Development of a High-Speed High-Performance Microfabricated Gas Chromatograph for Military Applications

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4th Microsensors Workshop

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Micro Gas Analyzers Program Plan: *Fast* GC separations

Phase II: Component-level Demonstration

- demonstrate separation using micromachined components
- demonstrate detectors/sensors
- control electronics (board level, not integrated)

Go-Ahead Milestones:

- size < 20 cm^3
- det. limit < 50 ppt
- 8/8 separation < 4sec
- Analytical channel capacity > 100
- energy/analysis < 3 J (PC, GC, Detector, pump)
- FAR < 1 in 200,000 for 8/8 mix
- Repeatability of elution time ±2 sec
- System reset time <30 sec
- Cold start time < 2 min
- *Total analysis time < 6 sec (not officially briefed)*

Phase III: System Integration

-Utilize arrayed approaches

-Process integration w/ IC's

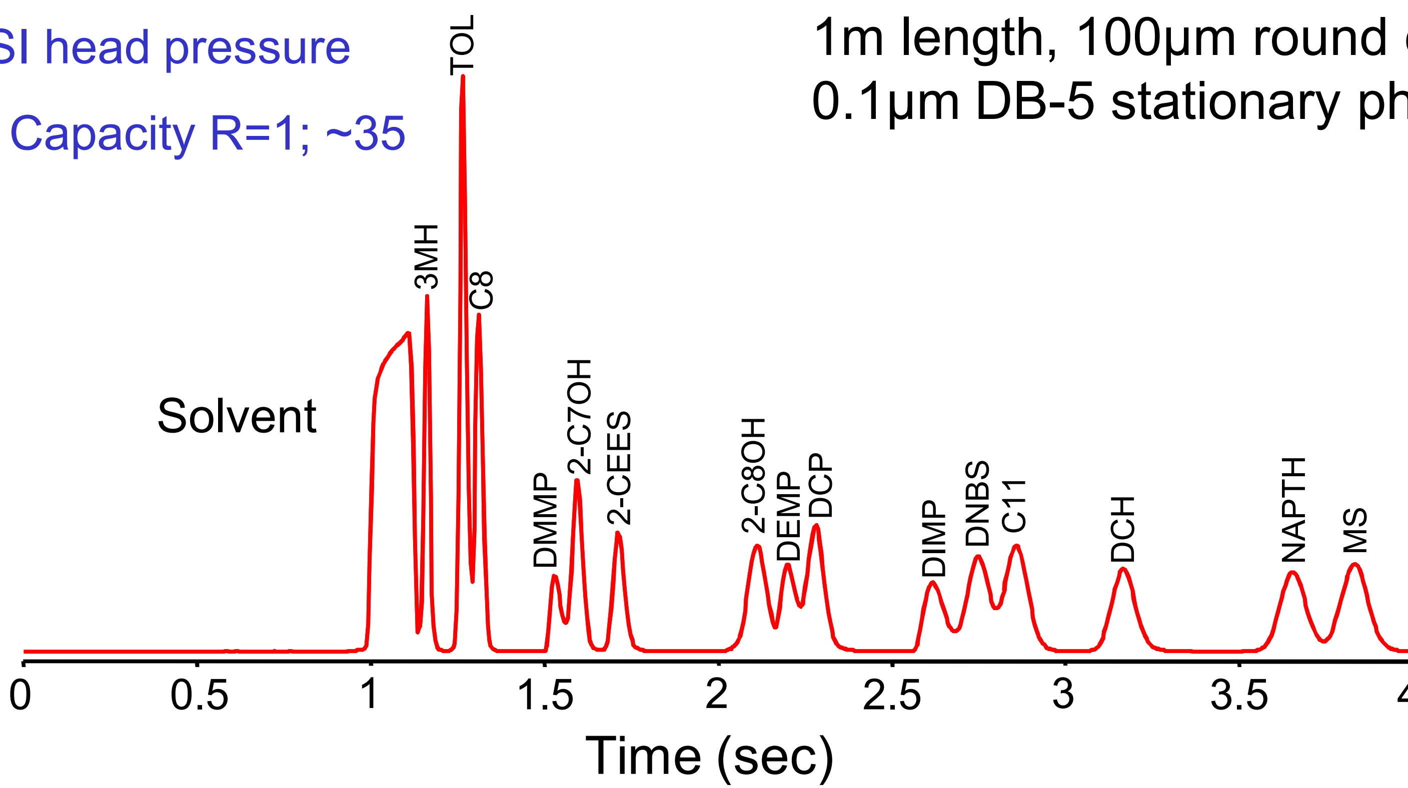
Program goals:

- size < 2 cm^3
- 20/10 separation < 4sec
- Peak capacity > 40 x 30
- det. limit < 1 ppt
- energy/analysis < 0.5 J
- FAR < 1 in 10^7 for 20/10 mix (block ROC)

Separation of 16 Compounds in < 4 sec (DARPA program milestone)

- Temperature Programmed from 59 to 87 °C
- 30 PSI head pressure
- Peak Capacity R=1; ~35

8 CWA simulants
8 interferents
1m length, 100µm round column
0.1µm DB-5 stationary phase



Modeling Predicts *System* Efficiency Using Rectangular GC Columns

1st 3 terms model column performance, 4th term connects column to system

$$H = \underbrace{\frac{2D_g f_1 f_2}{\bar{u}}}_{\text{Longitudinal diffusion}} + \underbrace{\frac{(1+9k+25.5k^2)}{105(k+1)^2}\frac{w^2}{D_g}\frac{f_1}{f_2}\bar{u}}_{\text{Mass Transport in the Mobile Phase}} + \underbrace{\frac{2}{3}\frac{k}{(k+1)^2}\frac{(w+h)^2 d_f^2}{D_s h^2}\bar{u}}_{\text{Mass Transport in the Stationary Phase}} + \underbrace{\frac{\Delta t^2 u^2}{L(k+1)^2}}_{\text{Extra-Column Band Broadening}}$$

$\bar{u}$ – average linear carrier gas velocity

D_g – binary diffusion coefficient in gas phase

f_1 –Giddings-Golay gas compression correction factor

f_2 – Martin-James gas compression correction factor

k – retention factor

w – channel width

h – channel height

d_f – stationary phase film thickness

D_s – binary diffusion coefficient in stationary phase

L – column length

Δt – time correlating to extra column band broadening

$$\Delta t = \frac{\text{inlet (or outlet) volume, cm}^3}{\text{gas flow rate, cm}^3\text{/sec}}$$

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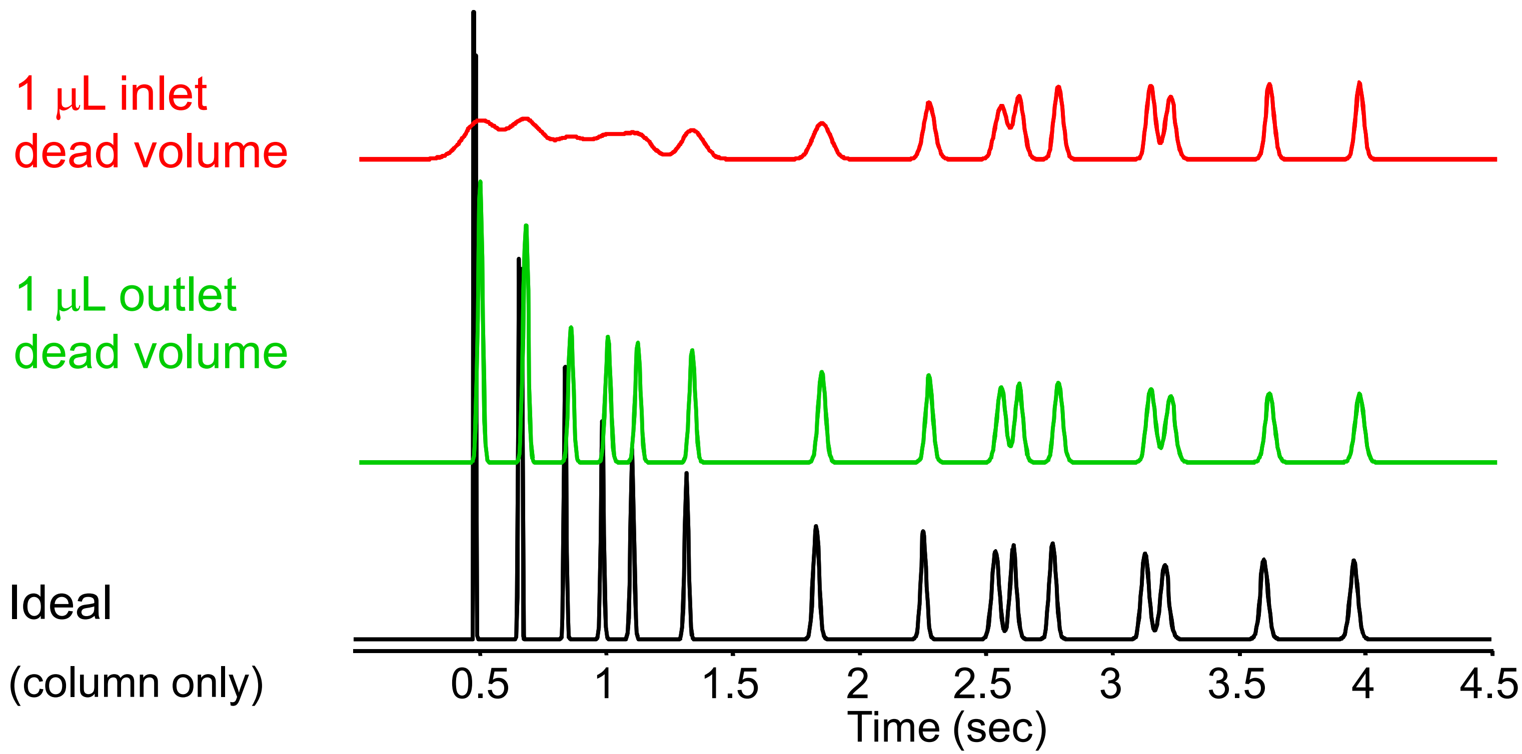
Integration Driver: Modeled GC Band Broadening

Ahn and Brandani Model – Dec. 2005 **T-programmed 8/8 separation**



Inlet dead volume costs more than outlet dead volume due to carrier gas compressibility: $(cm^3/sec)_{outlet} > (cm^3/sec)_{inlet}$

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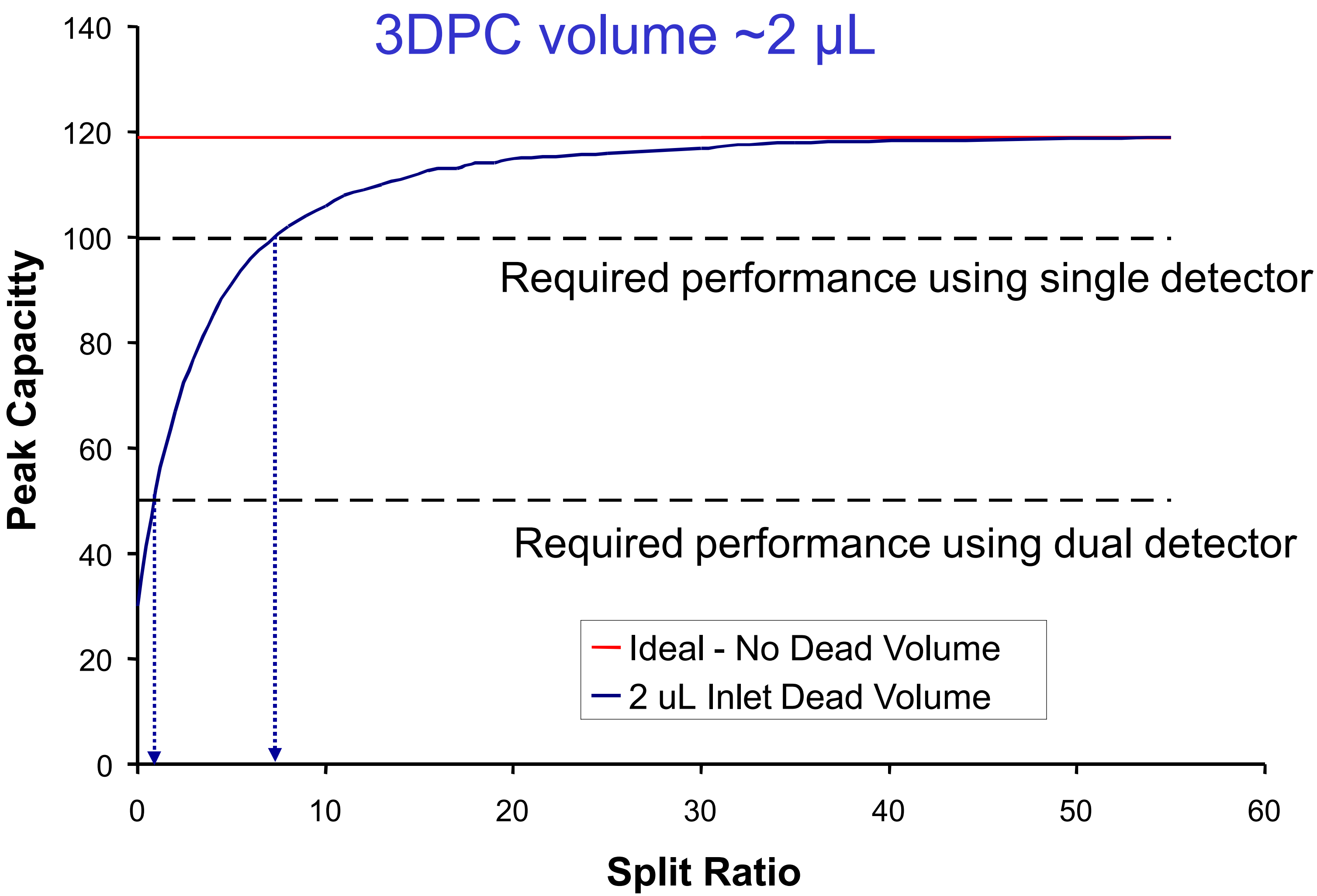
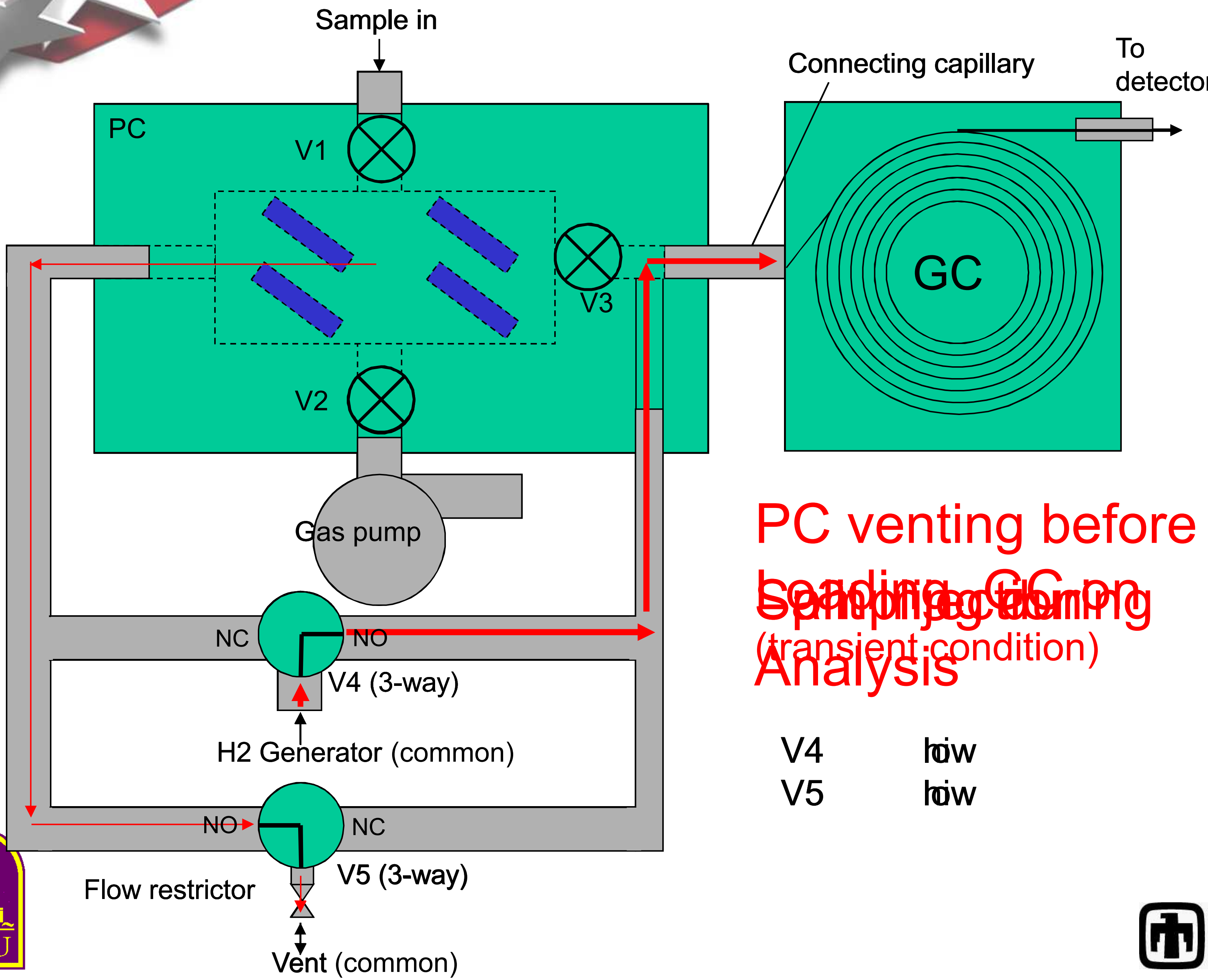
Mitigating the Effects of Inlet Dead Volume

GC Peak Capacity vs. Injection Split Ratio

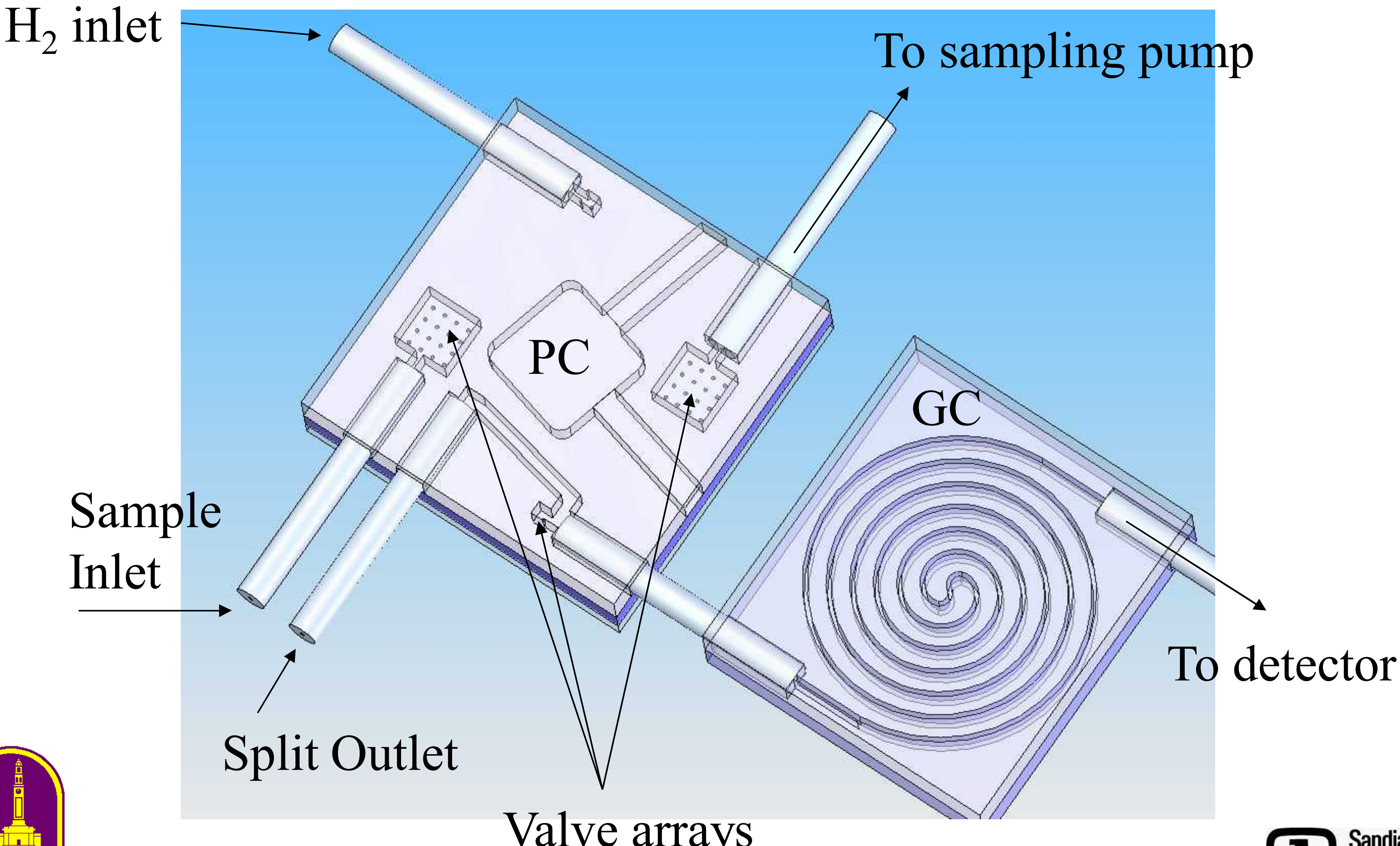


Phase 2: 2 External Valve System Schematic

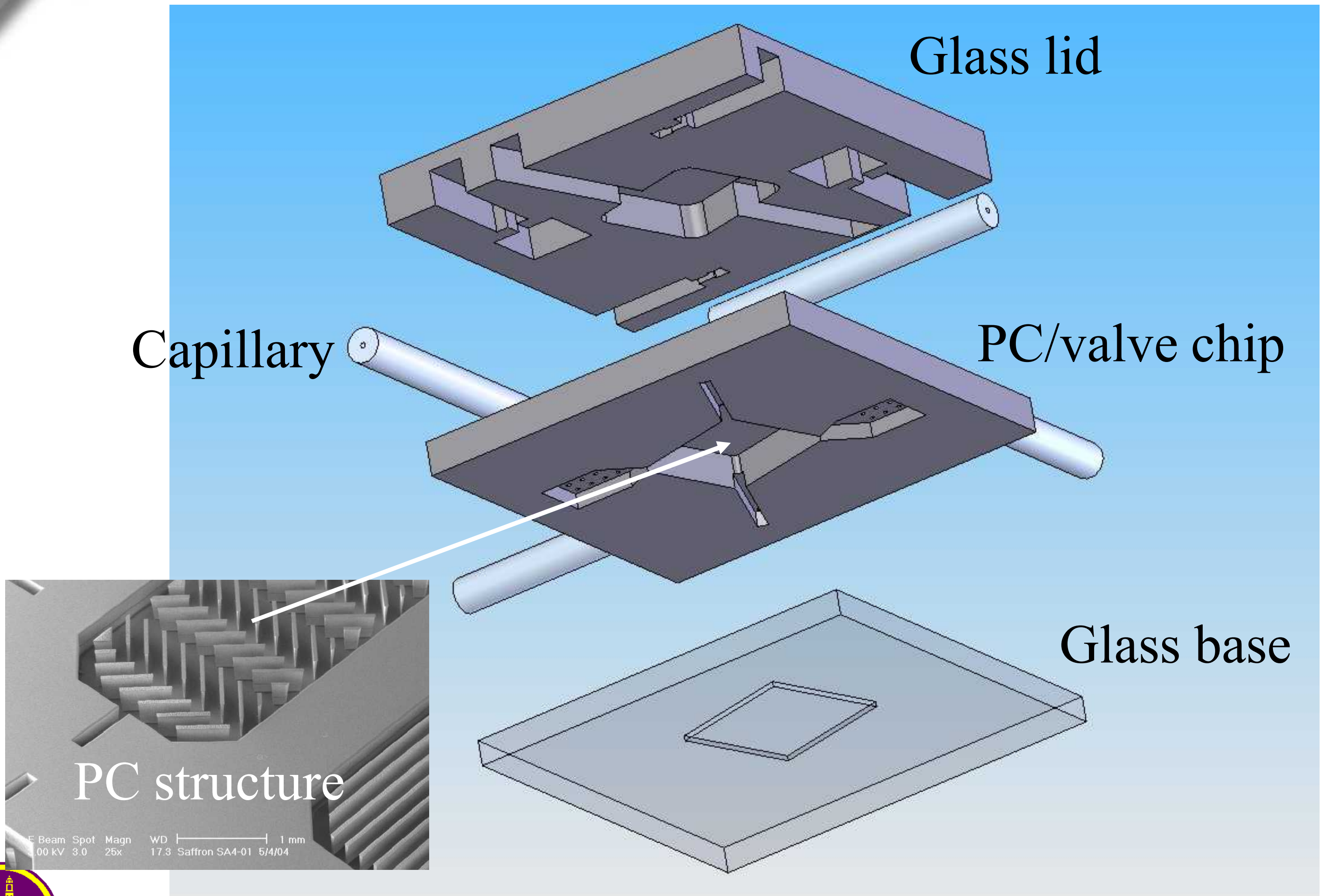


Phase 2 Hybrid Chips

MEMS valves on PC chip limit inlet volume



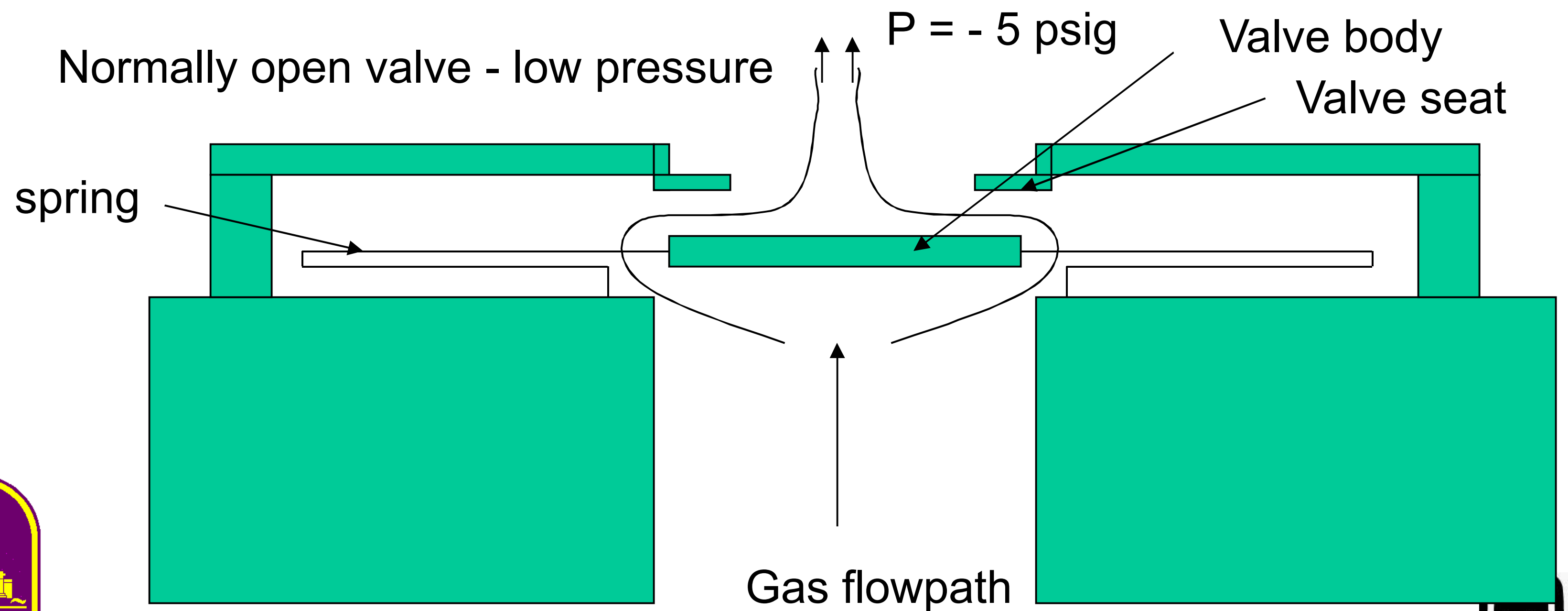
Exploded view from the bottom



Passive Offset Check Valve design concept (normally open valve)

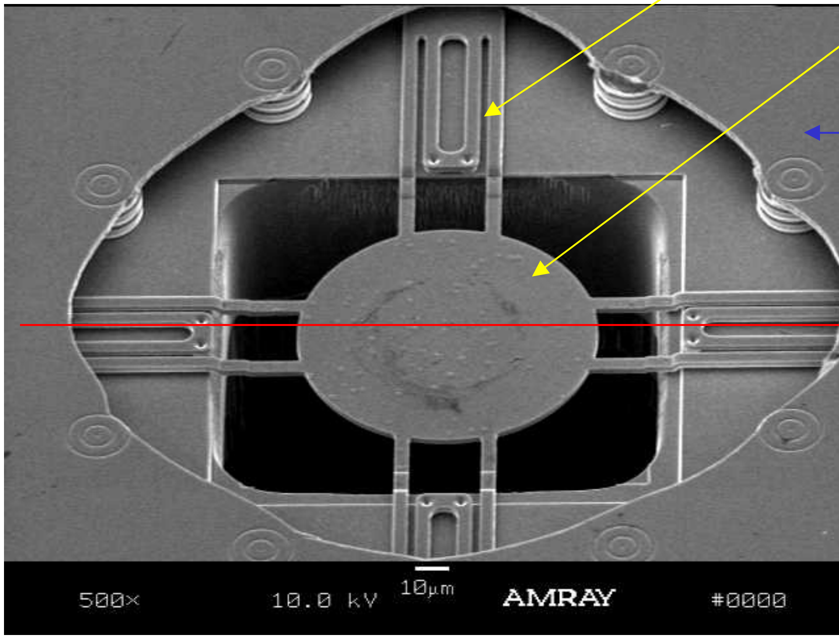
- Open one-way at low pressures
- Closed *in the same flow direction* at higher pressures
- A check valve with an offset.

- Our design uses a soft spring with properly selected stiffness, matched to:
  - Pressure requirement
  - Flow requirement
  - Orifice size

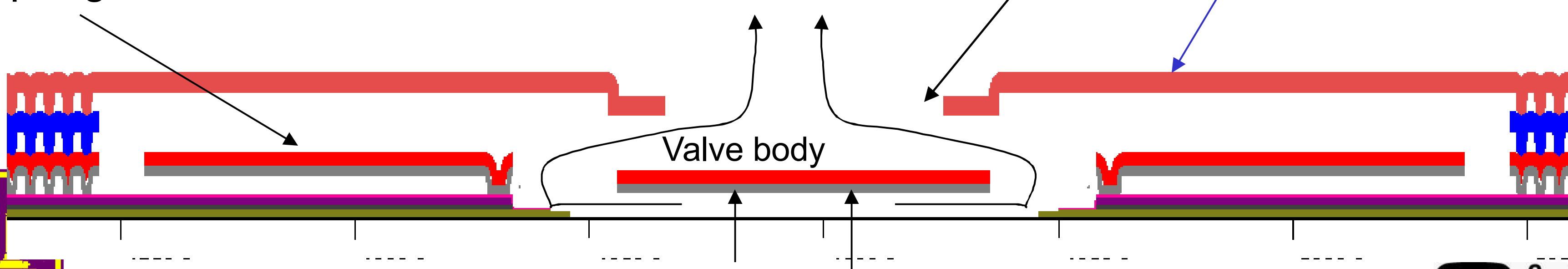


Valve 2 - SUMMiT™ design and fabrication

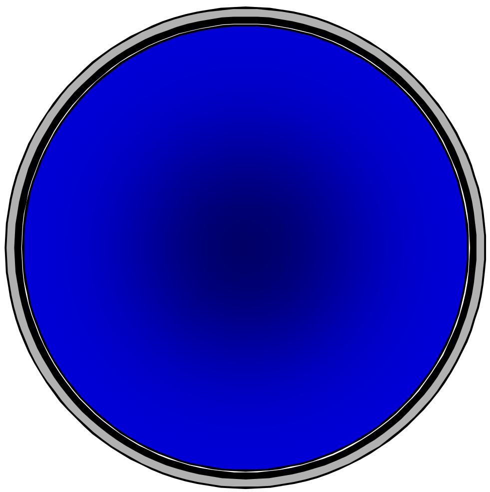
Valve size ~400 μm^2



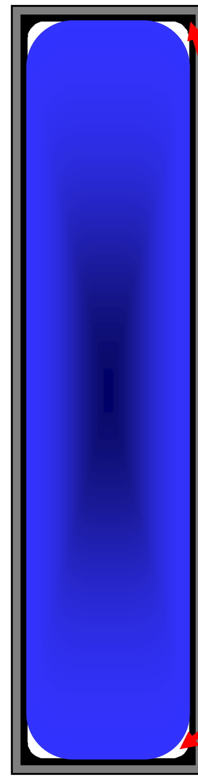
Upper poly-Si layer, which defines the valve orifice, is cut away in the micrograph



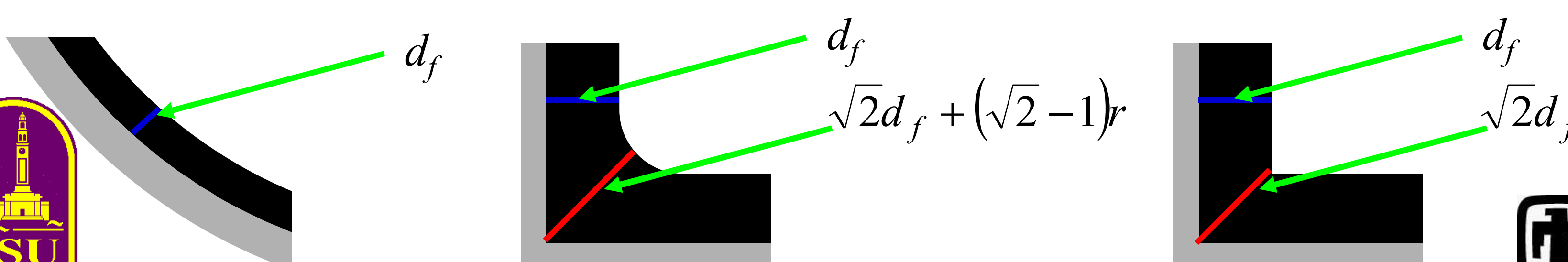
Round vs. HARM columns



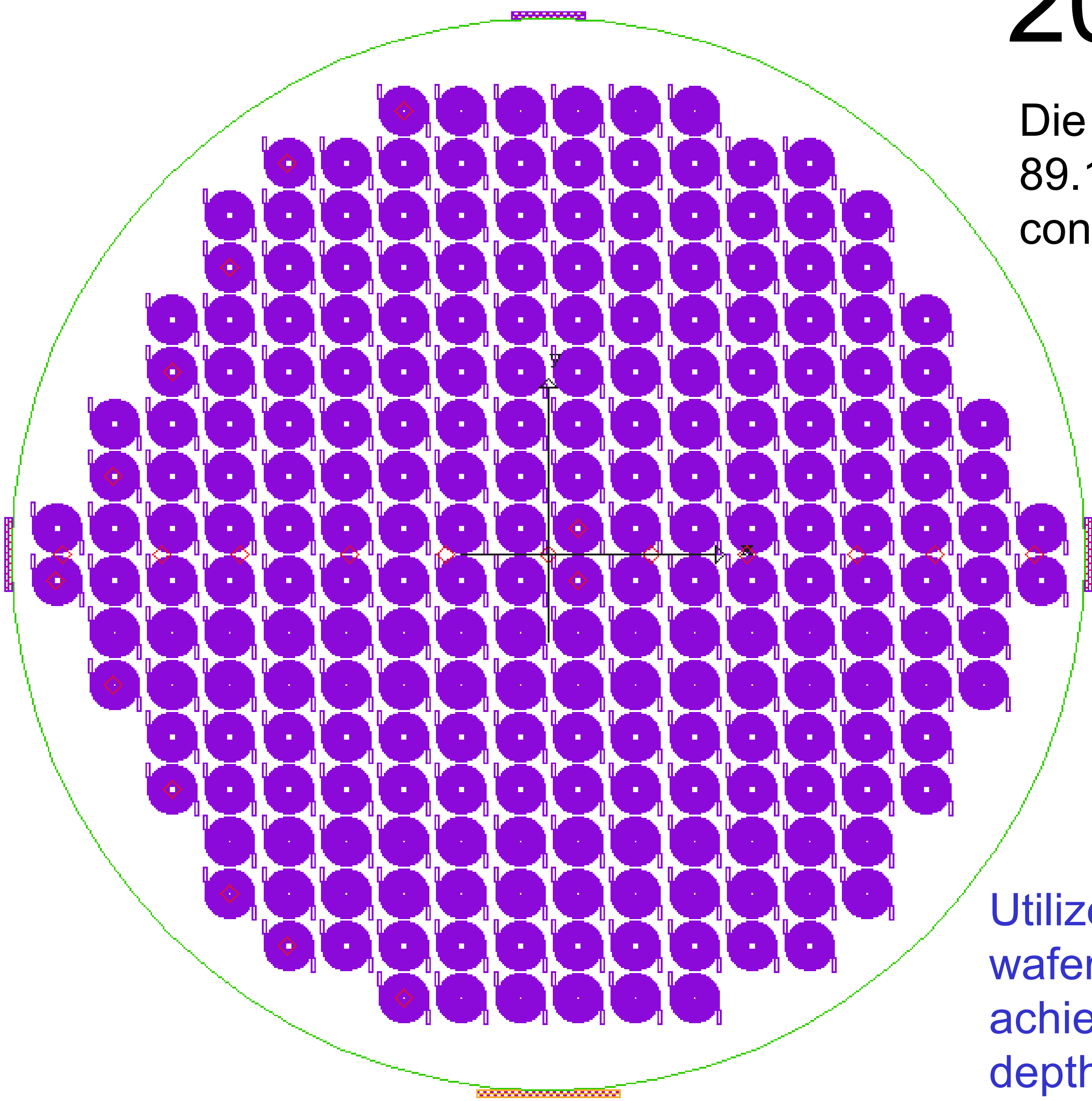
- Flow restriction and performance limited by radius
- Film deposition is uniform



- Flow restriction controlled by height
- Performance limited by width
- End effects
  - Film deposition often results in thicker phases in the corner
  - Dead spaces in corners



2090 GC



Die 1: 20 um wide, 20 um wall, 89.16 cm length between edge connections; 98 occurrences

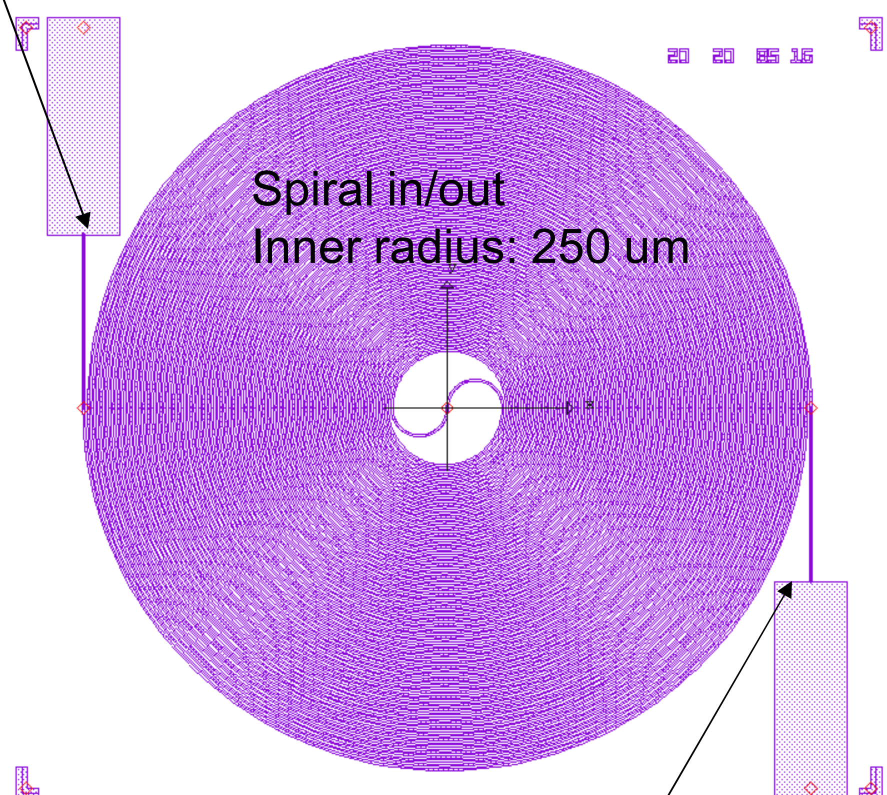
Die 3: 20 um wide, 30 um wall, 73.58 cm length; 68 occurrences

Die 2: Like Die 1 with slight taper before edge connections; 94 occurrences

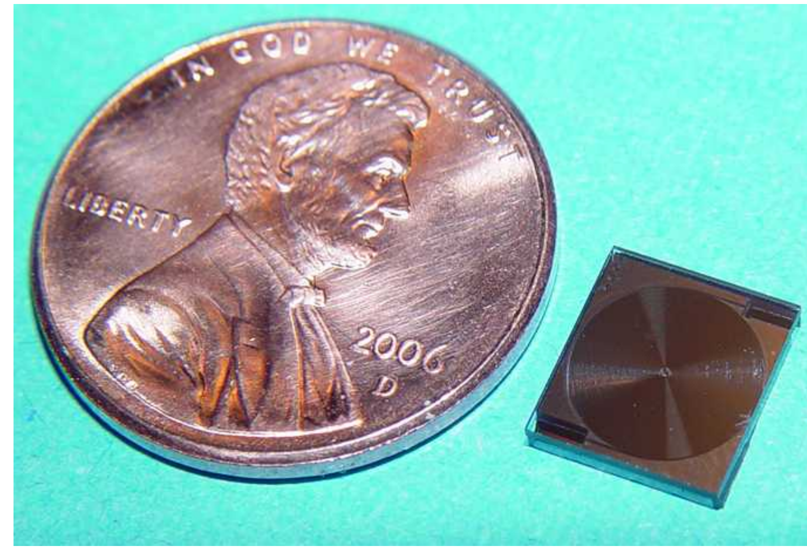
Utilize BOX layer of SOI wafer as etch stop to achieve required column depths

Sample Closeup: Die 1 fabricated on 20 um SOI (1 um BOX, 650 um Si)

Stated lengths are measured between here…



…and here

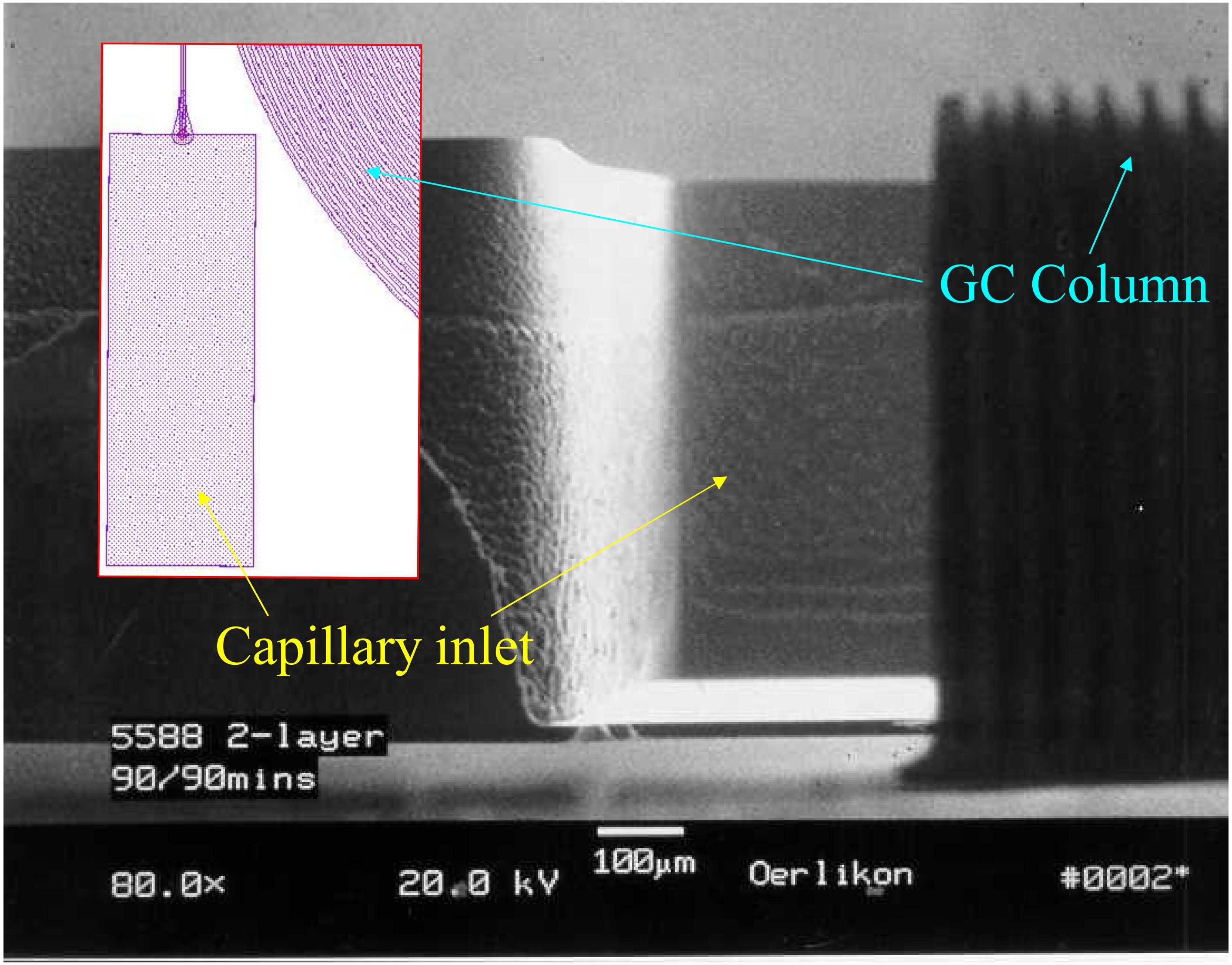


Die2 has a slight taper

$$Ctot = 0.097\frac{J}{K}$$

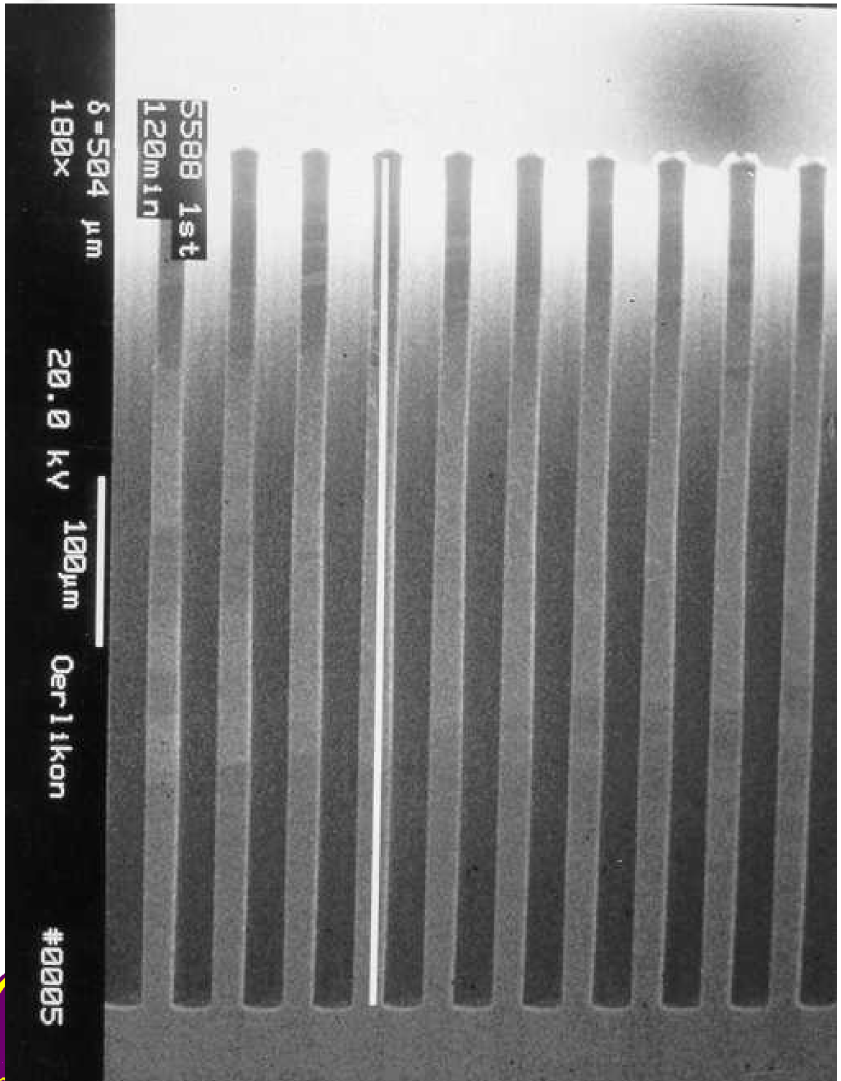
Delay layer has arrived and is awaiting processing

2090 GC test wafer - SEM

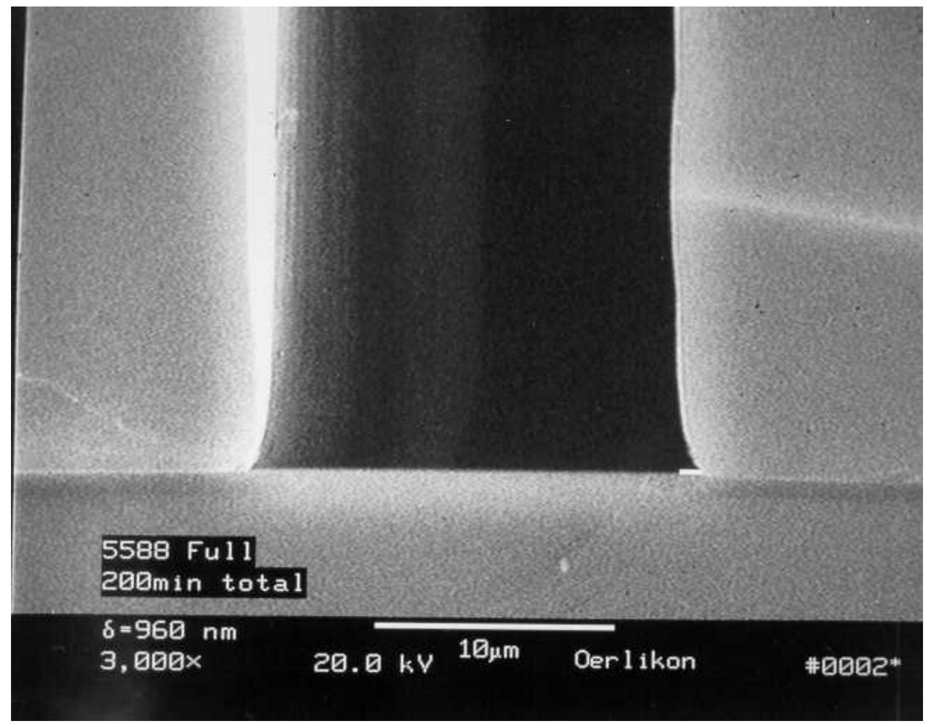


2090 GC test wafer - SEM

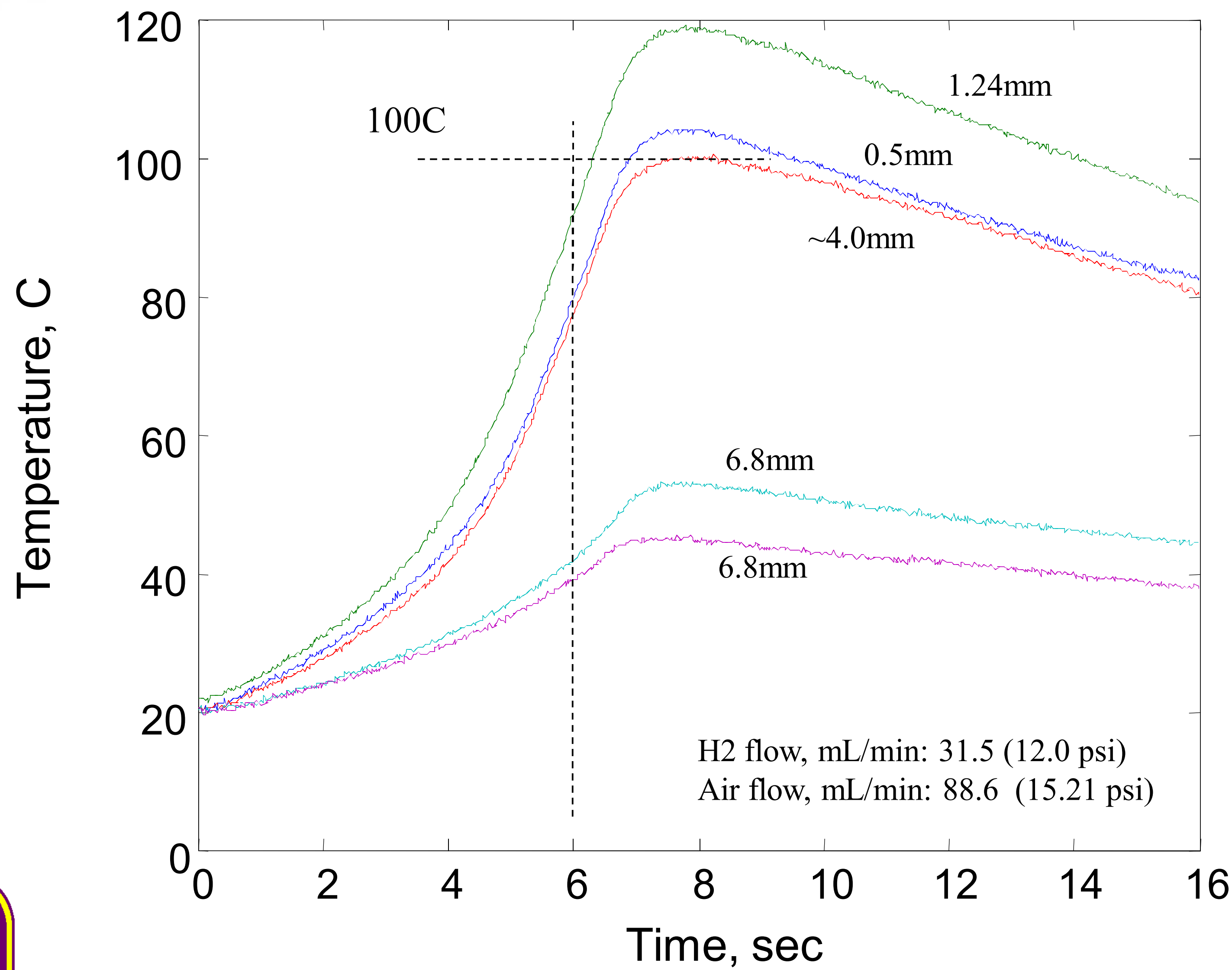
Column walls (first etch)



Bottom of column (2nd etch)



Example data, 2090 GC autocatalytic heating



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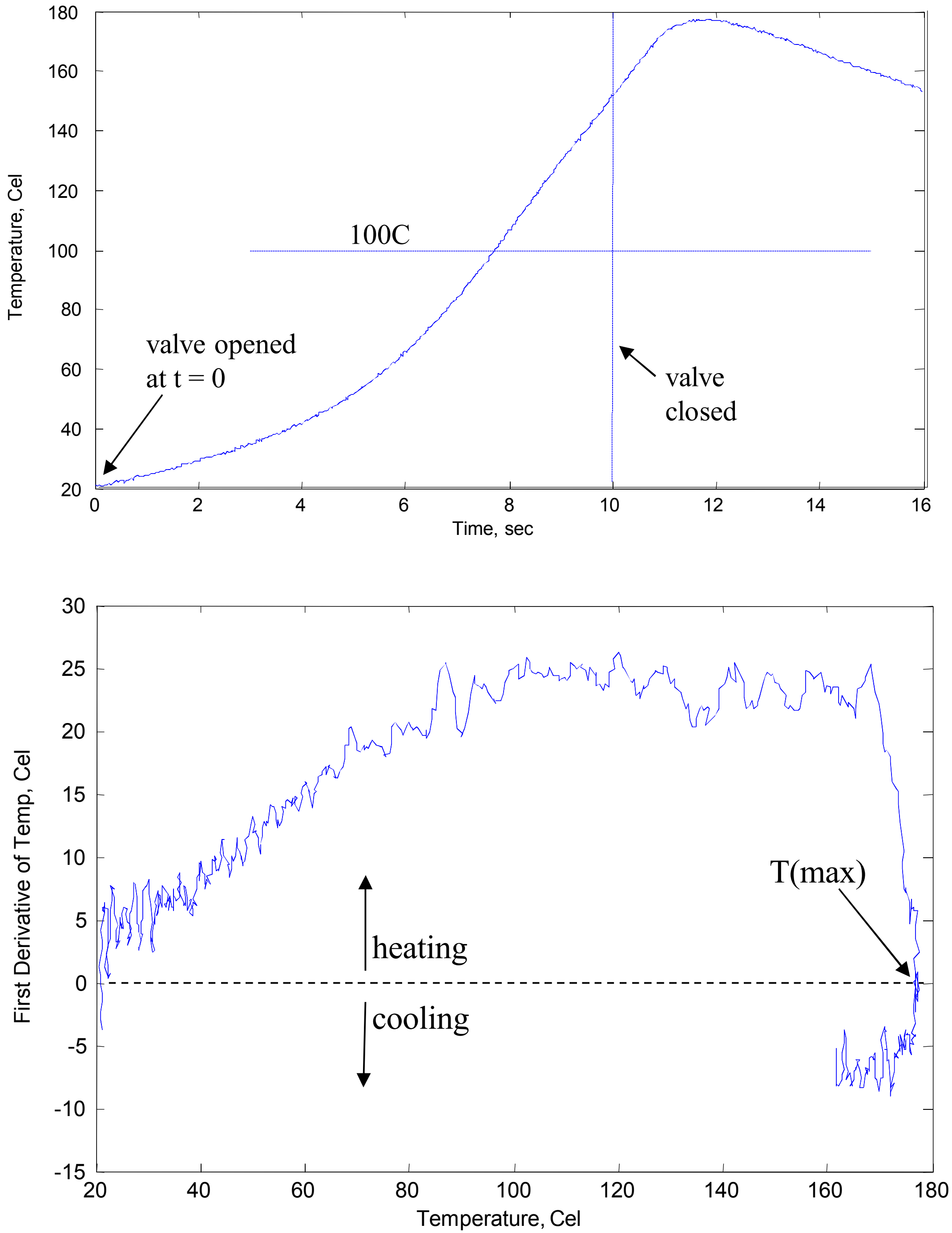
Catalytic GC Heating

- Fuel autoignites
- Thermocouple T lags fuel valve switching
- Efficiency ~25%, can be improved with “burner” design

dT/dt vs. T

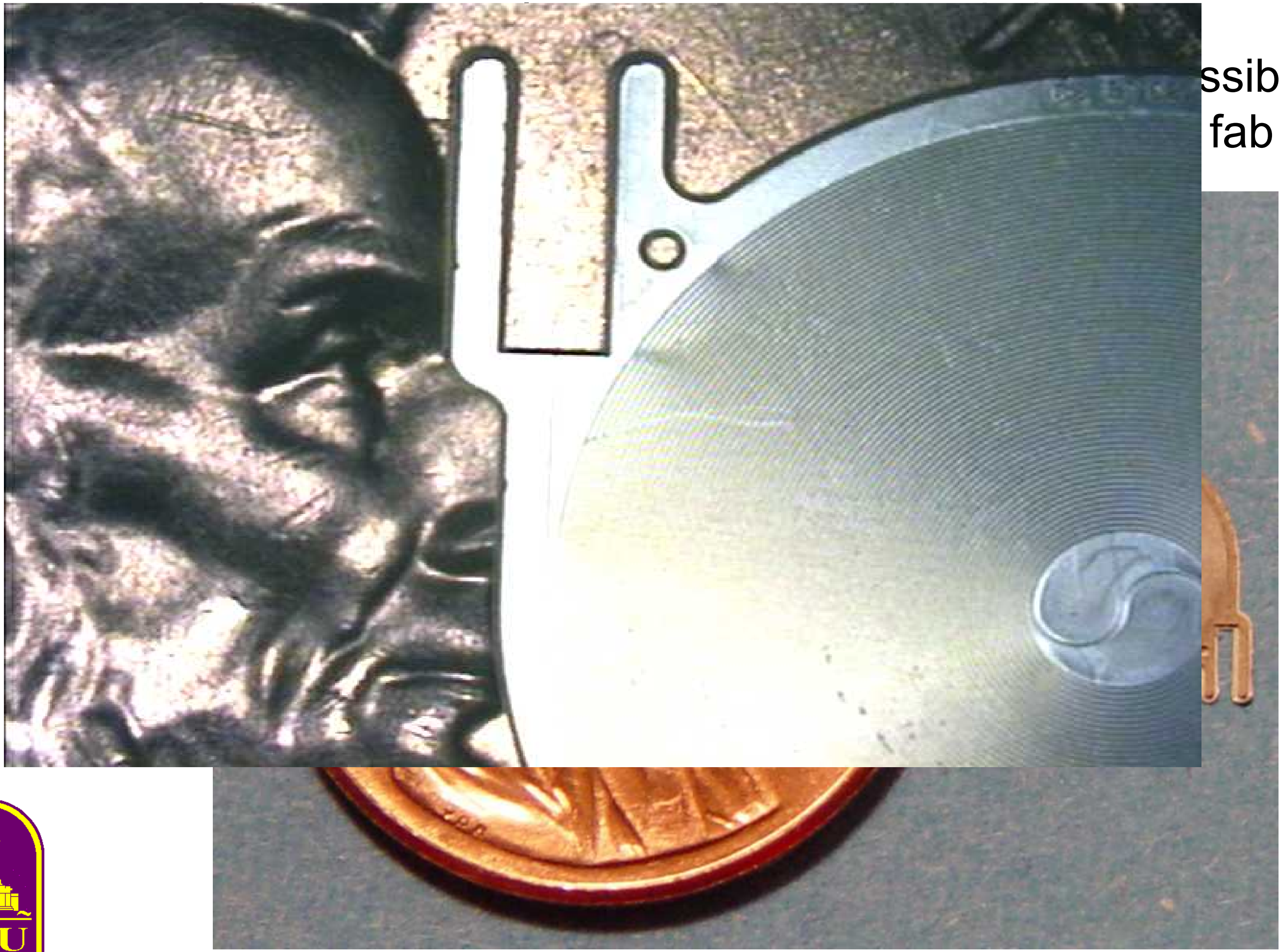


Single Spiral in/out LIGA GC Column

•Test structure: 20 μm wall, 20 μm column, 150 μm depth

ssible

fab

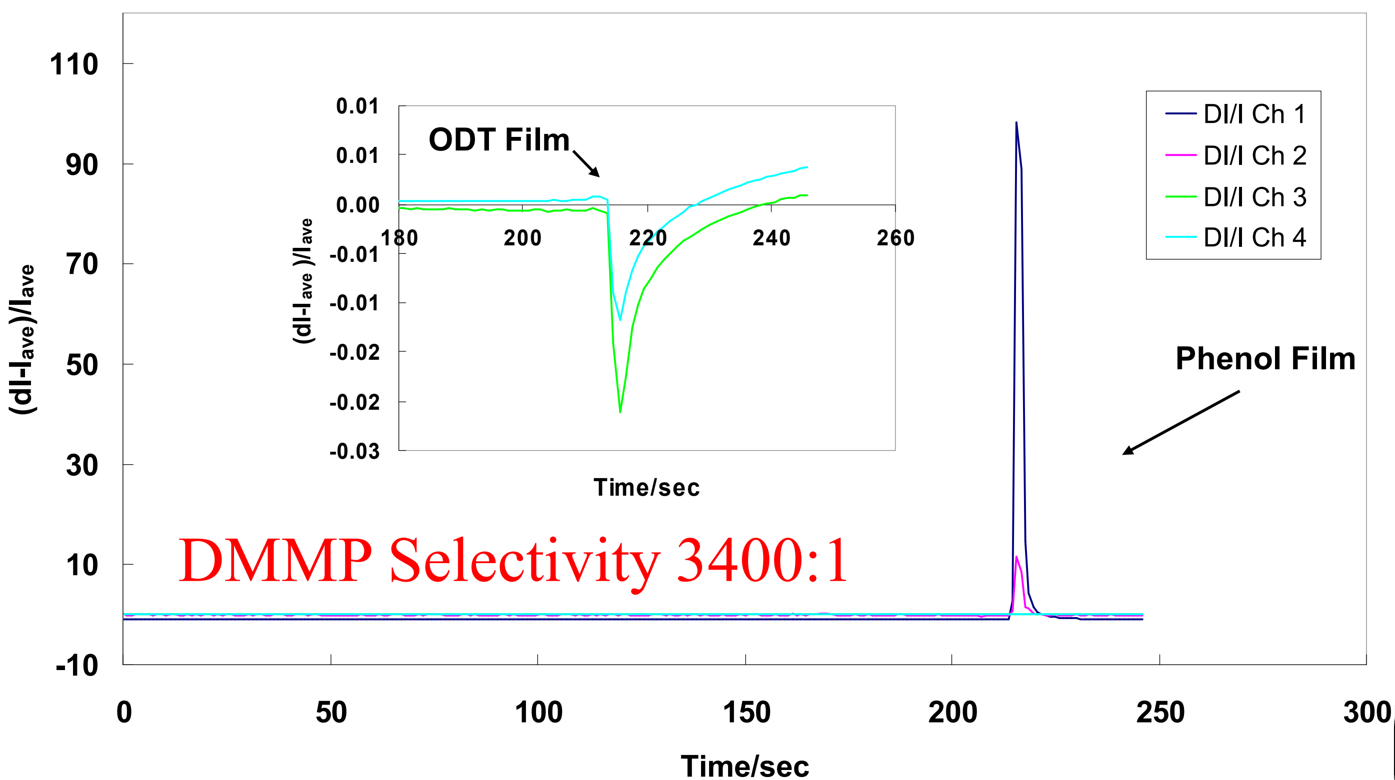


Initial Vapor sensing of DMMP using a protected phenol

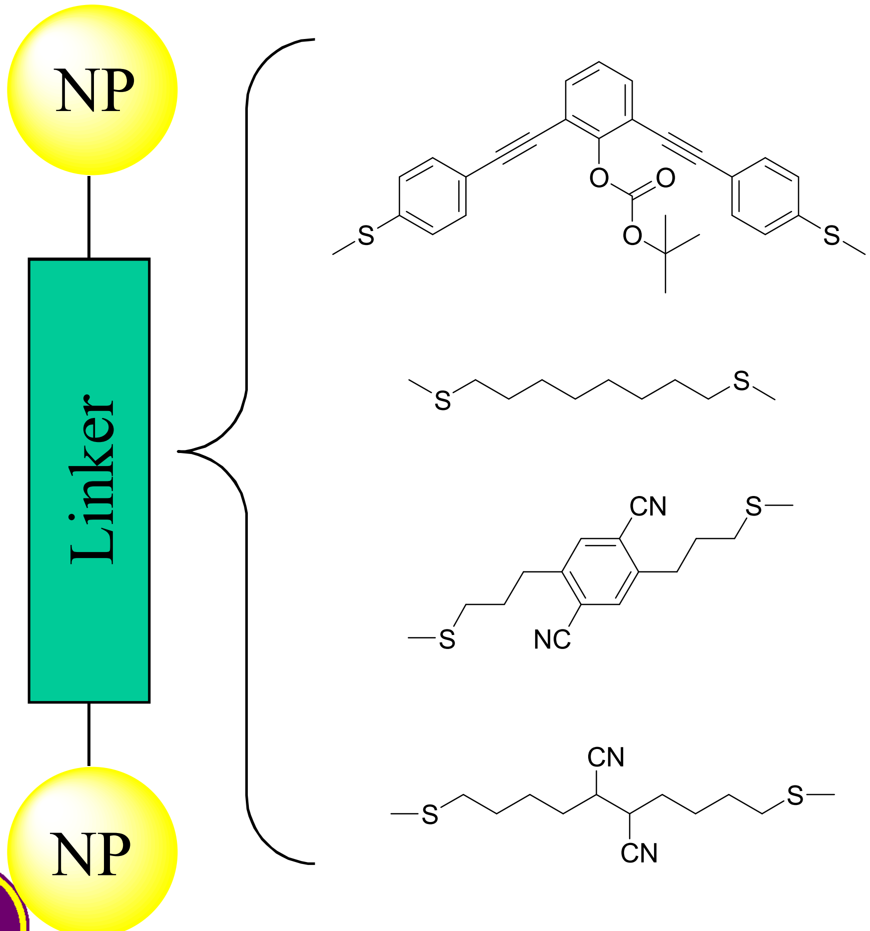
Our initial observations during exposure to DMMP show:

- **Protected phenol-Au films have dramatically increased conduction (molecular electronic effect)**
- **Control ODT-Au films have a slight decrease in conduction (swelling)**
- **10^{-4} J per detector channel per analysis!**

DMMP vapor from Tenax PC using Boc Protected Phenol Molecule as Ch 1 and Ch 2 and ODT as Ch 3 and Ch 4 both with Au nanoparticles



Additional Sensor Channel Candidates

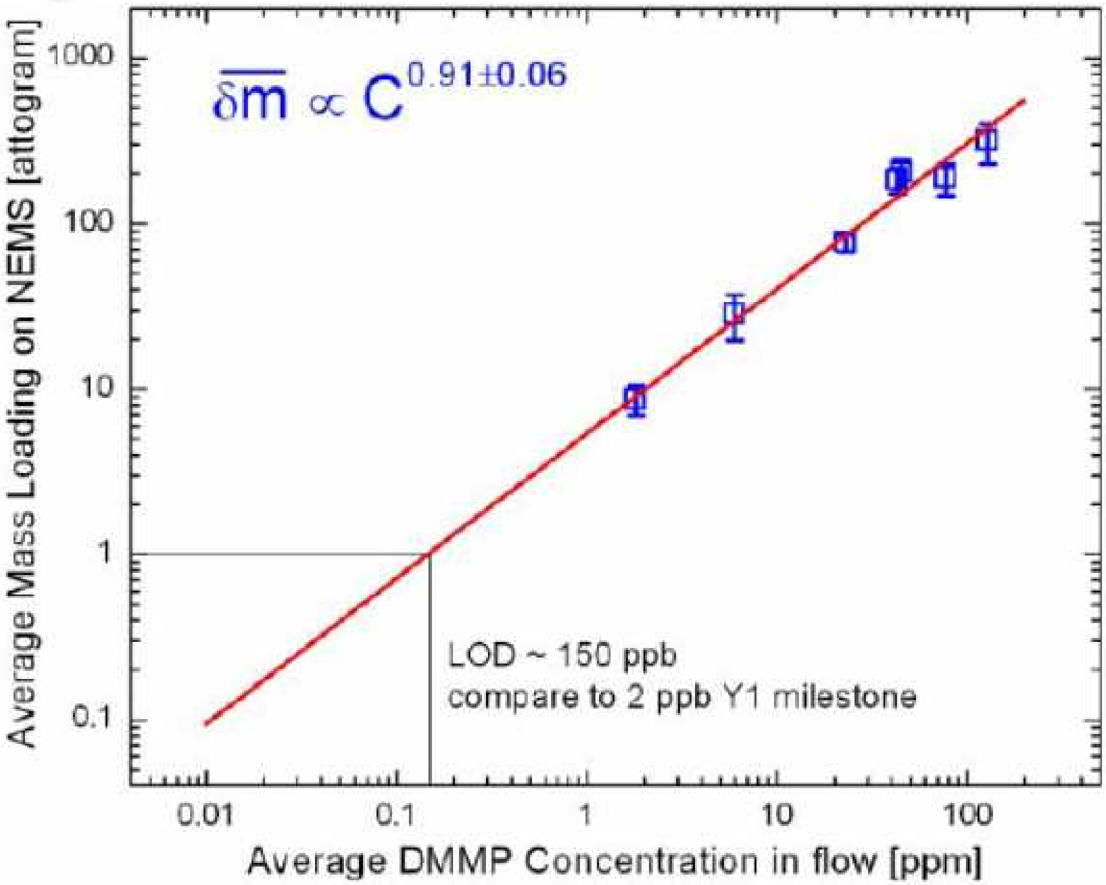


- Phosphonate-selective
- Electron hopping?

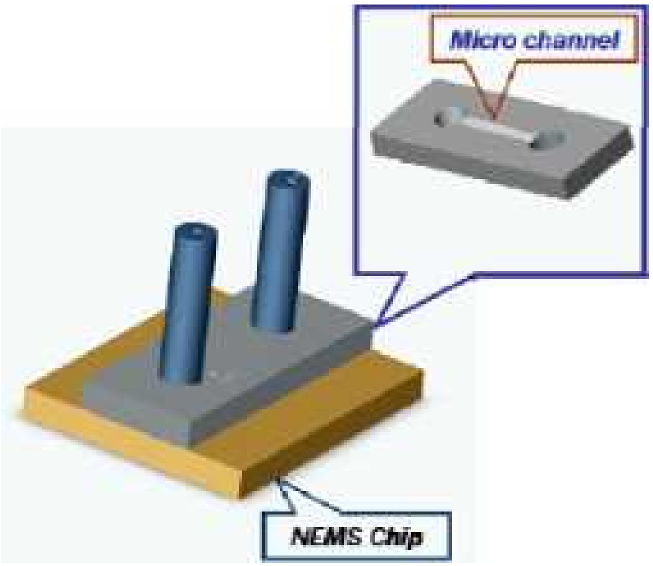
Swelling mechanism, nonpolar

- Swelling mechanism
- Vary polarity, polarizability
- Changing partition coefficients adds information to array response, increasing analytical power

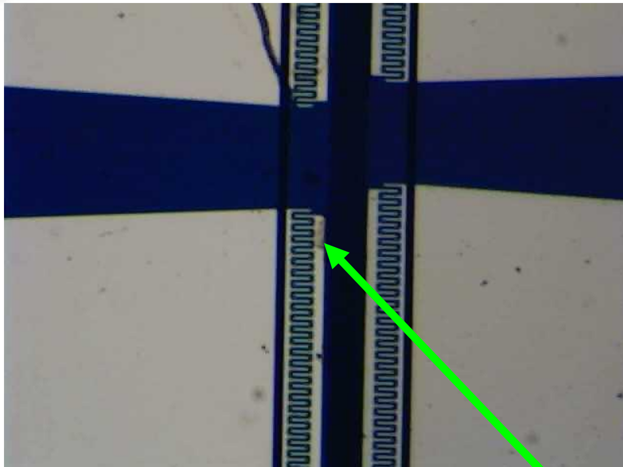
Linear Nanoresonator Response

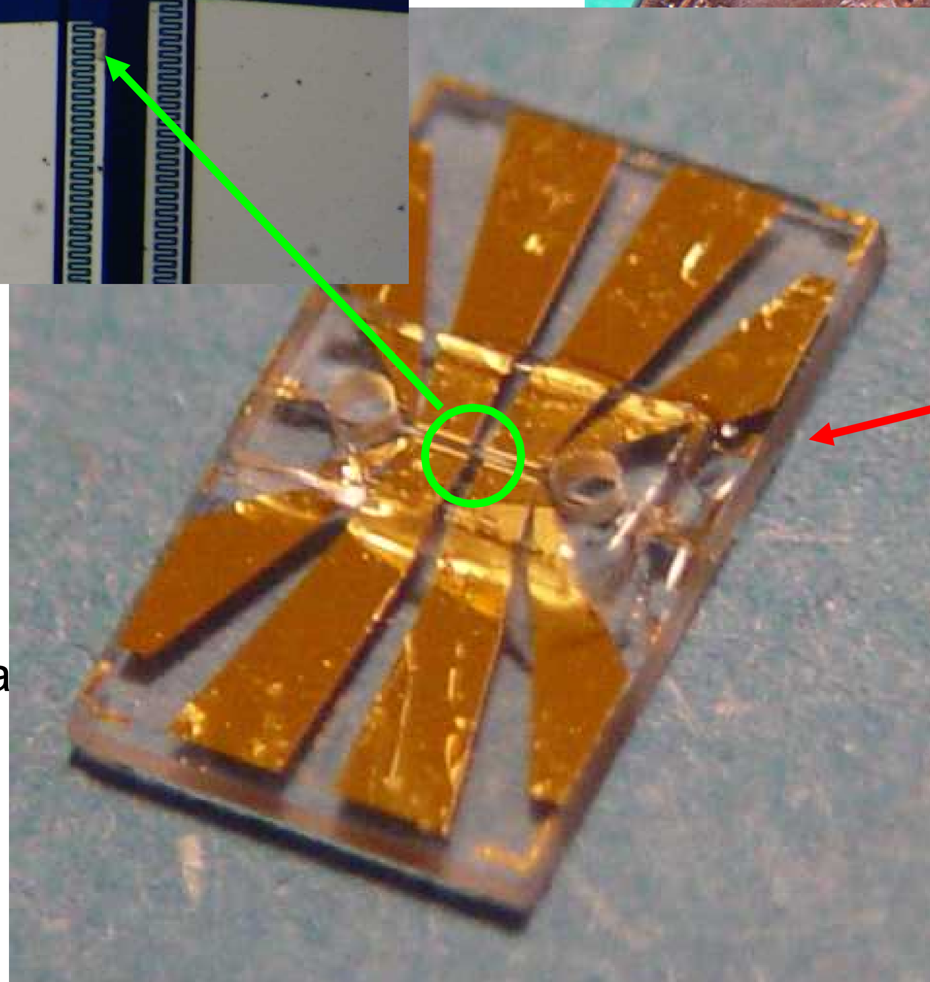


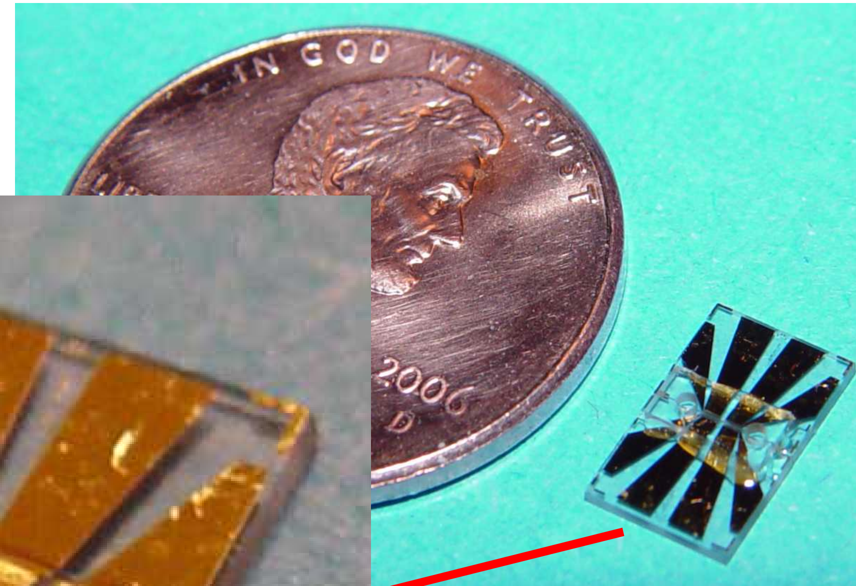
Next device package has 15 nL volume (3000x decrease), to improve both response speed and detector mass transport efficiency (lower LOD)



Nanoparticle IDT Arrays







Two quartz nanoparticle IDT chips covered by a flow lid

0.5 mm thick glass with 685 micron capillary holes

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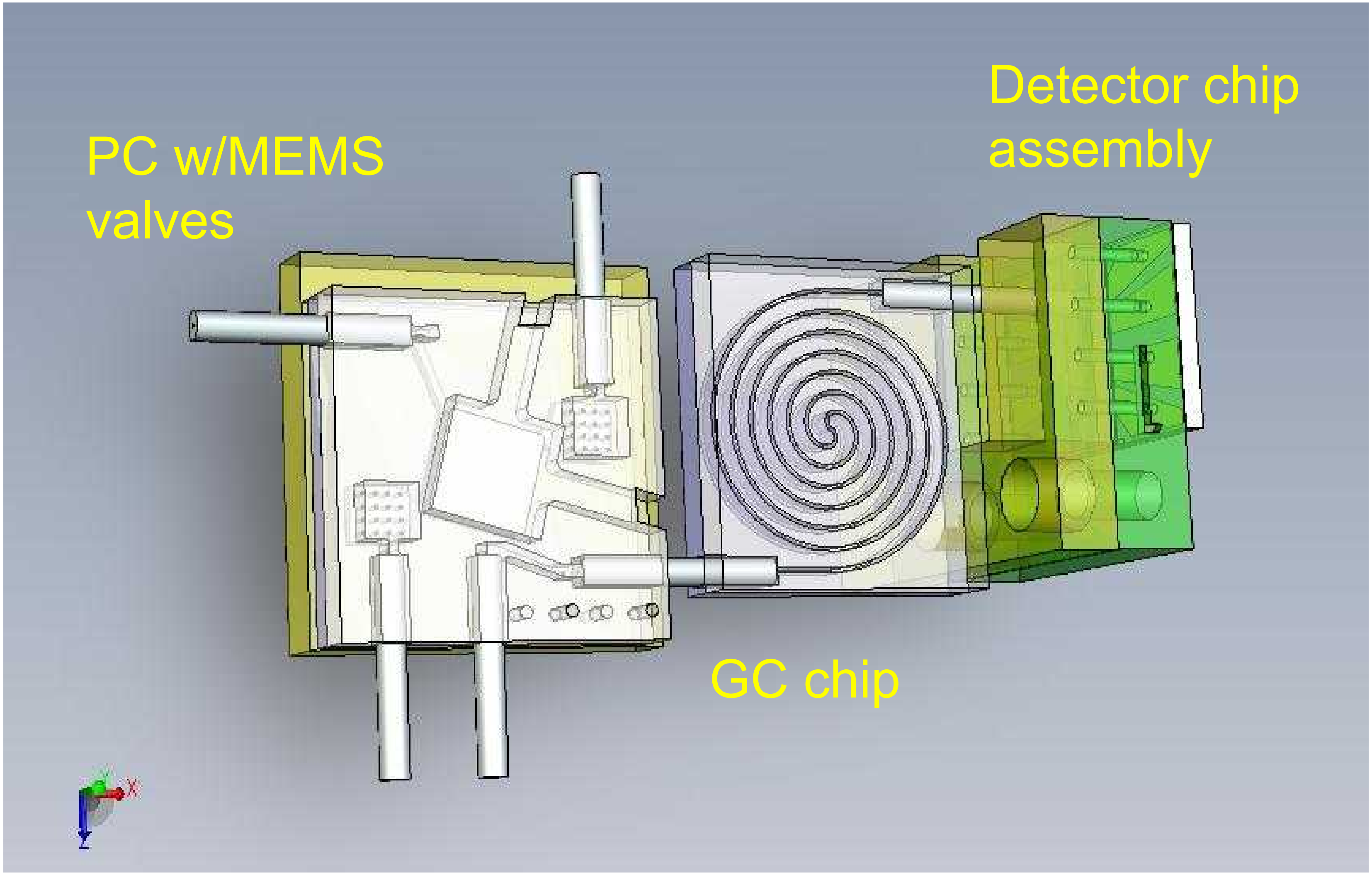
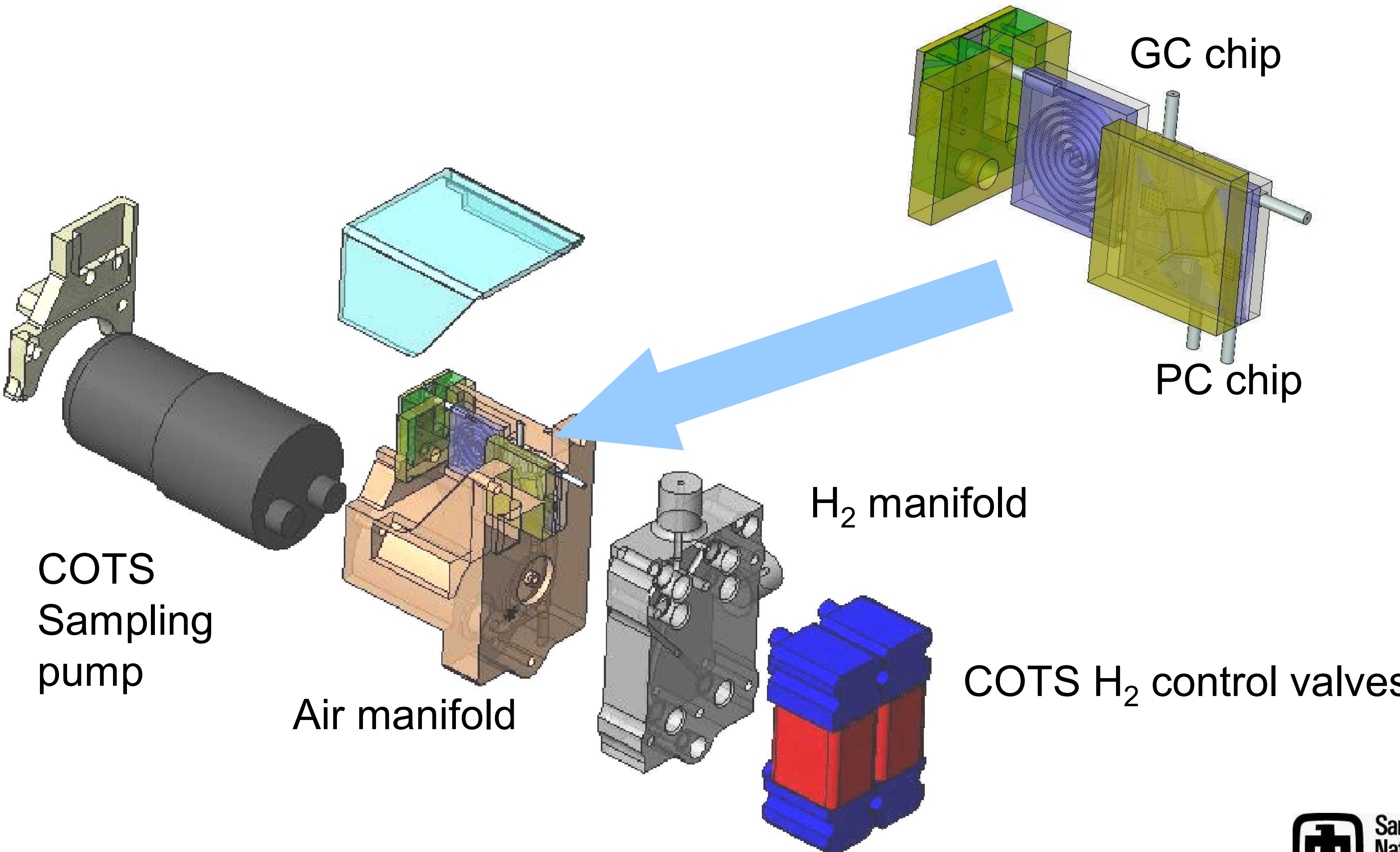
Phase 2 MGA System
Microfabricated Components



Phase 2 MGA System



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Summary: Phase II MGA Hybrid Integration Strategy

- Our Phase II prototype utilizes hybrid integration
- Disadvantages: System volume and interconnect dead volume
- Advantages: Yield, thermal isolation, system flexibility, LIGA column options
- Risk reduction for testing of prototypes
  - Use COTS pump, COTS valves for “active” gas switching
  - Use MEMS check valves, PC, GC, and detectors

- Modeling results drive custom microfabrication efforts (PC with integrated microvalves, GC column, detector fluidic packaging) to enable *high-speed* system performance

- We have demonstrated first GC detection results on nanofabricated cantilevers in collaboration with the Roukes group at Caltech

- We have fabricated initial designs for Phase II external manifold structures