

**ROCHESTER INSTITUTE OF TECHNOLOGY
MICROELECTRONIC ENGINEERING**

RIT CHEMICAL SENSORS

**Dr. Lynn Fuller, Ellie Brion,
Ellen Sedlack**

Dr. Fuller's Webpage: <http://www.rit.edu/~lffeee>

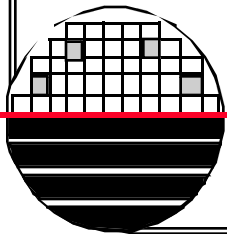
Microelectronic Engineering
Rochester Institute of Technology
82 Lomb Memorial Drive
Rochester, NY 14623-5604

Tel (585) 475-2035

Fax (585) 475-5041

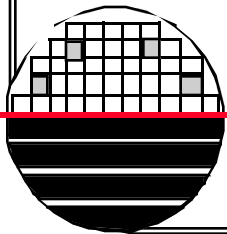
Email: Lynn.Fuller@rit.edu

Program webpage: <http://www.microe.rit.edu>



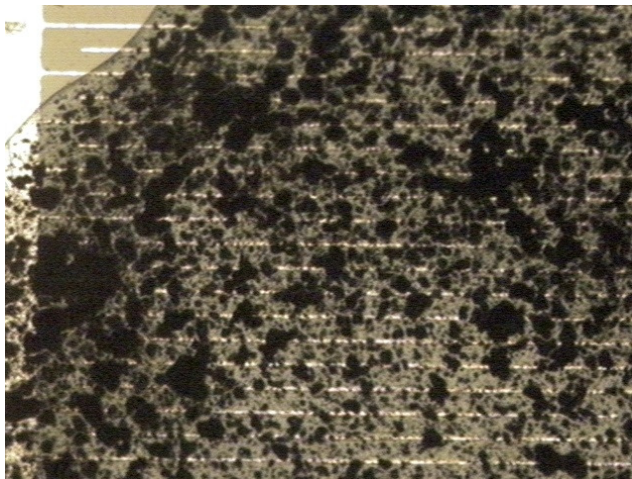
OUTLINE

Introduction
Chem Resistors
Modeling of Resistance Change
 Parallel
 Series
Coatings
Test Results

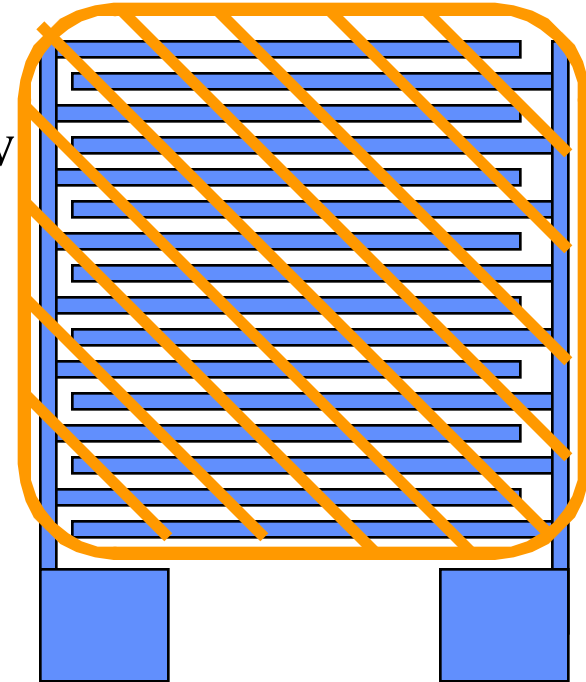


CHEMIRESISTOR

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



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



Resistor with
25 μ m gaps
25 μ m length
7250 μ m width

MODELING OF PARALLEL RESISTANCE CHANGE

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

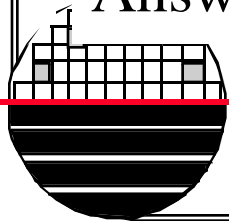
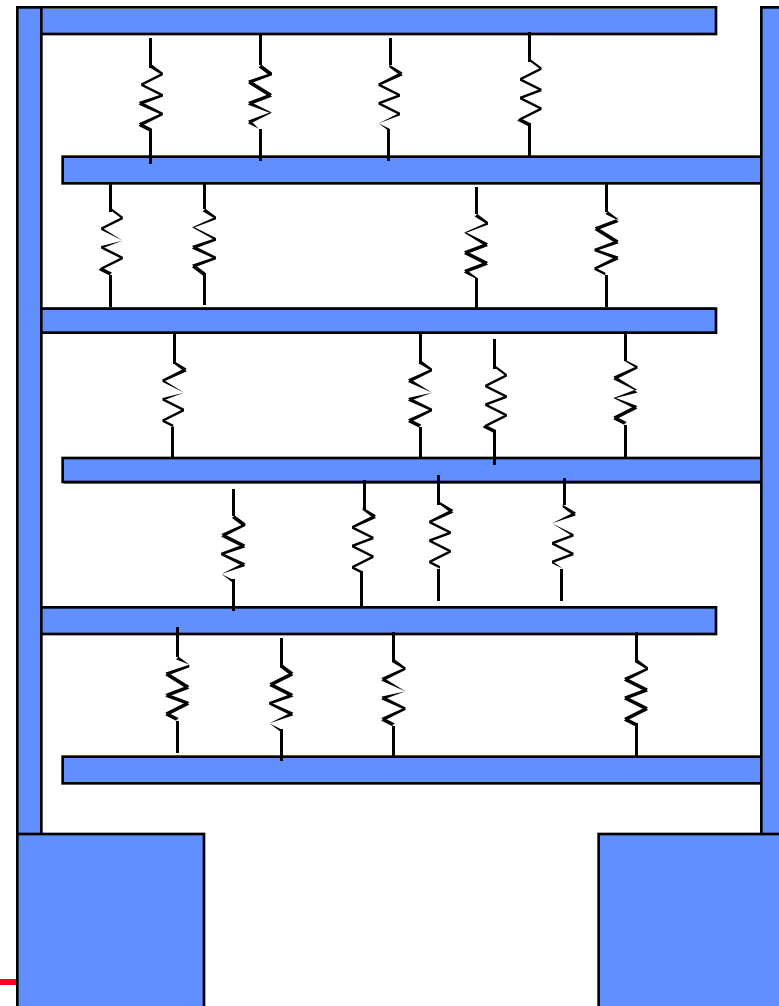
Answer 20 ohms

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?

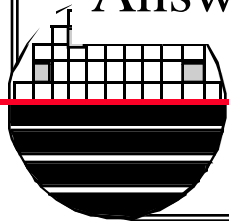
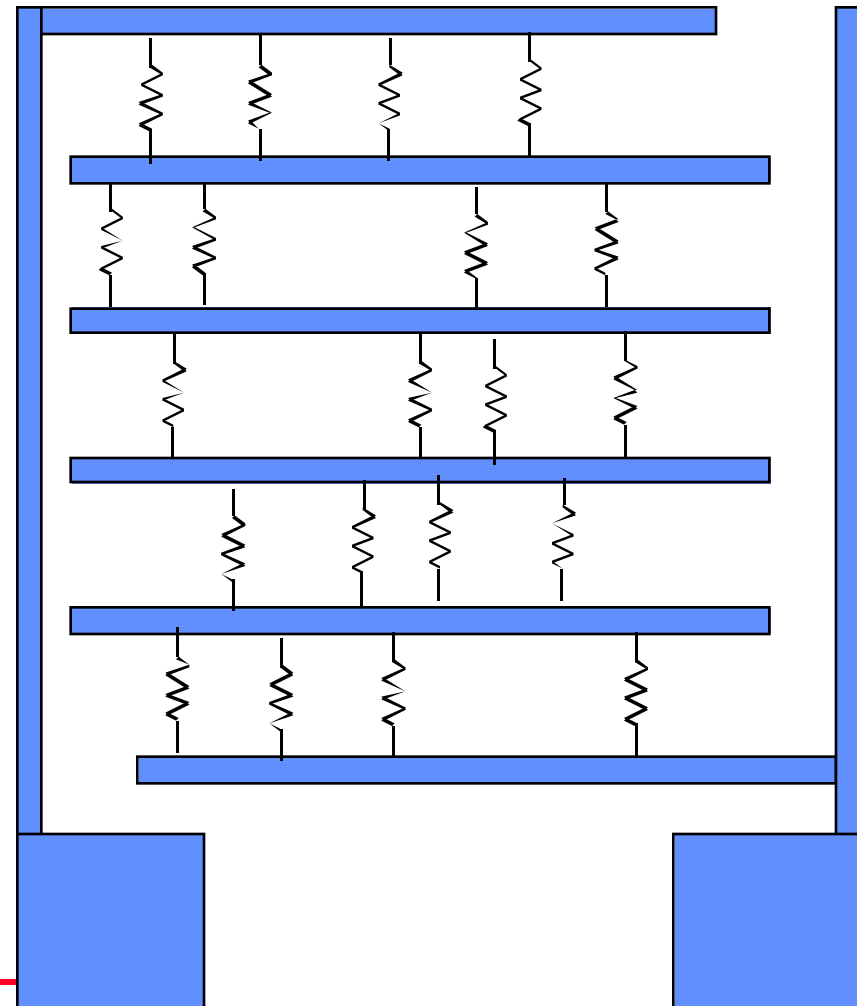
Answer 500 ohms

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%

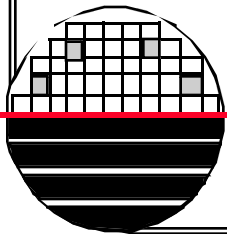


SUMMARY OF MODELING

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.



DEFINITION OF TERMS

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

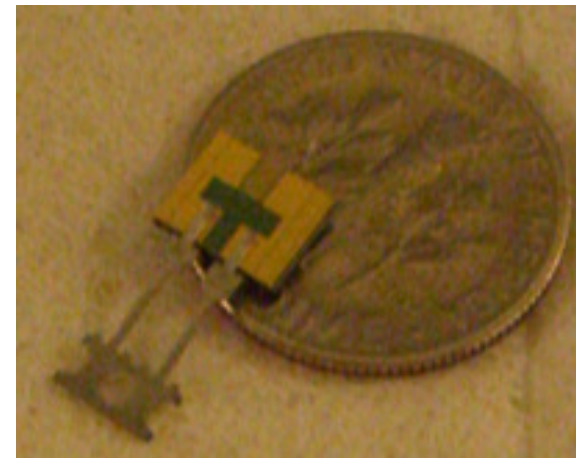
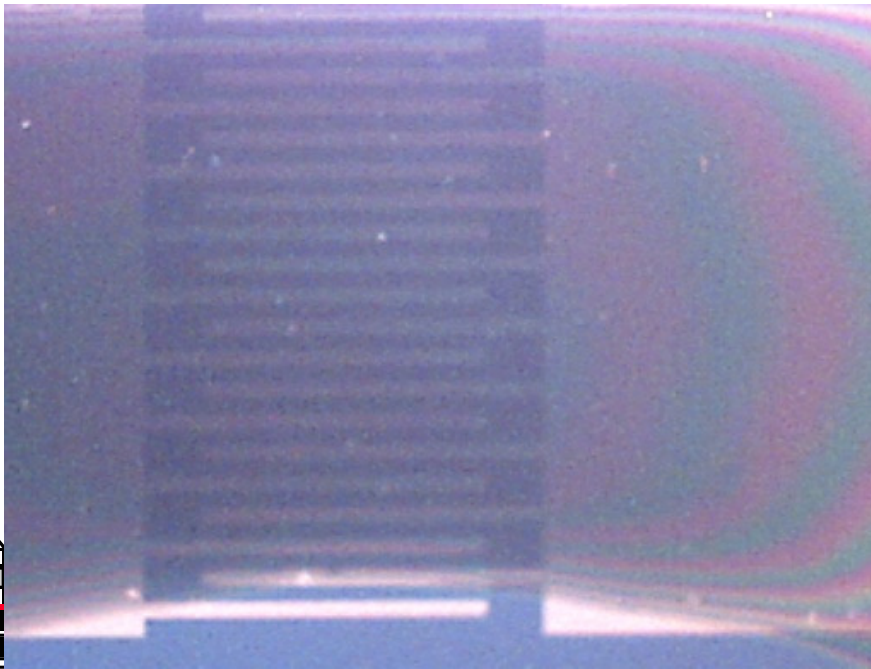
Rheological Properties – flow characteristics

Photoinitiator – causes cross linking in the presents of light

Crosslinker – used with low molecular weight monomers, causes cross linking

COATING TO DETECT ETHANOL

- ◆ 2 μm of (3,4-polyethylenedioxythiophene-polystyrenesulfonate) PEDOT polymer is applied to interdigitated electrodes and cured at 100 °C 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

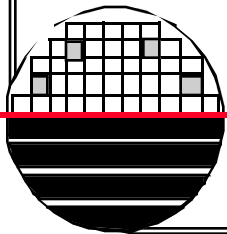


Steve Parshall, Dr. KSV
May 2006

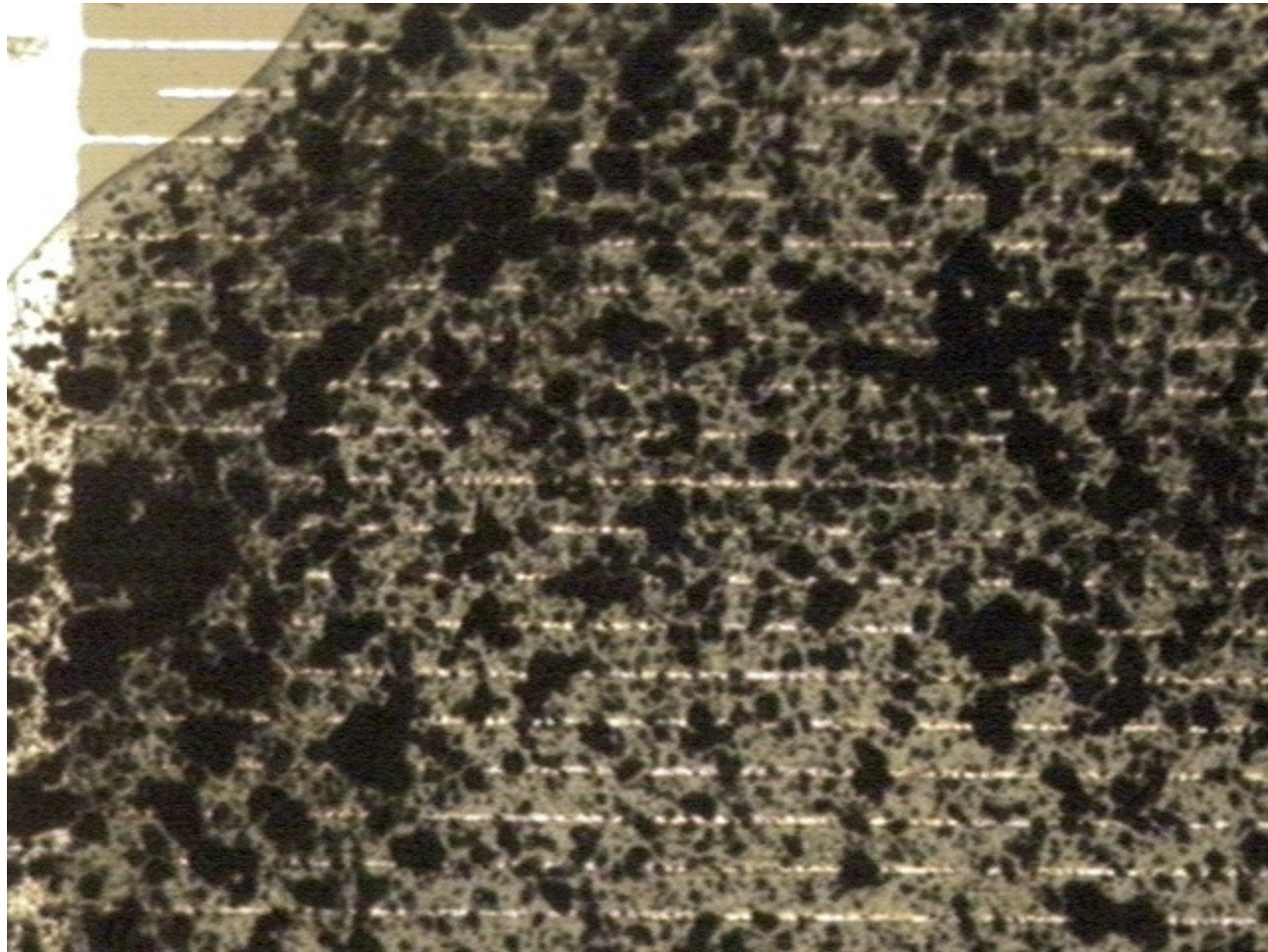
COATINGS

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

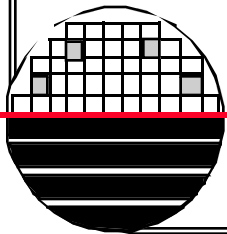
Carbon Black mixed with Nailpolish is sensitive to Acetone.



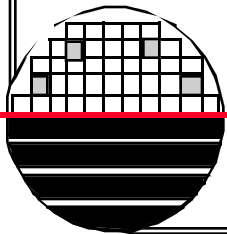
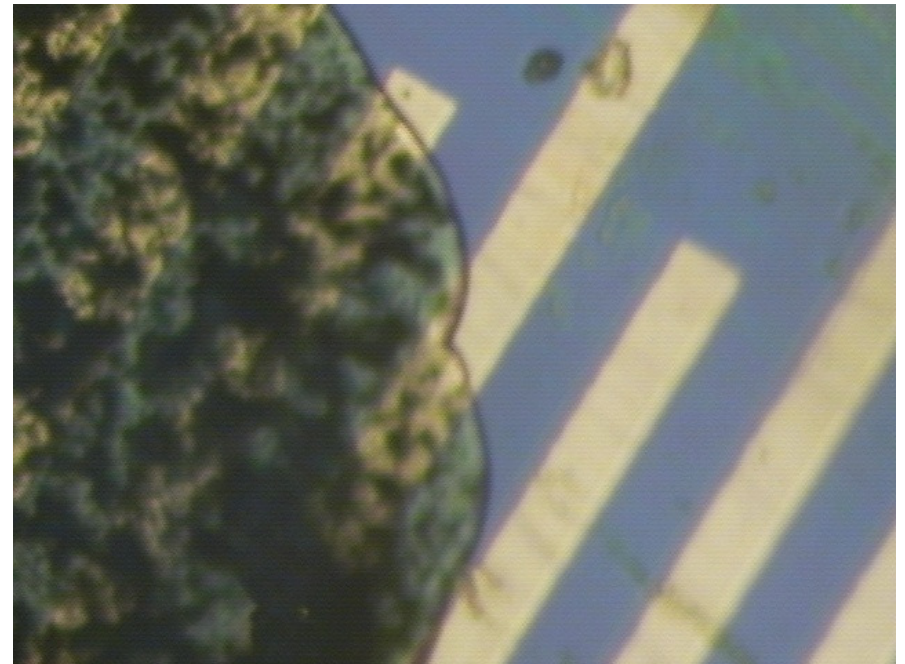
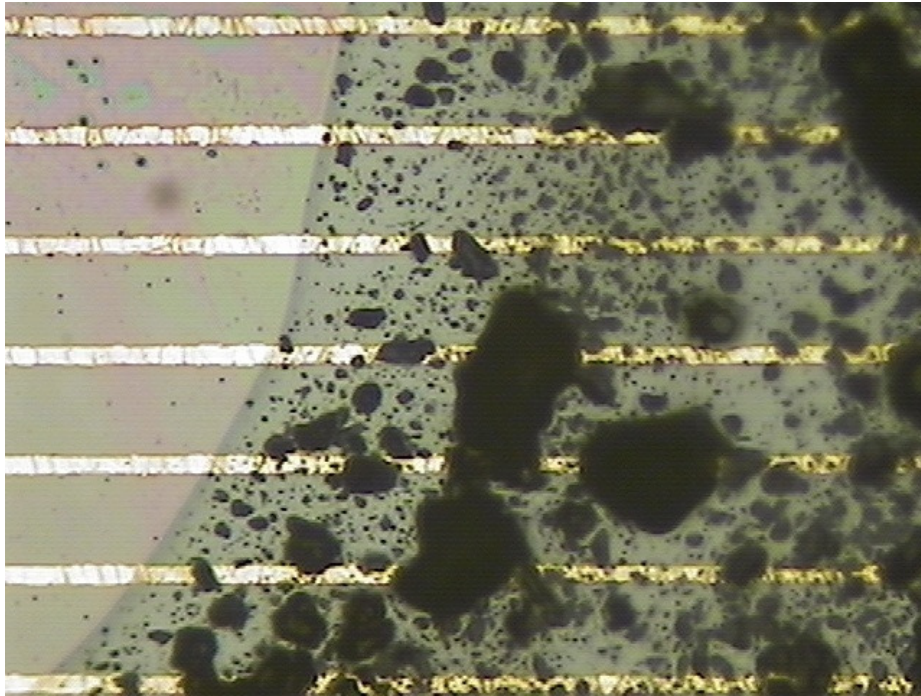
CARBON BLACK MIXED WITH AIRPLANE GLUE



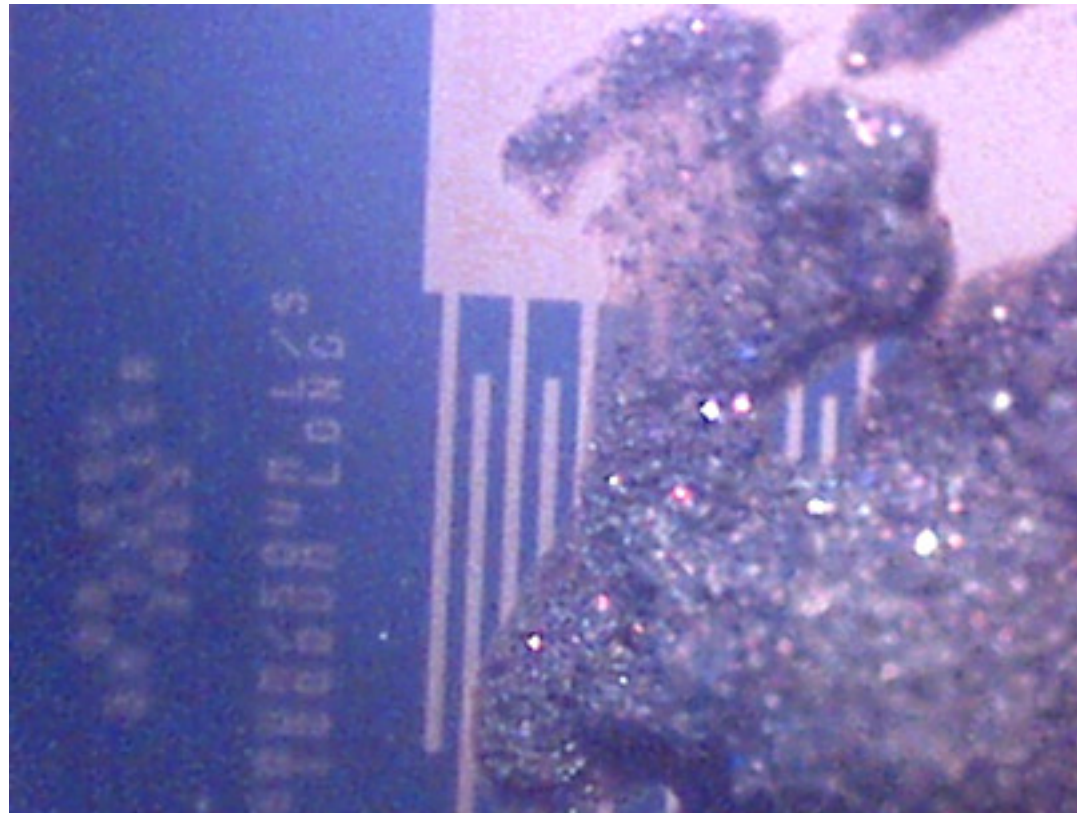
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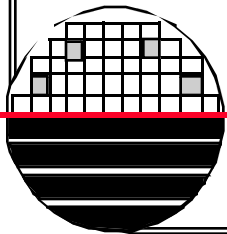
CARBON BLACK MIXED WITH AIRPLANE GLUE



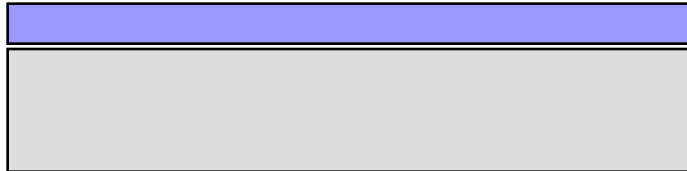
THICK COATING



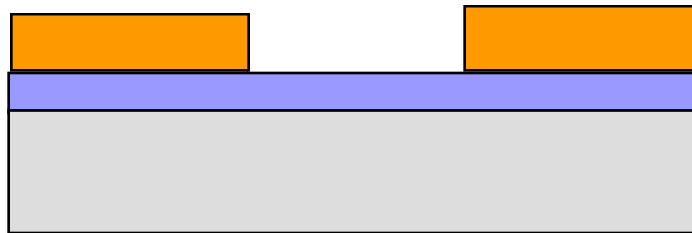
Thinner coatings are more sensitive



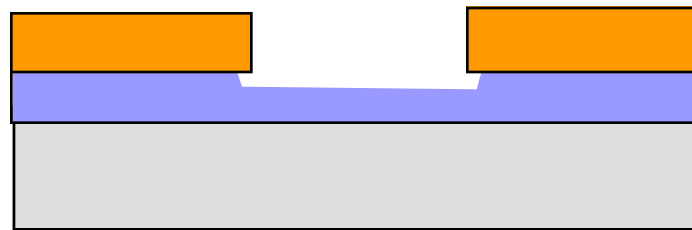
TYPICAL FABRICATION DETAILS



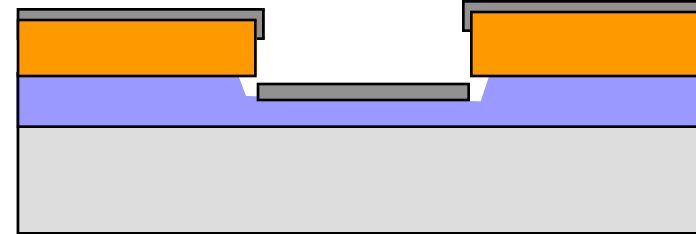
Glass wafer or Silicon wafer with 10,000Å oxide on it



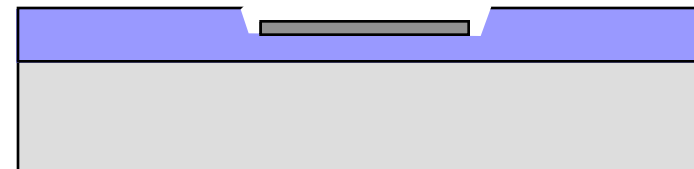
Normal Positive Photoresist Via



Over etch to create undercut

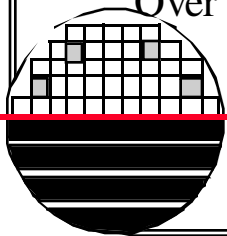


Deposit Metal for Fingers and Pads

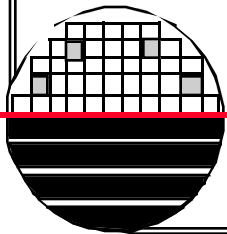
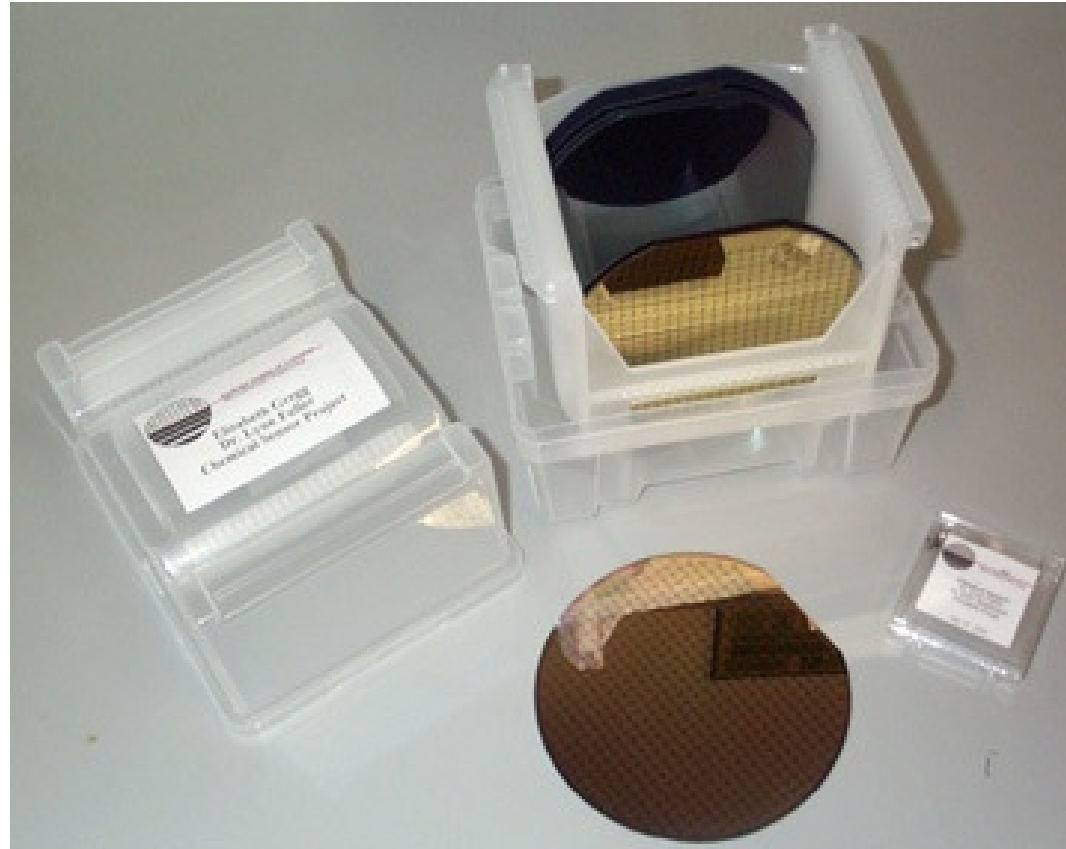


Lift-Off in Acetone and ultrasonic

Many variations exist including:
etch metal instead of lift-off,
different metals or multiple layers
of metal, solder bumps, etc

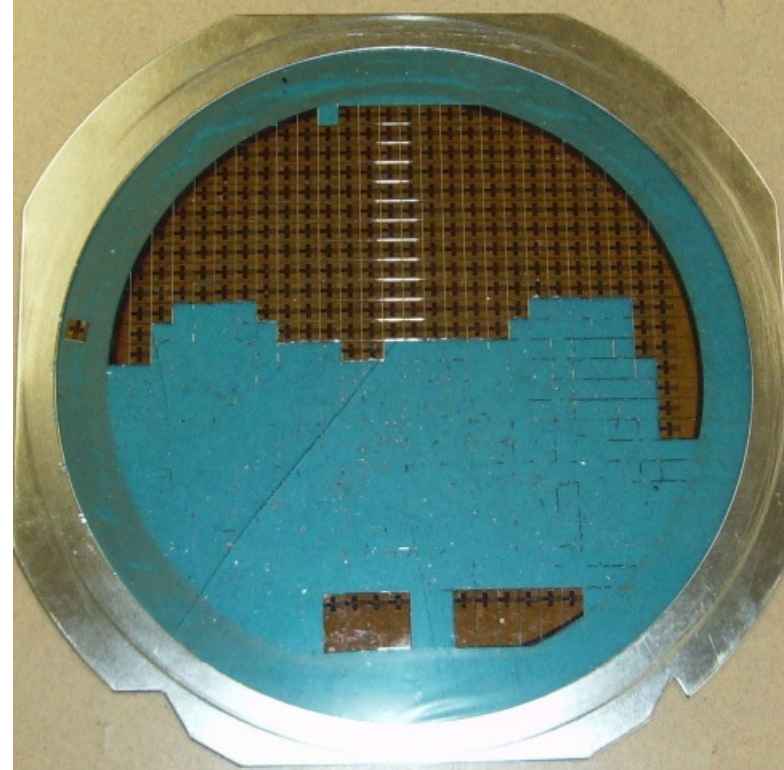
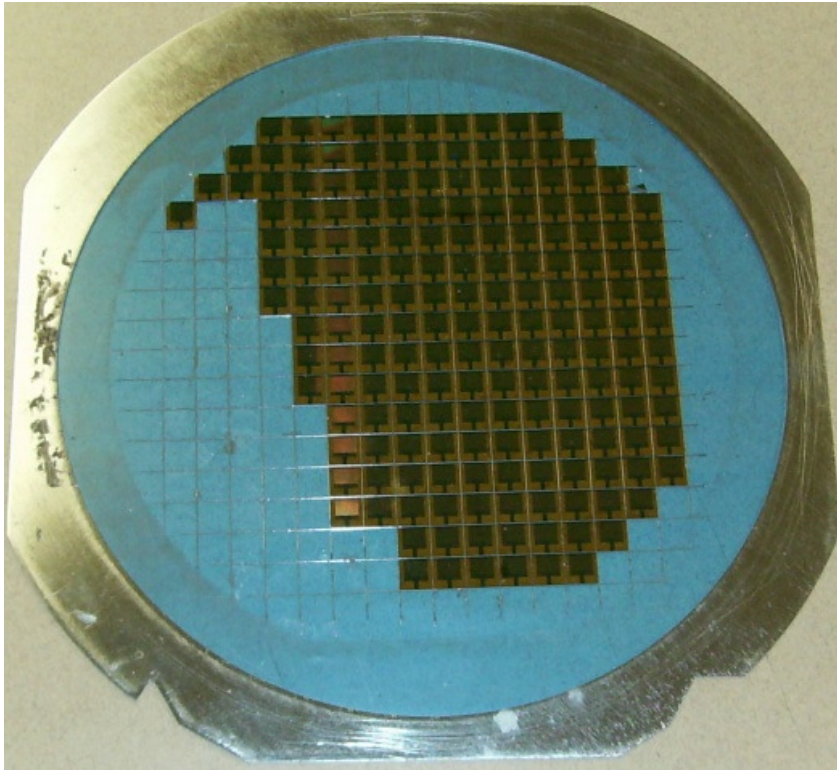


FINISHED WAFERS OF CHEMICAL SENSORS

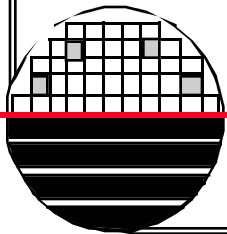


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WAFERS OF SENSORS CUT (SOME REMOVED)

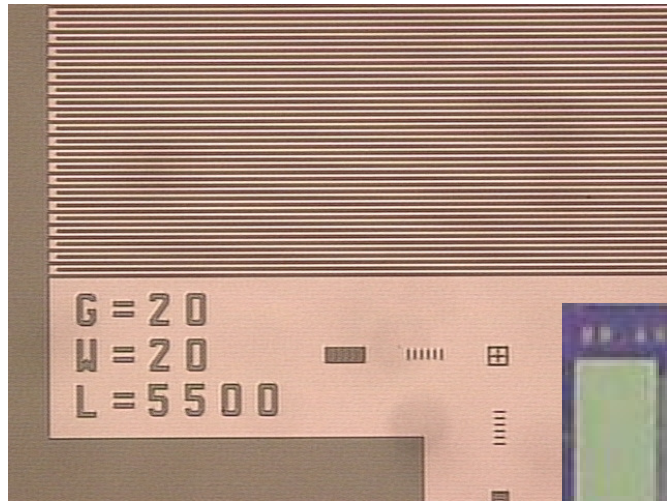


Ellen Sedlack

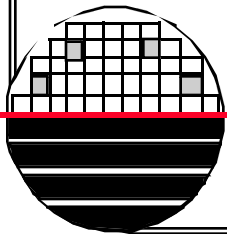
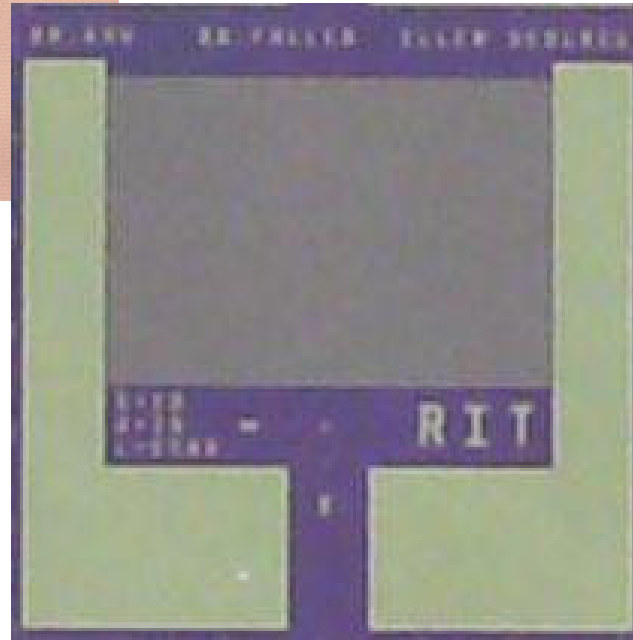


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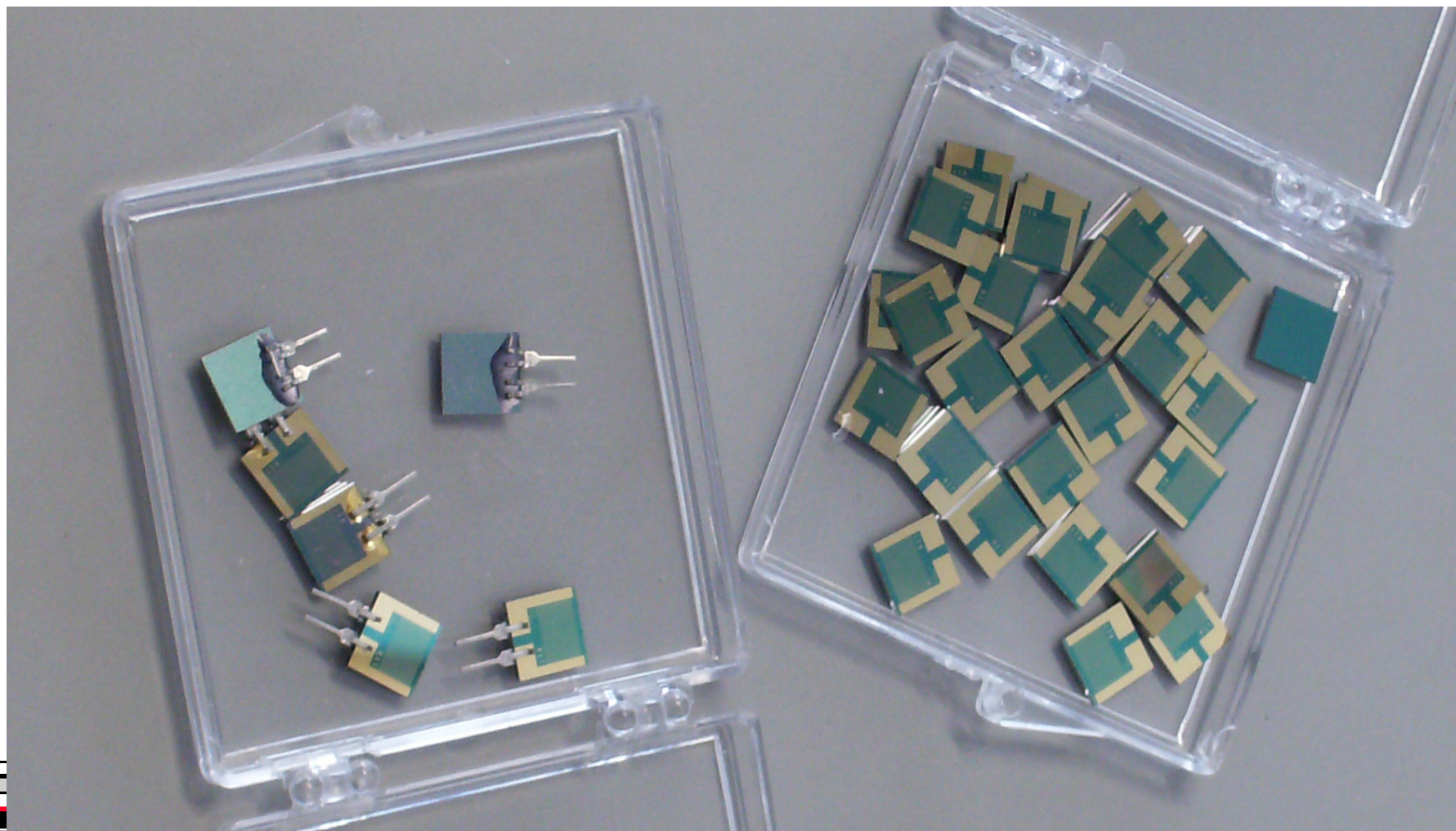
PARALLEL ARCHITECTURE



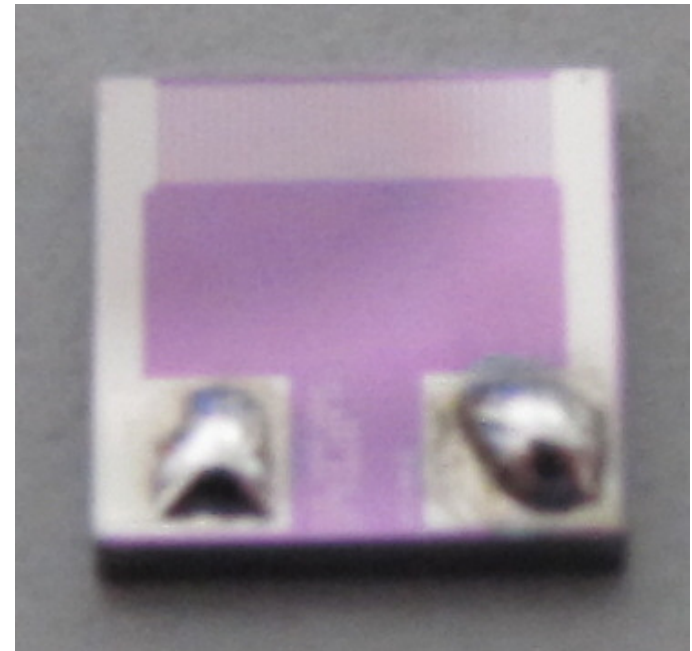
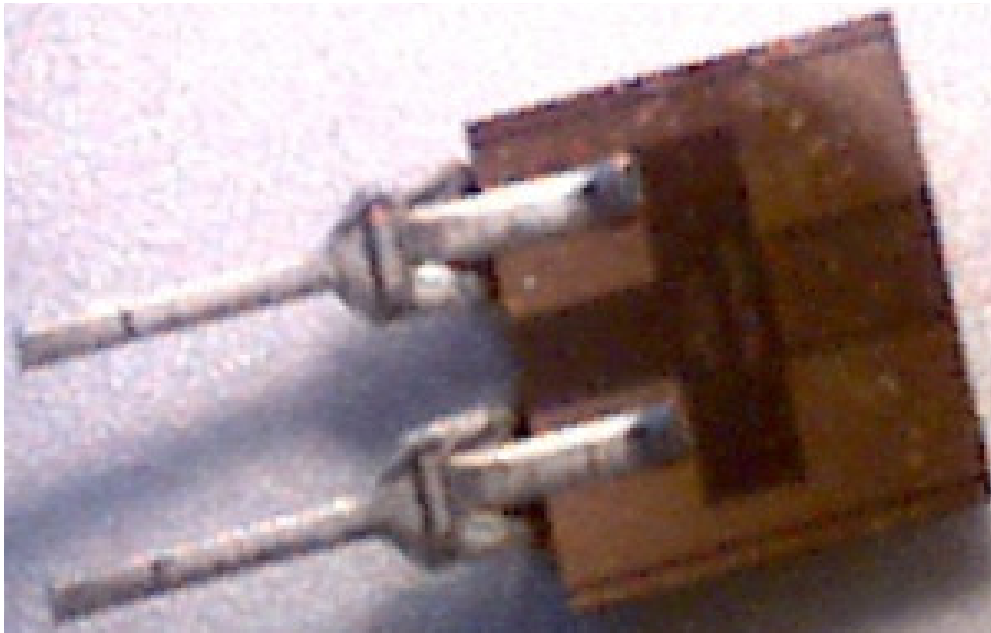
Ellen Sedlack



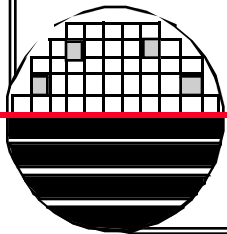
COMPLETED ELECTRODES



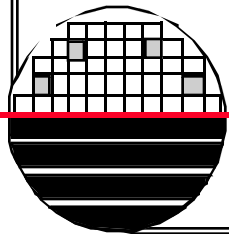
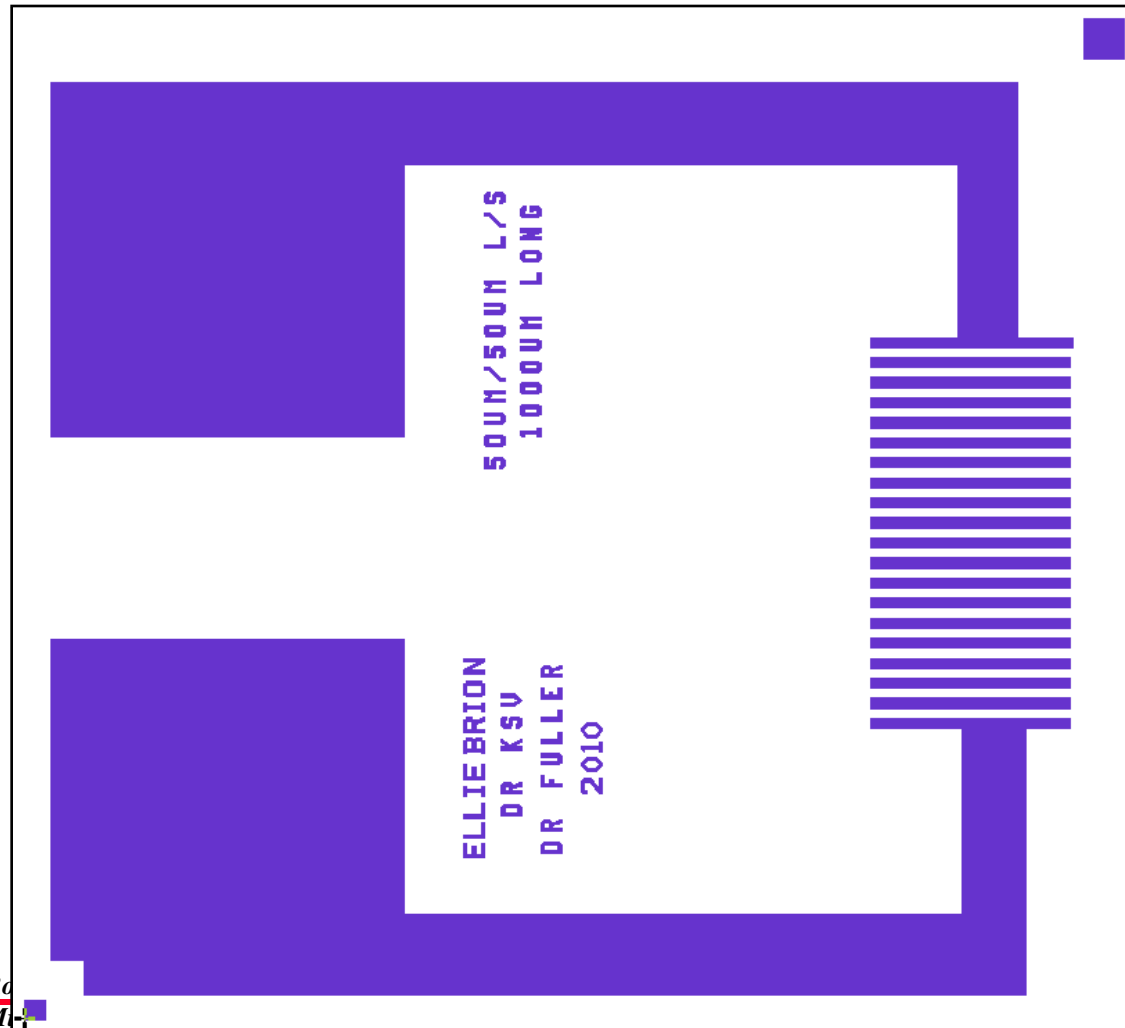
COMPLETED ELECTRODES



Left: Sensor chip (no coating) with clip on pins
Right: Sensor chip with solder connections



CHEMICAL SENSOR USING SERIES ARCHITECTURE



Rd
Mt

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 (m³)] X						BAC = Blood Alcohol Concentration BAC = wt. In gm of ethanol/100 BAC = wt. In gm of ethanol/210		
[Volume of one mole of air (L/mole) / Molecular weight of sample (g/mole)]								
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								
				Concentration in ppm =	346	ppm	Ex: 0.0002ml ethanol in 250 mL 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 ₃ OH	32.04243	810	0				
ethanol	CH ₃ CH ₂ OH	46.06952	816	1				
2-propanol	CH ₃ CH ₂ CH ₂ OH	60.09661	804.13	0				
acetone	CH ₃ COCH ₃	58.08	784.58	0				
Reference: http://www.ilpi.com/msds/ref/concentration.html								

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%

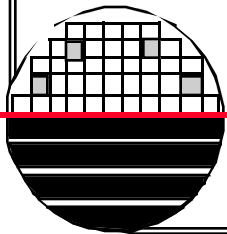
Nail Polish

Cellulose Acetate Solution

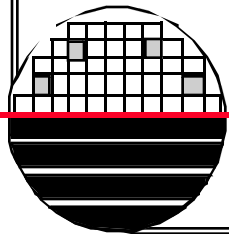
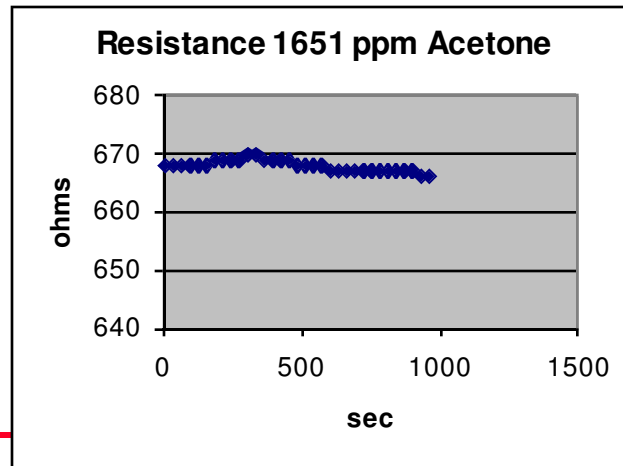
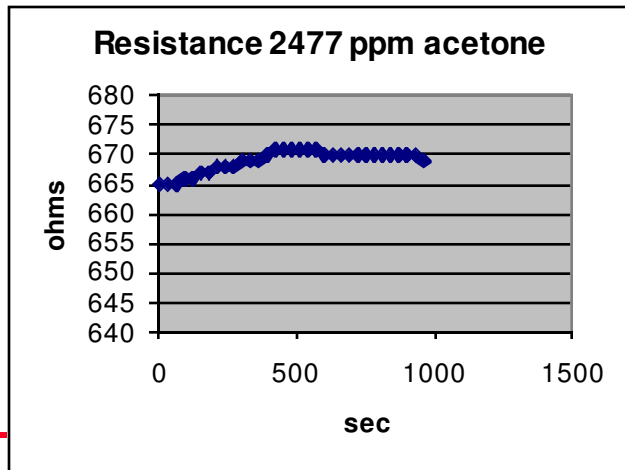
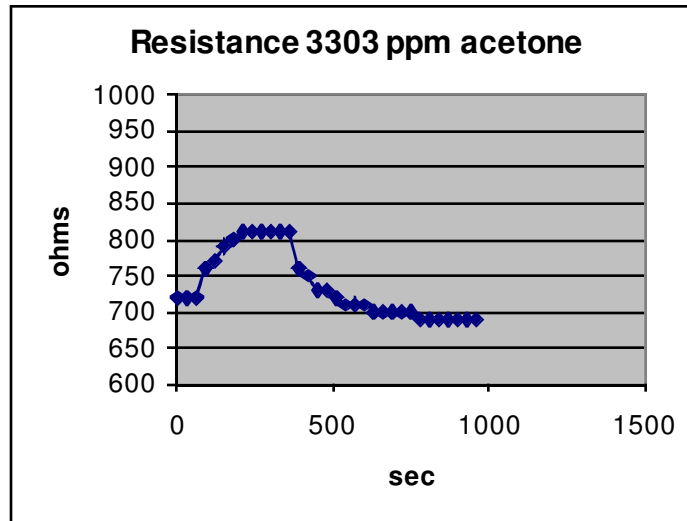
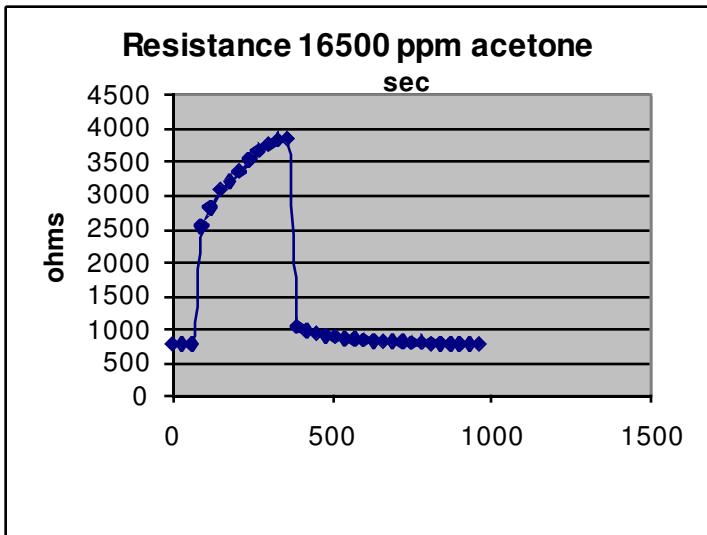
From the MSDS:	Nitrocellulose (polymer)	10%
	Di butyl Phthalate (plasticizer)	1%
	Camphor (aromatic)	5%
	Benzophenone-1 (UV Blocker)	1%
	Toluene (solvent)	5%
	Butyl acetate (solvent)	25%
	Ethyl Acetate (solvent)	45%
	Isopropyl Alcohol (solvent)	5%

MECHANISM OF POLYMER SWELLING

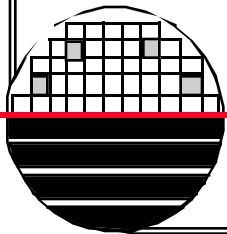
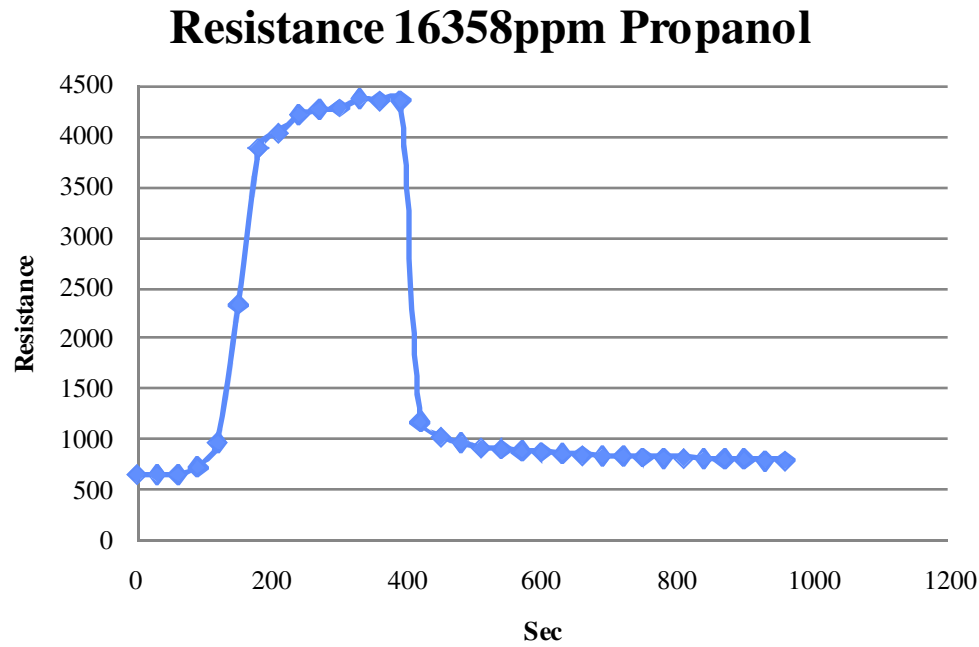
Solvents interact with the polymer, plasticizer or other additives in the film causing swelling. For example nail polish and airplane glue have the same base polymer, Nitrocellulose, which swells in the presence of acetone and both show acetone sensitivity. Nail polish does not show sensitivity to alcohol 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.



AIR PLANE GLUE / CARBON BLACK TEST RESULTS

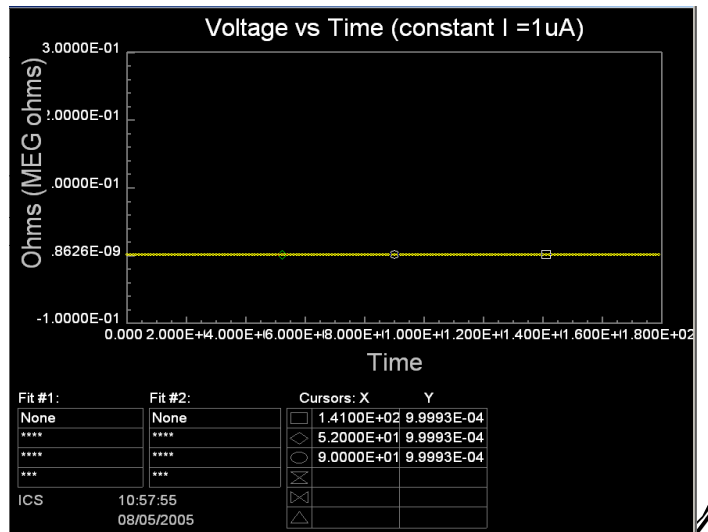
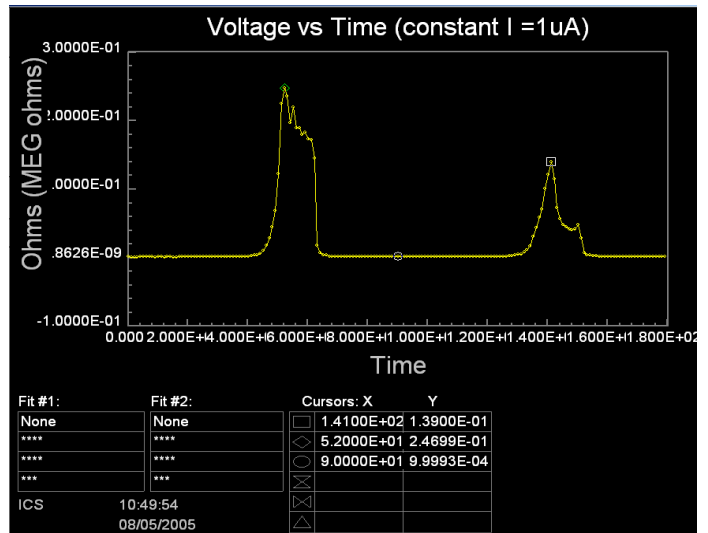


AIR PLANE GLUE RESPONSE TO PROPANOL

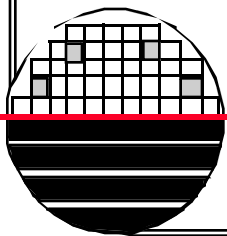


NAIL POLISH / CARBON BLACK RESPONSE TO ACETONE AND ISOPROPANOL

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



ELLIE BRION



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SIGMA ALDRICH – SENSOR APPLICATIONS

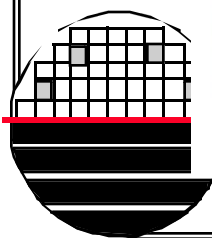
<http://www.sigmaaldrich.com/analytical-chromatography/analytical-reagents/sensoric-applications.html>

Interactive Periodic System of Elements

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

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc *	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La *	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po *	At *	Rn *
Fr *	Ra *	Ac *	Rf *	Db *	Sg *	Bh *	Hs *	Mt *	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
		Ce	Pr	Nd	Pm *	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		

* Lanthanides
 * Actinides
 * Radioactive
 ⚡ Datasheets available



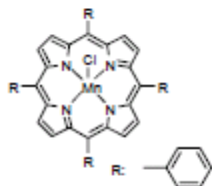
SIGMA ALDRICH ION SELECTIVE MEMBRANES FOR CHLORINE



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@stal.com

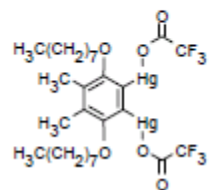
Two of 6 ionophores

Chloride



Chloride ionophore I
 (meso-Tetraphenylporphyrin manganese(III)-chloride complex; Mn(II)TPPCI)
 $C_{44}H_{28}ClMnN_4$ M, 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(mercuryltrifluoroacetate))
 $C_{22}H_{40}F_6Hg_2O_8$ M, 987.79 [1458889-57-2]

[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)

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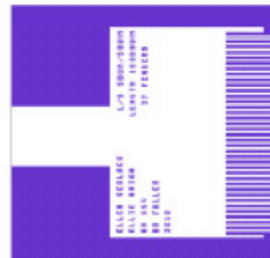
ELECTRODE ARRAYS AVAILABLE FROM RIT

ELECTRODE ARRAYS AVAILABLE FROM RIT

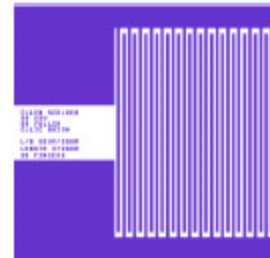
MODEL #	METAL MATERIAL	SUBSTRATE MATERIAL	TYPE	WIDTH	SPACE	LENGTH	NUMBER OF ELEMENTS	PRICE EACH
Ta50-10-37Si	Ni/Ta/TaN	Silicon*	SERIES	50 μm	50 μm	1000 μm	37	\$5.95 each
Ta50-37-20Si	Ni/Ta/TaN	Silicon*	PARALLEL	50 μm	50 μm	3700 μm	20	\$5.95 each
Ta20-37-40Si	Ni/Ta/TaN	Silicon*	PARALLEL	20 μm	20 μm	3700 μm	40	\$5.95 each
Ta10-37-100Si	Ni/Ta/TaN	Silicon*	PARALLEL	10 μm	10 μm	3700 μm	100	\$5.95 each

MODEL #	METAL MATERIAL	SUBSTRATE MATERIAL	TYPE	WIDTH	SPACE	LENGTH	NUMBER OF ELEMENTS	PRICE EACH
Ta50-10-37G	Ni/Ta/TaN	Glass	SERIES	50 μm	50 μm	1000 μm	37	\$9.95 each
Ta50-37-20G	Ni/Ta/TaN	Glass	PARALLEL	50 μm	50 μm	3700 μm	20	\$9.95 each
Ta20-37-40G	Ni/Ta/TaN	Glass	PARALLEL	20 μm	20 μm	3700 μm	40	\$9.95 each
Ta10-37-100G	Ni/Ta/TaN	Glass	PARALLEL	10 μm	10 μm	3700 μm	100	\$9.95 each

Dr. Lynn F. Fuller, Professor
 Electrical and Microelectronic Engineering
 Rochester Institute of Technology
 82 Lomb Memorial Drive
 Rochester, NY 14623-5604
 Email: Lynn.Fuller@rit.edu
 Dr. Fuller's Webpage: <http://people.rit.edu/lffeee>

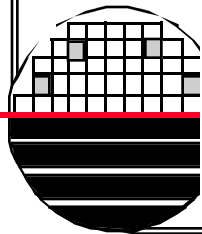


Series



Parallel

Silicon* is 6500Å oxide on silicon
 Size 4.8 mm x 4.8 mm x 0.67 mm
 Solder Pads for Interconnect
 Other metals available



RIT ELECTRODE ARRAYS



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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.

