Microelectromechanical Systems (MEMs) Chemical Sensors

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OUTLINE

INTRODUCTION

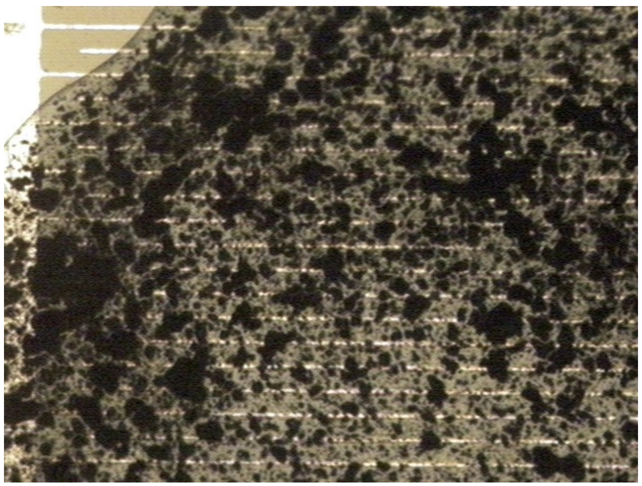
Physical Sensor - device that measures temperature, pressure, flow, light intensity, acceleration, motion, etc.

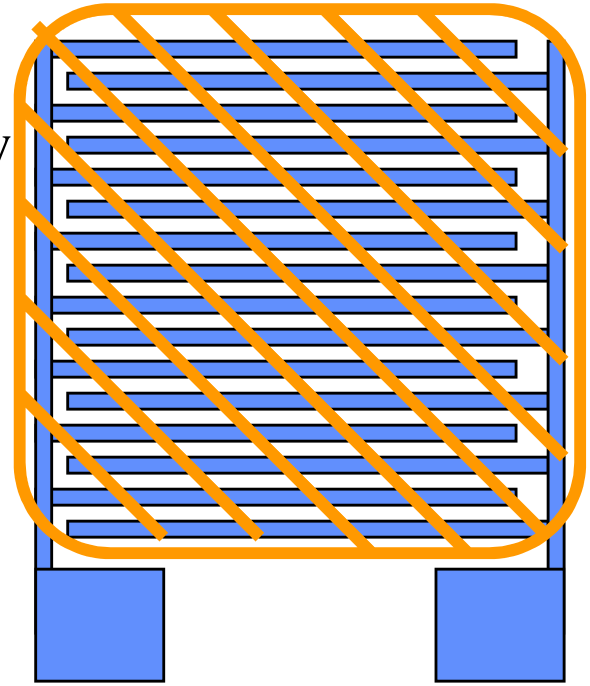
Chemical Sensor - measures chemical nature of its environment, while it may contain a physical sensor, it is usually incorporates a chemically selective membrane, film or layer.

Biological Sensor - a sensor that incorporates a biological entity (enzyme, antibody, bacteria, etc.)
or
Physical or Chemical that is used in bioanalytical measurements, sometimes called a **Bioprobe**. For example a pressure sensor used to measure blood pressure or a chemical sensor used to measure chemical concentrations in urine.

CHEMIRESISTOR

Simple interdigitated electrodes coated with a chemically sensitive layer that changes the resistance in response to a few ppm of some (or many) chemicals

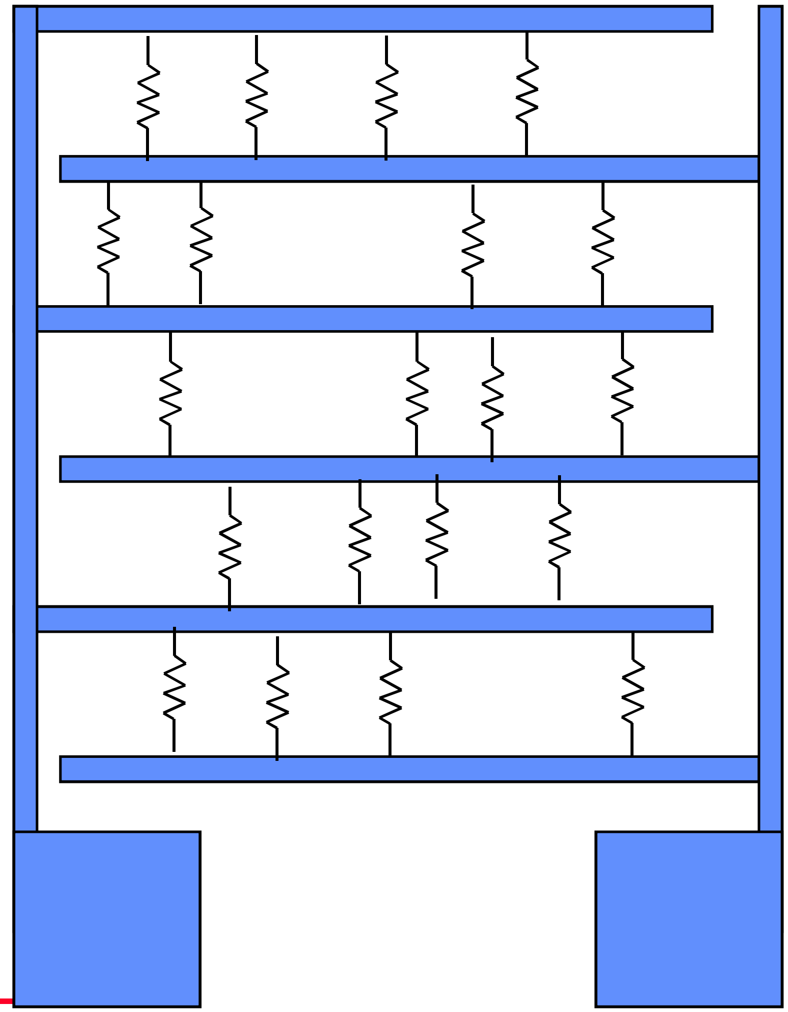




Resistor with
25µm gaps
25µm length
7250µm width

For example: carbon black mixed with polymer, the polymer swells breaking some of the carbon black connections increasing resistance of the sensor

MODELING OF PARALLEL RESISTANCE CHANGE



If each resistor is identical with value equal to 400 ohms, what is the total resistance?

Answer 20 ohms

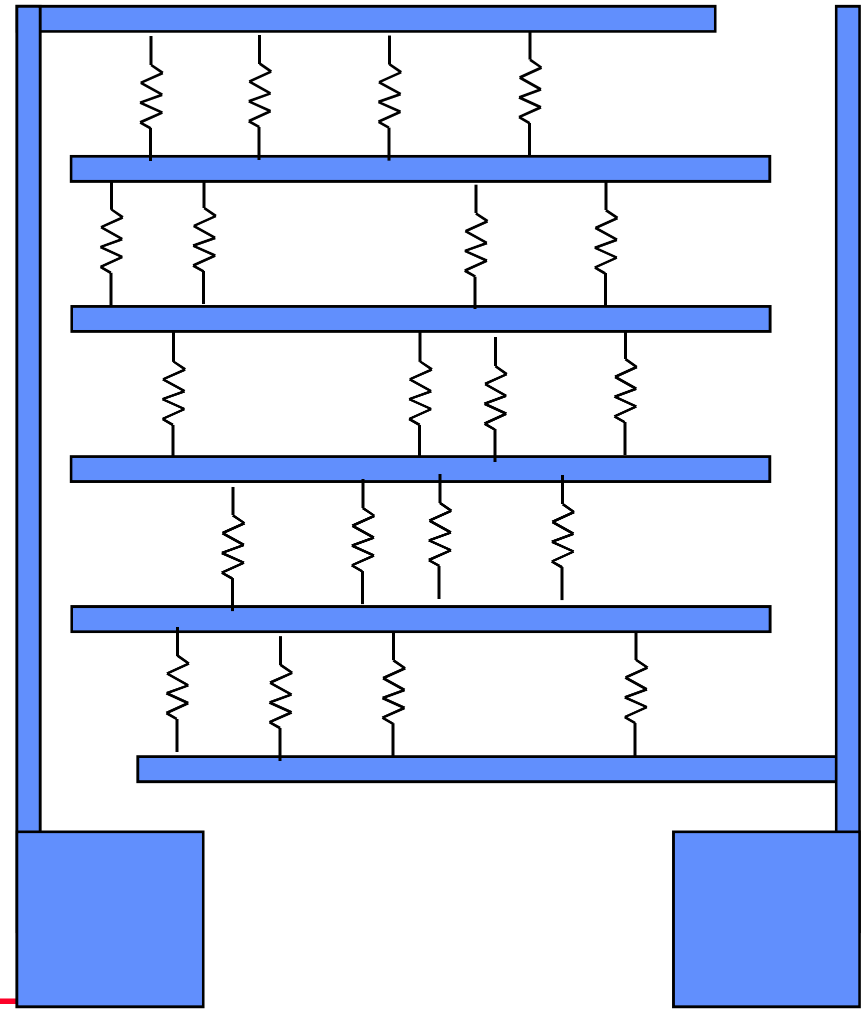
If two of the resistors in each row open circuits, what is the total resistance?

Answer 40 ohms

If two resistors in one row open circuits, what is the total resistance?

Answer 22.22 ohms or 11%

MODELING OF SERIES RESISTANCE CHANGE



If each resistor is identical with value equal to 400 ohms, what is the total resistance?

Answer 500 ohms

If two resistors in each row open circuits, what is the total resistance?

Answer 1000 ohms

If two resistors in one row open circuits, what is the total resistance?

Answer 600 ohms or 20%

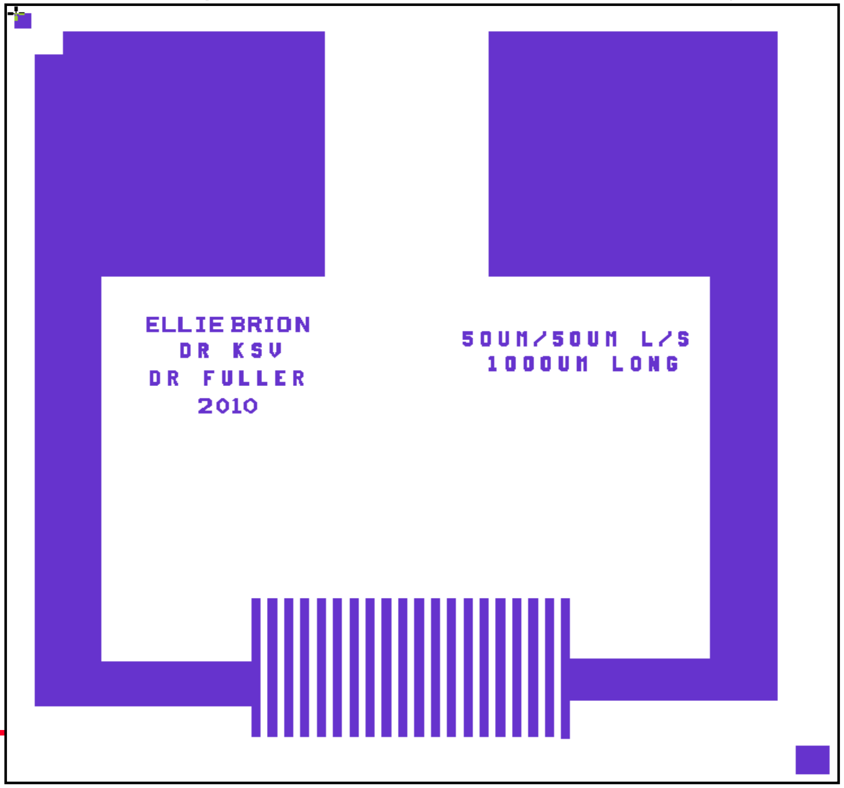
SUMMARY OF DESIGN ARCHITECTURE

Series architecture with coatings whose resistance increases in the presence of some chemical being detected gives more sensitivity

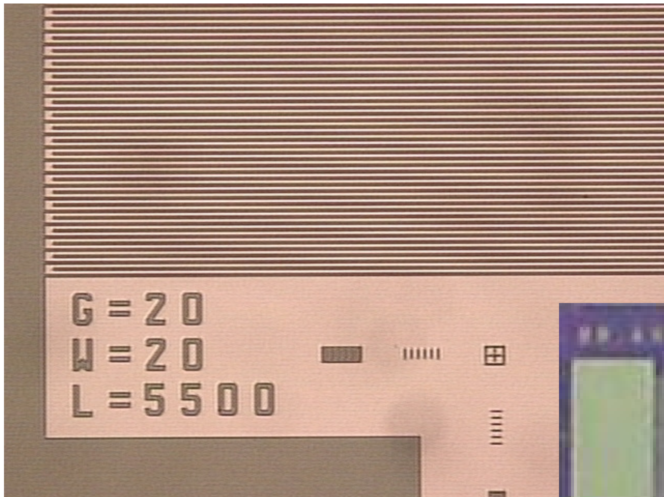
Parallel architecture with coatings whose resistance decreases in the presence of some chemical being detected gives more sensitivity.

If the coating is perfectly uniform and responds uniformly then both architecture approaches give identical results.

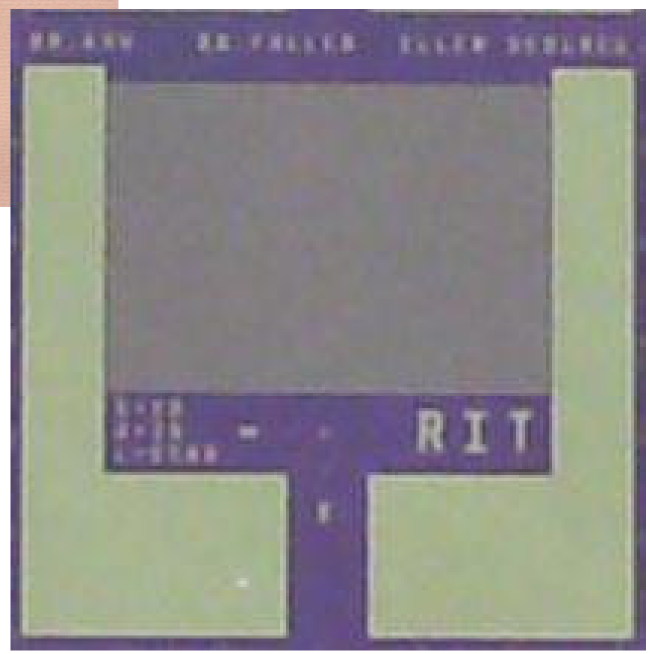
Series Sensor Design by Ellie Brion 2010

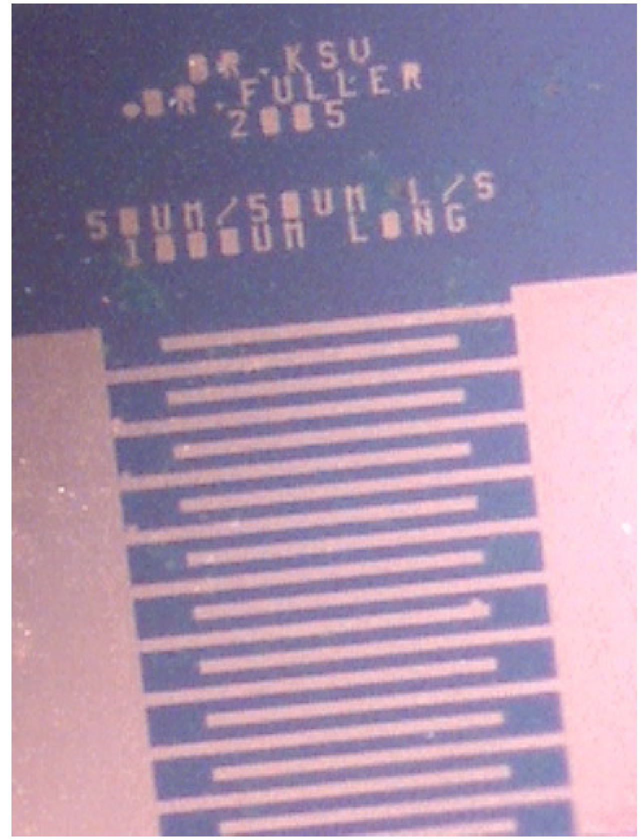


CHIPS MADE WITH PARALLEL ARCHITECTURE

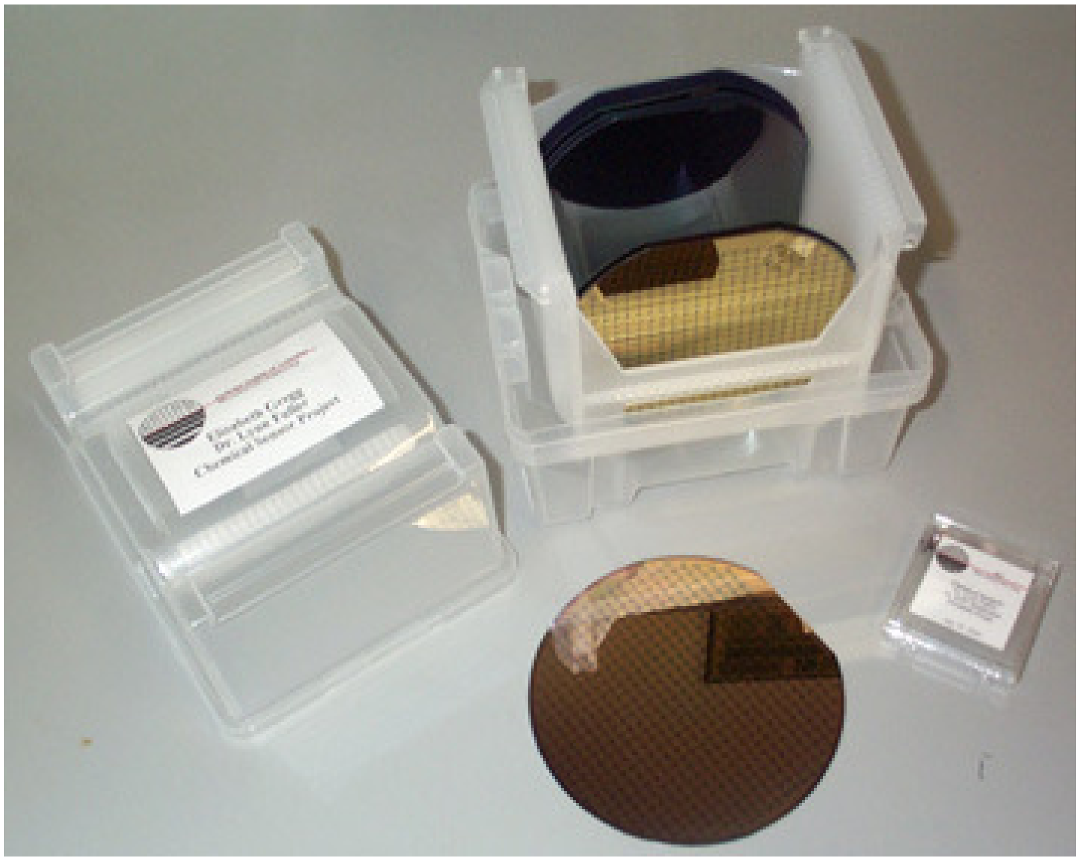


Ellen Sedlack

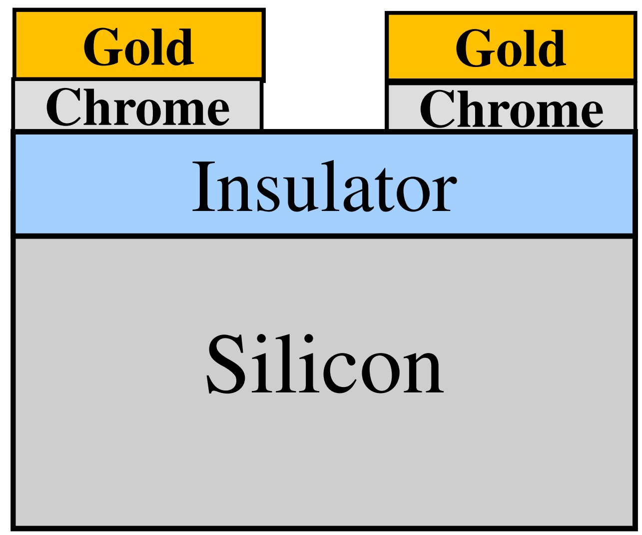




FINISHED WAFERS OF CHEMICAL SENSORS

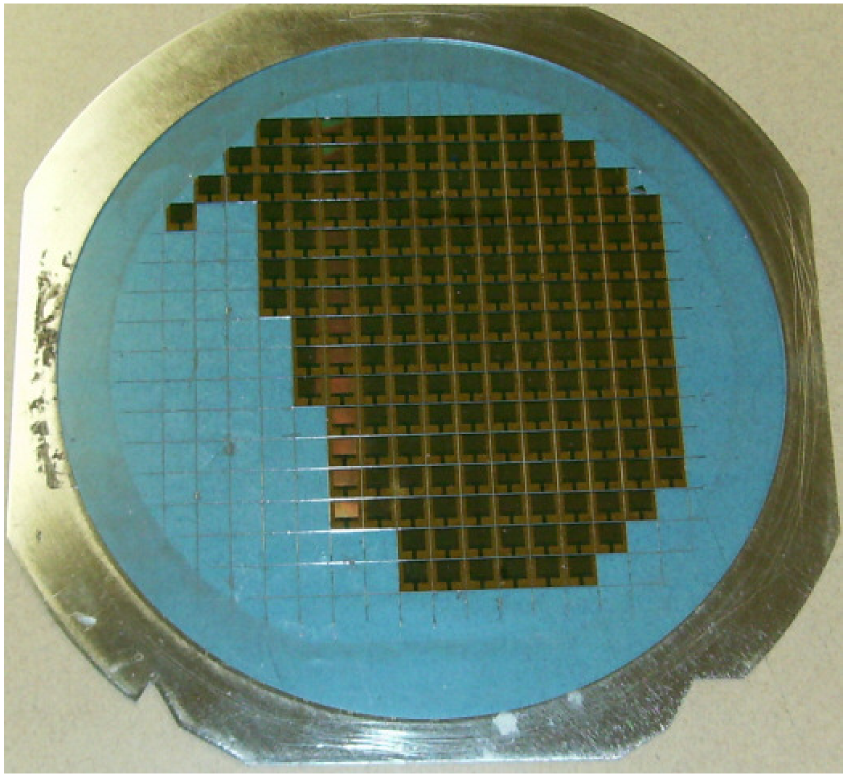


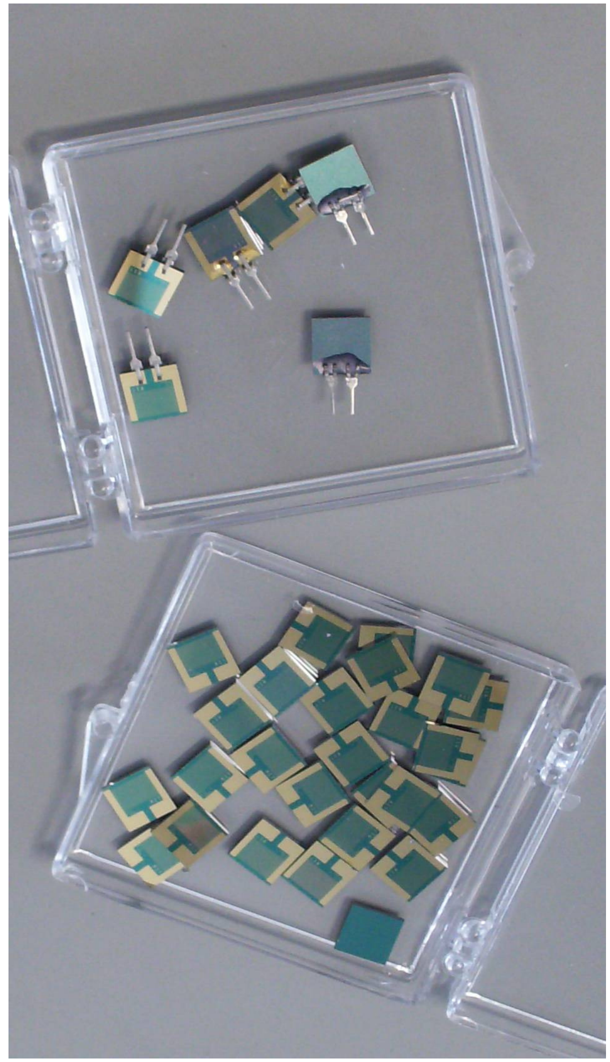
Au - 1000Å
Cr -300Å
SiO_2 - 5000Å



Gold on Chrome on Oxide on Silicon Wafers

DICED WAFER – CONNECTION LEADS

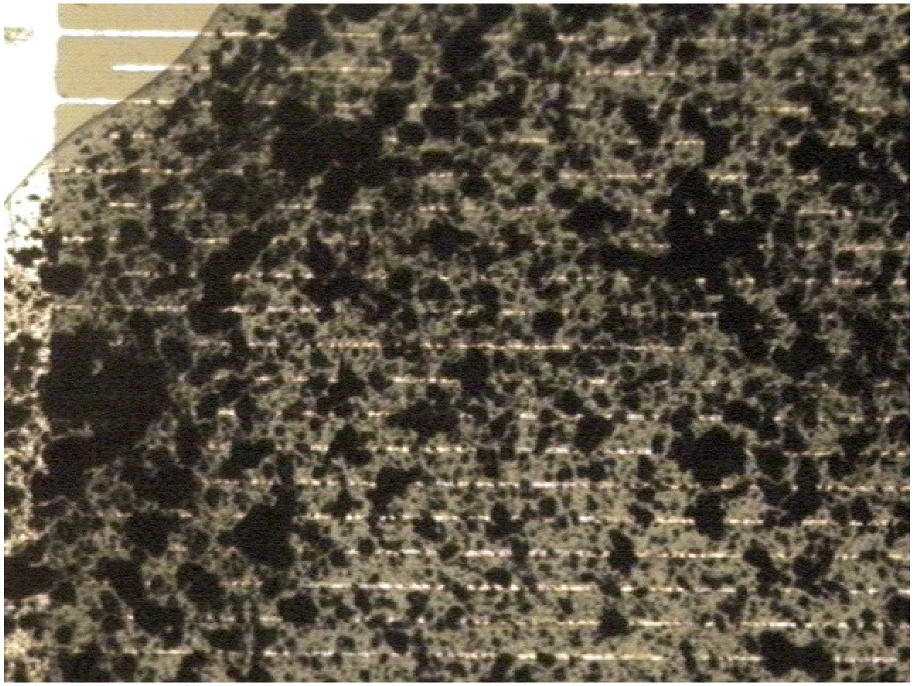


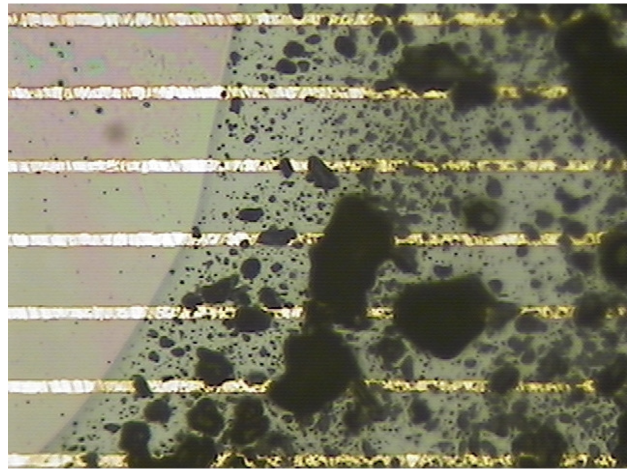


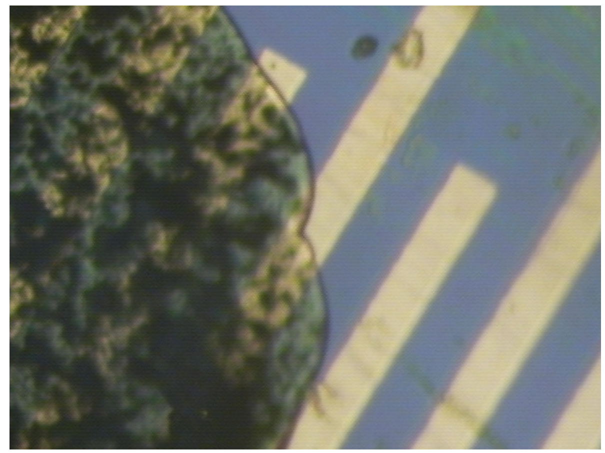
Fabrication by Ellen Sedlack 2010

Leads make contact by pressure or can be soldered to the gold

CARBON BLACK MIXED WITH AIRPLANE GLUE

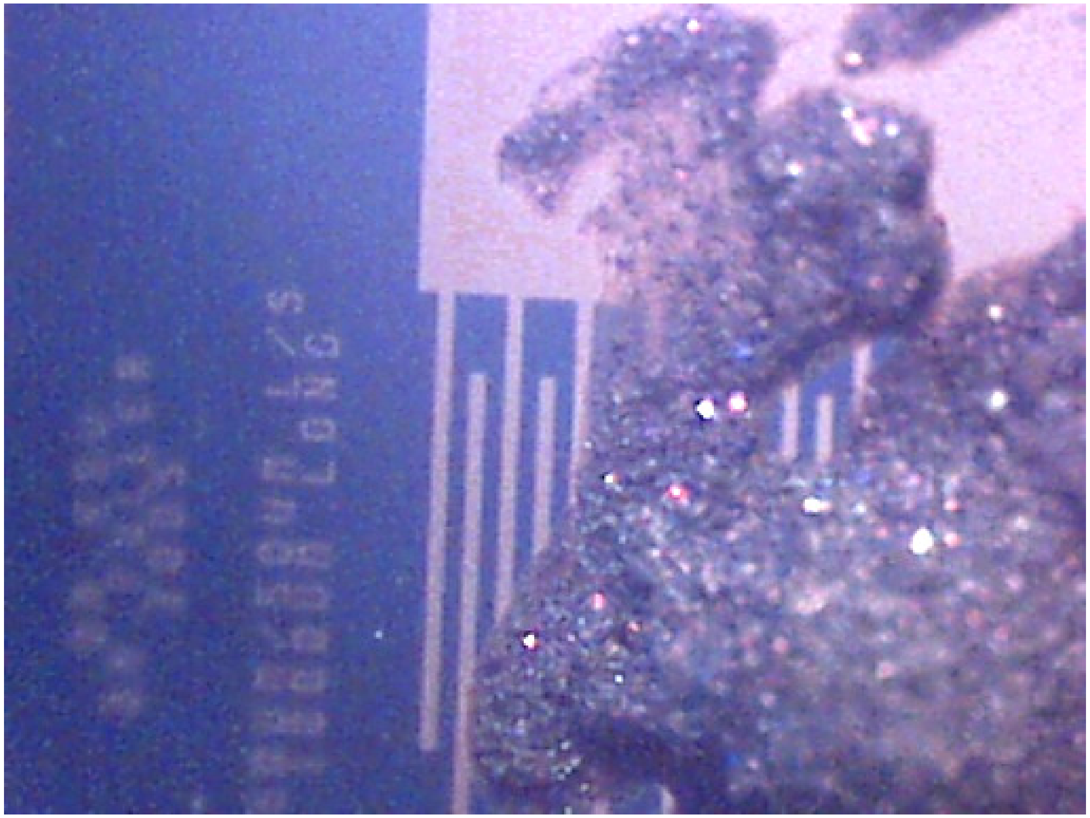






Glue and Carbon Black mixed by hand and diluted with a drop of acetone then applied by hand (painted) on the sensor chip

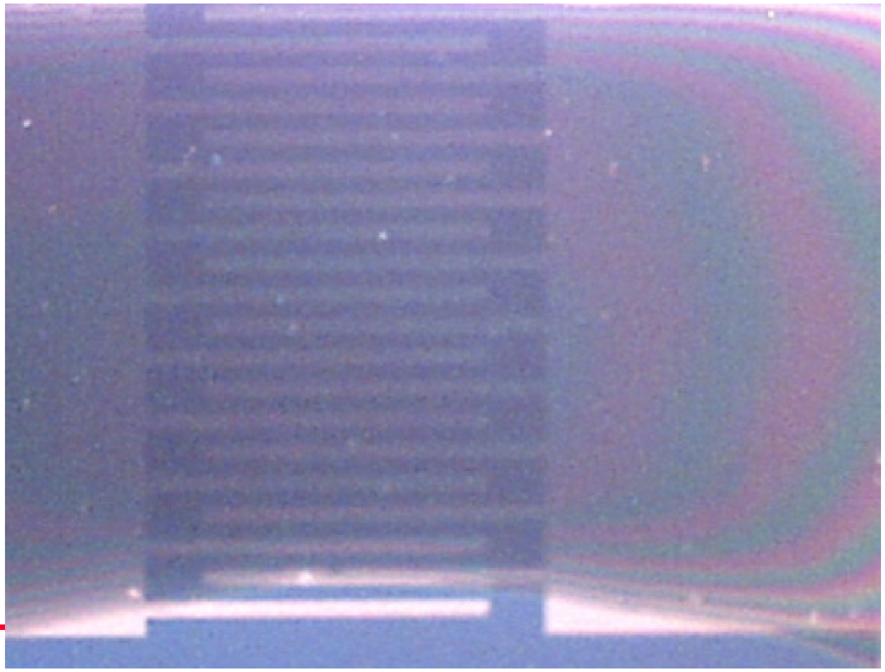
NAIL POLISH AND CARBON BLACK

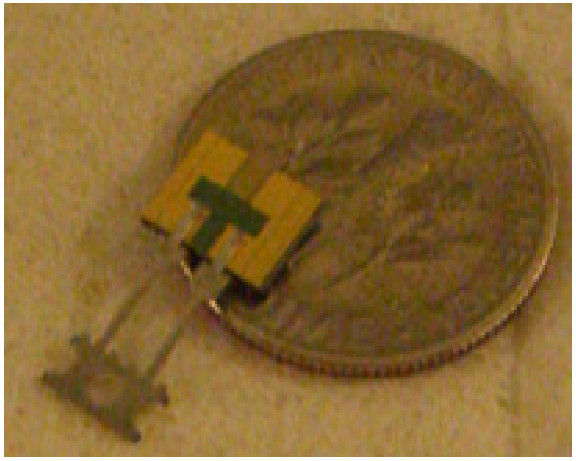


Thinner coatings are more sensitive

COATING TO DETECT ETHANOL

- ♦ 2 µm of (3,4-polyethylenedioxythiopene-polystyrenesulfonate) PEDOT polymer is applied to interdigitated electrodes and cured at 100 ºC for 30 minutes
- ▪ PEDOT is a conductive polymer which upon exposure to ethanol vapors, will adsorb the ethanol causing the polymer to swell which results in a measurable change of resistance across the electrodes





Steve Parshall, Dr. KSV
May 2006

DEFINITION OF TERMS – FOR COATINGS

ISE – Ion Sensitive electrodes
ISFET – Ion Sensitive Field Effect Transistor
Ionophore – compounds that allow specific ions to move through a membrane that they otherwise would not be able to pass through.
Oligomer – low molecular weight monomers often used with photocurable polymers
Polymer- major substance in a coating film, gives the film strength
Permselectivity – intrinsic ion selectivity of the polymer film itself
Plasticizer – increases the plasticity of a substance, making it more flexible, prevent cracking,
Solvent – any substance that dissolves another substance. Allows the substance to flow for coating purposes.
Phthalates – one type of plasticizer commonly used but is a Teratogen (causes birth defects) restricted use since 1976 in Europe
UV Blocker – blocks ultraviolet radiation
Rheological Properties – flow characteristics
Photoinitiator – causes cross linking in the presents of light
Crosslinker – used with low molecular weight monomers, causes cross linking

POLYMERS USED TO MAKE SENSORS

Air Plane Glue

Bond adhesives Co., Multipurpose Adhesive 527

From the MSDS:		
	Nitrocellulose (polymer)	25%-X%
	Trade Secret (plasticizer)	X%
	Acetone (solvent)	66%
	Isopropanol (solvent)	7%
	Propylene Glycol Monoethyl Ether (rheological properties)	4%

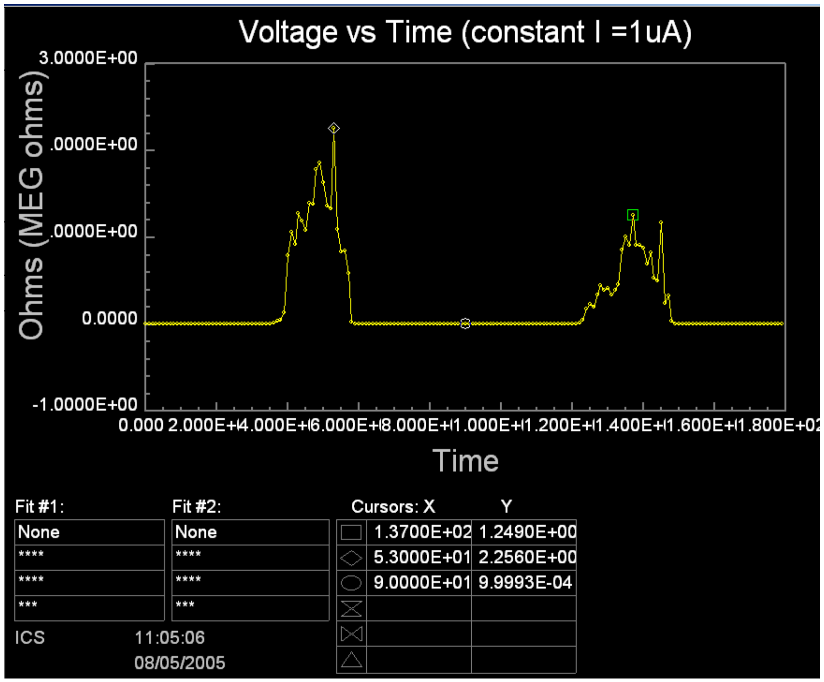
Nail Polish

Cellulose Acetate Solution

From the MSDS:		
	Nitrocellulose (polymer)	10%
	Di butyl Phthalate (plasticizer)	1%
	Camphor (aromatic)	5%
	Benzophenone-1 (UV Blocker)	1%
	Toluene (solvent)	5%
	Butyl acetate (solvent)	25%
	Ethyl Acetate (solvent)	45%
	Isopropyl Alcohol (solvent)	5%

TESTING OF RESISTIVE CHEMICAL SENSOR

Computer controlled ohmmeter measures resistance every second for 3 min.



30s off, 30s on, 60s off, 30s on, 30s off

GAS CONCENTRATION CALCULATOR

Rochester Institute of Technology — **20-Mar-06**

Microelectronic Engineering — **Dr. Lynn Fuller**

Concentration Calculations:

When testing chemical sensors it is important to know the concentration of the chemical to determine the sensitivity. For chemicals that are available as a liquid but evaporate in a volume of air, one can use the following equation to find the concentration in parts per million (ppm)

Concentration (in ppm) = [Weight (mg) / Chamber volume (m^3)] X [Volume of one mole of air (L/mole) / Molecular weight of sample (g/mole)]

BAC = Blood Alcohol Concentra
BAC = wt. In gm of ethanol/100
BAC = wt. In gm of ethanol/210

To use this spread sheet input values in the white boxes and results will be displayed in purple boxes

	volume of liquid =	0.0002	ml	Chamber Volume =	0.25
Example:	mass of liquid = volume x density	0.1632	mg		0.000163
Chamber of 1 Liter = 1000 cm^3 = 0.001 m^3	Chamber volume =	0.00025	m^3		210
Volume of air = 24.45 L/mole	Volume of air =	24.45	L/mole		0.137088
	molecular wt sample=	46.06952	g/mole		
note: valid at T=25°C and P=760 mm Hg				Ex: 0.0002ml ethanol in250 mL	
	Concentration in ppm =	346	ppm	which is equivalent to 346 ppm	

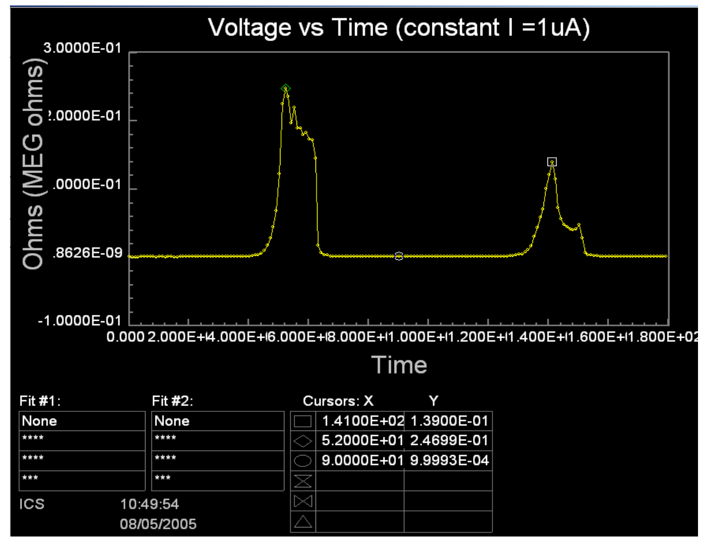
Data:

Chemical name	Chemical formula	Molecular weight	Density Kg/m^3	Select one entry =1, others = 0
methanol	CH_3OH	32.04243	810	0
ethanol	CH_3CH_2OH	46.06952	816	1
2-propanol	$CH_3CH_2CH_2OH$	60.09661	804.13	0
acetone	CH_3COCH_3	58.08	784.58	0

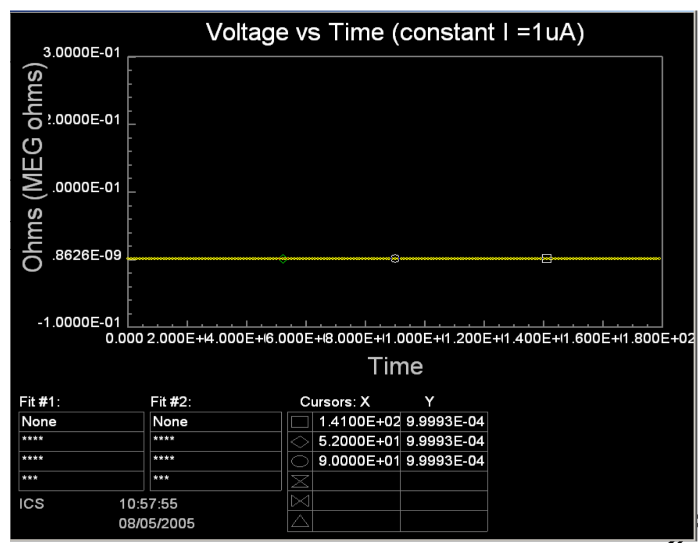
Reference: http://www.ilpi.com/msds/ref/concentration.html

NAIL POLISH / CARBON BLACKRESPONSE TO ACETONE AND ISOPROPANOL

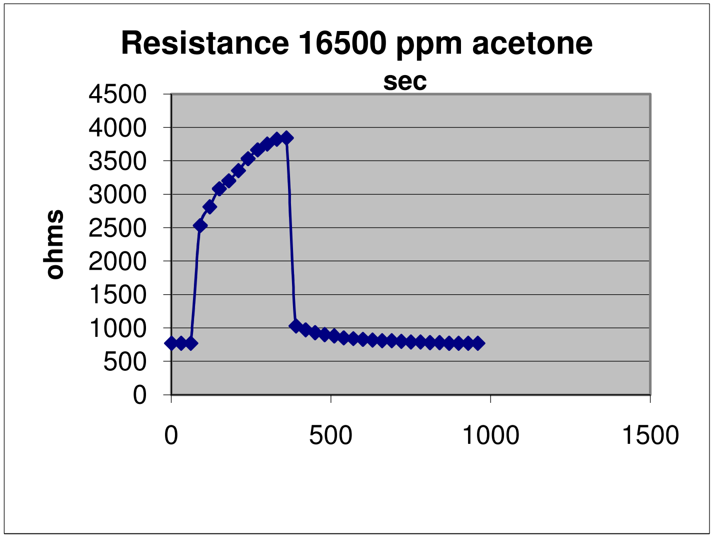
30s off, 30s on, 60s off, 30s on, 30s off
0.5 ml Acetone/ 125 ml bottle = 4000 ppm
Resistance goes from ~100 ohms (no vapor)
to ~ 100,000 ohms (with vapor)

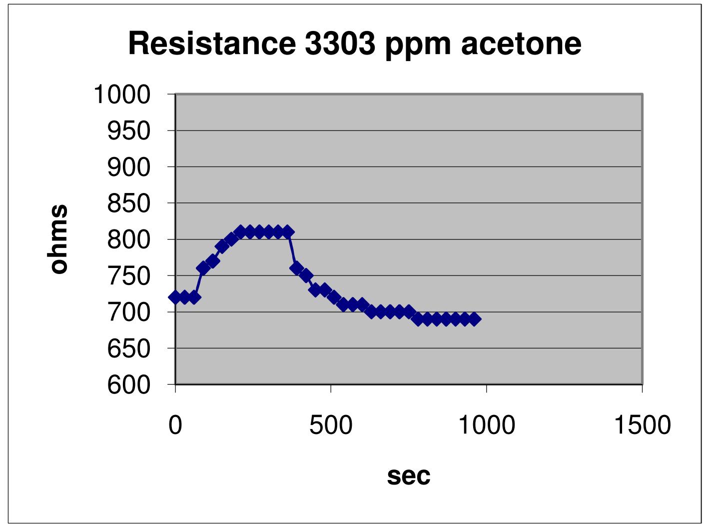


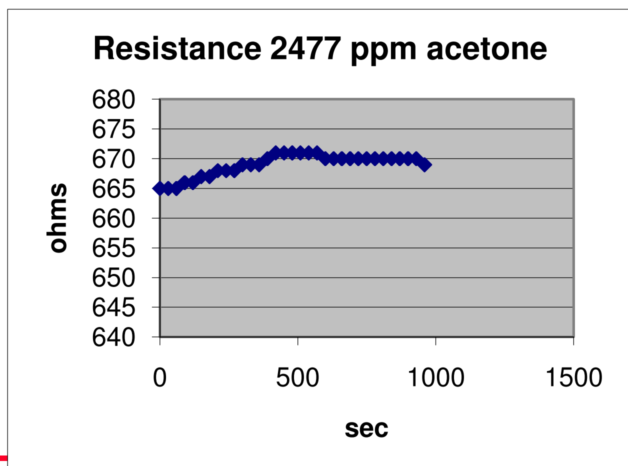
30s off, 30s on, 60s off, 30s on, 30s off
Isopropanol ~ 10,000 ppm
No Response

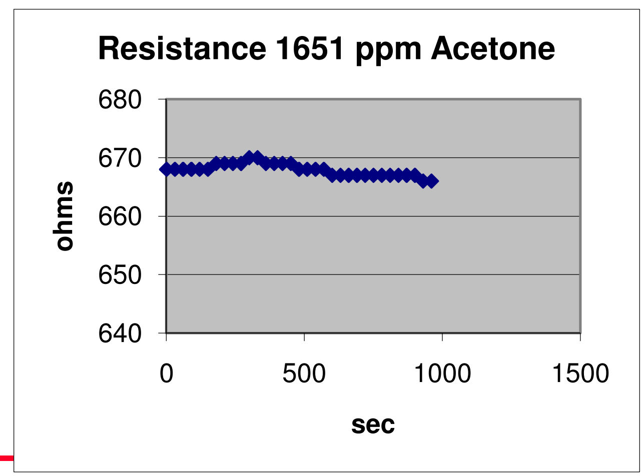


AIR PLANE GLUE / CARBON BLACK TEST RESULTS

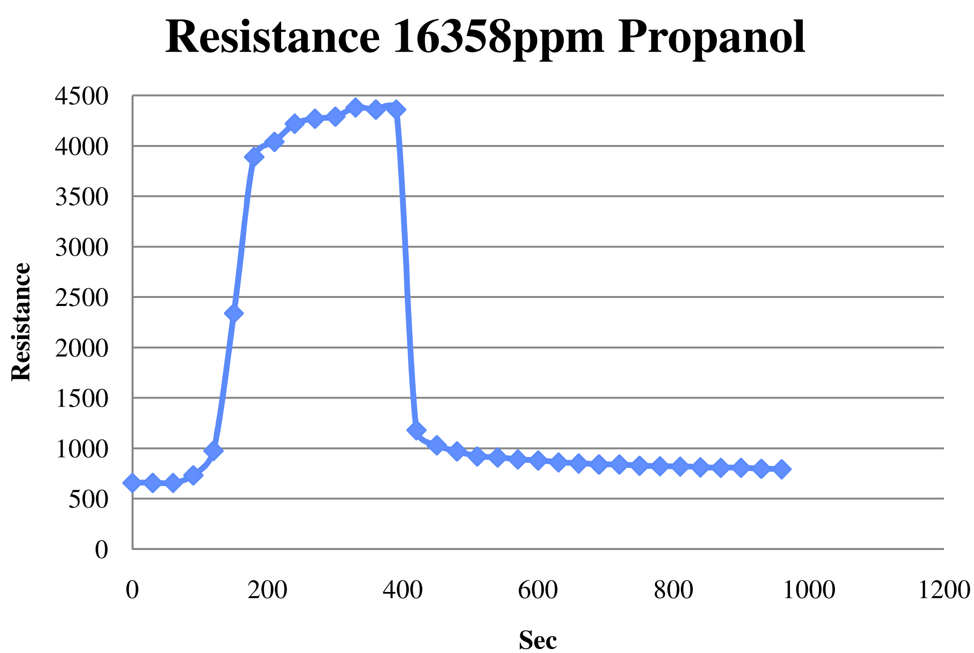








AIR PLANE GLUE RESPONSE TO PROPANOL



SUMMARY FOR TWO DIFFERENT COATINGS

Carbon Black mixed with Airplane Glue (Bond 527 Multipurpose Cement) is sensitive to Acetone and isopropynol

Carbon Black mixed with Nailpolish is sensitive to Acetone.

Solvents interact with the polymer, plasticizer or other additives in the film causing swelling. For example nail polish and airplane glue have the same base polymer, Nitrocellulose, which swells in the presence of acetone and both show acetone sensitivity. Nail polish does not show sensitivity to alcohol but air plane glue does so one explanation is that the alcohol sensitivity in air plane glue is due to the type of plasticizer used.

MEMS CHEMICAL GAS SENSOR (NOSE)

MEMS Chemical Gas Sensor

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Abstract-- We have developed a miniature polymer-based chemical gas sensor array on silicon using micromachining technology. The sensors use conductive polymer – carbon black composite films, which swell reversibly and induce a resistance change upon exposure to a wide variety of gases. Using a SU-8 photoresist, we have constructed high aspect ratio wells which can contain the polymer – carbon black – solvent liquid volume present during deposition and allow the sensor film to be placed reproducibly in a specific and well-constrained area while reducing its overall size. Two sizes of wells, 500×600 µm and 250×250 µm, have been fabricated and tested. Six polymer – carbon black composite films were deposited into an array of sensor wells and exposed to three chemical gases at five concentration levels. The sensors were able to uniquely detect these gas vapors and demonstrated a linear response to the concentration levels. This design allows the integration of circuits to process the changes in resistance which will permit the realization of a completely integrated miniature gas sensor.

1. INTRODUCTION

The ability to monitor and detect various chemical gases is important to many applications. One example is environmental monitoring, such as determining the air quality inside a room or closed chamber and detecting the presence and concentration of toxic or otherwise dangerous gases that may come from spills and leaks [1]. Another broad application area is quality control and industrial monitoring, particularly in such industries as food processing, perfume, beverage, and other chemical products where complex vapor mixtures need to be analyzed and classified [2,3]. Monitoring and determining the constituents of a sample gas or environment involves collecting samples and analyzing them in complex and expensive laboratory analytical instrument such as a gas chromatograph-mass spectrometer (GC-MS). [1] Although GC-MS systems work very well, many applications need sensor systems that are smaller, more portable, cheaper, and even disposable.

MEMS CHEMICAL GAS SENSOR (NOSE)

2. SENSOR DEVICE

We have developed a miniature polymer-based chemical gas sensor array on silicon using micromachining technology. The sensors use conductive polymer – carbon black composite films, which have been shown to swell reversibly upon exposure to gases [1,2]. This swelling induces a resistance change in the composite film. By depositing the film across two metal leads, this resistance change can be measured. Compared to conventional chemical sensors which use a specific receptor that selectively responds to a single analyte of interest [2], the polymer composite film is not specific to any one particular gas. However, when it is used in an array, with each sensor containing a different polymer composite film, gases and gas mixtures can be identified by the pattern of response of the array. This allows a much more general-purpose chemical gas sensor capable of broadly detecting and identifying various constituents.

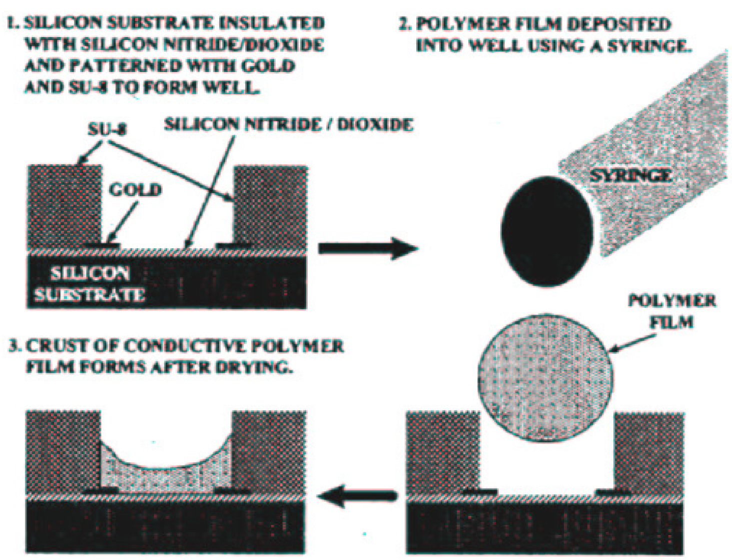

Figure 1: Fabrication of the gas sensor on the silicon surface using SU-8 photoresist.

A. Design

Conductive polymer – carbon black composite films have been used as a sensing medium in several gas sensors or "electronic noses" [1,2]. They have been deposited on co-fired ceramic substrates [1] and on glass slides [2]. Most of these sensors have large-area composite film deposits (>mm^2). During deposition, the composite film is dissolved into a solvent mixture, which evaporates and leaves behind the thin sensing film. We have designed micromachined reservoirs or wells to contain the large liquid volume present during deposition. The well allows the polymer – carbon black film to be placed reproducibly in a specific, well-constrained, and smaller area.

MEMS CHEMICAL GAS SENSOR (NOSE)

B. Fabrication

The sensor array was fabricated on the surface of a silicon wafer by building high aspect ratio wells using thick-film photolithography. The starting material was a <100>-silicon wafer coated with either silicon nitride or silicon dioxide. Gold was deposited by an e-beam evaporation system and patterned using a lift-off process into 100-µm-wide leads which define the electrical contacts to the sensor. The wells were constructed on the surface of the wafer using a SU-8 photoresist (MicroChem Corp.). SU-8 is an epoxy-based negative imaging resist developed for thick-resist applications where high aspect ratios and resistance to harsh conditions are required. The SU-8 photoresist was patterned into 200 µm thick square-ring wells with ~50 µm of the gold leads exposed on opposite sides for contact with the polymer film. This fabrication process is shown in Figure 1. These wells can be post-processed onto silicon CMOS chips, which would allow for integration of on-chip electronics for measurement, signal processing, and analysis. The well sizes that we have fabricated and tested are 500×600 µm and 250×250 µm, shown in Figure 2.

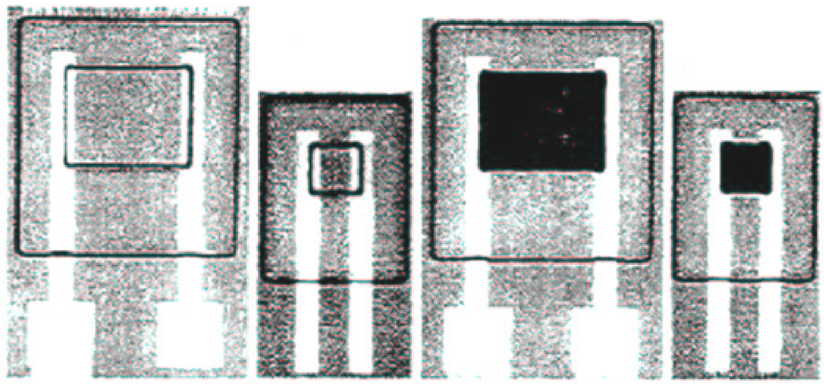

Figure 2: 200 µm high SU-8 square ring on silicon surface forming 500×600 µm and 250×250 µm wells in the middle with gold leads on each side (left two images) before and (right two images) after polymer deposition.

MEMS CHEMICAL GAS SENSOR (NOSE)

C. Composite Film Deposition

The polymer – carbon black composite film was deposited into the well using an automated syringe (Nanojet II by Drummond Scientific Comp.) which is capable of reproducibly injecting nanoliter volumes. The tip of the syringe is a disposable, pulled-glass capillary with a 10 μm diameter. The tip was changed between the deposition of different polymer composite films. In general, the polymer was first dissolved in a solvent or solvent mixture and agitated in an ultrasonic bath. [1,2] Once the polymer had fully dissolved, carbon black was added to the solution and sonicated further to promote uniform dispersion. Depending on the height of the wells, approximately 50 nl was injected into the 500×600 μm wells and 12 nl was injected into the 250×250 μm wells. After depositing the film solution, the solvents would immediately start to evaporate and within minutes, a polymer – carbon black residue crust was left between the two metal leads on each side of the well. The resistance of the film was measured and adjusted by additional injections of the composite film solution. The targeted resistance for these films was between 5 - 30 kΩ.

3. EXPERIMENT

The sensor array was evaluated by exposing it to several chemical gas vapors in a closed and controlled gas flow system. The micromachined gas sensor array was custom packaged and placed in a sealed chamber within the gas flow system and connected to a data acquisition system.

Six polymer – carbon black films were used to evaluate the sensor array which were: styrene/butadiene, aba block copolymer; poly (ethyl methacrylate); polyisoprene, chlorinated; styrene/ethylene/butylene aba block copolymer; polypropylene, isotactic, chlorinated; polyepichlorohydrin. The polymers were dissolved in toluene.

Three different chemical gas vapors at five concentration levels for each were used. Each gas sample was repeated five times sequentially. The gas vapors were methanol, methyl ethyl ketone, and methylene chloride. The concentration levels tested were 2,000, 4,000, 6,000, 8,000 ppm, and at the saturated vapor pressure for the gas. The gas was turned on for 4 min. and then turned off for 10 min.

MEMS CHEMICAL GAS SENSOR (NOSE)

4. RESULTS

The response of the sensors was measured as a percentage change in resistance divided by the baseline resistance. Figure 3 shows the time-domain response of the polyepichlorohydrin film when exposed to five concentrations of methanol vapor. The baseline to peak heights, representing the response of the sensor to the sample chemical vapor, are extracted from this series of data. Figure 4 shows the responses of four of the polymer – carbon black films when exposed to the three sample chemical vapors each at 8000 ppm. Each of the polymer sensor films responded differently to each of the gas vapors. By integrating the responses from the sensor array, a unique pattern or signature is produced for each chemical gas vapor as shown in Fig. 5. The response of the polymer – carbon black sensors increases proportionally as the concentration of the gas vapor increases. Figure 6 shows the linearity of the response of six polymer sensors with concentration ranging from 2,000 to 10,000 ppm. Thus, using pattern recognition techniques such as principle component analysis (PCA), data clustering, or artificial neural networks, the identity of the gas vapor and its concentration can be determined from the response of the sensor array.

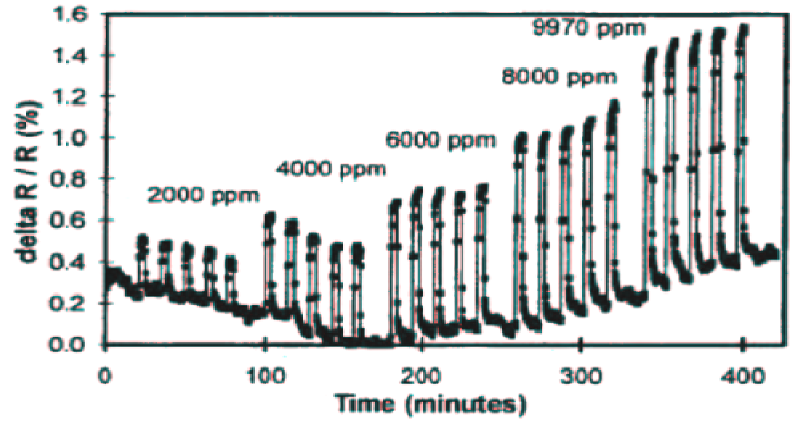

Figure 3: Time-domain response of polyepichlorohydrin sensor film when exposed to 5 concentrations of methanol.

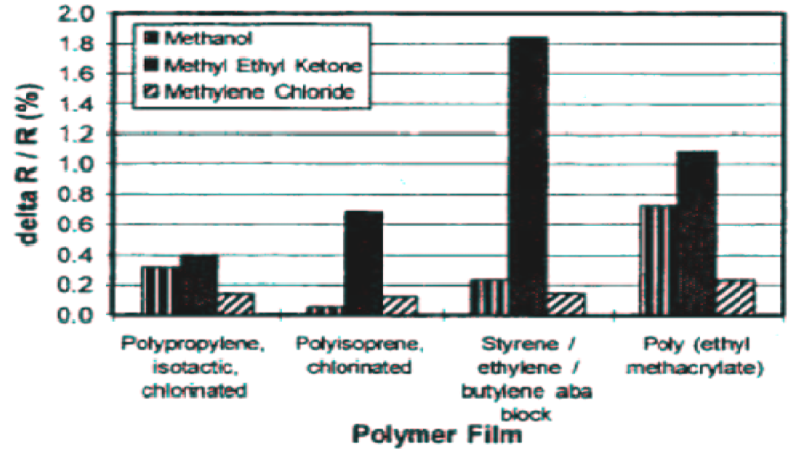

Figure 4: Responses of four polymer – carbon black sensor films when exposed to three gases at 8000 ppm.

MEMS CHEMICAL GAS SENSOR (NOSE)

5. CONCLUSIONS

An arrays of different polymer – carbon black composite films, whose resistances change uniquely with gas species and proportionally with vapor concentration, can be used effectively as a chemical gas sensor. Micromachining technologies can be used to miniaturize the sensor. Specifically, SU-8 photoresist can be patterned into 200 μm high wells ranging in size from 500×600 μm to 250×250 μm which can precisely contain the large liquid volume present during deposition of the composite films. The design of this array of wells is compatible with silicon IC's and would permit the realization of a completely integrated miniature gas sensor.

ACKNOWLEDGEMENT

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REFERENCES

[1] M. A. Ryan, M. L. Homer, M. G. Buehler, K. S. Manatt, F. Zee, and J. Graf, "Monitoring the Air Quality in a Closed Chamber Using an Electronic Nose," *Proceedings of the International Conference on Environmental Systems*, Society of Automotive Engineers, Lake Tahoe, Nevada, 1997.

[2] M. C. Lonergan, E. J. Severin, B.J. Doleman, S. A. Beaber, R. H. Grubbs, and N. S. Lewis, "Array-Based Vapor Sensing Using Chemically Sensitive, Carbon Black-Polymer Resistors," *Chem. Materials*, **8**, 2298, 1996.

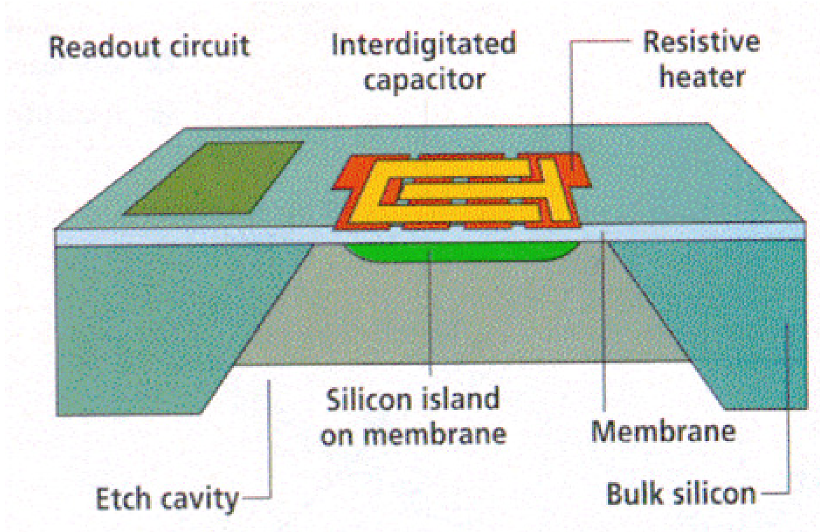
[3] J. W. Gardner, T. C. Pearce, S. Friel, P. N. Bartlett, and N. Blair, "A Multisensor System for Beer Flavor Monitoring Using an Array of Conducting Polymers and Predictive Classifiers," *Sensors and Actuators*, **B18**, 240, 1994.

CHEMICAPACITOR

Two conductors separated by a material that changes its dielectric constant as it selectively absorbs one or more chemicals.

Some humidity sensors are made using a polyimide layer as a dielectric material.

Heaters can help increase the response time.



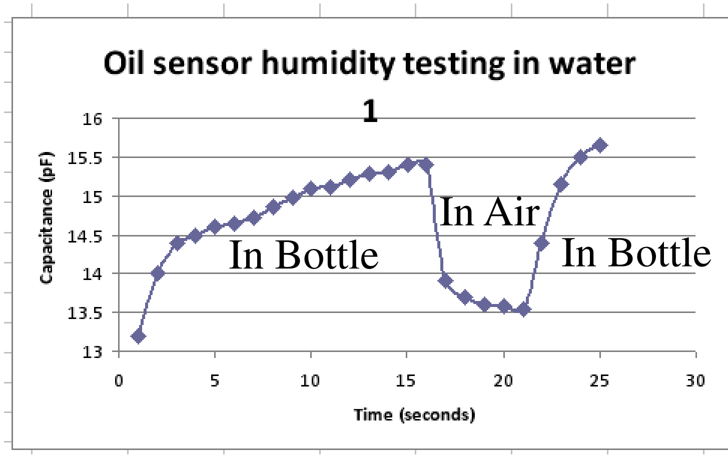
DIELECTRIC CONSTANT OF SELECTED MATERIALS

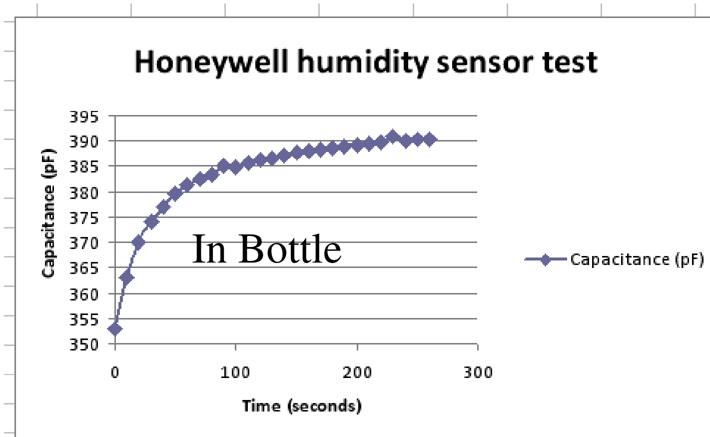
Vacuum	1
Air	1.00059
Acetone	20
Barium strontium titanate	500
Benzene	2.284
Conjugated Polymers	6 to 100,000
Ethanol	24.3
Glycerin	42.5
Glass	5-10

Methanol	30
Photoresist	3
Plexiglass	3.4
Polyimide	2.8
Rubber	3
Silicon	11.7
Silicon dioxide	3.9
Silicon Nitride	7.5
Teflon	2.1
Water	80-88

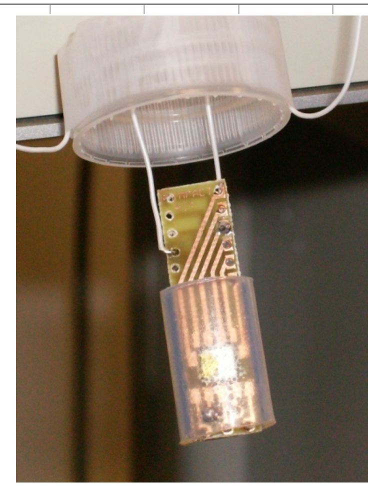
http://www.asiinstruments.com/technical/Dielectric%20Constants.htm

RIT HUMIDITY SENSOR TEST RESULTS





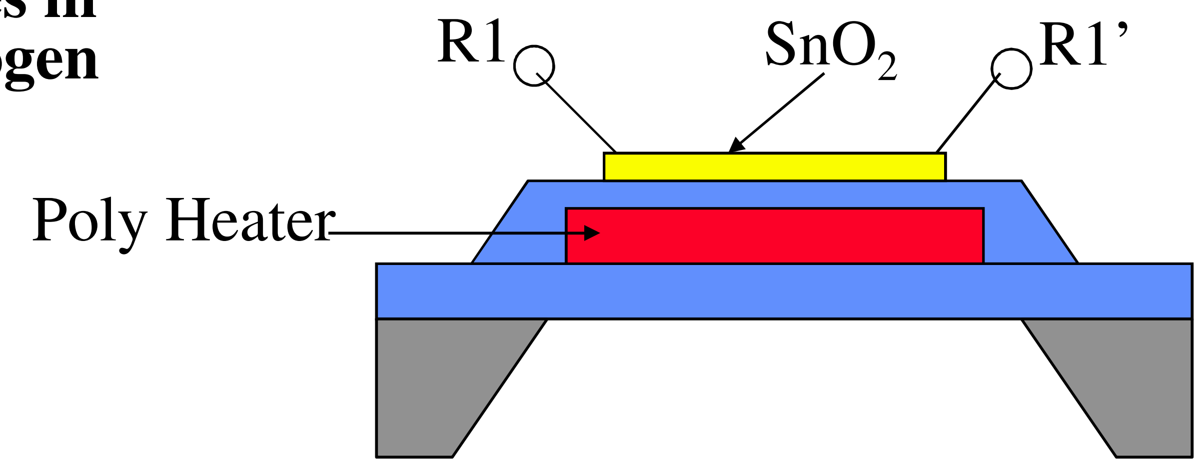
We put a small quantity of water in a 1000ml bottle. The sensor was put into the bottle and the capacitance increased, when removed from the bottle the capacitance decreased.



Packaged RIT Humidity Sensor

METAL OXIDE GAS SENSOR

Resistance changes in presence of Hydrogen



The metal oxide (SnO_2, TiO_2, In_2O_3, ZnO, WO etc.) will react with adsorbed ambient oxygen to form an electron trap (O-) on the surface **increasing** the resistance R1-R1'. When combustible gases are present (H_2 for example) the hydrogen reacts at the surface to reverse the effect of the adsorbed oxygen **reducing** the resistance. The heater keeps the film at a fixed but elevated temperature (250 °C)

METAL OXIDE GAS SENSOR

Inorganic Coating for Chemical Sensors

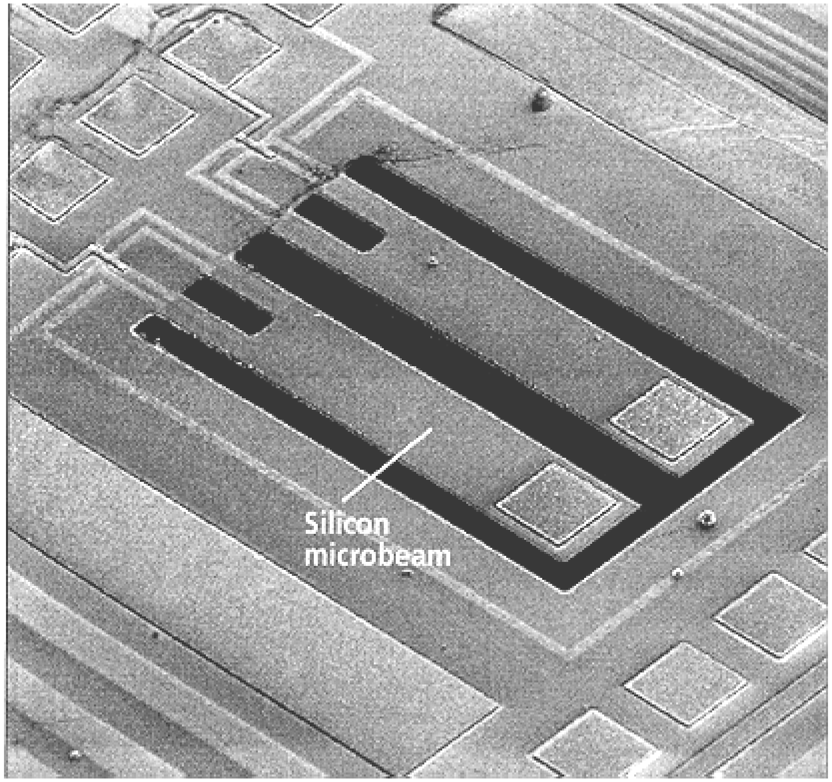
Semiconductor	Suggested Additives	Gas to Be Detected	Reference
$BaTiO_3/CuO$	La_2O_3, $CaCO_3$	CO_2	Haeusler and Meyer (1995)
SnO_2	Pt + Sb	CO	Morrison (1994)
SnO_2	Pt	alcohols	Morrison (1994)
SnO_2	Sb_2O_3 + Au	H_2, O_2, H_2S	Morrison (1994)
SnO_2	CuO	H_2S	Tamaki, et al. (1997)
ZnO	V, Mo	halogenated hydrocarbons	Morrison (1994)
WO_3	Pt	NH_3	Morrison (1994)
Fe_2O_3	Ti-doped + Au	CO	Morrison (1994)
Ga_2O_3	Au	CO	Schwebel, et al. (1997)
MoO_3	none	NO_2, CO	Guidi, et al. (1997)
In_2O_3	none	O_3 (ozone)	Wlodarski, et al. (1997)

From: <u>Micromachined Transducers</u>, Gregory T.A. Kovacs,

Table of example semiconducting metal oxides suitable for use in gas sensors, additives to improve performance, and gases that can be detected.

CHEMOMECHANICAL

The two cantilever structures have piezoresistive sensors to measure the change in the resonant frequency of the beams due to additional mass. The beams have a chemical selective film at the end of the cantilever that reacts or absorbs the chemical to be sensed. The additional mass is detected in a change in resonant frequency.



From: Micromachined Transducers, Gregory T.A. Kovacs,

CHEMOMECHANICAL

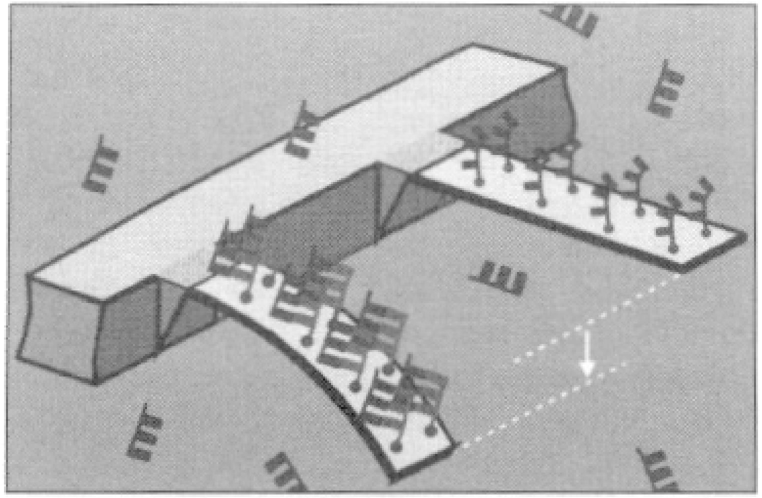


Fig. 2. Schematic illustration of biomolecule hybridization transduced to cantilever deflection. The cantilevers are functionalized on one side with different oligonucleotide base sequences. The differential signal is set to zero and a complementary oligonucleotide is injected. Hybridization with the matching oligonucleotide is shown on the left cantilever where surface stress induces bending and increases the differential signal.

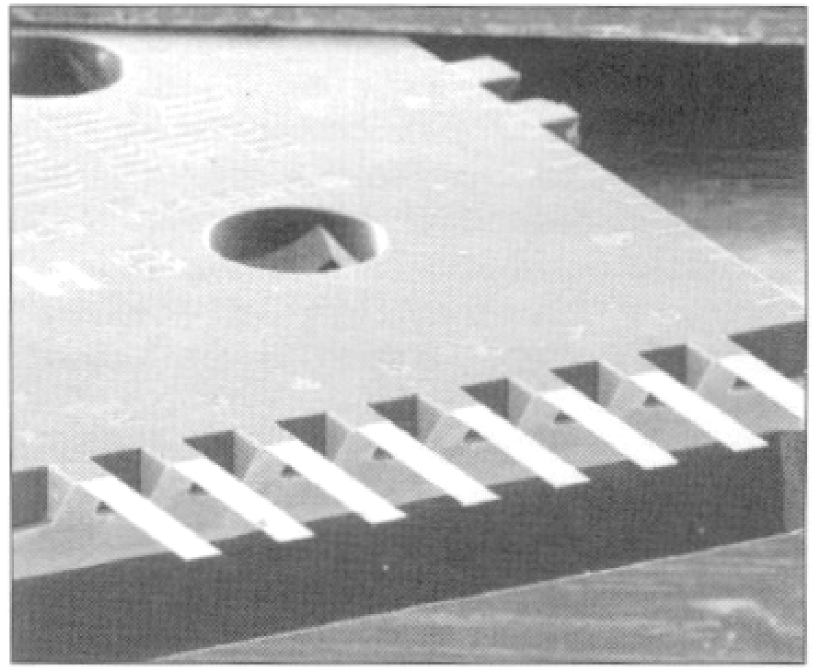
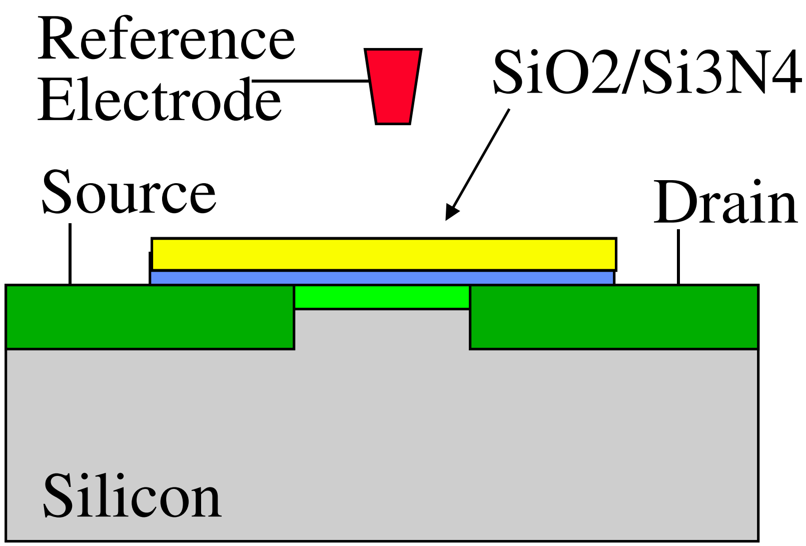


Fig. 1. Microfabricated silicon cantilever array. Each cantilever is 1 μm thick, 500 μm long, and 100 μm wide on a pitch of 250 μm.

From: Micromachined Transducers, Gregory T.A. Kovacs,

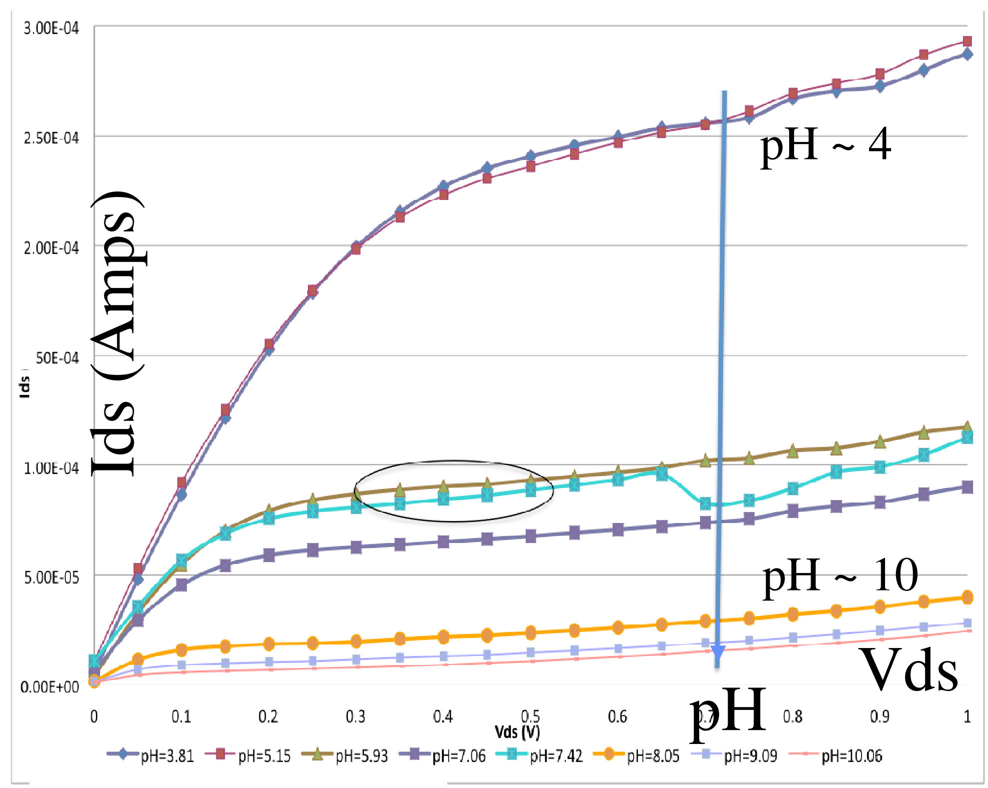
ION-SENSITIVE FETS ISFETS



2010 Murat Baylav

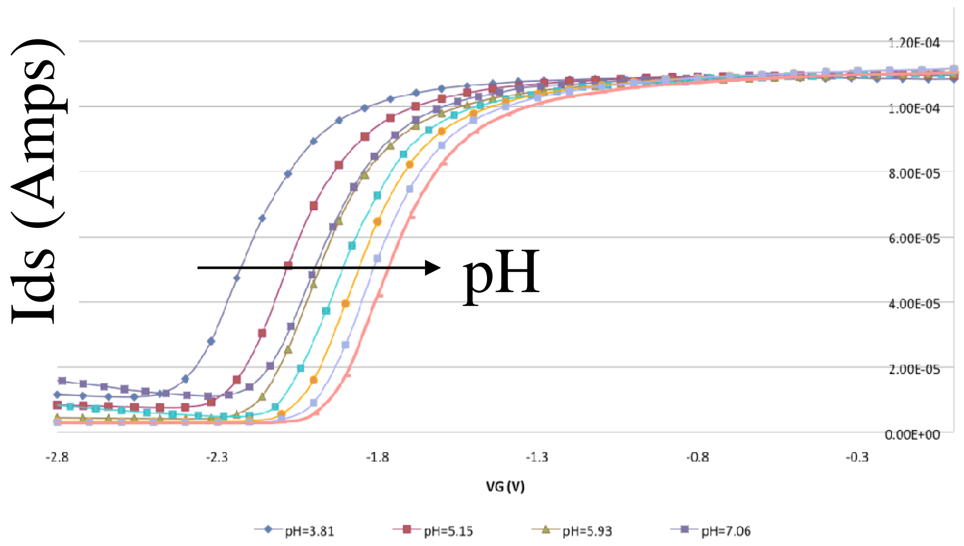
RIT's First ISFETs

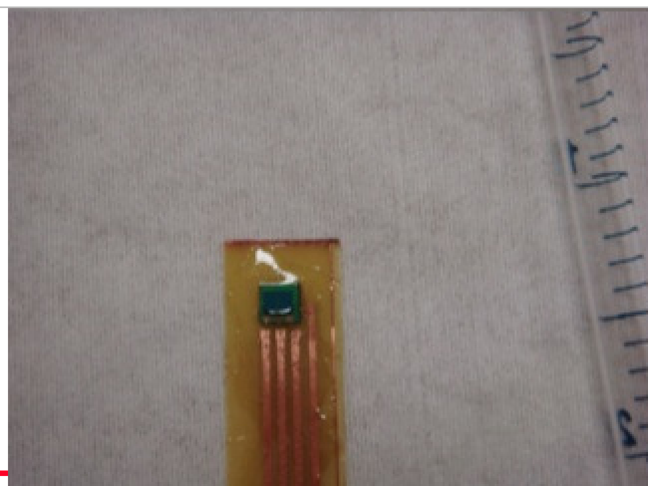
When immersed in a solution containing ions, the ions at the surface of the gate insulator change the threshold voltage of the FET.

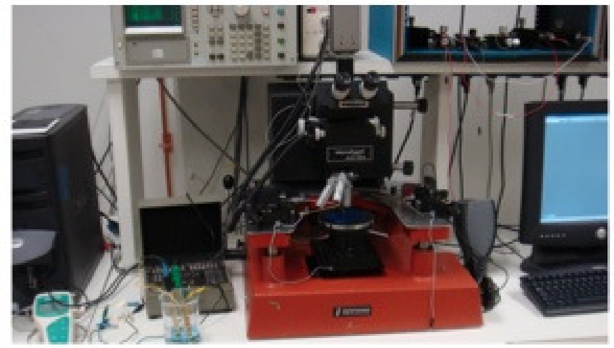


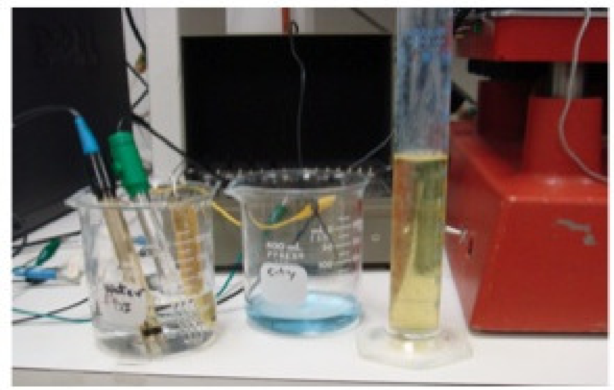
Vref = -2 volts

MEMS ISFET PH TESTING

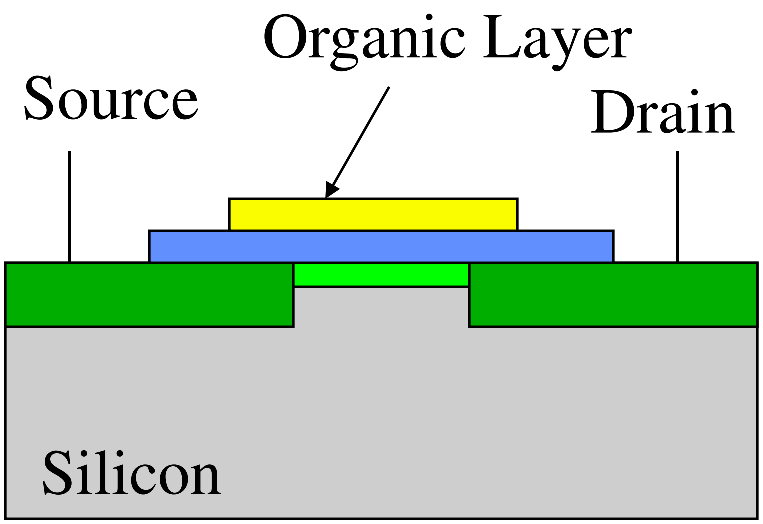








ION-SENSITIVE FETS (CHEMFETS)



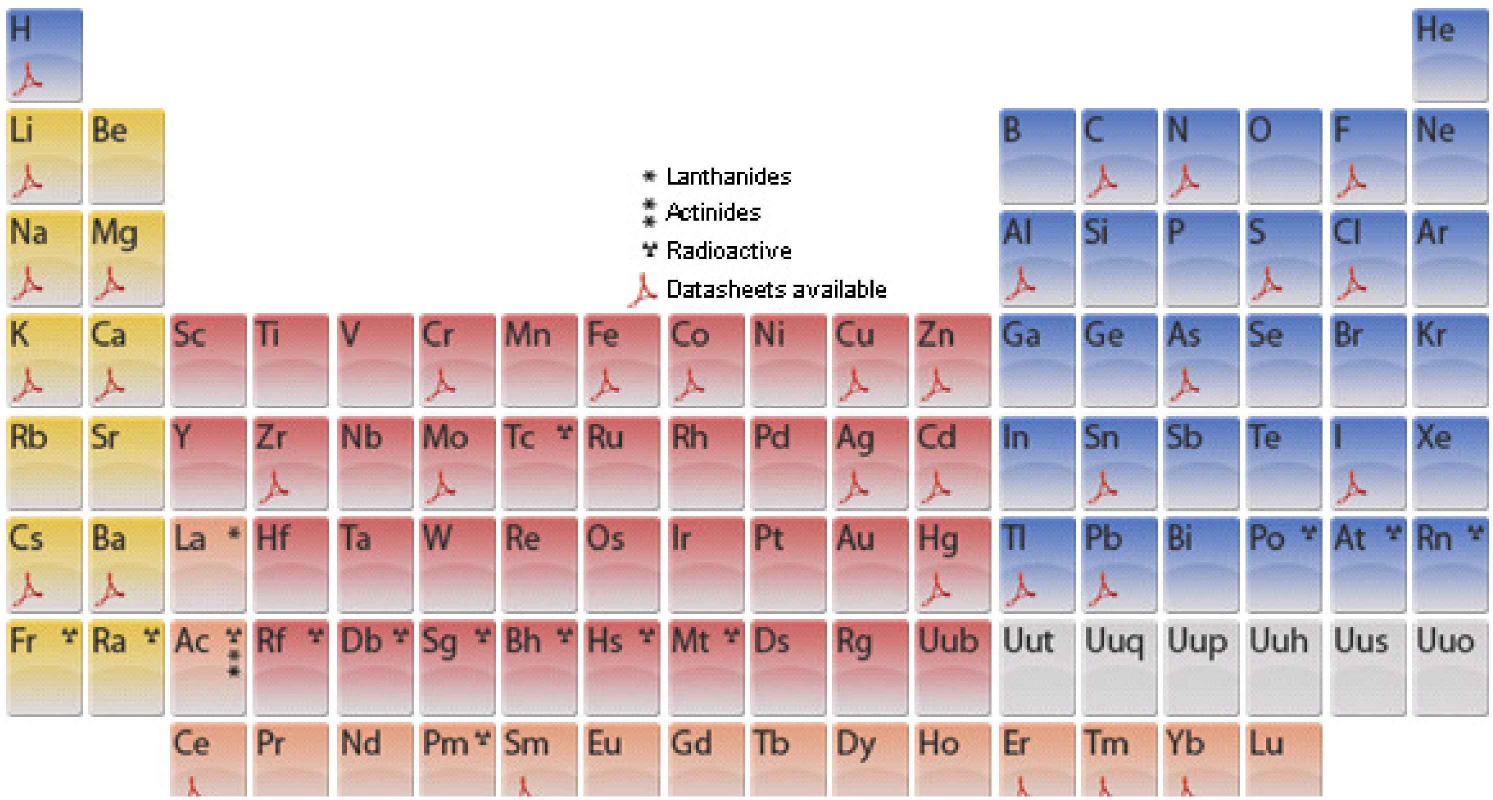
In the Chem FET the organic layer is selective allowing the device to respond specifically to certain ions. Specific compounds can be sensed by using the high specificity of biological molecules such as enzymes and antibodies in the membrane.

SIGMA ALDRICH – SENSOR APPLICATIONS

http://www.sigmaaldrich.com/analytical-chromatography/analytical-reagents/sensoric-applications.html

Interactive Periodic System of Elements

Explore the interactive periodic table below to locate available data sheets that describe the preparation of the membranes, applicati guides, technical data and references.



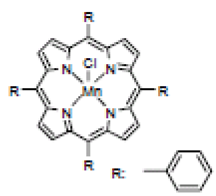
SIGMA ALDRICH ION SELECTIVE MEMBRANES FOR CHLORINE

Fluka Analytical

sigma-aldrich.com
Sigma-Aldrich Chemie GmbH · Industriestrasse 25 · Postfach · CH-9471 Buchs / Schweiz
Tel. +41 / 81 755 25 11 · Fax +41 / 81 756 54 49 · Flukatec@sial.com

Two of 6 ionophores

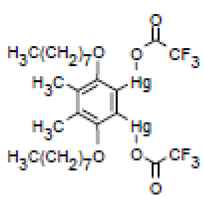
Chloride



Chloride ionophore I

(*meso*-Tetraphenylporphyrin manganese(III)-chloride complex; Mn(III)TPPCl)
$C_{44}H_{28}ClMnN_4$ M_r 703.12 [32195-55-4]

24897 **Selectophore®, function tested** 50 mg



Chloride ionophore II

(ETH 9009; 4,5-Dimethyl-3,6-dioctyloxy-o-phenylene-bis(mercurytrifluoroacetate))
$C_{28}H_{40}F_6Hg_2O_6$ M_r 987.79 [145889-57-2]

24901 **Selectophore®, function tested** 25 mg

One of several Cocktail Recipes

Electrochemical Transduction

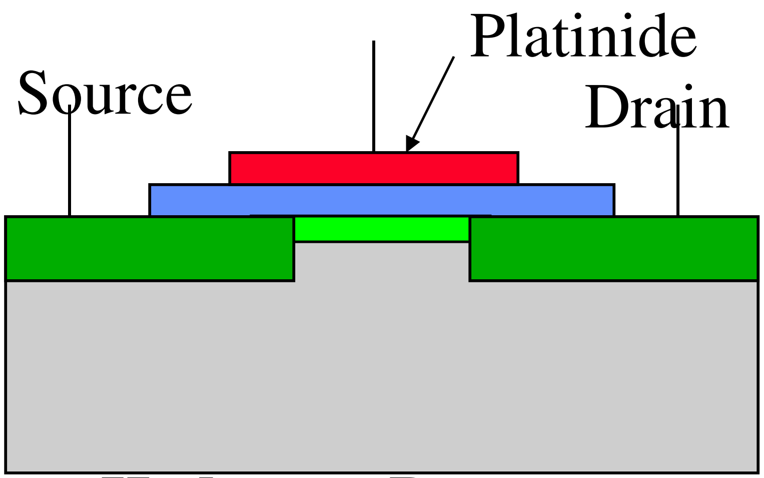
Ion-Selective Electrodes

Application 1 and Sensor Type [1,2]
Assay of Cl^- activity with solvent polymeric membrane electrode based on Chloride ionophore II.

Recommended Membrane Composition

2.00	wt%	Chloride ionophore II (24901)
0.03	wt%	Tridodecylmethylammonium chloride (91661)
64.97	wt%	Bis(2-ethylhexyl) sebacate (84818)
33.00	wt%	Poly(vinyl chloride) high molecular weight (81392)

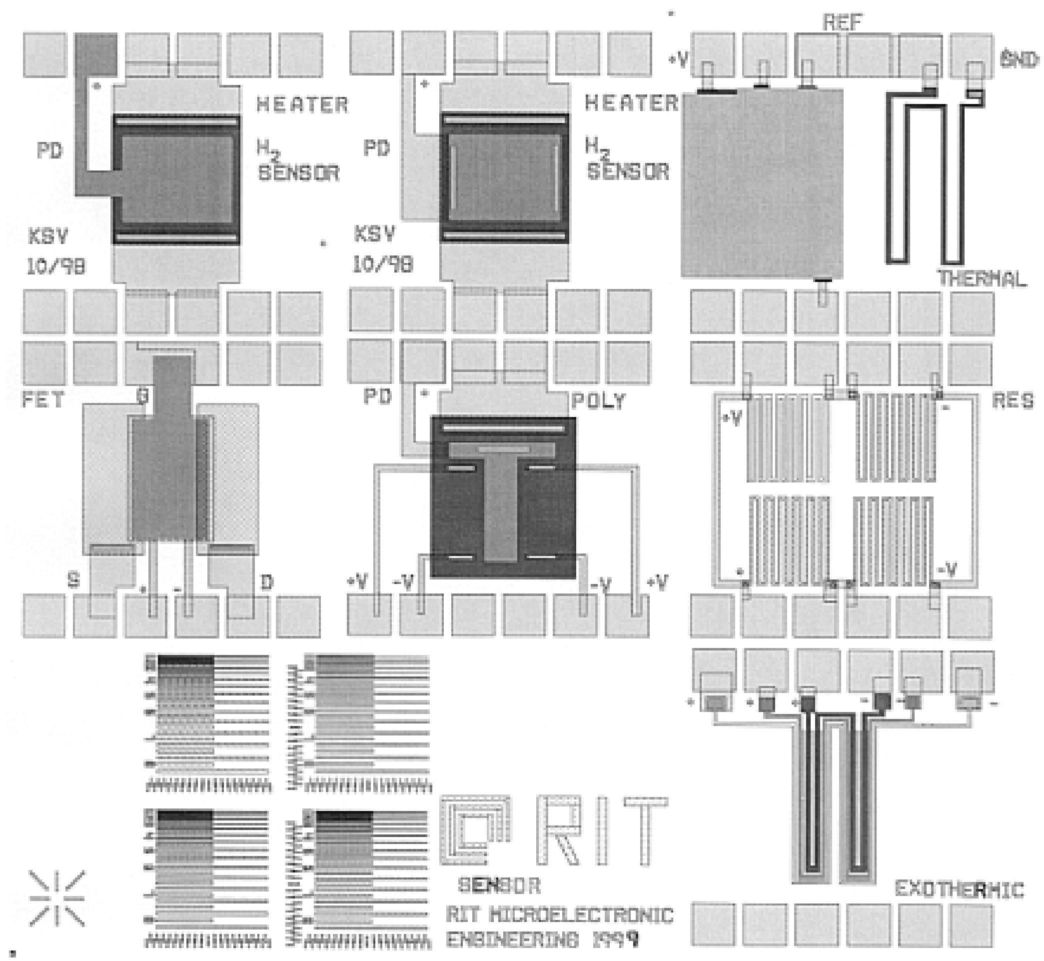
PLATINIDE-BASED HYDROGEN SENSORS



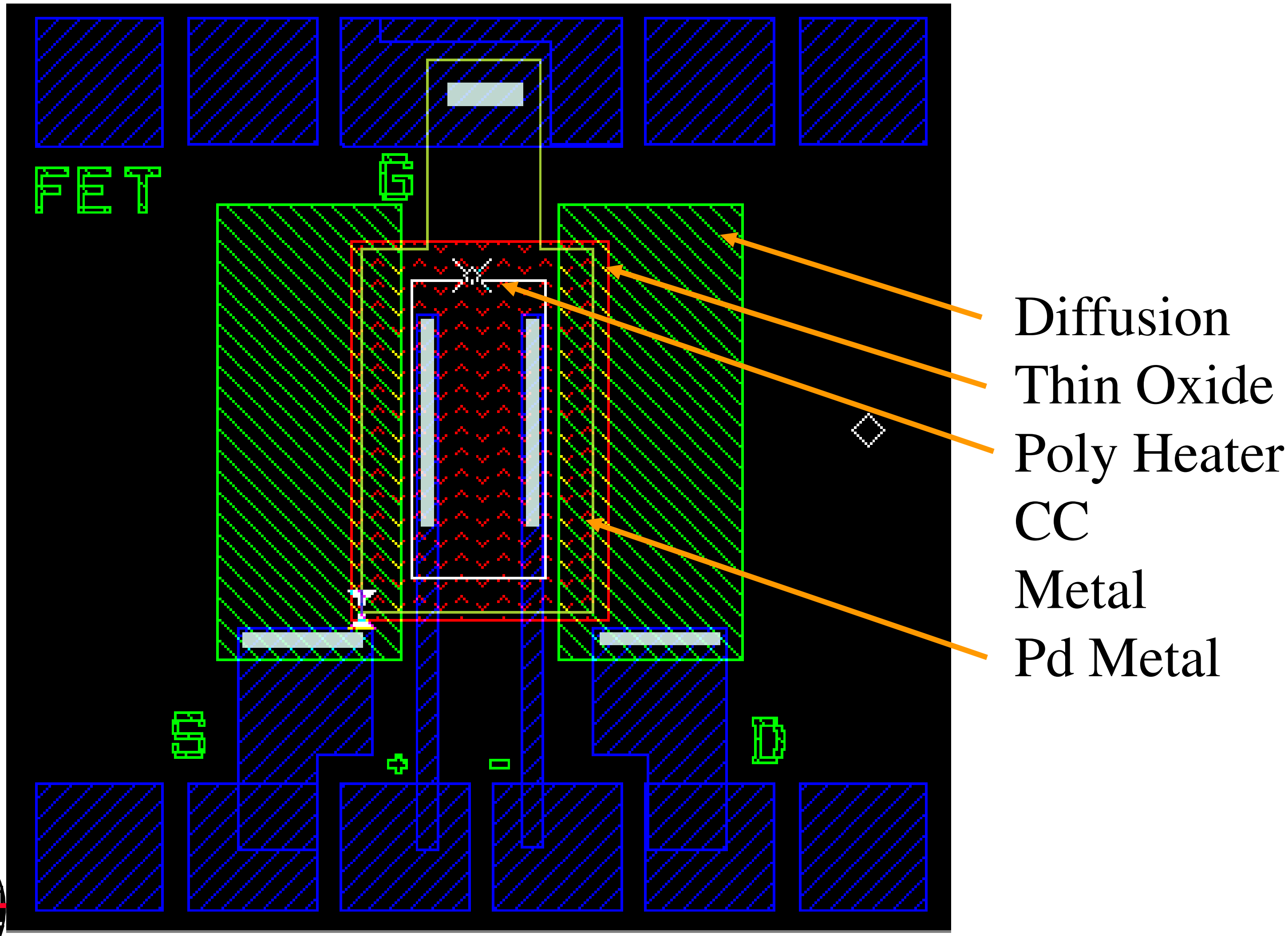
Hydrogen Detector

H2 adsorbs readily onto the Pt (Pt, Pd, Ir, etc.) gate material and dissociates into H atoms. The H atoms can diffuse rapidly through the Platinide and adsorb at the metal/oxide interface, changing the metal work function. This shifts the drain current through a shift in threshold voltage Vt via flatband voltage.

LAYOUT OF RIT HYDROGEN SENSOR TESTCHIP



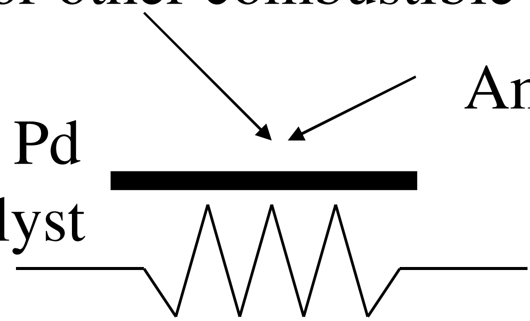
PALADIUM PMOSFET H2 SENSOR



CALORIMETRIC

$$P = Q(-\Delta H) = C\ dK/dt\ (-\Delta H)\ \text{ in W}$$

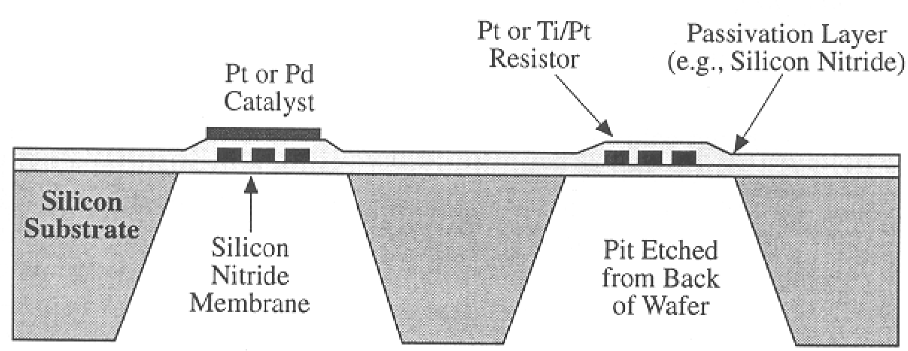
Hydrogen or other combustible gas



Ambient oxygen

Pt or Pd Catalyst

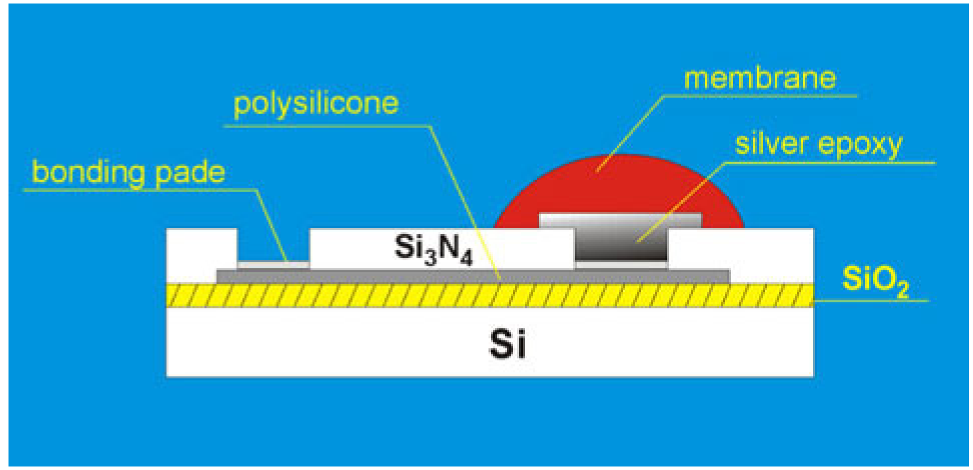
Temperature Sensor and Heater

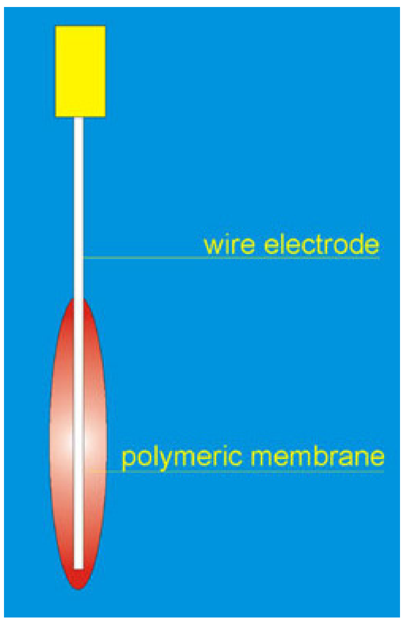


From: Micromachined Transducers, Gregory T.A. Kovacs,

POTENTIOMETRIC SENSING

Sensors for Ca^{2+}, NO_3^-, K^+, Cl^-, Li^+ and ClO_4^- have been developed. Platinum or other reference electrode in solution. Output is the open circuit voltage.





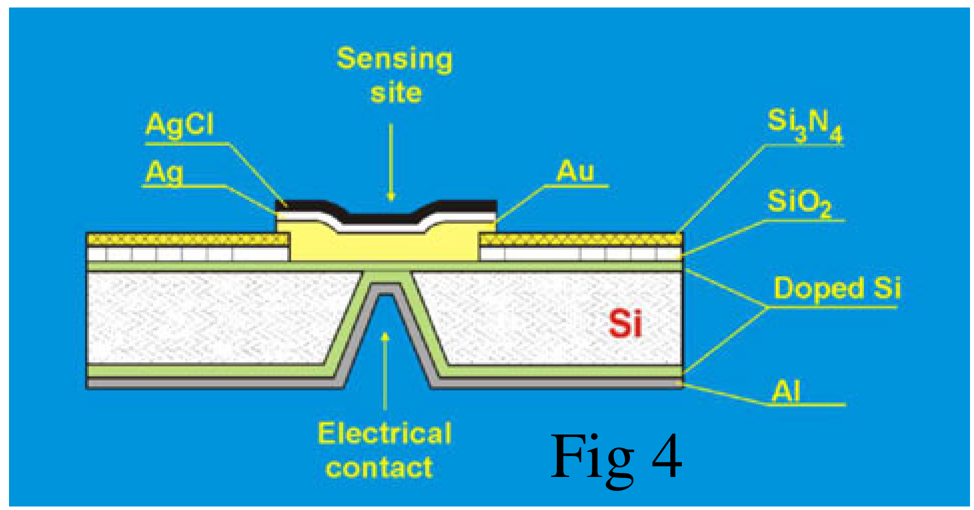
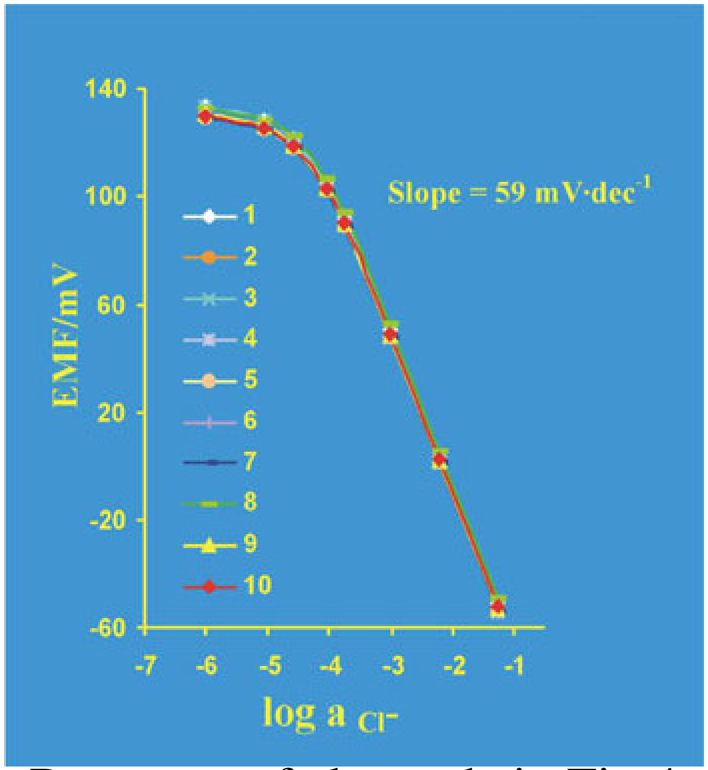


Fig 4

http://csrg.ch.pw.edu.pl/

POTENTIOMETRIC SENSING



Response of electrode in Fig 4 to changes in Cl- concentration

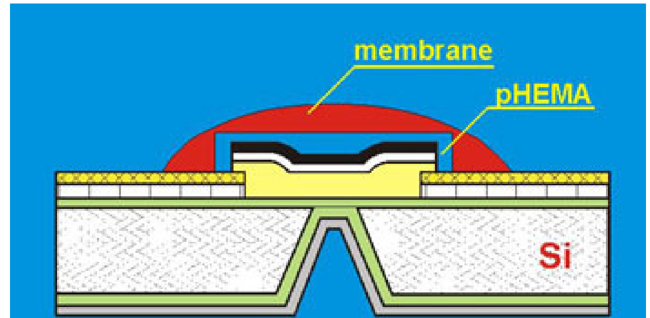
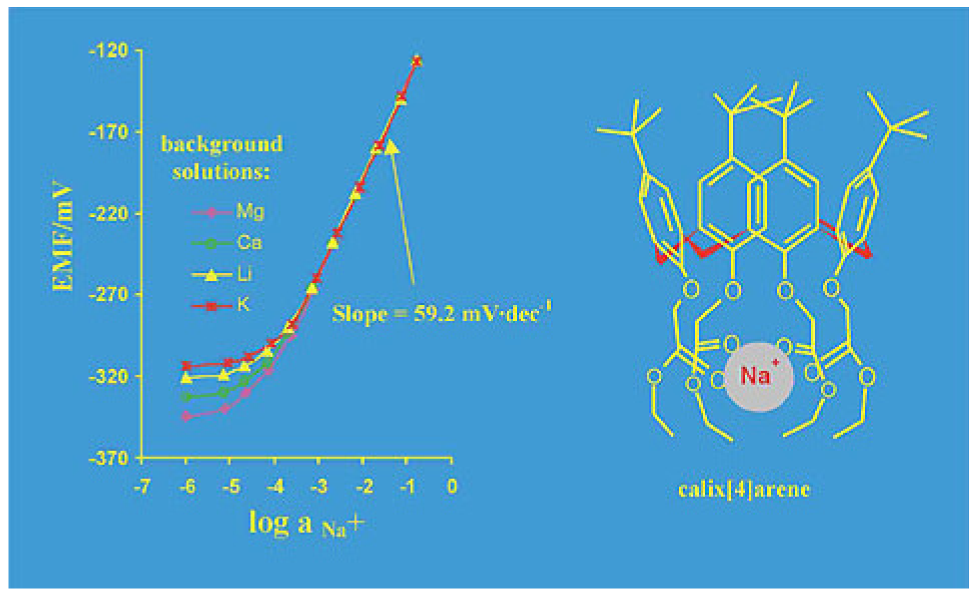


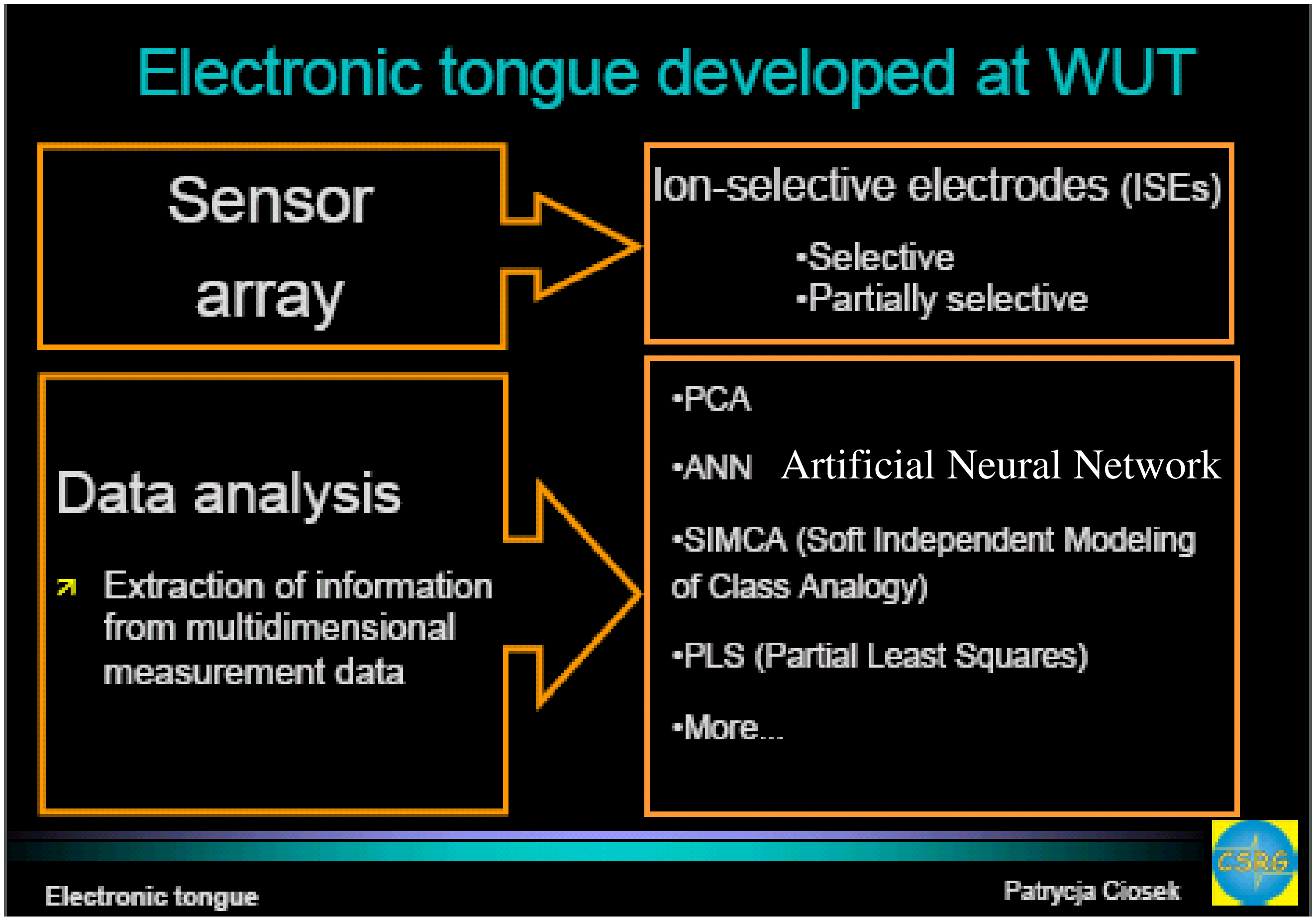
Fig 5



http://csrg.ch.pw.edu.pl/

Response of electrode in Fig 5 to changes in Na+ concentration

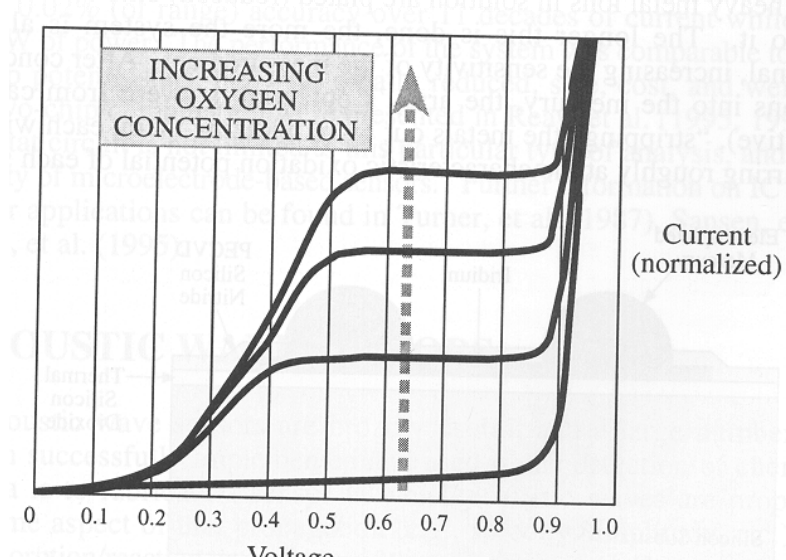
CHEMICAL NOSE / TOUNGE



http://csrg.ch.pw.edu.pl/tutorials/electronicT_N/etongue1.pdf

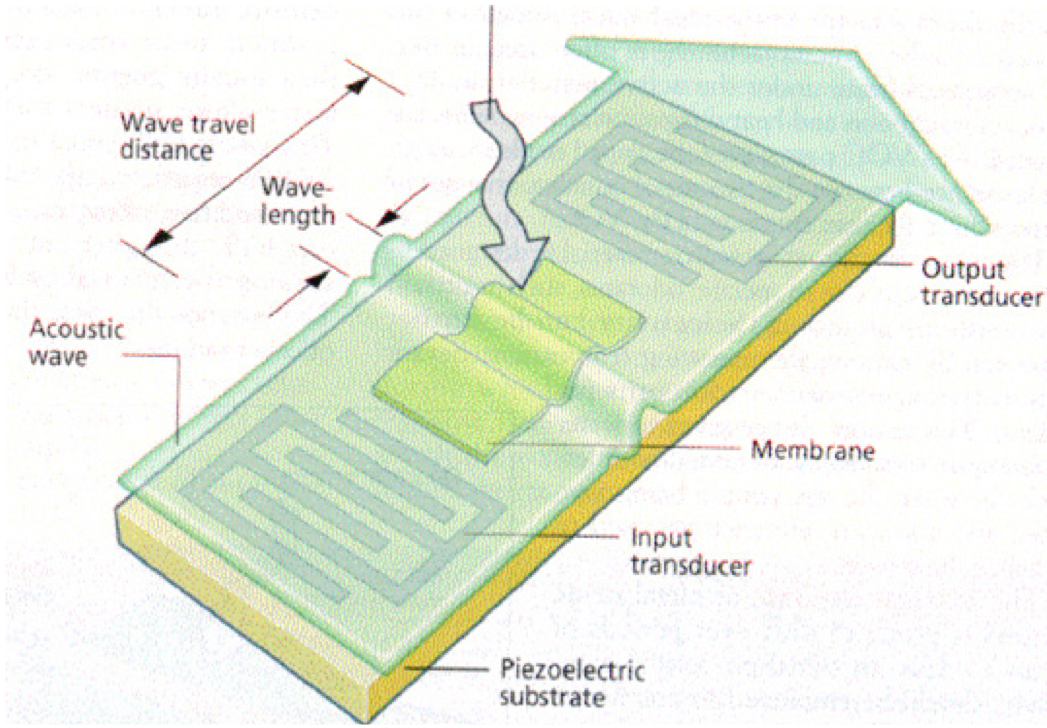
AMPEROMERIC SENSING

Apply a step in voltage sufficient in amplitude to immediately locally deplete the reactant species of interest at the surface, the resulting limiting current is theoretically given and can be related to the concentration of the gas being detected. For example: a noble metal (Au, Pt, etc) cathode in solution, coated with an oxygen permeable membrane, such as Teflon, polyethylene and apply a voltage between the measuring electrode and a larger counter electrode. The reaction involving oxygen at the cathode occurs at a relatively low voltage (less than 1 volt). The current at which plateau occurs is proportional to the oxygen concentration.



From: Micromachined Transducers, Gregory T.A. Kovacs,

SURFACE ACOUSTIC WAVE SENSORS



A surface acoustic wave is launched from a high voltage, high frequency, electrical signal applied to the interdigitated electrodes at one end of the sensor. The surface acoustic wave travels toward the other end of the sensor and there a set of interdigitated electrodes record a voltage. The time delay is sensitive to the coating and any adsorbed chemical in the chemically selective coating.

CHEMICAL SENSORS IN BIOSENSORS

The term biosensor refers to sensors wherein biologically derived molecules are used to perform an intermediate transduction between the desired measurand and some parameter readily measurable with a solid-state sensor. This approach takes advantage of the amazing selectivity of many biomolecule interactions, but unfortunately, some of the underlying binding or other chemical events are not easily reversible. Typically, an enzyme (protein), antibody (protein, polysaccharide, or nucleic acid is chosen to interact with the measurand.

ENZYME-BASED BIOSENSOR

The glucose oxidase based sensor is used to monitor glucose levels in diabetes and industrial fermentation processes. The enzyme is immobilized on a platinum electrode, and covered with a thin polyurethane membrane to protect the enzyme layer. Glucose oxidase, in its oxidized form, oxidizes glucose entering the sensor to gluconic acid; resulting in the conversion of the enzyme to its reduced form. The enzyme does not remain in this form for long. It interacts with oxygen entering through the membrane. The products of this interaction are the oxidized form of the enzyme, two hydrogen ions and two oxygen ions. The hydrogen is detected by the a platinum catalyzed hydrogen chemical sensor.

BLOOD ANALYSIS CHIP

I-stat Corp, Princeton, N.J. sells a unit that uses micromachined electrochemical sensors to analyze a 60 μL drop of blood for sodium, potassium, chloride ions, urea, glucose, and hematocrit concentrations. The hand-held unit, with disposable cartridges, plugs into a bench top instrument for readout.

What we would like to measure……

MICRO GAS CHROMATOGRAPHY

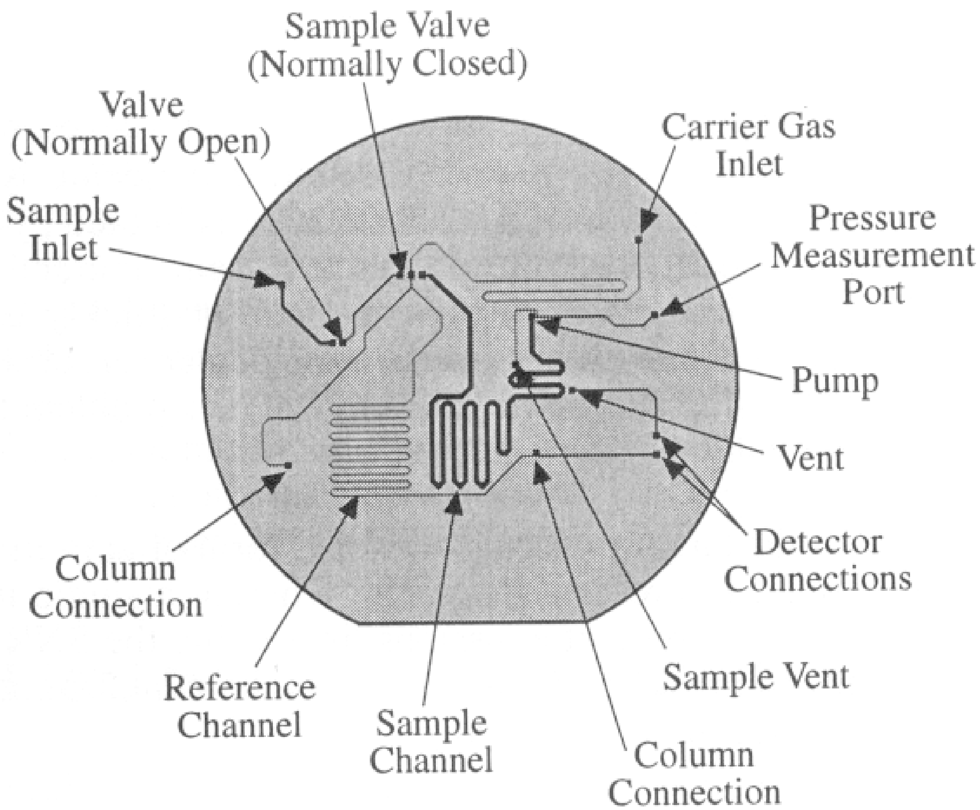


Illustration of a micromachined gas chromatography system. After Terry, et al. (1979).

GAS CHROMATOGRAPH

784 IEEE SENSORS JOURNAL, VOL. 6, NO. 3, JUNE 2006

Recent Advancements in the Gas-Phase MicroChemLab

Patrick R. Lewis, Ronald P. Manginell, Douglas R. Adkins, Richard J. Kottenstette, David R. Wheeler, Sara S. Sokolowski, Daniel E. Trudell, Joy E. Byrnes, Murat Okandan, Joseph M. Bauer, Robert G. Manley, and Gregory C. Frye-Mason

***Abstract*—Sandia's hand-held MicroChemLab system uses a micromachined preconcentrator, a gas chromatography channel, and a quartz surface acoustic wave array detector for sensitive/selective detection of gas-phase chemical analytes. Requisite system size, performance, power budget, and time response mandate microfabrication of the key analytical system components. In the fielded system, hybrid integration has been employed, permitting optimization of the individual components. Recent improvements in the hybrid-integrated system, using plastic, metal, or silicon/glass manifolds, is described, as is system performance against semivolatile compounds and toxic industrial chemicals. The design and performance of a new three-dimensional micropreconcentrator is also introduced. To further reduce system dead volume, eliminate unheated transfer lines, and simplify assembly, there is an effort to monolithically integrate the silicon PC and GC with a suitable silicon-based detector, such as a magnetically-actuated flexural plate wave sensor or a magnetically-actuated pivot plate resonator.**

***Index Terms*—Acoustic detection microanalytical system, gas**

functions were performed by three microfabricated components, coupled via electrical/fluidic packaging, and housed in a hand-held system, complete with system-level control, and a rugged, simple-to-use interface.

The initial system application was the selective detection of chemical warfare agents (CWA), though the range of analytes has been expanded over the years to include pharmaceutical solvents, petrochemicals, toxic industrial chemicals (TICs) and tri-halo-methanes (THMs). In any of these cases, but particularly with CWA detection, rapid response, low power consumption, small size, and minimization of false positives are essential system requirements. Integrated sampling and sample preparation functions, as well as fast chemical separations via micro gas chromatography (GC), are likewise critical. The diversity of these attributes dictates a multidisciplinary approach: microfabrication was used to provide small, low-power critical com-

GAS CHROMATOGRAPH

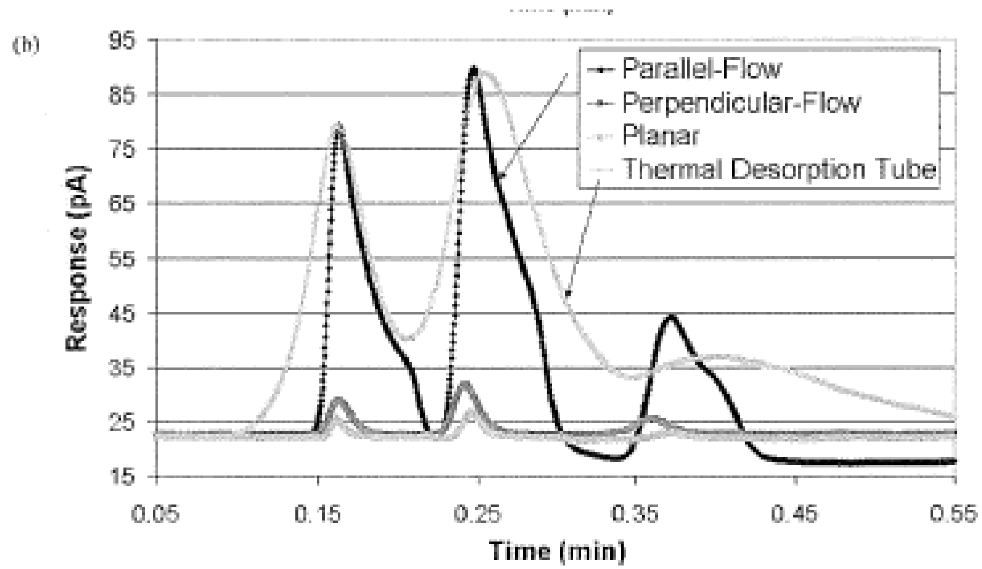


Fig. 4. (a) Desorption peaks from the planar and perpendicular flow 3D-PC as seen by a downstream flame ionization detector (FID). (b) Comparison of the desorption response of various preconcentrator devices with the adsorbent Tenax TA. Device response with TIC analytes after a 300-s collection. The parallel-flow micropreconcentrator has improved performance compared with the conventional desorption tube; the former takes 0.6 W, while the latter 3 W. (Color version available online at http://ieeexplore.ieee.org.)

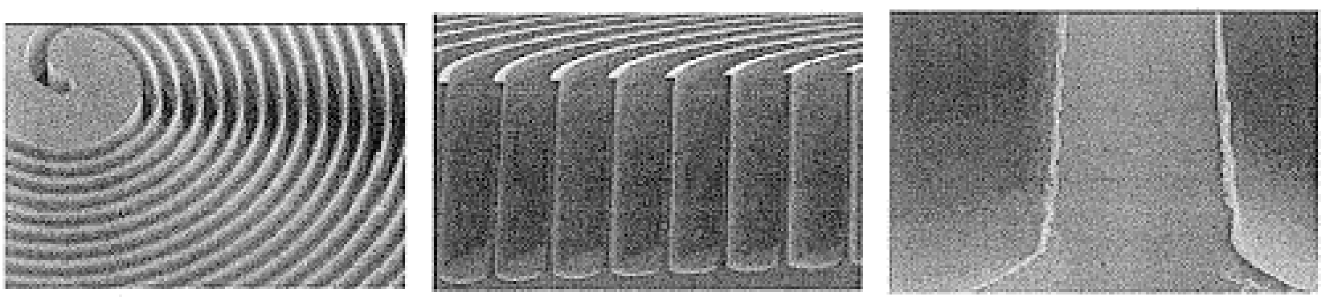


Fig. 5. SEMs of the deep-etched, spiral GC column. Far right shows a stationary phase. For scale, the channels are 100 micron wide with 25-micron-thick walls. (Color version available online at http://ieeexplore.ieee.org.)

REFERENCES

1. Micromachined Transducers, Gregory T.A. Kovacs, McGraw-Hill, Ch.8 - Chemical and Biological Transducers, pp687-778., 1998.

2. Principles of Chemical and Biological Sensors, Edited by Dermot Diamond, John Wile and Sons, 1998.

3. “Microfabricated Sensor Arrays Sensitive to pH and K+ for Ionic Distribution Measurements in the Beating Heart”, Cosofret, Erdosy, Johnson, Buck, Ash, Neuman, U of North Carolina, American Chemical Society, Journal of Analytical Chemistry, Vol 67, No. 10 May 15, 1995.

4. “Acrylated Polyurethane as an alternative Ion-Selective Membrane Matrix for Chemical Sensors”, A Bratov, et.al., Sensors and Biosensors Group, Department of Chemistry Universitat Autonoma de Barcelona, Spain, Transducers ‘95, IEEE 8th International Conference on Solid State Sensors and Actuators, and Eurosensors IX, Stockholm, Sweden June 25-29, 1995.

REFERENCES

5. Fabrication and Fabrication of a Resistive Chemical Sensor, Elizabeth Gregg, RIT Intern, Summer 2005

6. Microfabtication of a Chemical Gas Sensor, Senior Project Report by Steve Parshall, May 2006.

7. "Recent Advances in the Gas-Phase MicroChem Lab", Patrick R. Lewis, et.al., IEEE Sensors Journal, Vol 6 No. 3, June 2006

8. "MEMS Chemical Gas Sensor", Frank Zee and Jack Judy, UCLA, IEEE UGIM Conference

9. http://csrg.ch.pw.edu.pl/tutorials/electronicT_N/ Chemical Sensor Research Group, Warsaw University of Technology, Warsaw, Poland, Professor Zbigniew Bruzozka

10. Sigma Aldrich – Sensor Applications, http://www.sigmaaldrich.com

HOMEWORK - CHEMICAL SENSORS

1. Calculate the amount of liquid needed to prepare a sample of 8000 ppm acetone in air.
2. Design a sensor that can distinguish between methanol, ethanol and isopropyl alcohol.
3. How can carbon monoxide be detected.
4. How can methane (CH_4) be detected.