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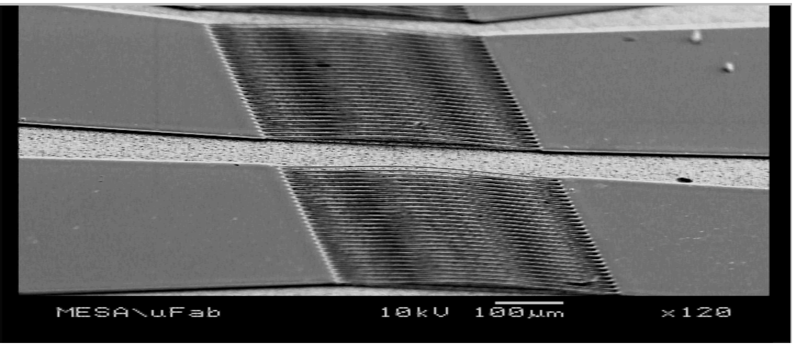

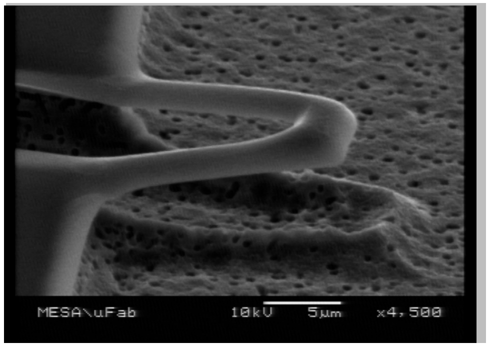

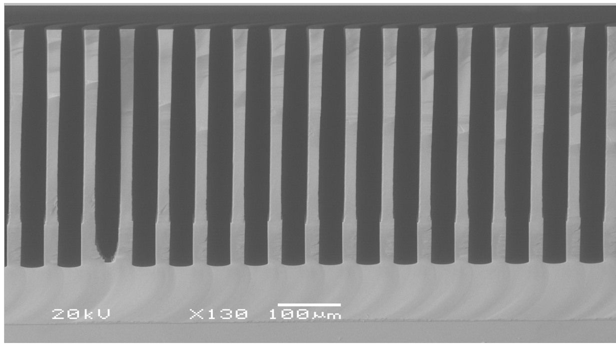

Chemoselective Sensor Development for WR Applications

Cody M. Washburn [a], Gregory Von White II [a], James M. Hochrein [b], Shawn M. Dirk [a], Jonell N. Smith [b], Robert Bernstein [a], Jennifer M. Strong [a], and Patrick Finnegan [a]

Org. 1821 – Organic Materials [a] and Org. 1825 – Materials Reliability [b]

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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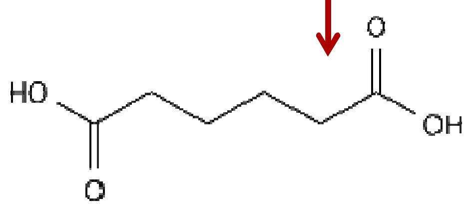
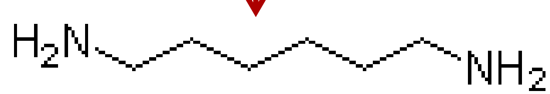
Outline

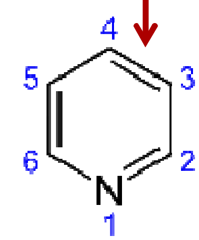
- Why is a low cost micro sensor interesting to WR?
  - Nylon degradation products.
- Down select of sensors
- Why Carbon based devices?
- Device and material development.
- Device electronic and fluidic package.
- Results
- Discussion and Future Work

Degradation Products

- If one can detect the signs of early aging → pathways can be developed to minimize problems associated with material degradation. (Material lifetime cycle)
- Ideally, develop a real-time health and stability monitor using lower power embedded evaluation using chemical sensors.
- Leveraging WR environment gas sampling studies and materials degradation studies using GC/MS the Karnaugh Map (Logic Table) can be developed and understood.
- Nylon 6,6 – adipic acid, 1,6 hexanediamine and pyridine

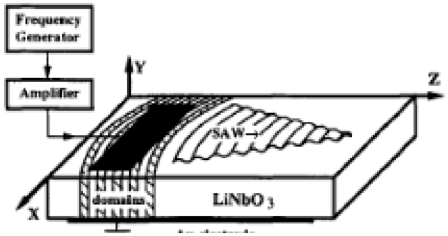






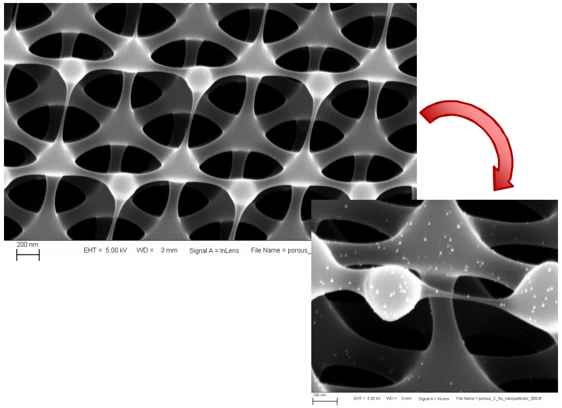
Down select of sensor options

- Quartz Crystals and Surface Acoustic Waveguides
  - Temperature dependence on signal.
  - Crystalline material choice (direction) and operating frequency.
  - Expensive electronics and challenging to scale.



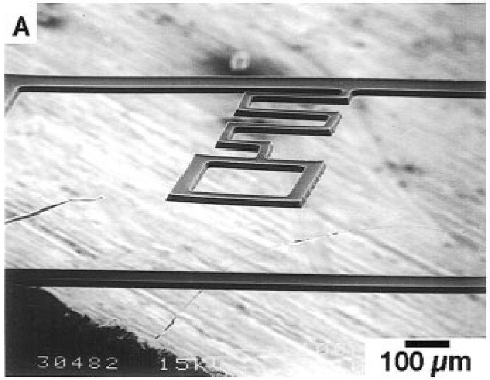
Dmitry V. Roshchupkin and Michel Brunel

- MEMS/ NEMS Resonators
  - Temperature dependence.
  - Multi-step MEMS processing becomes costly.
  - Operating frequency drives design and electronics.
- Chemiresistor based
  - Coating dependent drives performance.
  - How about a carbon based Chemiresistor and increase interaction of the surface area?
  - Decrease Temperature dependence and use DC electronics to lower cost.

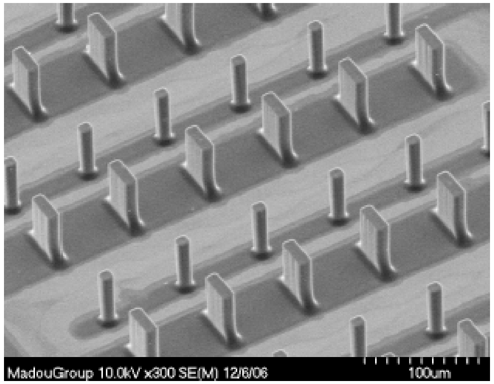

Burkel, Polsky, Washburn, Wheeler 08’

Device and Material Development

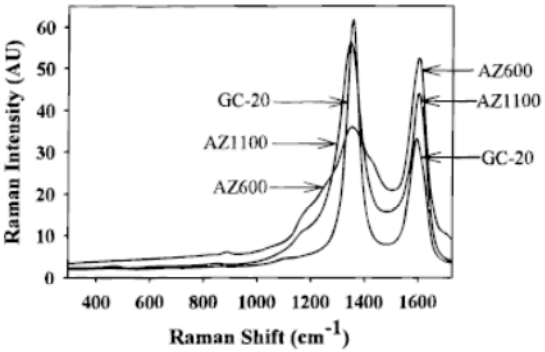
- Pyrolytic Carbon
  - Derived from photosensitive polymers (novalac and Epon(SU8)).
    - G. Whitesides, M. Madou, and R. McCreery
    - Has electrochemical sensitivity towards Redox compounds.
    - Demonstrated at Sandia to have broader capabilities. Polsky, Burkel, Washburn, and Wheeler for 3-D engineered porous carbon.
    - Carbon MEMS as structures and beams using Xenon Di-fluoride (XeF2) silicon etch release techniques, the material has a much lower internal stress compared to a metal of equivalent dimension.



Whitesides, et. al.



Madou, et. al.



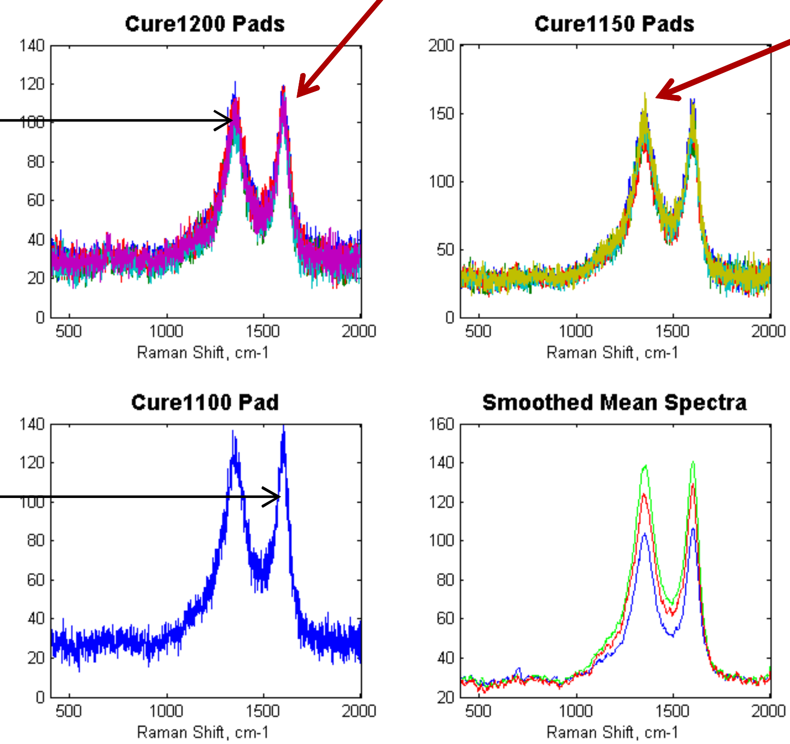
McCreery, et. al.

Material Development

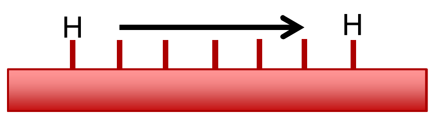
Comparing Raman results. HOPG ~1582 cm-1, Diamond ~ 1332 cm-1

~1360 cm-1
D

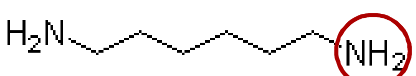
~1582 cm-1
G



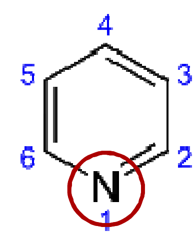
Sp2 to Sp3 with
~ 1000 S/cm conductivity



Carbon Surface



Hexanediamine

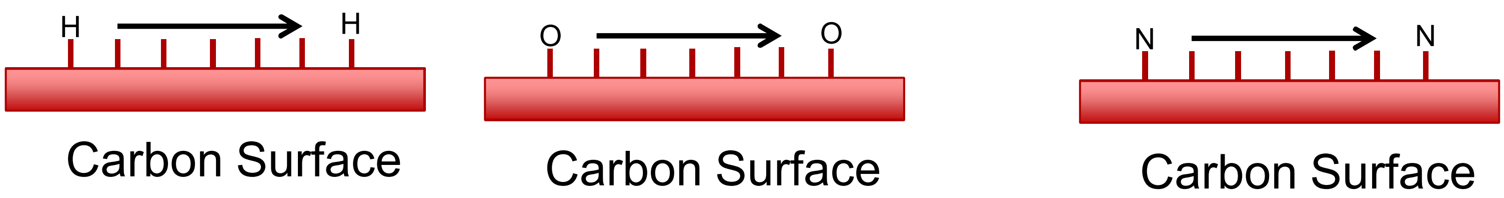


Pyridine

G peak - Defines how structured the carbon lattice is becoming more graphitic due to heat.
D peak – Defines the number of graphitized layers present on the surface.
2D- Defines the sheet stacking of the graphitized layers (graphene and/or graphite)

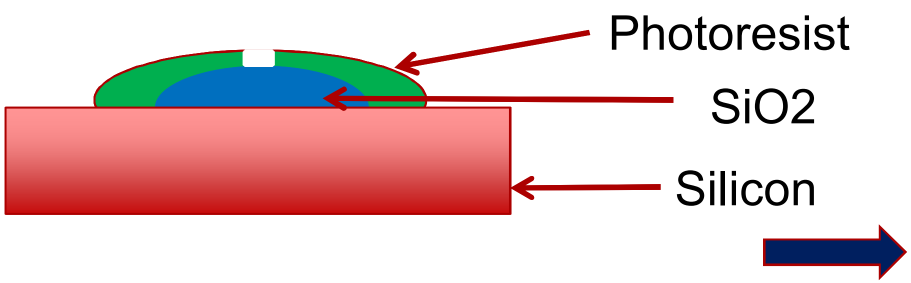
Surface Mechanism

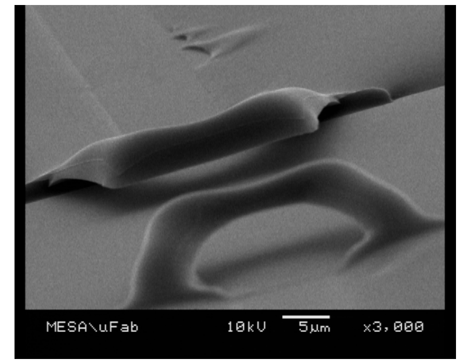
- Oxygen bonding to the carbon surface will increase resistance and lower conductivity.
- Nitrogen bonding to the carbon surface will in theory decrease resistance and increase conductivity.
  - N-type dopant to Carbon Nantubes, Graphene , and Amorphous carbon.



Device Development

- First attempt at free standing beams.
  - Choose a Silicon oxide etch release technique.

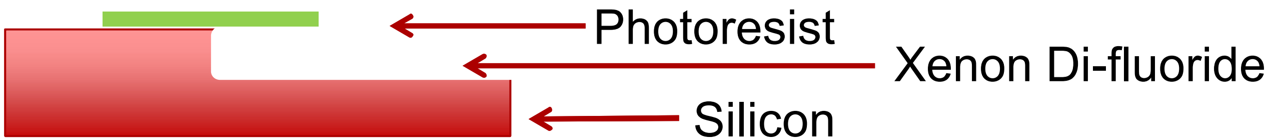


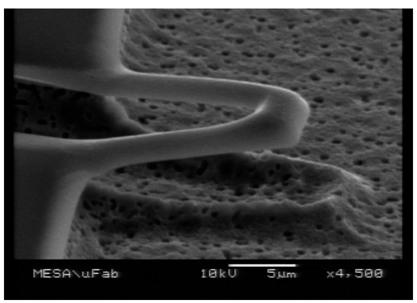


  - Low yield on devices.
    - 49% HF found porosity in the carbon and would etch away the full device.
  - Critical bake steps in air helped maintain dimensions (lowered reflow issues).
  - Adjusted the process flow on the pyrolysis step to before release.
  - 80% of the starting material thickness is the final device thickness after a 3 C/min ramp from room temperature to 1150C under a 95% Nitrogen and 5% Hydrogen reducing atmosphere.
  - Commonly start ~ 3.3 micron and finish with ~ 1.1 to 1.3 micron

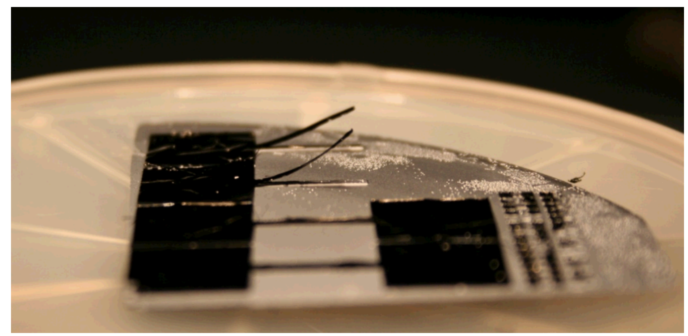
Device Development

- Moved to a XeF2 silicon etch process (Pad:Device surface area ratio)
- Straight forward manufacturing, lends scaling on full wafer.

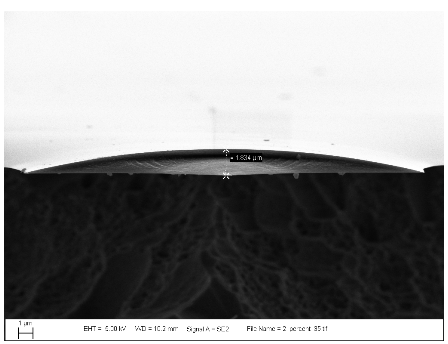




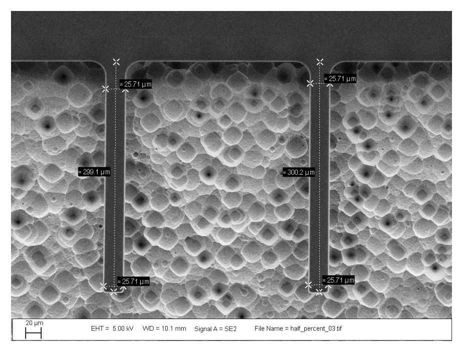
10 micron wide X 30 micron long



1mm X 10mm beam released



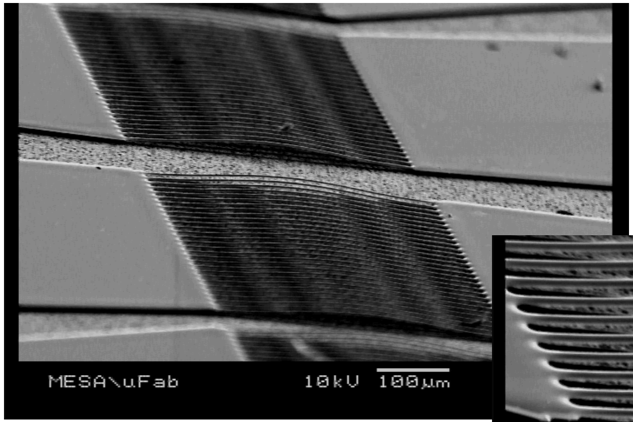
Air craft
Wing X-section

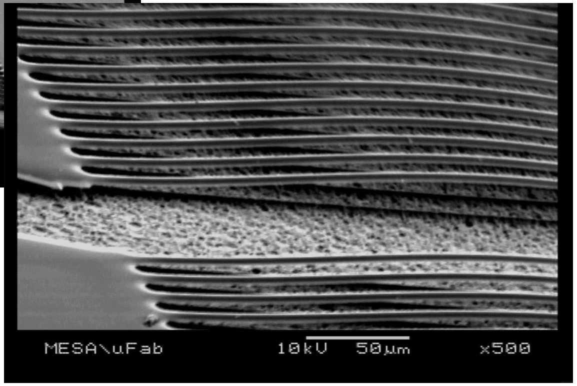


Design specific
Beams for testing

Carbon MEMS Bridge

- Developed a series of 1, 5, and 10 micron wide bridge which are 400 microns in length.
- 4-channels on a die (4mm X 8mm)
- Each has a resistance ~ 200 ohms
- Devices is tested in a parallel resistance layout (80-90 ohms) using 3VDC.





Device interfacing using fixtures

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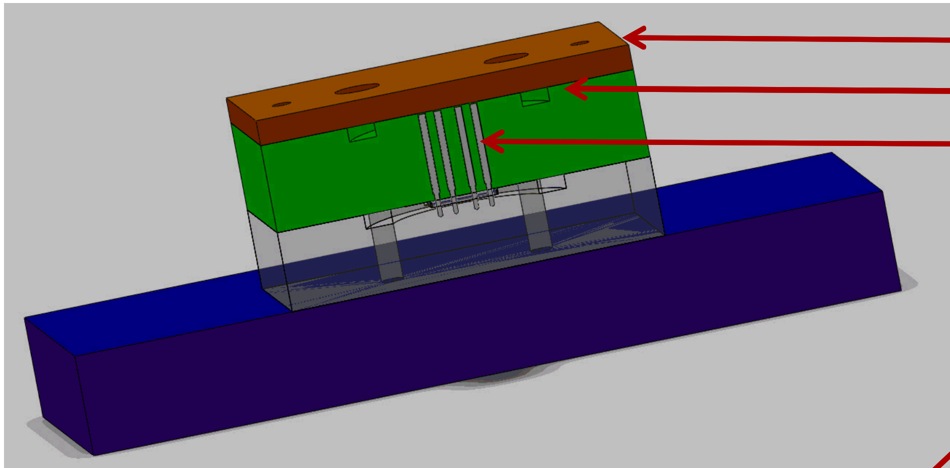
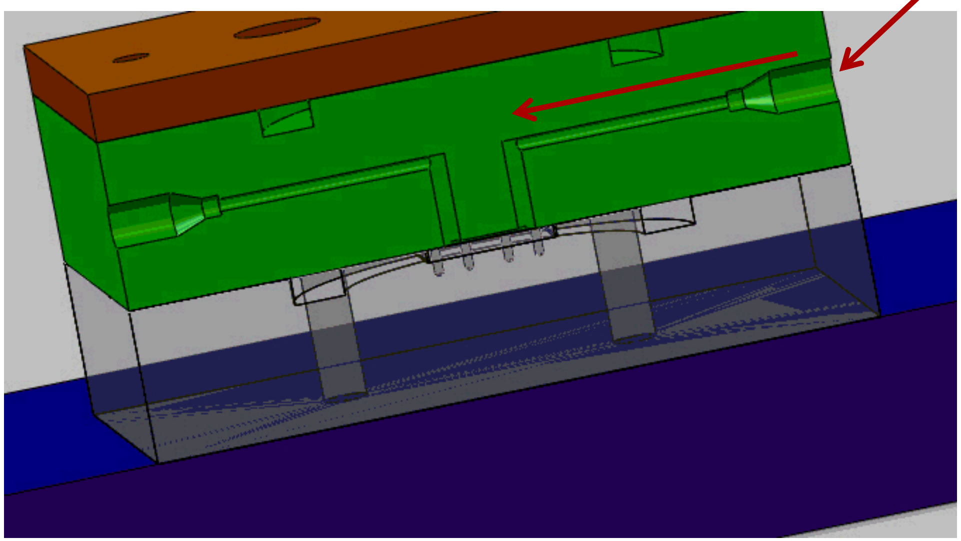


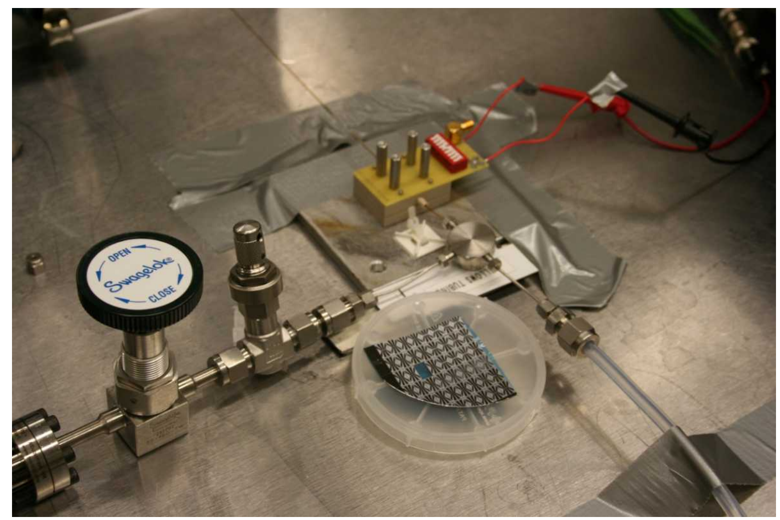
PCB board

Viton O-ring at PCB/PEEK interface

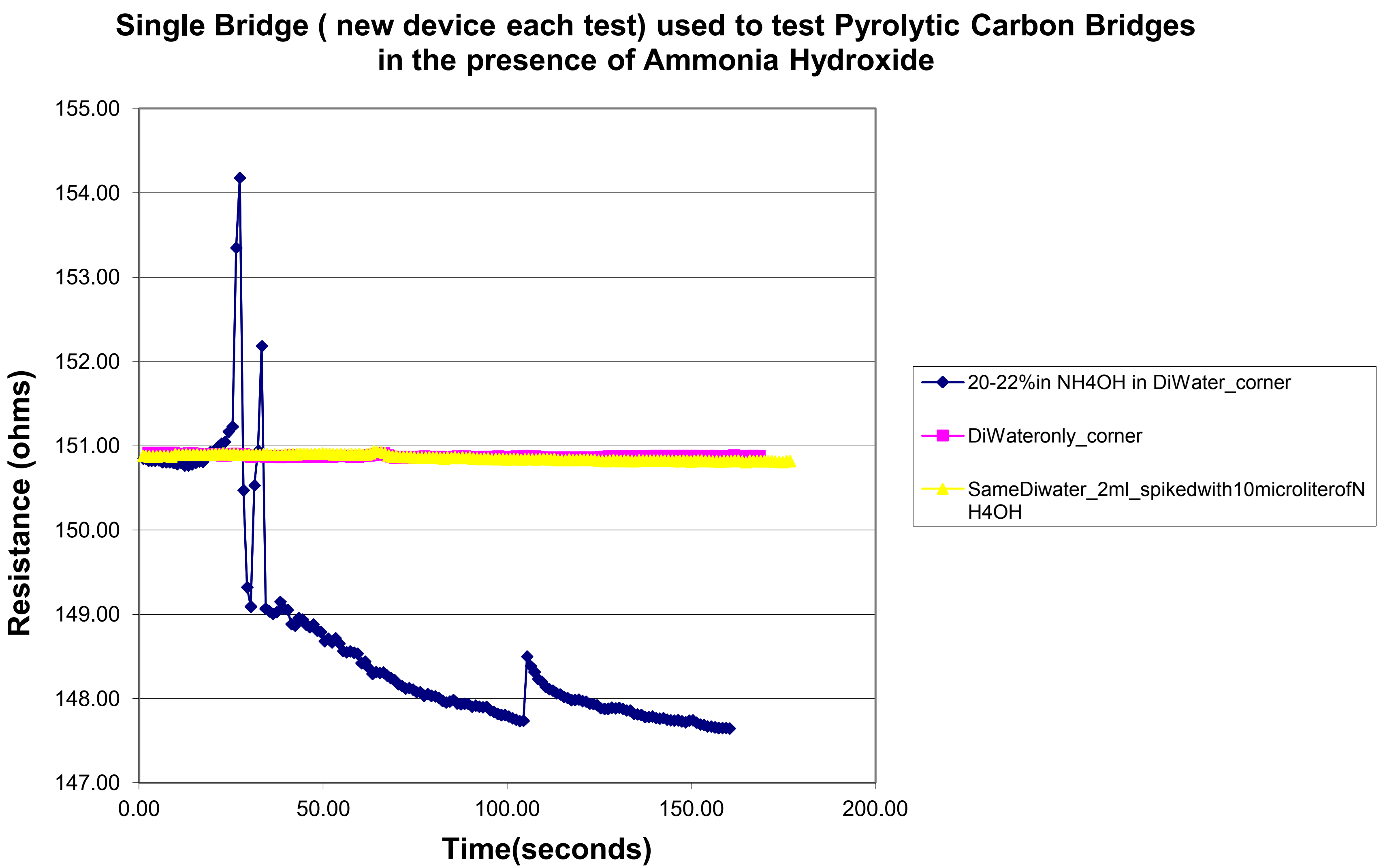
Pogo Pins for electrical contact

Gas Inlet using Micro-tights (Sandia R. Renzi design)
And Mega-bore capillary tubing (~530 O.D.)
Using only 20-30 sccm Nitrogen or Air.

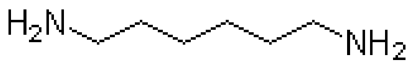


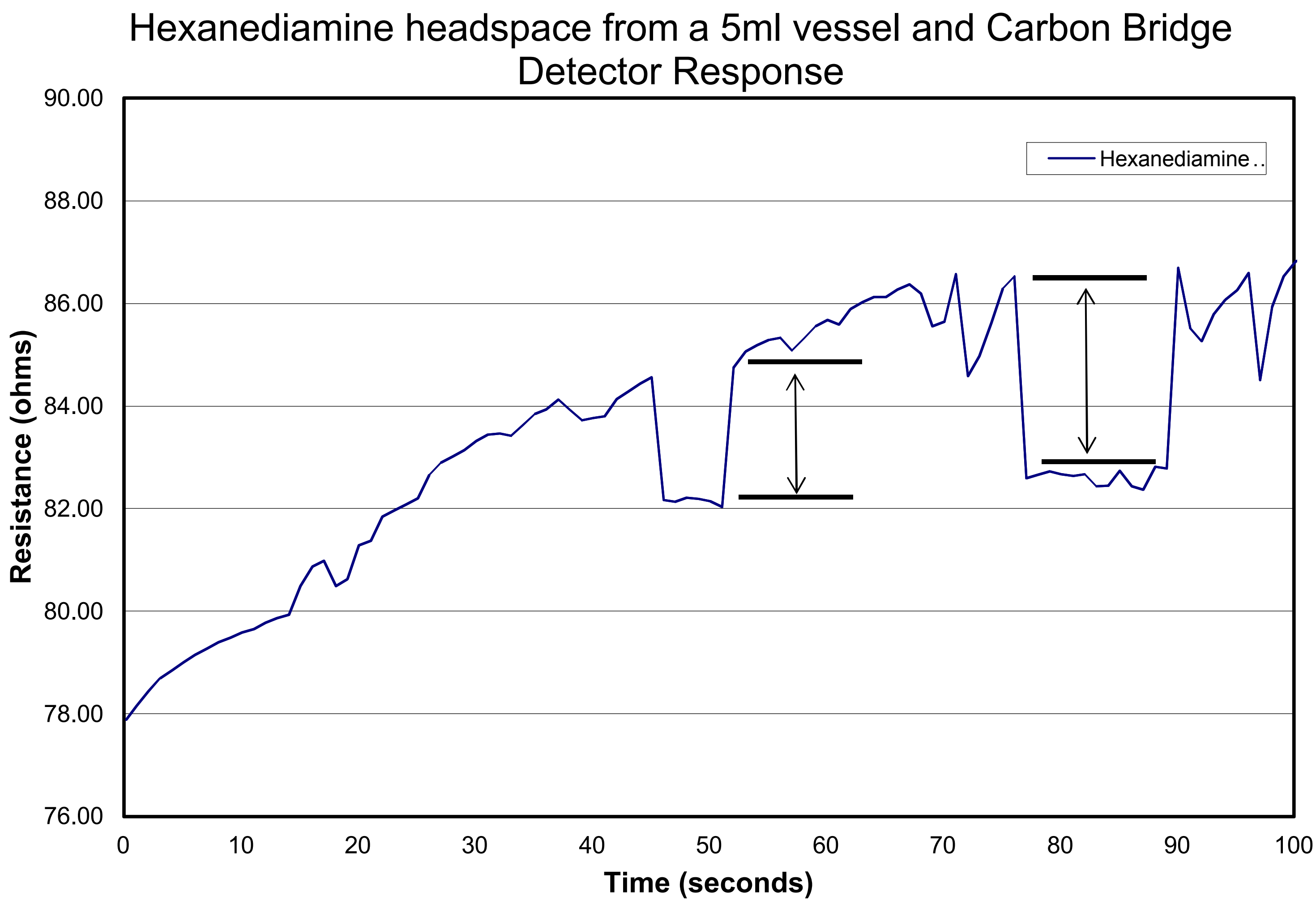


Initial concept for N-type dopant



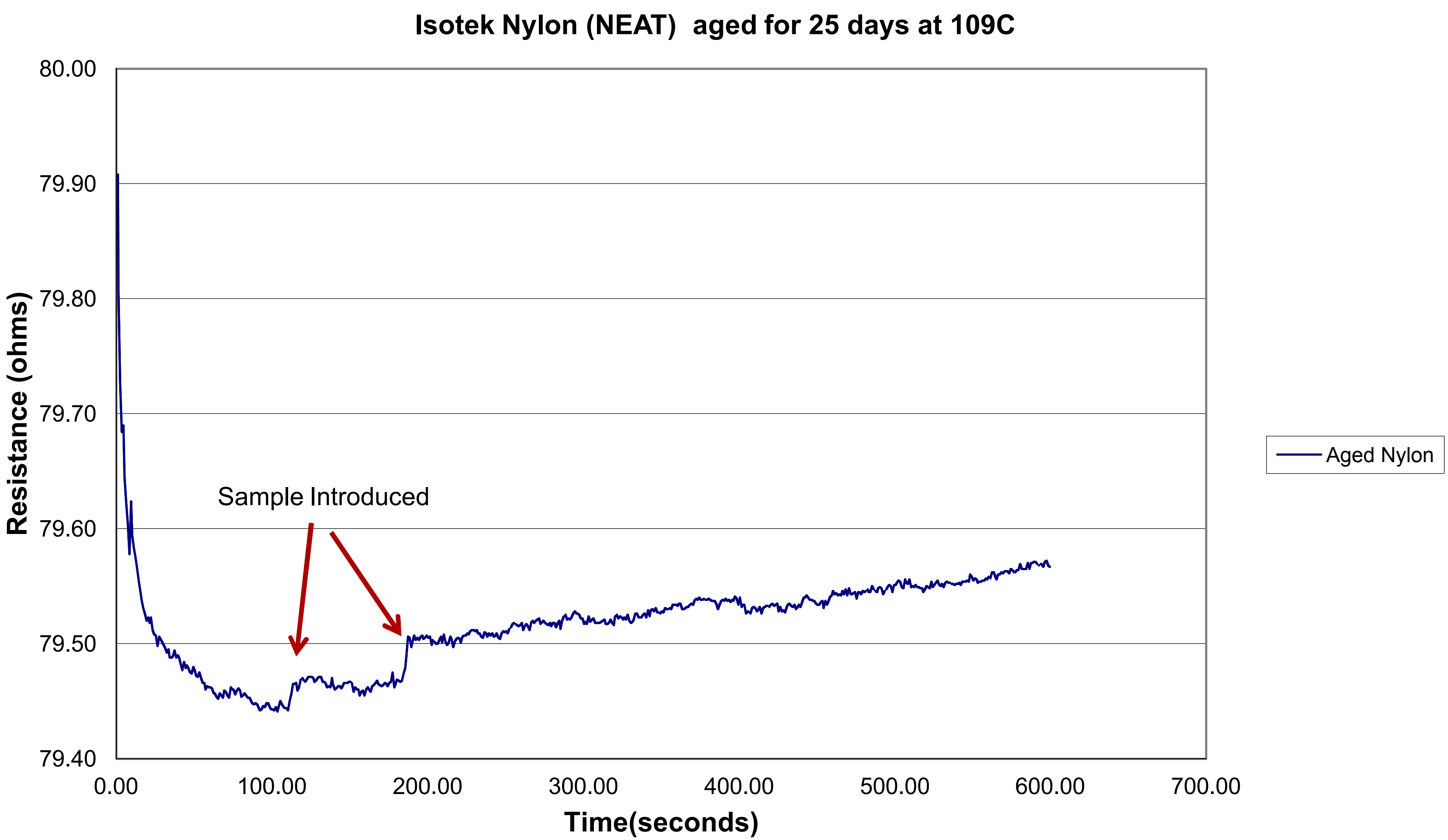
1,6 Hexanediamine





~4%
Delta R/ R

Nylon Degradation

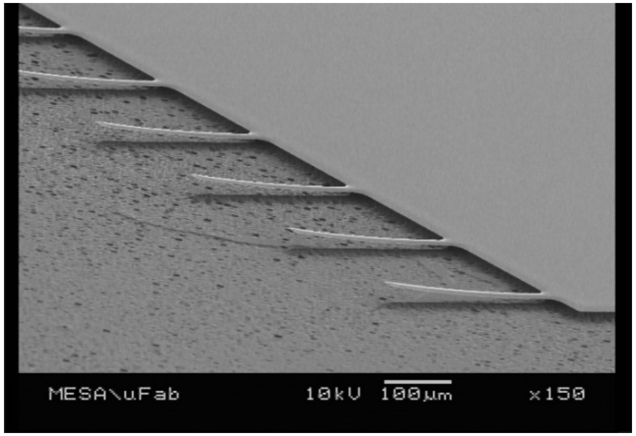


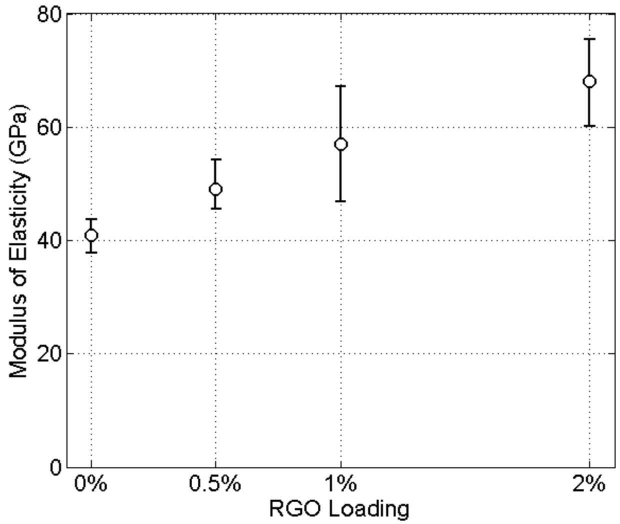
Tuning the sensor surface

- Did not see pyridine, adipic acid, and ammonia hydroxide.
  - Considering additional surface chemistries to assist in enhancing this binding event.
    - Diazonium covalently linked to the surface.
    - Graphene doping to improve conductivity and strength.
      - Decrease pressure sensitivity.
  - Not seeing NH_4OH
- Adding in a pre-concentration phase before the sensor to help concentrate the gas stream.
- Using a Micro-machined GC column along with an electronic amplifier circuit will increase signal to noise.

Tuning using Graphene Nano-fillers

- Reduced graphene oxide (RGO)
  - Placed this into the photoresist and patterned the same devices.
  - Using laser doppler vibrometry (LDV) – a resonant frequency analytical technique – material properties can be extracted.





Electrochemical Society – PRiME
ECS Transaction full paper

Tunable Young's Modulus in Carbon MEMS using Graphene-based Stiffeners
Cody Washburn*, Jill Blecke, Timothy N. Lambert, Danae Davis, Patrick Finnegan, Brad Hance, and Jennifer Strong

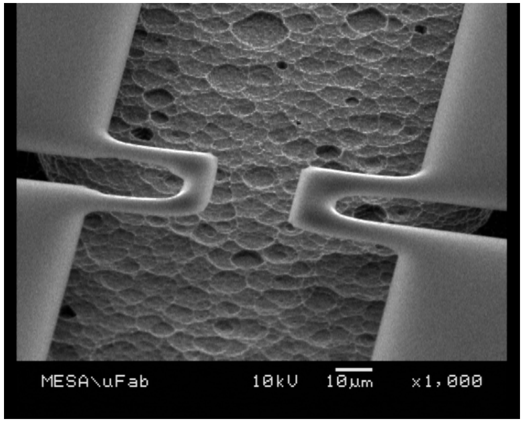
900 S/cm for 0 wt.% filler
1800 S/cm for 2 wt.% filler

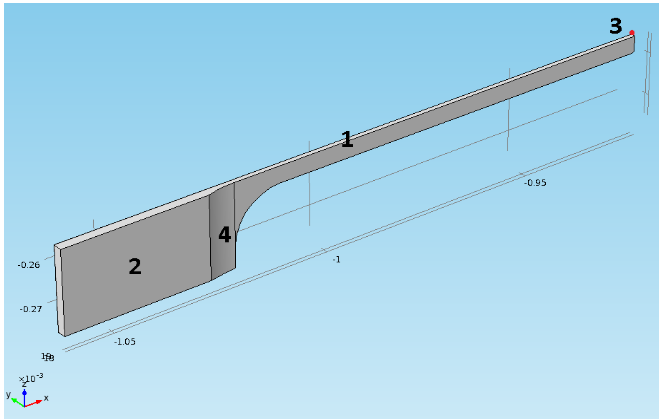
Discussion and Future Work

- Demonstrated releasable Carbon Bridge Devices.
- Still working sensor platform and N-type dopant activity.
- Investigate surface chemistries to help push the sensing mechanism.
- Demonstrated tunable electro-mechanical properties.
- Recently shown graphene fillers with 5 and 10 wt.% loadings are possible to resolve.

Acknowledgement

- NNSA and DOE funding under the Enhanced Surveillance Campaign (ESC).
- COMSOL multi-physics package to assist in design for testing.





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