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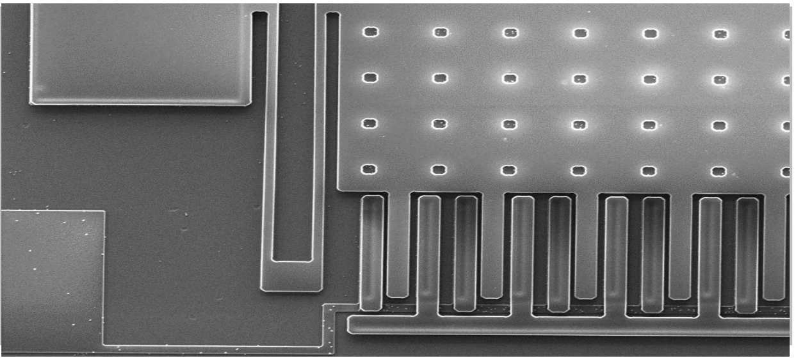

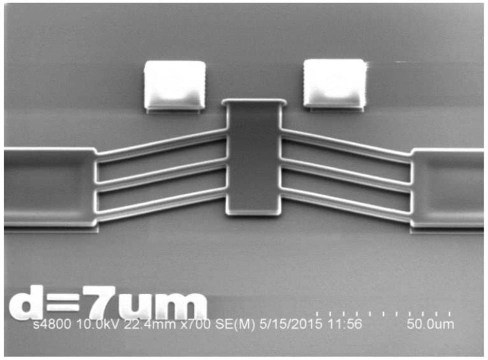

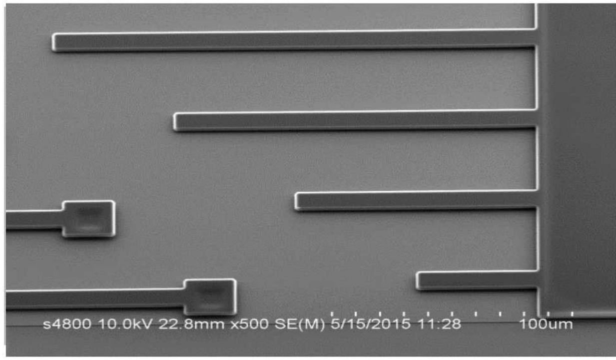

Novel Pyrolyzed Carbon Processing and Applications

Patrick Finnegan [a], Cody Washburn [b], Christopher Dyck [b], Bruce Burckel [c], Jill Blecke[d], Michael Rector[b], Kent Pfeifer [e], and Michael Satches[f]

Org. 1816– Electronics, Optical and Nano Materials [a], Org. 5865 – Applied Technologies [b], Org. 5265- Applied Photonic Microsystems [c], 1512-Diagnostic Sci. & Engineering [d], 8634- Nano and Micro Sensors [e], 5219- MEMS Technologies [f]

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Outline

- **Why Carbon based devices?**
- **Common approaches to CMEMS fabrication**
- **Bulk film Procssing vs pre pattenred, pyrolized approach**
  - Variable thickness control
  - Photo definable devices
  - Dry etched devices
- **Micromachining carbon- Production lot scalable**
- **Post silicon processing integration & Multilayered CMEMS device fabrication**
- **Tuning photo definable patterns for desirable characteristics**
  - Loading with Nano material
  - Reinforcing carbon with carbon
- **Discussion and Future Work**

Why Carbon?

- **MEMS for harsh environments**
  - High temperature operation
    - CMEMS fabricated at 1050C
  - General radiation environments
    - Radiation tolerance
  - Chemically inert
- **Photo-patternable materials & bulk film processing**
  - Ability to photolithographically define features before or after pyrolysis makes MEMS feasible
  - Can etch features out of a bulk film
- **Tunable Young's modulus and resistivity using graphene fillers**
- **Conductors and other materials can be deposited and patterned on carbon MEMS structures**
- **Applications: accelerometer, thermal actuator, chemical sensing, microfluidics?**

Faces of Carbon

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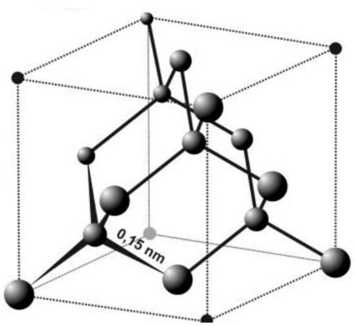
C
6

- Highest elemental melting point (sublimes at ~3900K)
- Forms ~ 10 million different compounds
- Resistant to acids, bases and all but the strongest oxidizers
- Biologically compatible

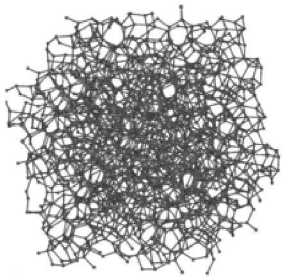
sp^3 bonds

Diamond



Hardest material
Good abrasive
Electrical insulator
Good thermal conductor
Optically transparent

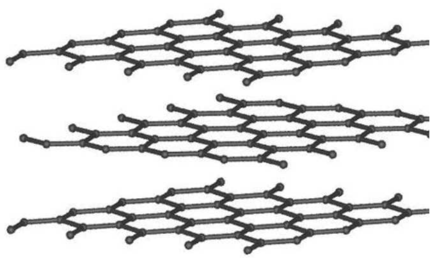
Amorphous Carbon



High Modulus
Tunable DC Conductor
Optically Opaque

sp^2 bonds

Graphite

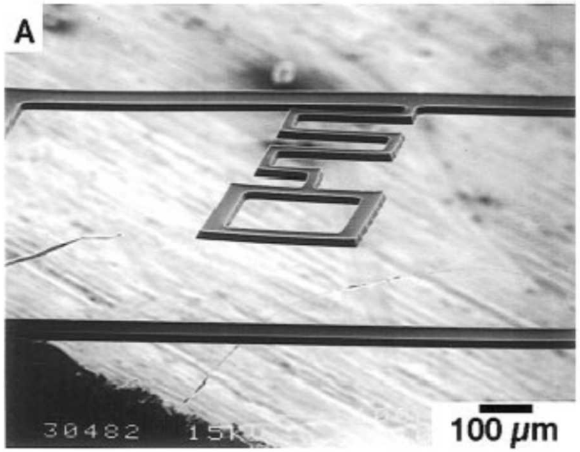


One of the softest materials
Good lubricant
Electrical Conductor
Can act as thermal insulatio
Optically opaque

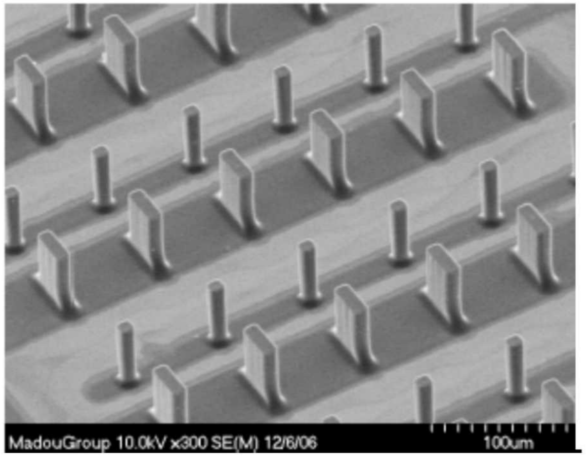
Images from Wikipedia

Device and Material Development

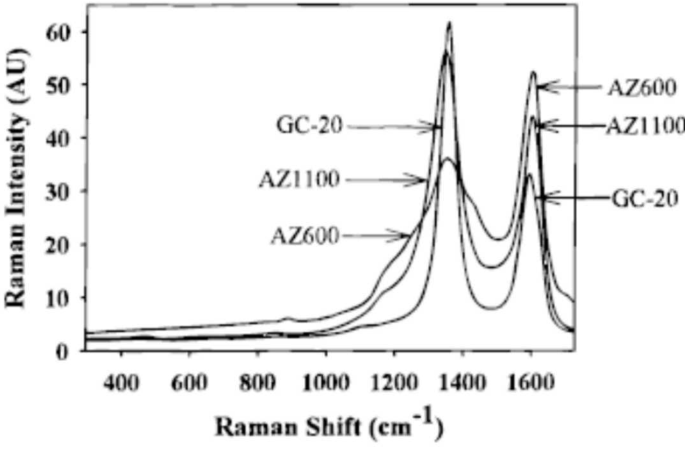
- **Pyrolytic Carbon**
  - Derived from photosensitive polymers (novalac and Epon(SU8)).
    - G. Whitesides, M. Madou, and R. McCreery
    - Has electrochemical sensitivity towards Redox compounds.
    - Demonstrated at Sandia to have broader capabilities. Polsky, Burkel, Washburn, and Wheeler for 3-D 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.



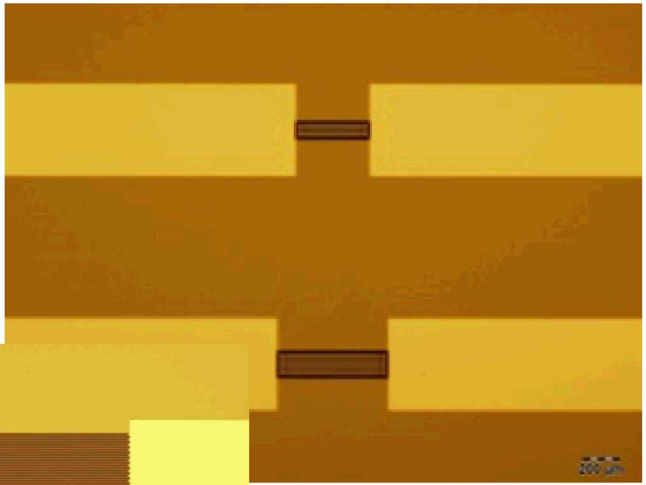
Madou, et. al.



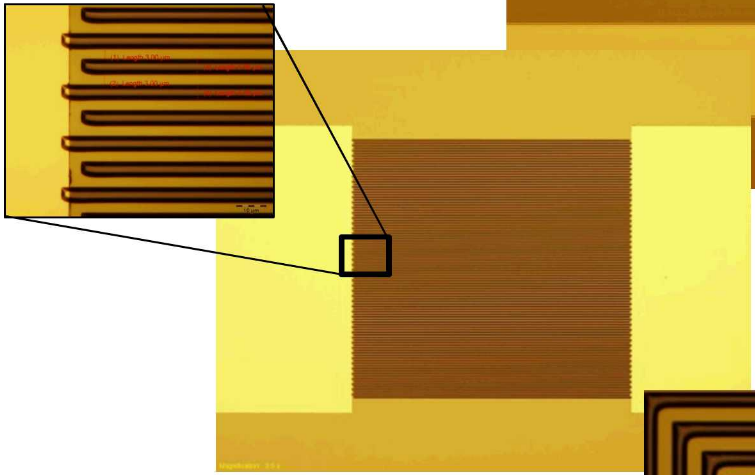
McCreery, et. al.

Rapid manufacturing simple devices

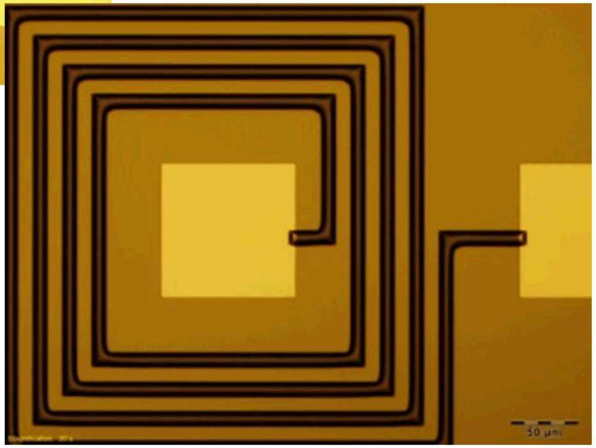
RESISTORS 4:1 aspect ratio resistors – Resistor behavior as a function of frequency.



CAPACITORS Inter-digitated electrodes – for fringe field capacitance modeling

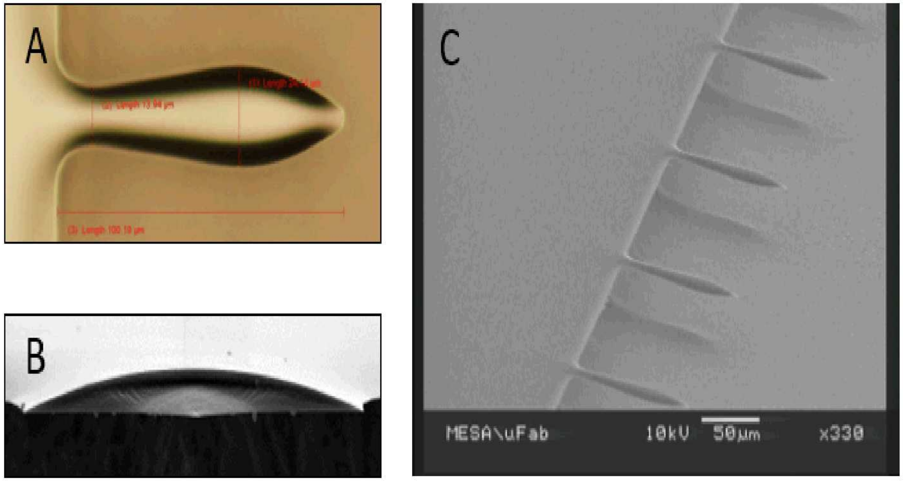


INDUCTORS 4-turn square spiral inductors – inductance behavior.



Pre patterned vs post patterning

Patterned before pyrolysis



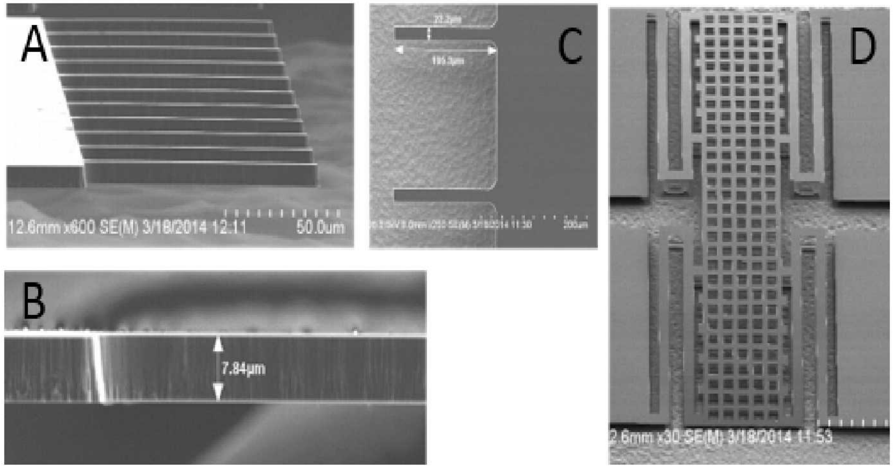
- **Post pyrolysis images of PPR cantilevers patterned prior to pyrolysis AZ9260 photoresist**
- **Reflow deformity that occurred during pyrolysis.**

A. Microscope image of an unreleased cantilever structure.

B. SEM cross section of cantilever

C. SEM of Cantilevers released in XeF_2

Patterned after pyrolysis



- **Thick-film carbon process: micromachining blanket pyrolyzed photoresist films (SiO_2 hard mask, ICP etch, XeF2 Si etch release) Results in controlled geometries for mathematical approximations and FEA modeling**
- **7.2 µm thick cantilever**

A. 100µm long x 10µm wide cantilevers with improved Dimensional control and vertical sidewall profile

B. profile of cantilevers ~8µm thick carbon process

C. top down view of released cantilevers

D. Prototype of an inertial sensor shows a net compressive strain.

Carbon Electrical Devices from Polymer Precursors for Harsh Environments

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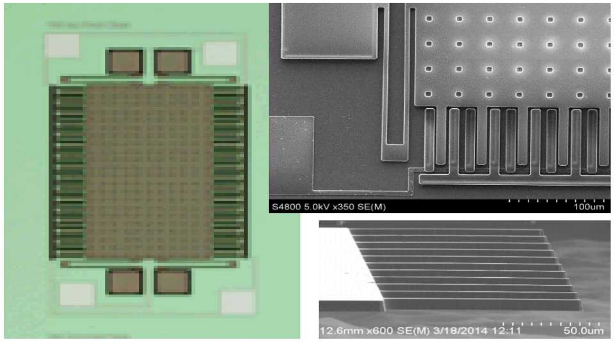


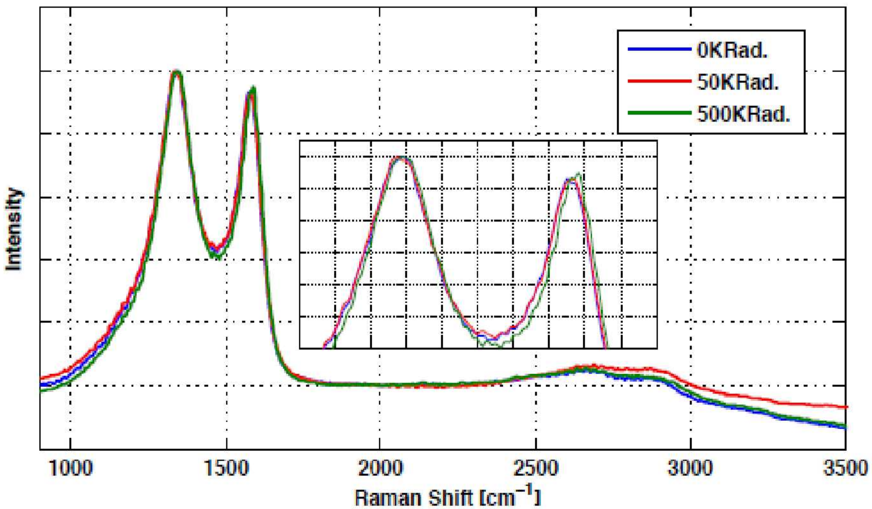
Carbon MEMS accelerometers and Cantilevers

Pyrolytic Carbon from Photoresist

- Produced using commercially available photoresist pyrolyzed at 1050°C- Heat tolerant
- Demonstrated Tunable conductivity 1-150 ohms/sq
- Demonstrate feasibility – Simple electrical components and rapid prototyping cantilevers, bridge, and accelerometer devices
- Single step photolithography, a high temperature furnace and a Xenon Difluoride etch
- Variable thicknesses capable for specific tunability .02μm -7.8μm has been demonstrated
- Adaptable into integrated circuits and circuit components

Electrically and mechanically tolerant in radiation environments

The amorphous carbon produced from pyrolysis of photoresist remained stable in Gamma radiation doses of 50, 100 and 150Krad exposed at 0.75-1Krad/second. Raman surface analysis before and after suggests the SP2 to SP3 ratio was not influenced by radiation tolerance.



Blanket Carbon Films of various Thickness on Si

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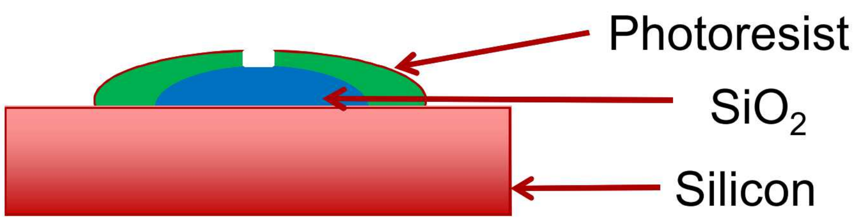
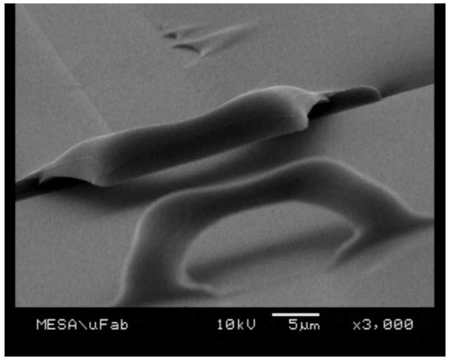
- Spin coat photoresist on Si wafers followed by pyrolysis at 1050°C
- Ability to adapt common CMOS tooling and micromachining processes
- Thickness control for specific component needs (conductivity, rigidity, etc.)
- Increased sample size: small pieces/quarter 4” Si wafer to large batch 6” wafer lots

Photoresist type	Spin Velocity [rpm]	Post-pyrolysis thickness[μm]
nLof 2020	4000	.35
AZ4330	4000	.70
nLof 2035	4000	.90
AZ 40XT	2000	2.50
AZ 50XT	3000	4.30
AZ 50XT	1300	7.84
nLof 2070 triple spin	3000	9.00
AZ9260	1000	9.20

Cantilever Device Development

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

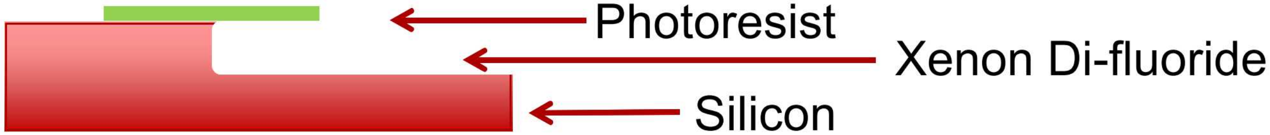


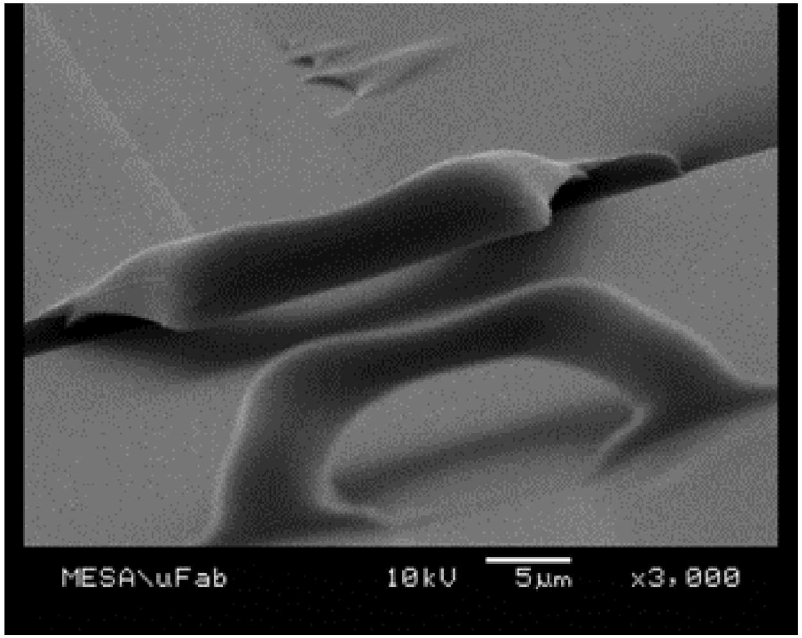


  - Low yield on carbon devices.
    - 49% HF found porosity in the carbon and would etch away the full device.
  - Critical bake steps in air helped maintain dimensions (lowered reflow issues).
  - Adjusted the process flow on the pyrolysis step to before release.
  - 80% of the starting material thickness is the final device thickness after a 3° C/min ramp from room temperature to 1050C under a 95% Nitrogen and 5% Hydrogen reducing atmosphere.
  - Commonly start ~ 3.3 micron and finish with ~ 1.1 to 1.3 micron

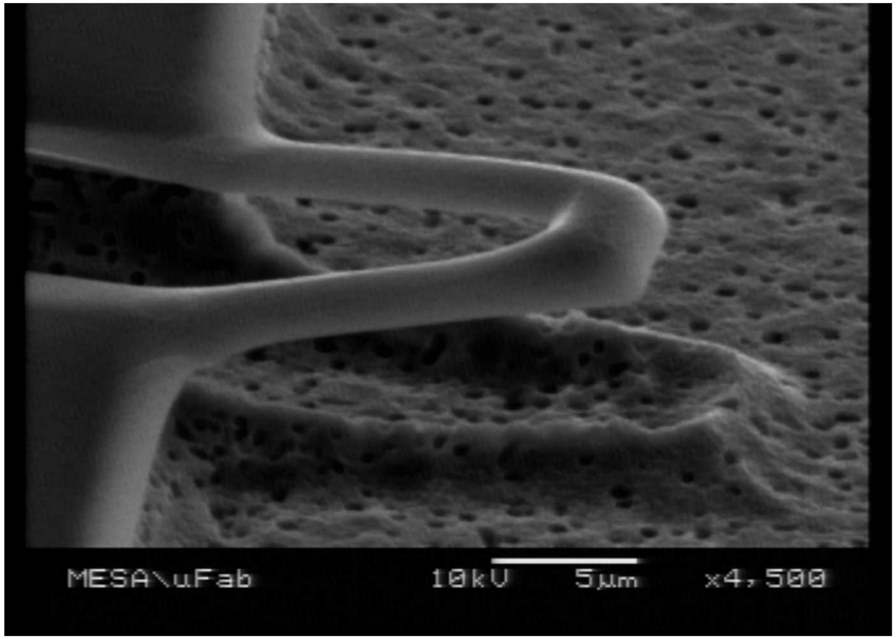
Device Development

- Moved to a XeF_2 silicon etch process (Function of Pad : Device surface area ratio)
- Straight forward manufacturing: Simple photoresist patterning> pyrolysis> XeF_2 release





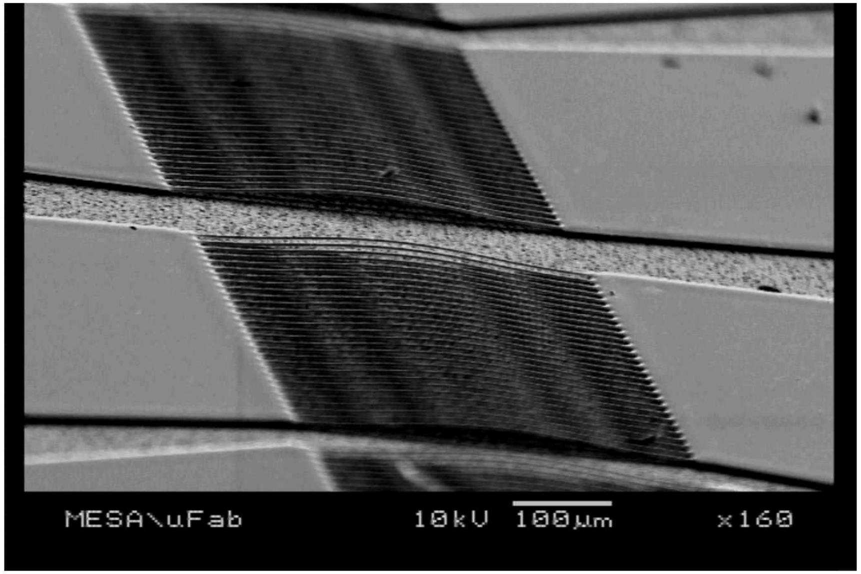
Patterned then pyrolized AZ4330 cantilever
SiO_2 sacrificial material with HF release

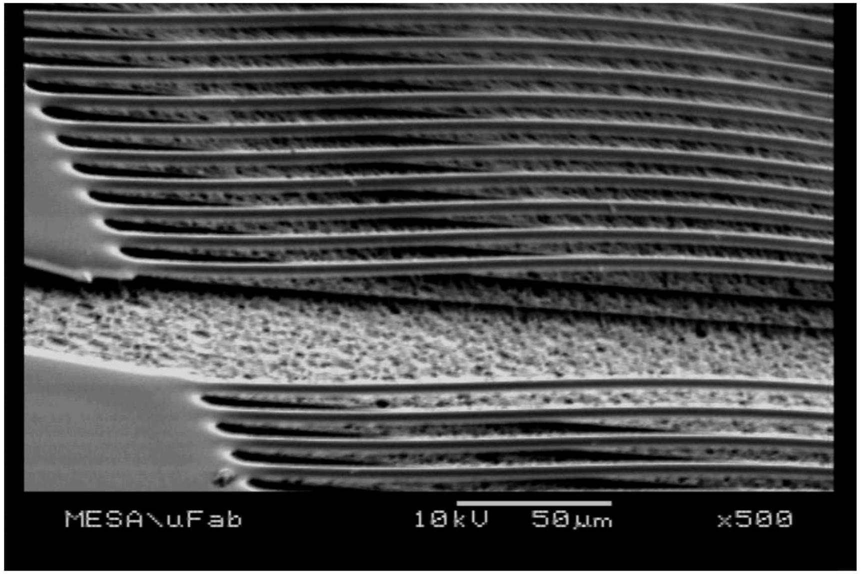


Patterned then Pyrolized AZ4330 cantilever
XeF2 Si etch release

Carbon MEMS Bridge

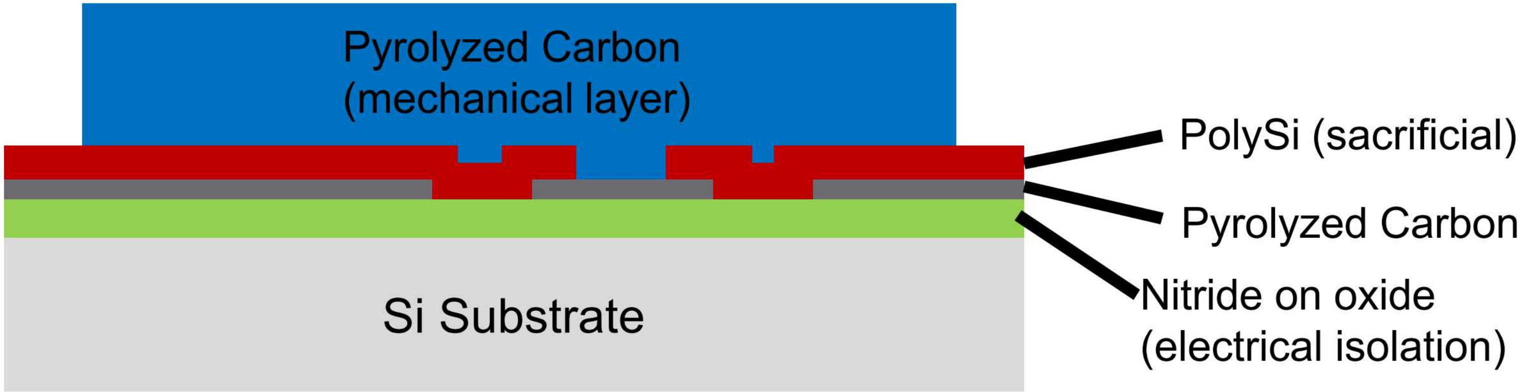
- Developed a series of 1, 5, and 10 micron wide bridge which are 400 microns in length.
- 4-channels on a die (4mm X 8mm)
- Each has a resistance ~ 200 ohms
- Devices tested in a parallel resistance layout (80-90 ohms) using 3VDC.





Carbon-Carbon Process

- Use pyrolyzed carbon as the conductive layer
  - This should survive a second high-temperature process when the mechanical carbon layer is pyrolyzed
- Thick polySi sacrificial layer
- XeF_2 dry release process
- All processing in the Microfab
- Pyrolyze in AMPL facility
- 6” wafers



Carbon on carbon processing

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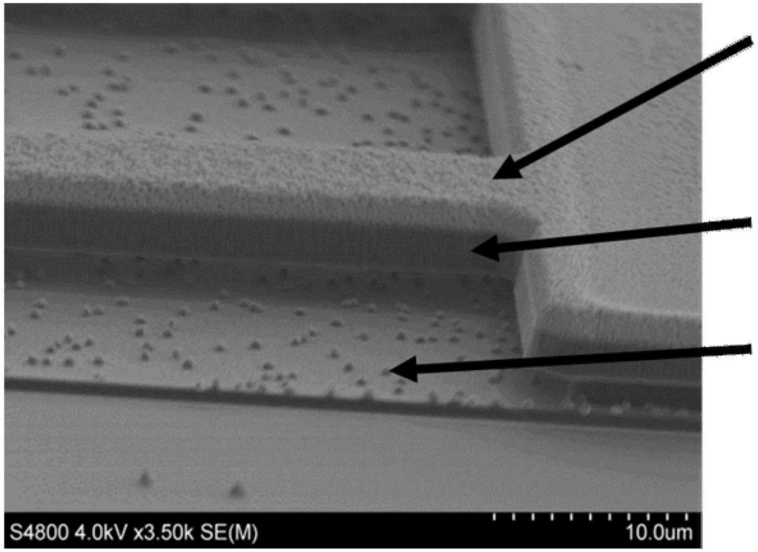
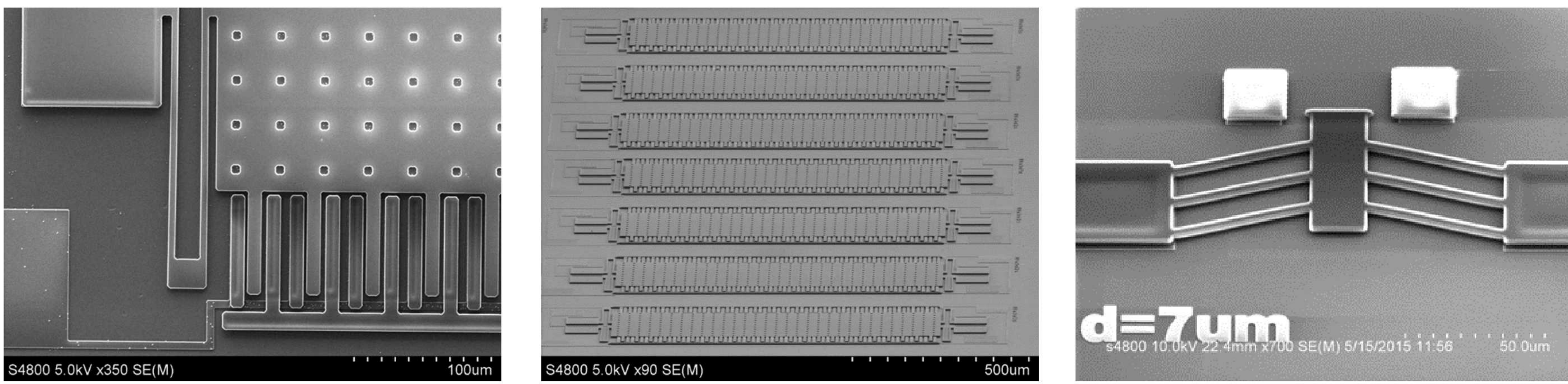


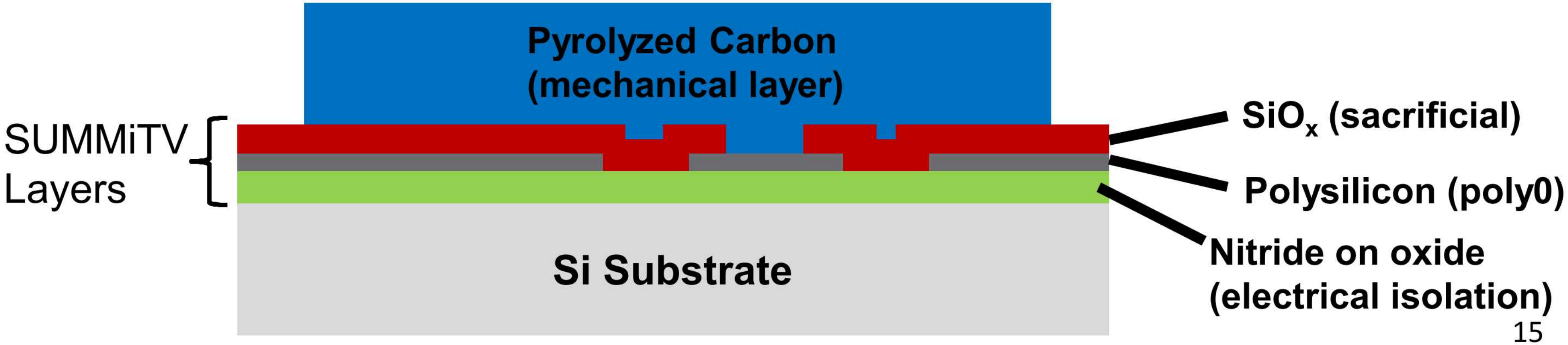
- SiO_2 hard mask grown in O_2/Ar/SiH_4 high-density plasma PECVD and patterned using standard photolithography and CHF_3 based RIE
- Carbon cantilever etched from a blank film of carbon derived from photoresist precursor
- Carbon bottom signal/actuation pad. Small bumps appear when using polysilicon sacrificial layer



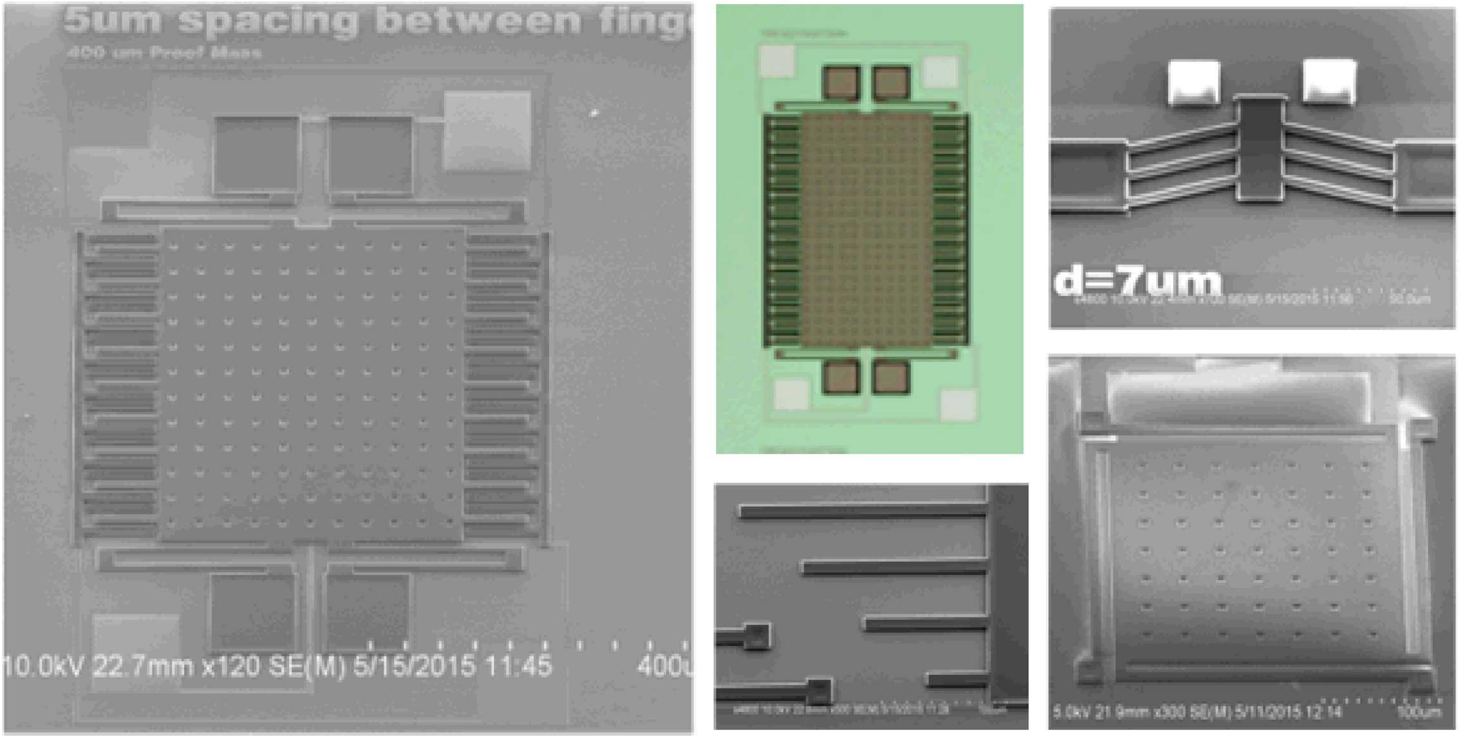
Carbon-on-carbon process. Pyrolyzed carbon over a conductive (non-mechanical) layer of pyrolyzed carbon. Polysilicon was used as the sacrificial layer. This was removed by selective XeF_2 etching.

Carbon on Si. Post Si process integration

- Use Poly0 as the conductive layer
  - SUMMiT materials undergo 1100C anneal during normal processing
- Poly0 and Sac_cut layers processed in the MDL
  - Known and controlled volume processes
- Carbon mechanical layer processed in the Microfab
- Pyrolyze in AMPL facility (up to 6 x 6" diameters wafers)
- <u>Move from processing small diameter wafers and pieces to an all 6" wafer process</u>



Si carbon integration

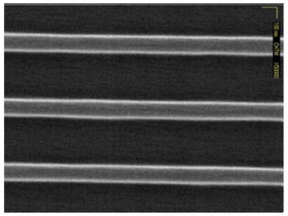


Images: carbon structures fabricated using the carbon-on-SUMMiTV™ process.

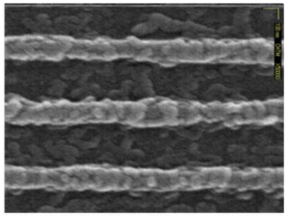
- **SEM image of prototype of a capacitive comb-drive accelerometer**
- **Accelerometer prototype defining bottom contact and conductive signal routing with mechanical carbon proof mass**
- **simple cantilever structures**
- **prototype of a capacitive thermal actuator with doped silicon feedback contacts**
- **plate capacitive inertial sensor prototype**

Photopatterning Loaded Photoresist

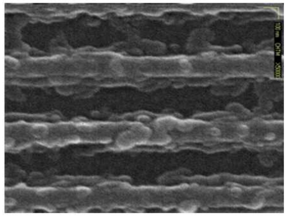
- **AZ 4330 Photoresist: loaded with Nano-materials**
- **Photo-patterning of a loaded photoresist**
- **Blending techniques to optimize quantity of materials, material size and suspension times, opens up a whole new filed of study.**
- **Carbon can be tuned to provide specific performance behaviors.**



control sample of carbonized patterned polymer with no Nano material loading



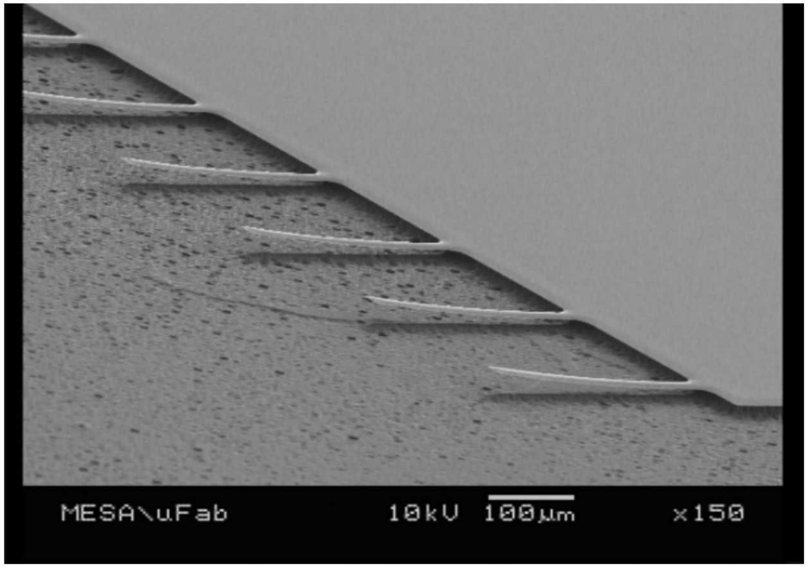
patterned carbonized polymer with 1% Graphene loading

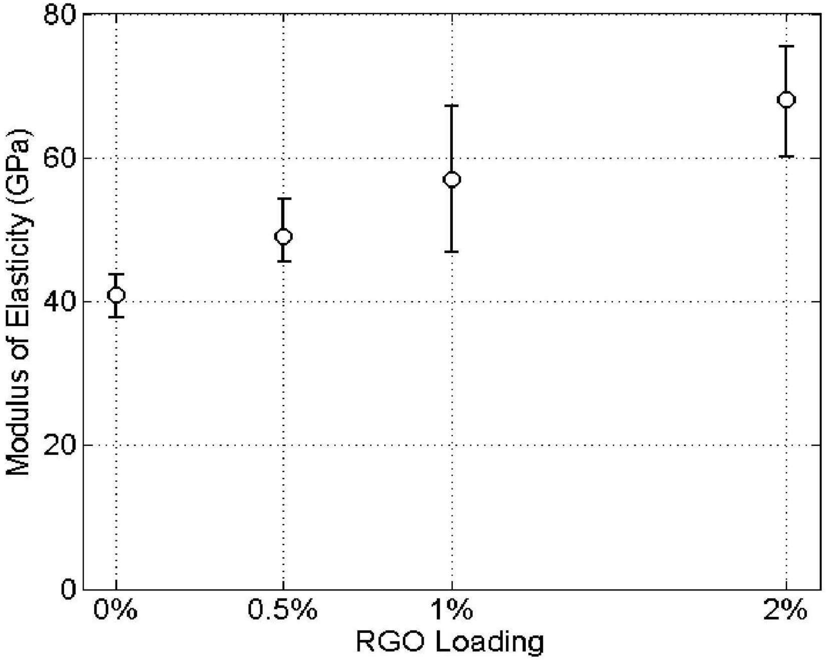


carbonized polymer loaded with 3%

Tuning using Graphene Nano-fillers

- **Reduced graphene oxide (RGO)**
  - RGO suspended in photoresist; patterned and released cantilevers
  - Using laser doppler vibrometry (LDV) – material properties observed



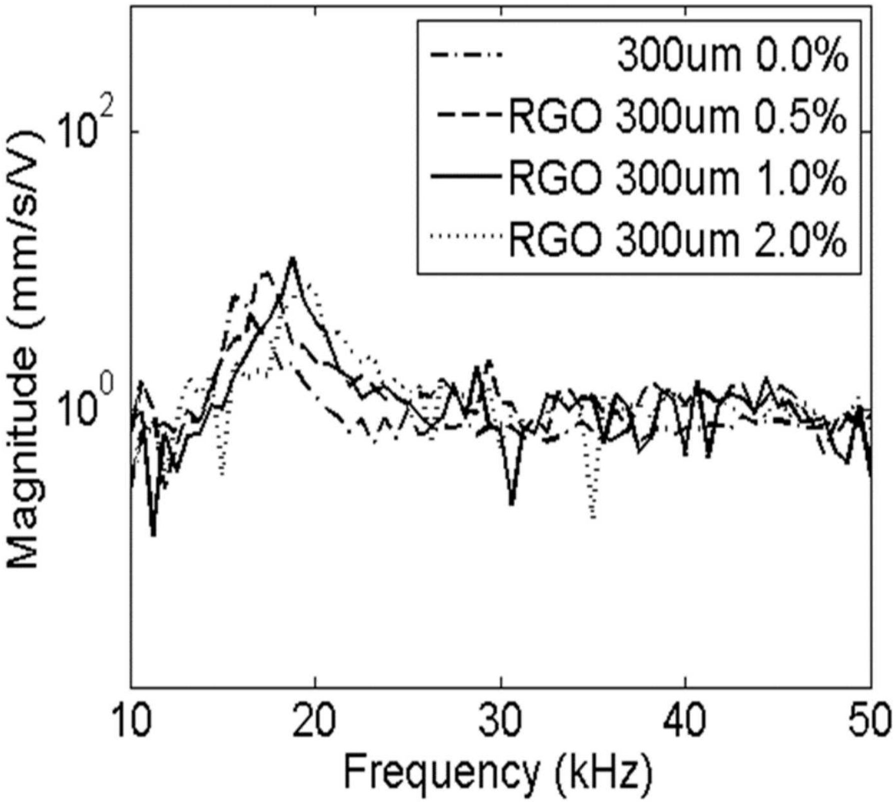


Electrochemical Society – PRiME
ECS Transaction full paper

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

Tuning photo-definable carbon via nano materials

- **Nano material loading into novolac photoresist precursor results in changes in Young's modulus and resistivity**

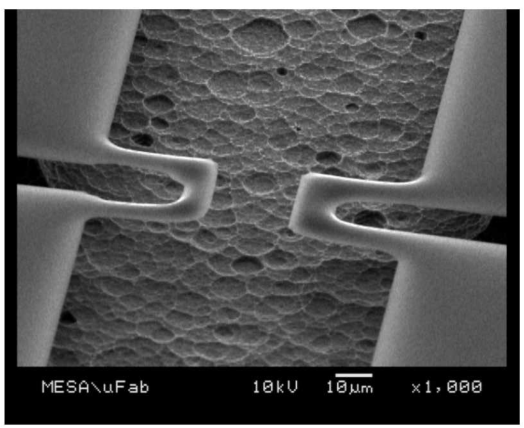


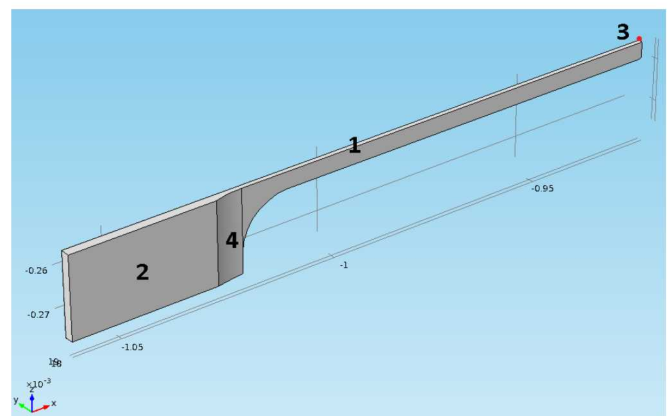
Tune carbon with carbon

- ideal material properties while maintaining a high degree of flexibility for design and processing.
- Tunability of Young's Modulus Tuned devices also displayed a high fracture toughness under loading (stress vs. strain) with a less abrupt failure mode than silicon crystals.

Acknowledgement

- NNSA and DOE funding under the Enhanced Surveillance Campaign (ESC) now known as Aging and Life Time Studies
- COMSOL multi-physics package to assist in design for testing.





Discussion and Future Work

- Brief history overview of SNL carbon device work
- Demonstrated releasable Carbon Bridge Devices:
  - Carbon on carbon platforms
  - Carbon integration on Si platforms.
- Demonstrated tunable electro-mechanical properties.
- Recently showed graphene fillers with 5 and 10 wt.% loadings are possible to resolve.
- Future: Micromachining of nanomaterial loaded blanket films
- Acquire test data from manufactured devices

Questions?

References

- G.Whitesides, et. al. “Fabrication and Characterization of Glassy Carbon MEMS”, Chem. Mat. 1997, 9, 1399-1406
- M. Madou, et. al. “Fabrication of suspended carbon microstructures by e-beam writer and pyrolysis”,2006, (13), 2602-2607
- R. McCreery, et. al. ” Photoresist-Derived Carbon for Microelectomechanical Systems and Electrochemical application” Journal of The Electrochemical Society, 147, (1) 277-282
- Polsky, et. al.” Lithographically Defined Porous Carbon Electrodes”, vol. 5, (24), 2792-2796
- T. Yamada, et. al.” A stretchable carbon nanotube strain sensor for human motion detection”, Nature NanoTech., 3/27/2011, DOI: 10.1038
- T. Ramanathan, et. al. “Functionalized graphene sheets for polymer nanocomposites”, Nature NanoTech., 6/2008, vol.3, DOI: 10.1038

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Synthesis Route to Amorphous Carbon: Pyrolysis of Organic Polymers

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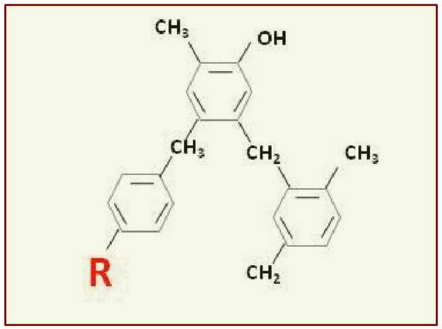
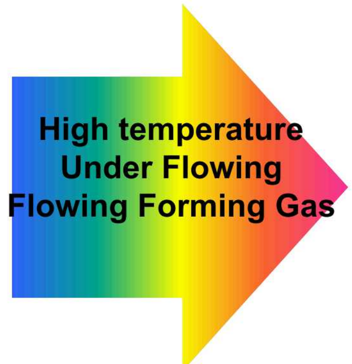
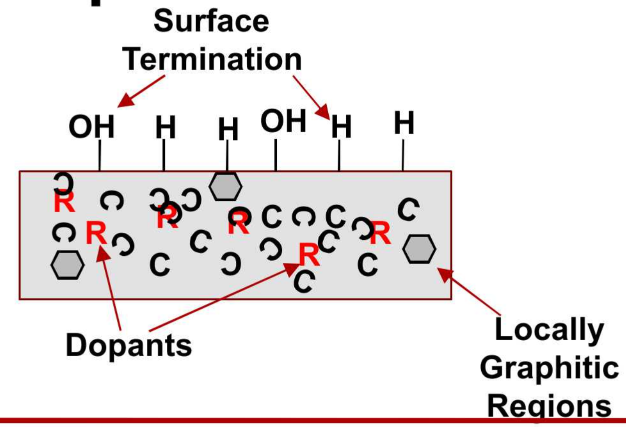
Organic Polymer → Pyrolysis → Amorphous Carbon

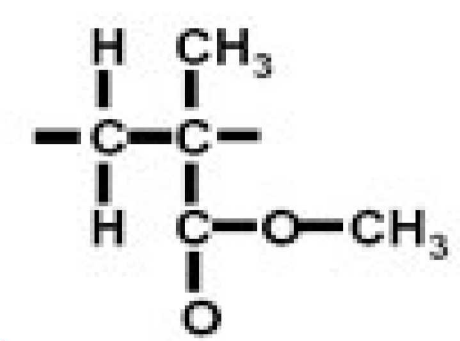




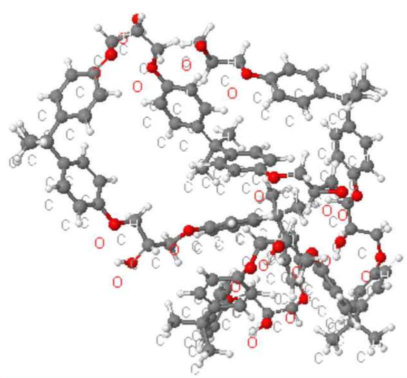


Typical Photopatternable Organic Polymers

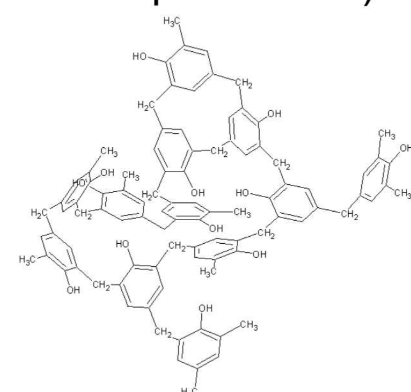
Polymethyl Methacrylate (PMMA)



Epoxide Resist (SU 8)



Phenol formaldehyde resin (novolac photoresist)

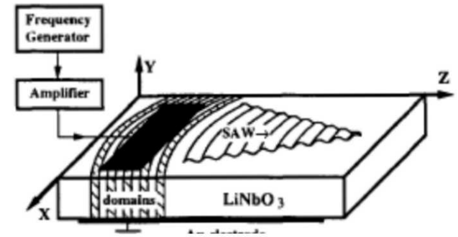


http://www.3dchem.com/moremolecules.asp?ID=326&othername=Epon

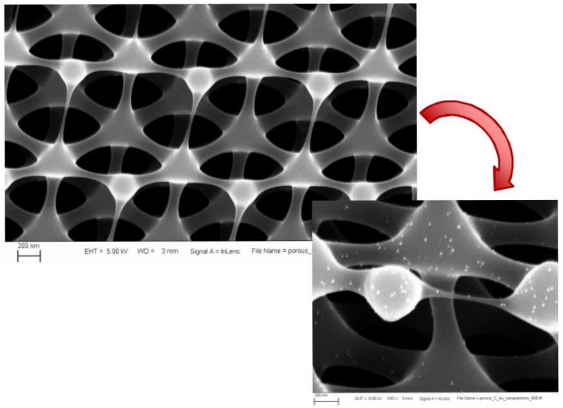
Wikipedia – Phenol fomaldehyde resin

Down select of sensor options

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

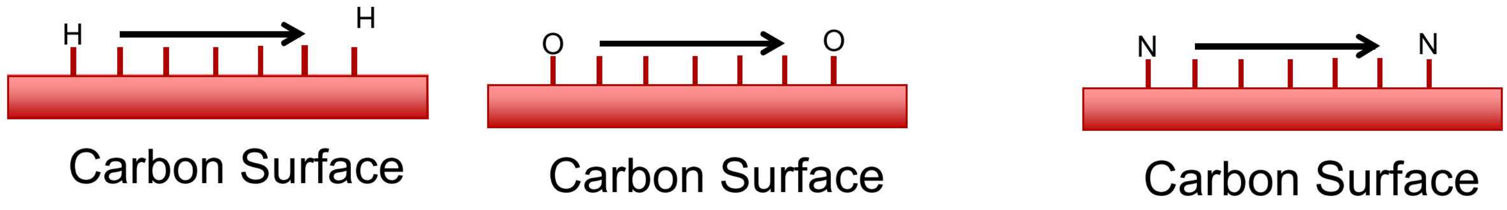


Dmitry V. Roshchupkin and Michel Brunel


Burckel, Polsky, Washburn, Wheeler 08'

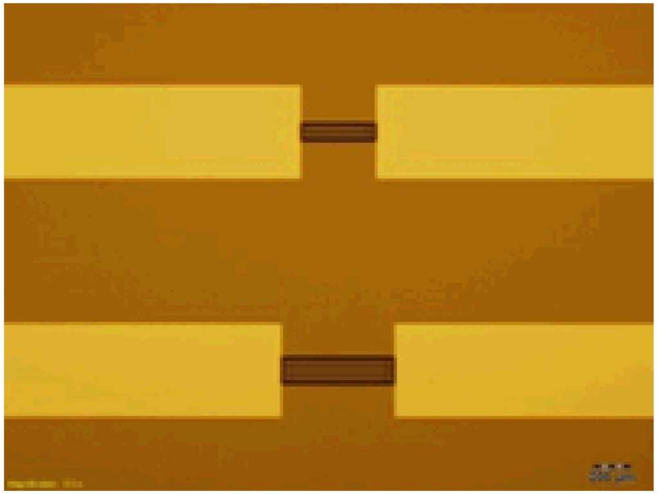
Surface Termination

- 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 Nanotubes, Graphene , and Amorphous carbon.



Hermetic Packaging

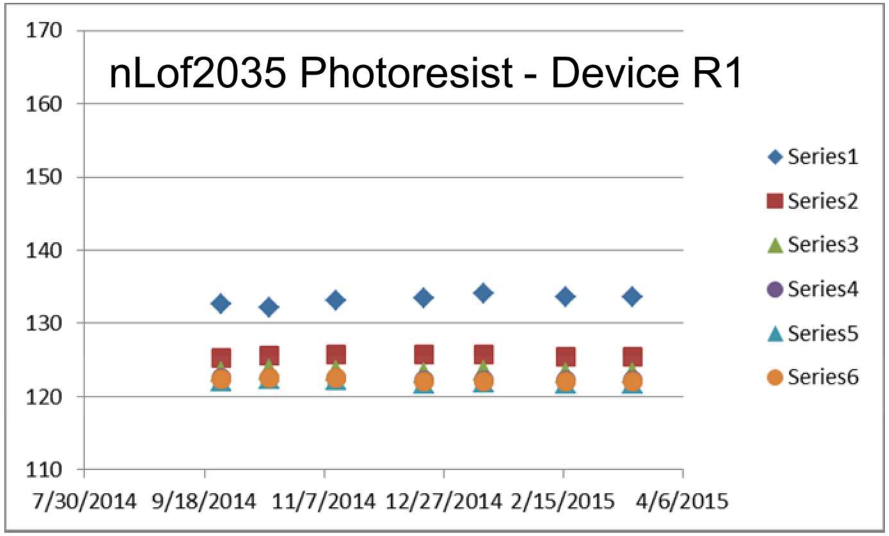
- Question: Why is the resistance not Stable?
- Answer: Water and Oxygen needed to be removed from the films in order to reach steady state.
- Can the resistance be stabilized by hermetic sealing?

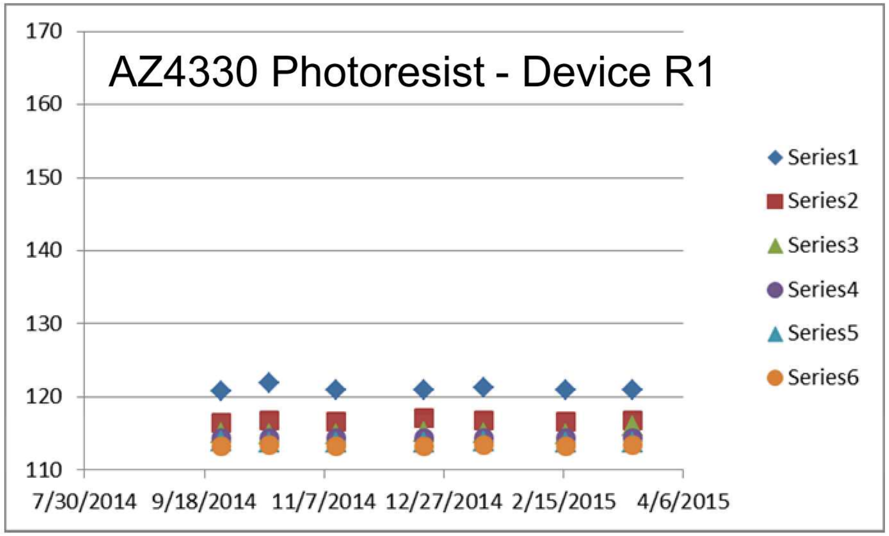


- Packaging process
  - 24-pin DIP, HTCC packages
  - Ribbon bond resistors
  - Vacuum bake – 150C, $4x10^{-4}$ Torr for 2 hours
  - Belt furnace in AMPL - N_2 ambient, 80/20 Au/Sn lid seal (280C melting point)

Hermetic Packaging – Typical Results

Monthly testing for 6 months

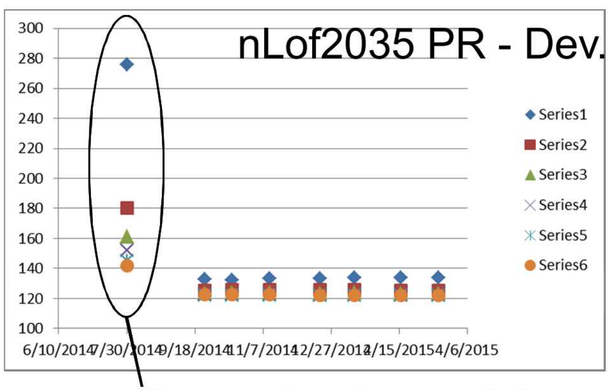




Series 1 = 50 x 200 [μm^2]
Series 2 = 100 x 400 [μm^2]
Series 3 = 150 x 600 [μm^2]
Series 4 = 200 x 800 [μm^2]
Series 5 = 250 x 1000 [μm^2]
Series 6 = 300 x 1200 [μm^2]

1mA test current – simulations indicate negligible resistor heating due to the test current

Note: The packaging process caused a large decrease in the resistance of all devices



Pre-packaging resistance

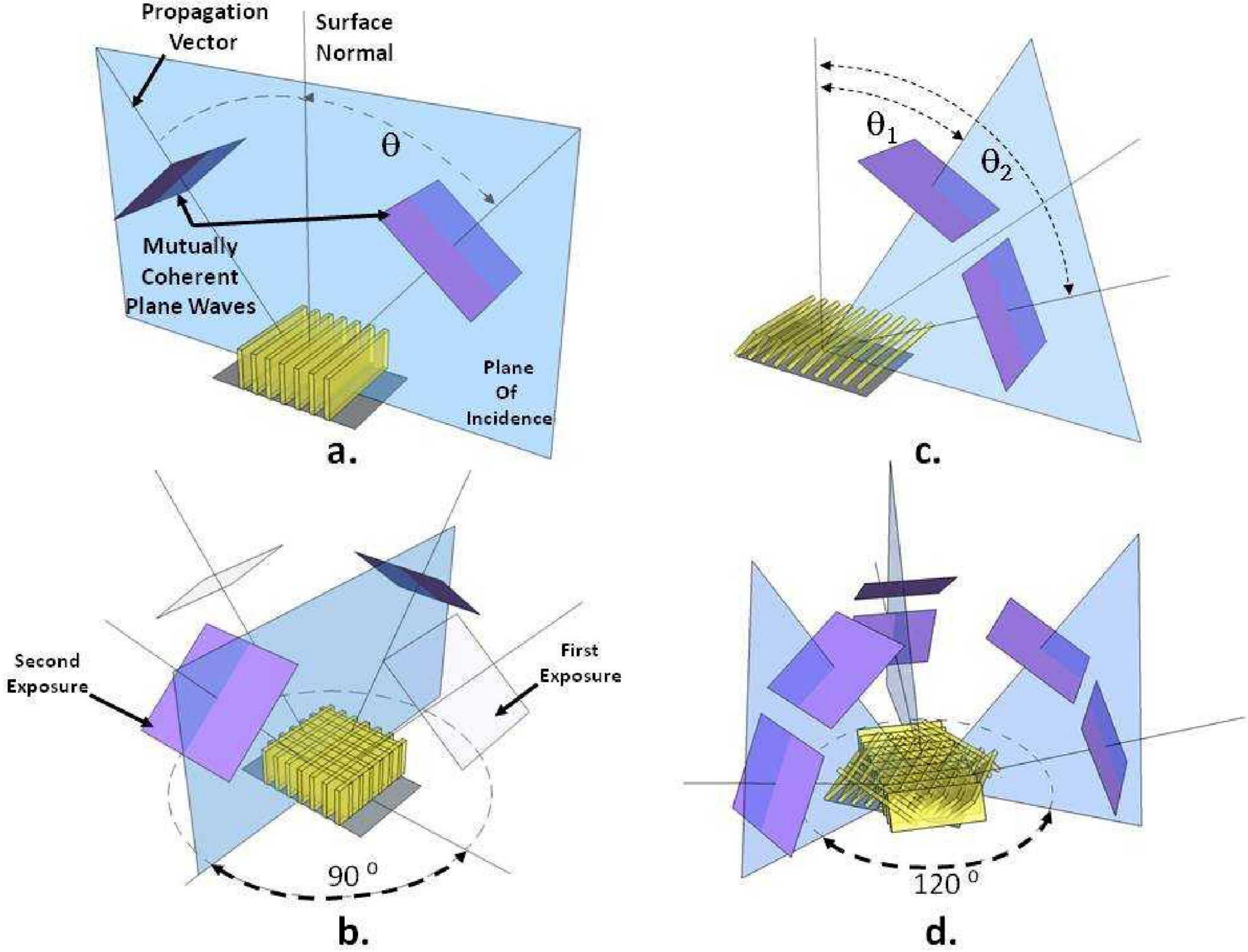
Interferometric Lithography

1-D Lines

Tilted 1-D Lines

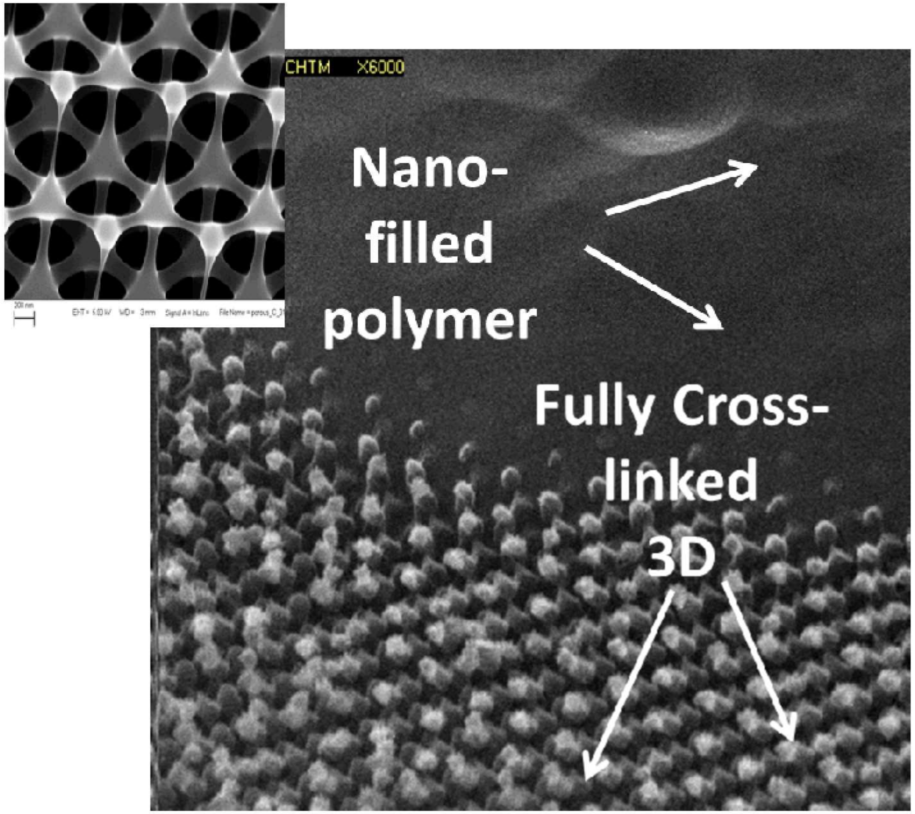
2-D Crystal

3-D Crystal



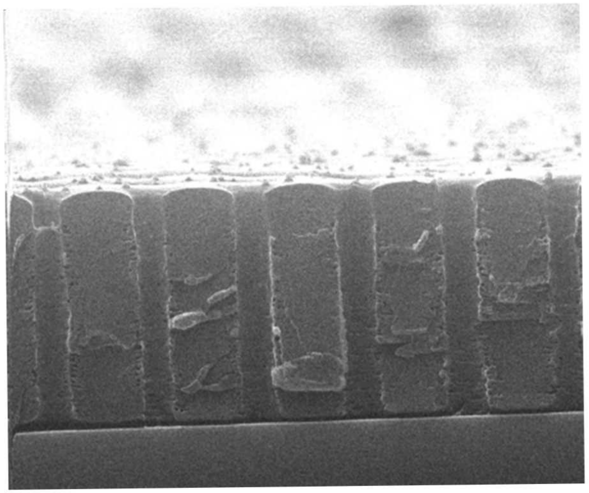
Burckel et al, *JVST B*, **28**, C6P14 (2010).

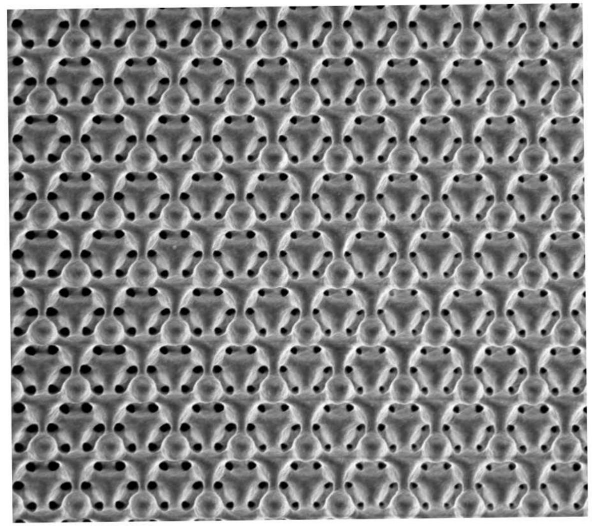
Reinforced carbon-carbon using interference lithography

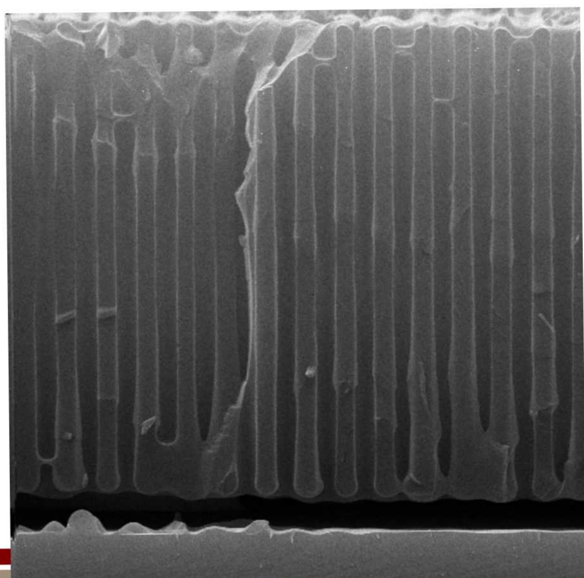


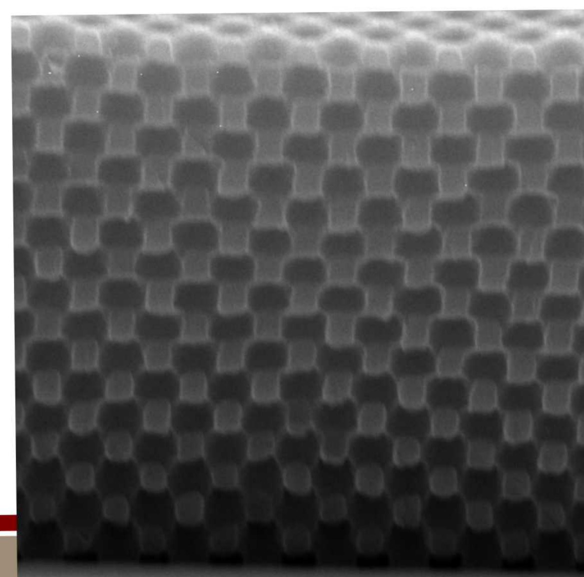
- Using a 3D carbon matrix formed using interference lithography provides a reinforcement structure that can be back-filled.
- Reinforces carbon like re-bar in concrete for strength to mitigate torsional stress

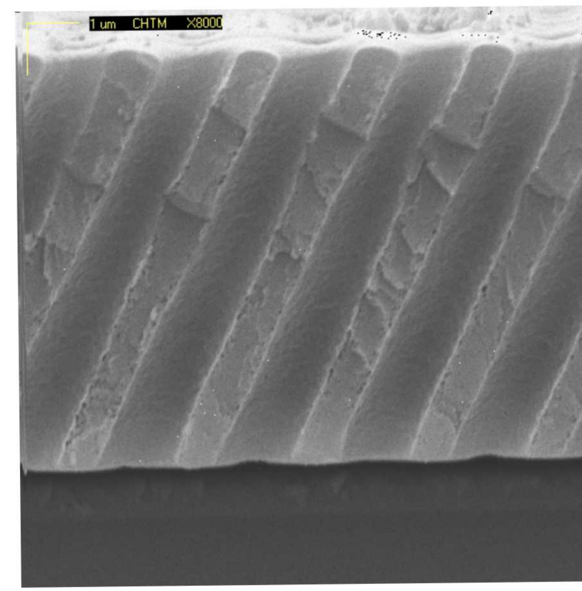
Sub-Micron 3D Resist Patterns Via Interferometric Lithography





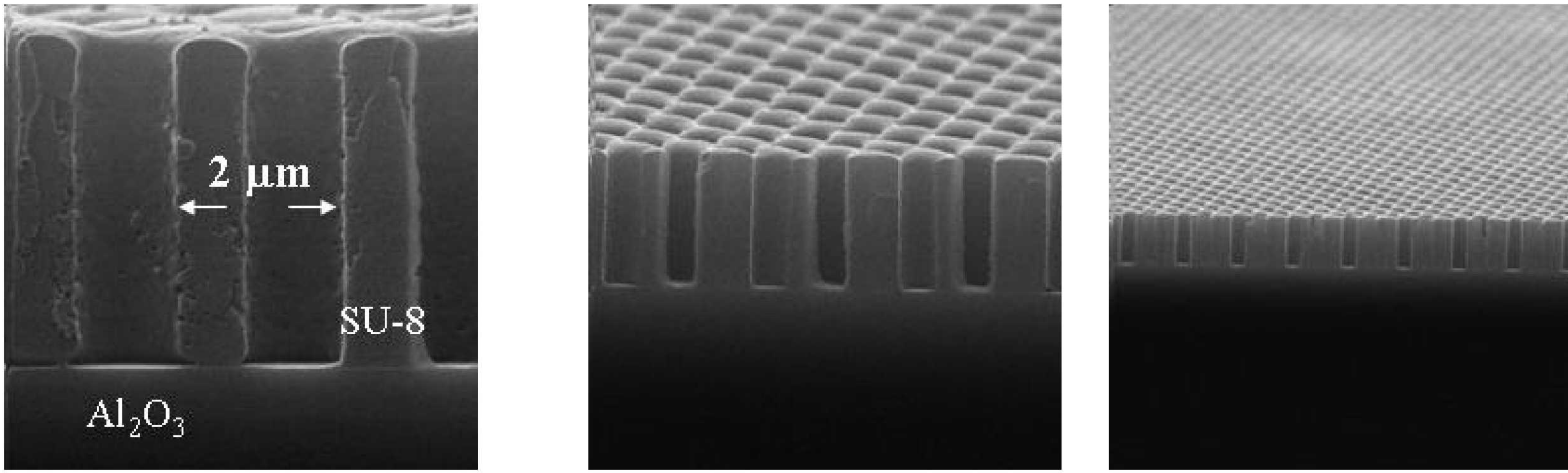




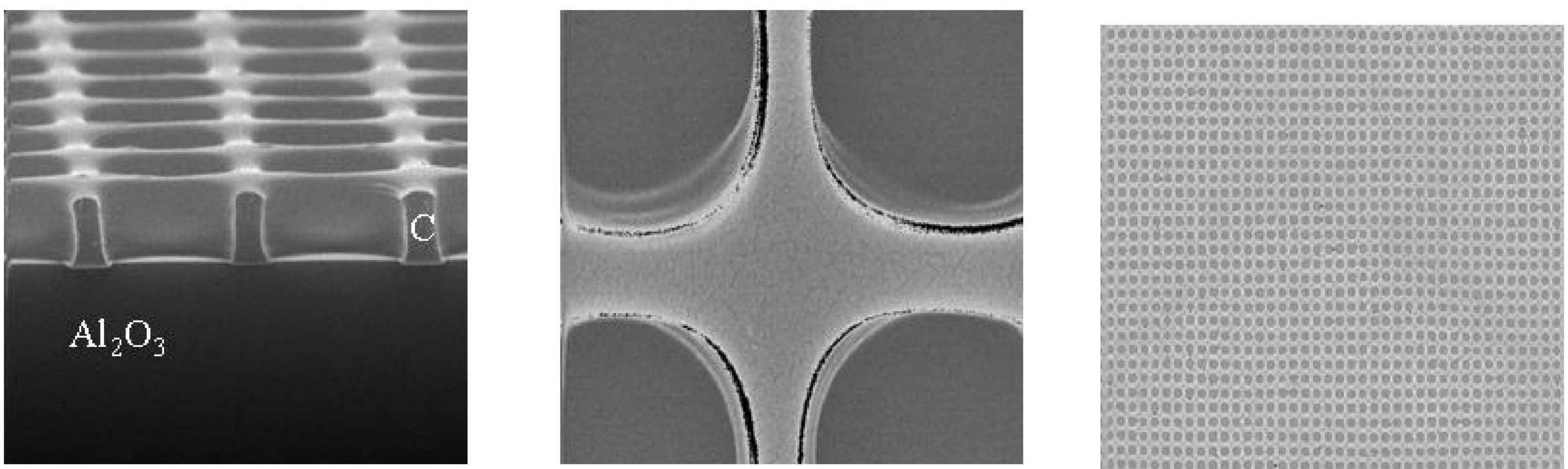


Conversion of 2-D Resist Structure to 2-D Carbon Structure

Resist



Carbon



Conversion of 3-D Resist Structure to 3-D Carbon Structure

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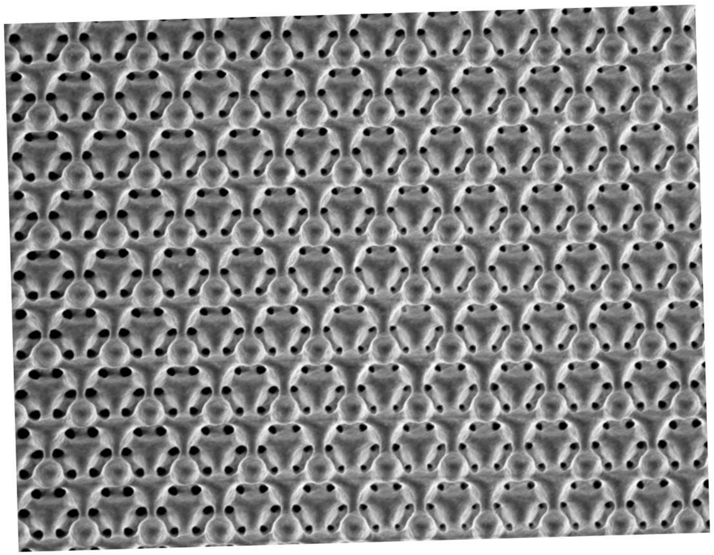
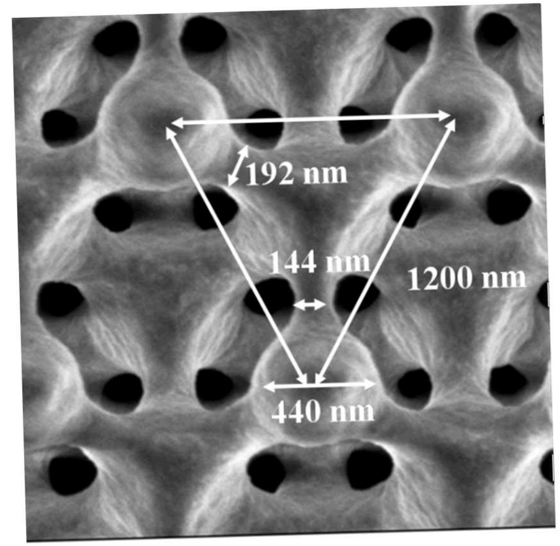
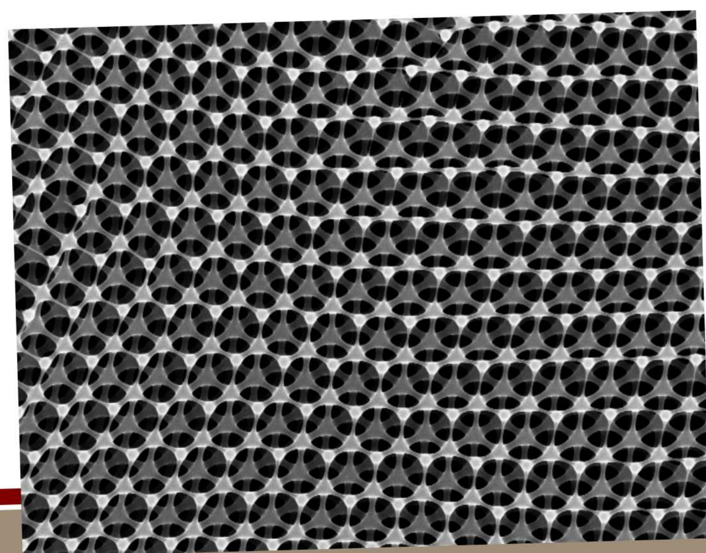
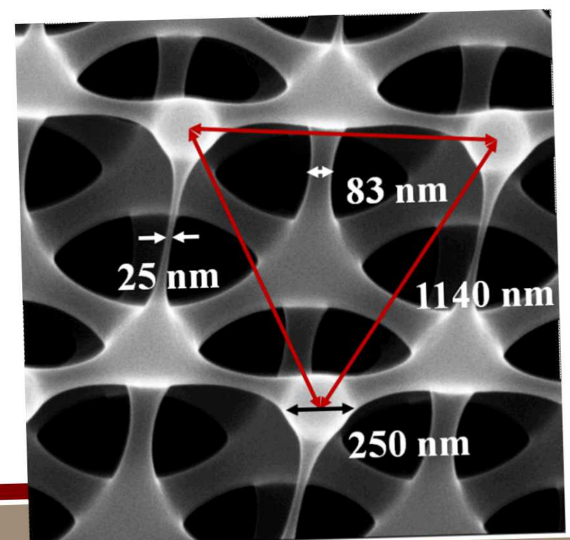
Resist





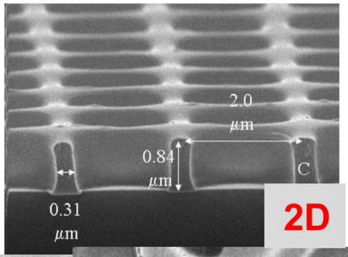
Carbon

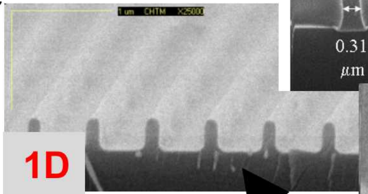


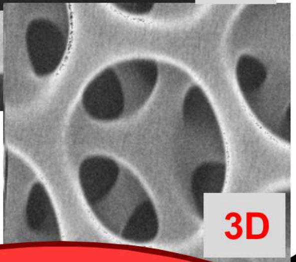


Interferometrically Patterned Carbon

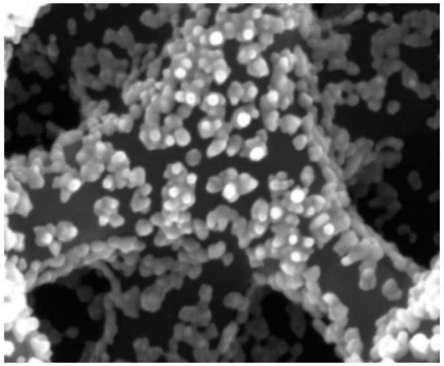
Carbon Photonics





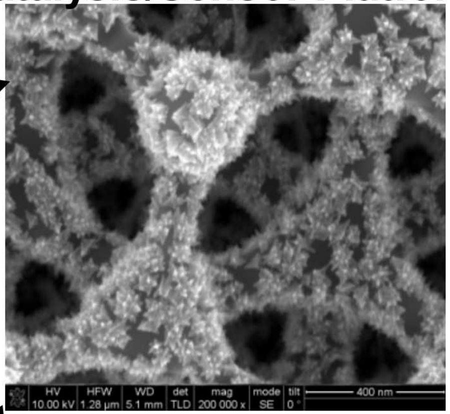


Ultra-Capacitor/Energy Storage

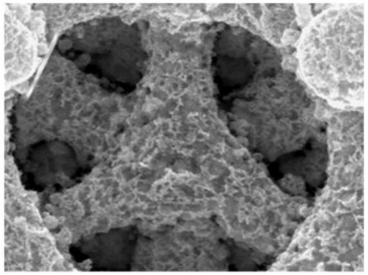


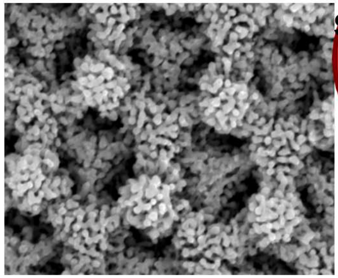
Structured Thermal Emitters

High Surface Area Catalysis/Sensor Platform



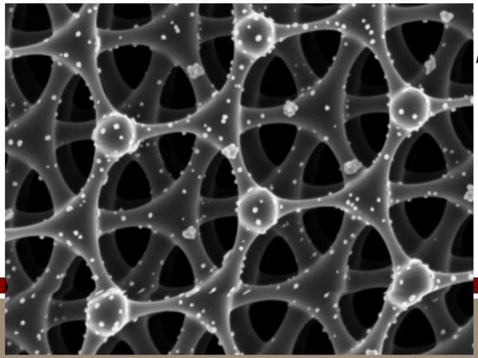
Hierarchical Porosity

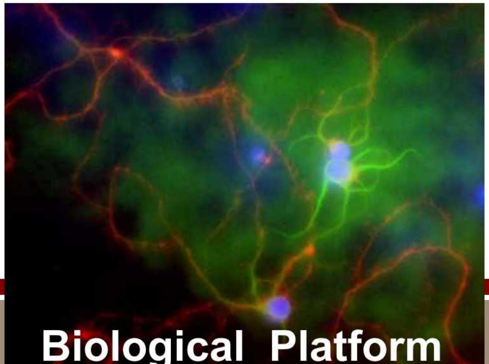




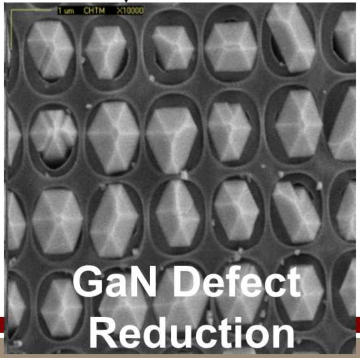
Convert 1D, 2D and 3D sub-micron photoresist patterns created with interferometric lithography into pyrolytic carbon

Fuel Cell Electrode

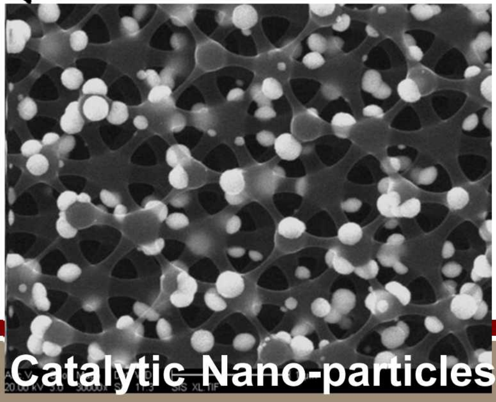




Biological Platform



GaN Defect Reduction

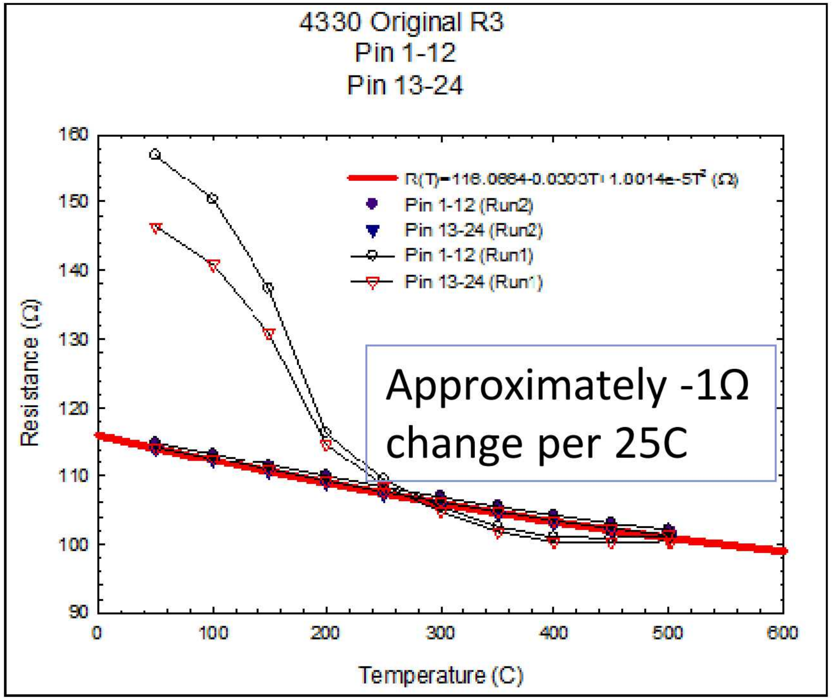


Catalytic Nano-particles

Thermal Coefficient of Resistance

Sandia National Laboratories

- 24-pin HTCC DIP exposed to ambient (no lid)
- Part cycled from RT to 500C in tube furnace with N_2 ambient
- Resistance was initially high, but dropped after cycling
- Non-linear temperature dependence over large temperature range
- Comparable to resistance obtained by hermetic packaging



$$R_1(T) = 116 \cdot (1 - 3.39 \times 10^{-4} \cdot T + 1.55 \times 10^{-7} \cdot T^2)\ [\Omega] \qquad T \text{ in } [^{\circ}C]$$

Sample	Temperature Range	α_o [1/°C]	2b [1/°C]^2
PPR – Cody	RT to 250C	-3.73×10^{-4}	Linear
PPR – Kent1	RT to 500C	-3.39×10^{-4}	1.55×10^{-7}
PPR – Kent2	RT to 500C	-3.53×10^{-4}	1.57×10^{-7}
Glassy Carbon – Strojnik (2006)	RT to 800C	-4.14×10^{-4}	Linear

Data referenced to T = 0 °C

Material Development

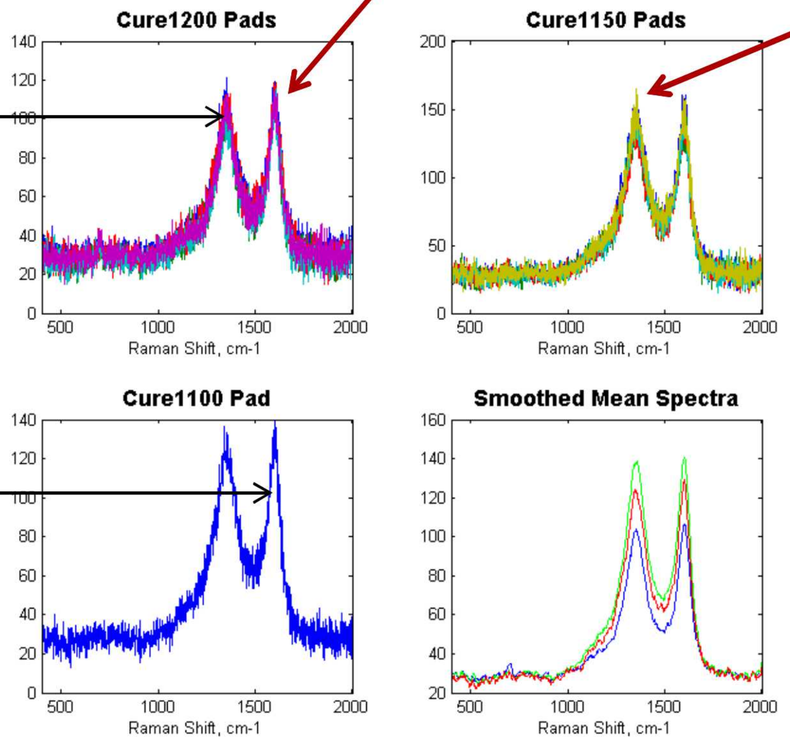
Comparing Raman results. HOPG ~1582 cm-1, Diamond ~ 1332 cm-1

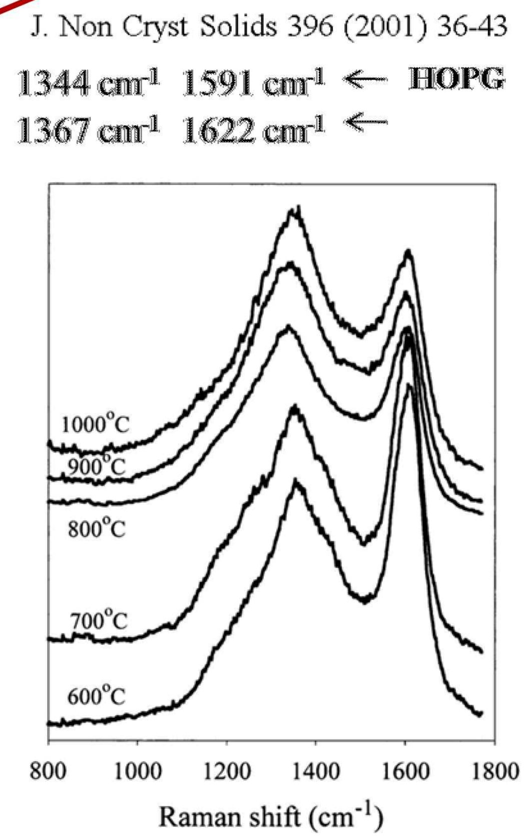
~1360 cm-1

D

~1582 cm-1

G





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)