

# Metal-Insulator-Metal Ensemble (MIME) Chemical Detectors

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## ABSTRACT

A new class of nanometer-scale, low power, solid-state devices is being investigated for the detection of hazardous vapors. These chemical vapor sensors are comprised of nanometer-sized gold particles encapsulated by monomolecular layers of alkanethiol surfactant deposited as thin films on interdigitated microelectrodes (Fig. 1). These new, alkylthiol-stabilized, gold nanocluster materials are appropriately categorized as metal-insulator-metal ensembles (MIME). When chemical (agent, hazmat) vapors reversibly absorb into these thin MIME films, a large modulation of the electrical conductivity of the film is observed. The measured tunneling current between gold clusters is extremely sensitive to very small amounts of monolayer swelling or dielectric alteration caused by absorption of vapor molecules. For chemical agent simulants, a large dynamic range (5-logs) of sensitivities is observed and extends down to well below sub-ppm vapor concentrations. Tailored selectivities of the sensors are accomplished by incorporation of chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure. Current research efforts are focused on examining the molecular mechanism(s) of conduction and mapping the selectivity and sensitivity of sensor elements. Targeted applications include: low-cost, low-power CB agent sensors, filter residual life indicators and orthogonal detector applications.

## 1. SENSING PRINCIPLE

Chemical vapors, reversibly absorbing into these thin films, effect large changes in the electrical conductivity of the film (Fig. 1). Tunneling currents between gold clusters are extremely sensitive to

very small amounts of monolayer swelling or dielectric alteration caused by absorption of vapor molecules. Response times are extremely fast for monolayers. Selectivity depends on chemical functionalization of the alkanethiol. For simulants, a large dynamic range (5-logs) of sensitivities is observed and extends down to well below sub-ppm vapor concentrations.

## 2. CONCEPT

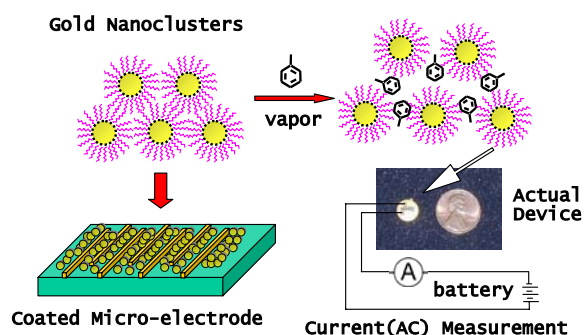


Fig. 1. MIME nanosensor concept.

## 3. NANOCLUSTER SIZES

Individual nanoclusters (Fig. 2) are prepared by the controlled reduction of gold chloride in the presence of suitable alkylthiols. As colloidal gold particles form, a monomolecular layer of alkylthiol molecules adsorbs on their surface producing a highly stable dispersion of uniformly sized gold particles. Colloidal dimensions

(nanometers) are determined by the molecular ratio of gold to alkylthiol reactants.

Cn/(X:Y)	(1:3)	(1:1)	(3:1)	(5:1)	(8:1)	R <sub>Shell</sub> (nm)
C <sub>16</sub>						1.0
		8 x 10 <sup>-11</sup>		1 x 10 <sup>-8</sup>	4 x 10 <sup>-7</sup>	
C <sub>12</sub>						0.80
	2 x 10 <sup>-9</sup>	1 x 10 <sup>-8</sup>	5 x 10 <sup>-8</sup>	1 x 10 <sup>-6</sup>	3 x 10 <sup>-6</sup>	
C <sub>8</sub>						0.60
	5 x 10 <sup>-9</sup>	1 x 10 <sup>-6</sup>	7 x 10 <sup>-6</sup>	2 x 10 <sup>-5</sup>		
C <sub>6</sub>						0.50
	8 x 10 <sup>-8</sup>	6 x 10 <sup>-6</sup>	2 x 10 <sup>-4</sup>	6 x 10 <sup>-4</sup>		
C <sub>4</sub>						0.40
	2 x 10 <sup>-6</sup>	2 x 10 <sup>-4</sup>				
R <sub>Core</sub> (nm)	0.65	0.88	1.2	1.8	2.4	

Fig. 2. Sizes & conductivities of gold nanoclusters.

As might be expected for unfunctionalized thiol ligands, electrical conductivities (ohm-cm<sup>-1</sup>) of these nanoclusters increase with an increase in core size or a decrease in ligand shell thickness.

#### 4. SENSOR RESPONSE

Tailored selectivities of MIME sensors can be accomplished by incorporation of chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure. Differing responses are observed for the various functionalized MIME coatings. In some cases, in fact, a conductivity *increase* is observed upon exposure. This was observed for several phosphorus and nitrogen-containing compounds (viz., Fig. 3).

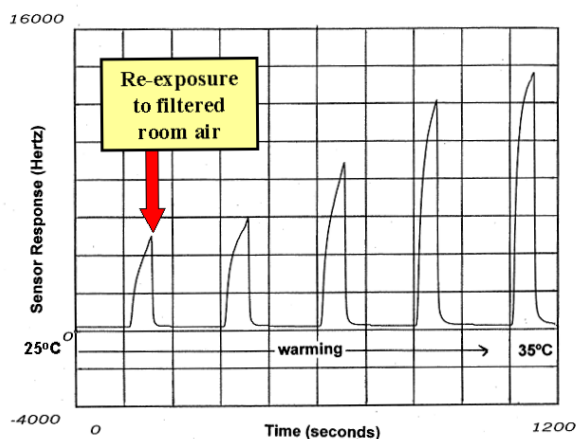


Fig 3. Headspace detection - 5% TNT in sand.

#### 5. ADVANTAGES

Some significant advantages of this sensor class include:

- Low power devices (microwatts)
- Reversible sensing activity
- Fast responding (vis-à-vis polymer films)
- Large array size possible (minimal crosstalk)
- Large dynamic range (4-6 logs)
- Low humidity response

#### 6. POTENTIAL APPLICATIONS

Potential applications (a non-exhaustive list) which are suggested include:

- Handheld chemical vapor monitors
- Drop-off/expendable chemical sensors
- Filter residual life indicators
- Orthogonal detector applications
- Explosives detectors

#### 7. PROTOTYPE



#### 8. ACKNOWLEDGEMENT

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#### 9. REFERENCES

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