

Present-day chemical detection and characterization technologies are based primarily on adaptation of laboratory instruments. For example, many spectroscopic methods have been introduced during the past twenty years that are based upon methods such as optical absorption, laser scattering, luminescence, atomic fluorescence spectroscopy, or changes in refractive index. Most chemical characterization instruments do not have sufficient sensitivity to analyze small concentrations. In addition, they are expensive and complicated, sample preparation is long and complicated, and analysis times are relatively long.

There are a number of excellent competing technologies on the commercial market. The closest competing technologies that we could compare our chemical sensor are discussed briefly below. The first device, the NET+PEL/D Gas Sensor available from Sensitron Srl, is a catalytic type of chemical sensor. This chemical sensor is based on oxidation of a hot-wire sensing element. The sensing element is a platinum filament covered with a special catalyst for oxidizing combustible gases. This spindle-shaped element is 0.8 to 1.0 mm in length and 0.5 to 0.6 mm in diameter. A chemical reaction (oxidation) occurs when a combustible gas reaches the surface of the sensing element, which is kept at 300 to 400°C. This oxidation causes a rise in the temperature of the element proportional to the specific energy of the detected gas. This temperature rise is then transmitted to the platinum heater coil, which in turn causes an increase in the electrical resistance of the wire.

The second instrument is based on changes of electrical conductivity due to chemical interactions. This system, available from Siemens Electromechanical Components GmbH & Co. KG, is a gas sensor based on gallium oxide. Gallium oxide is a semiconducting metal oxide, the conductivity of which changes upon interaction with reactive gases. The operating temperature of the sensor chip lies between 600 and 900 °C. To achieve optimal selectivity and sensitivity (methane, propane, butane,

hydrogen) the sensor must be operated at a sensor chip temperature of 800°C, which corresponds to a heating resistance of 68 W.

The third competing sensor is based on ultraviolet photon absorption technology. The device is rather bulky and requires a relatively large power supply. This type of product is available from Cole-Parmer and is used as a small (suitcase-size) transportable gas analyzer. This instrument has an ultimate detection sensitivity of 10 ppm.

## 10B. Comparative matrix

**Table 1. Comparison of the APCS with its closest competition**

Product	ORNL APCS	NET+PEL/D <sup>a</sup>	V23990-C1210-A <sup>b</sup>	P05500-20 Gas Analyzer <sup>c</sup>
Principle of operation	(Photon-enhanced) molecular adsorption-induced surface stresses in microsensors	Hot wire (catalytic) type	Electrical conductivity changes	UV absorption/photometry
Detection limit (ppm)	<0.001–100	10–100	0.1–100	10–100
Gas/liquid operation	Yes	No	No	No
Response time (s)	0.5–1	10	5	1
Detection mode	AC or DC	DC	DC	DC
Integrating sampling mode	Yes	No	No	Yes
Sensor area (mm <sup>2</sup> )	0.15 × .050	0.5 × 1	1.4 × 2.2	
Dimensions (in. <sup>3</sup> )	4 × 3 × 2	3 × 2 × 1	0.85 × 0.31 × 0.5 <sup>d</sup>	6 × 12.5 × 4.5
Weight (lb)	1	0.5	0.5	5
Operating temperature (°C)	! 50–500	300–400	600–900	300
Continuous operation	Yes	Yes	Yes	Yes
Readout	Digital/analog	Digital	Digital	Digital/analog
Expected lifetime (years)	10	10	10	15
Annual maintenance costs (\$)	<50	< 100	>500	> 200
Consumption (W)	0.05	300	1000	1000
Power	12 V dc	2.6 V dc	5 to 10 V dc	110/200 Vac
Price (\$)	500 <sup>e</sup>	500	450	3500

<sup>a</sup> NET+PEL/D available from Sensitron Srl, via A. Manzoni 19, 20010 - Pogliano M.se (MI), Italy.

<sup>b</sup> V23990-C1210-A Combustible Gas Sensor available from Siemens Electromechanical Components, GmBH & Co, KG Gustav-Heinemann-Ring 212, D-81739, Munich, Germany.

<sup>c</sup> P05500-20 Gas Analyzer available from Cole Palmer Instrument Company, Niles, Illinois.

<sup>d</sup> Sensor head dimensions not including electronics.

<sup>e</sup> Price does not reflect the cost of the required palmtop computer.

## 10C. Improvements upon competitive products or technologies

Present-day chemical detection technologies are based primarily on adaptation of laboratory instruments. They are expensive and complicated to use, sample preparation is long and complicated, and analysis times are relatively long. The technology used in the APCS device can provide real-time monitoring in a cost effective manner and can reach much lower detection thresholds in both gas and liquid environments.

- The ORNL APCS determines the presence of extremely low levels of chemical vapor in the air with a sensitivity that is 1000 times better than other comparable chemical detection instruments in the market. It has high sensitivity and a large dynamic range. The sensitivity is in the sub-part-per-billion level, and the dynamic range spans six orders of magnitude.
- The recent availability of high-performance micromechanical detectors allows APCS to detect extremely small amounts of chemicals.
- The APCS provides real-time response (response time < 1 s). Moreover, its micromechanical detector can be easily reset by heating, and because of the low thermal masses involved, each heating cycle can last less than 1 s, allowing continuous chemical monitoring and characterization.
- The modest power requirements allow the whole device to be powered by batteries.
- The APCS sensing element is less than one-tenth the size of other competing products and weighs less than 1 lb. The detector's size and weight make it ideal for portable field applications.

## 11A. Principal applications

The principal applications of APCS are the detection and identification of target molecules in the following areas:

- environmental monitoring,
- explosives detection (airport security),
- natural gas sensing, and
- chemical warfare agents detection.

## 11B. Other applications

The APCS can also be used in the following applications:

- personal dosimeters for toxic gases or metal vapor;
- air-quality monitors in airplanes, mines, or other closed spaces;
- monitoring and characterization in the U.S. Department of Energy's weapons facilities;
- industrial hygiene monitoring;
- industrial process monitoring;
- indoor air-pollution monitoring;
- engine exhaust monitoring; and
- smoke and fire constituent detection.

The ORNL APCS has direct application to virtually any type of chemical detection. Although the product is currently engineered to operate in air, operation under water or in viscous environments is also possible, making it a versatile miniature chemical sensor for many environments.

## 12. Summary

Chemical microsensors that are sensitive, chemically selective, fast, rugged, and low-cost are desirable in numerous applications. Gravimetric-based chemical microsensors suffer from the fact that they require highly selective chemical coatings that are often difficult to find and implement. APCS makes it possible to tailor the response characteristics of a given coating by using photo-induced stress in semiconductor microstructures. This is a revolutionary step towards the coupling of the physical and chemical properties of a microdevice to enhance chemical sensing. The APCS technology requires only a handful of chemical coatings, and by changing their reaction properties, it can achieve both high chemical selectivity and sensitivity.

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