Precursor-Derived Nanostructured SiC-Based Materials for MHD Electrode Applications

Program Manager: Dr. Jason Hissam

YiHsun Yang*, Fumio S. Ohuchi (PI)*, Amir H. Tavakoli**, and Rajendra K. Bordia(Co-PI)**

Department of Materials Science and Engineering

*University of Washington
Box 352120, Seattle, WA 98195

** Clemson University
Clemson, SC 29634

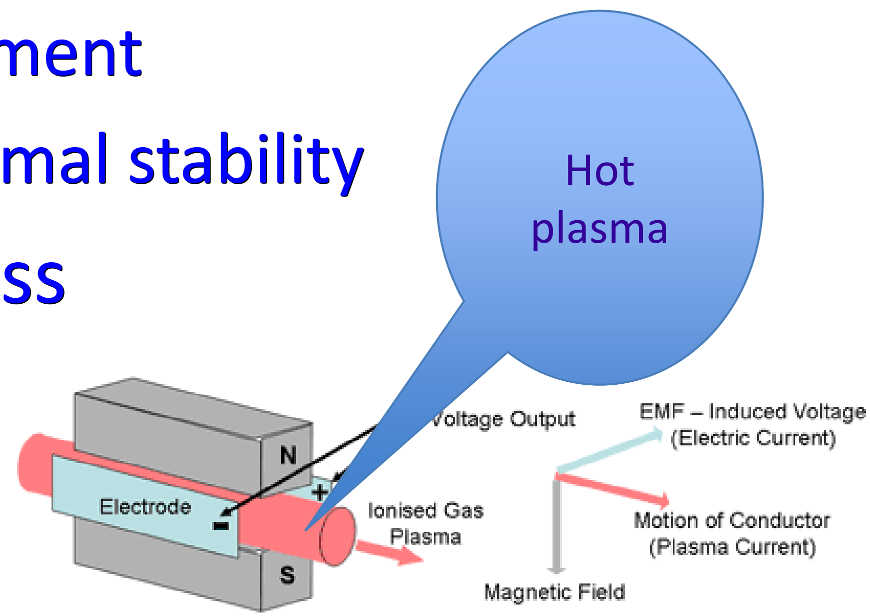
Grant No. DE-FE0023142
April 21, 2016

Technology advancements may bring new opportunities for legacy projects

1974

SiC ZrB$_2$+SiC

- Withstand MHD environments:
  - Oxidation resistivity at high temperature
  - ion bombardment
  - plasma impingement
  - Mechanical thermal stability
- Conformal process
- Low resistivity



Magnetohydrodynamic Power Generation (Principle)

Reference: R-1656-ARPA Dec 1974 report by George Rudins)

Long term goal

To develop a novel class of SiC based ceramic composite materials with tailored compositions for channel applications in MHD generators.

Today's Focus

Controlling and understanding the effect of the nature of the excess carbon and boron additive on the structural and electrical properties.

- Role of excess carbon and boron
  - ✓ Polymer based synthesis
  - ✓ Structural information
  - ✓ Electrical resistivity
  - ✓ Work function from thermionic emission

Project Team Tasks

TASK 1: PROCESSING AND STABILITY OF NANOSTRUCTURED SI-C-X CERAMICS

Sub-Task 1.1: Effect of stoichiometry and temperature on the nanostructure

Sub-Task 1.2: Effect of temperature and stress on the stability of the nanostructure

TASK 2: MECHANICAL AND THERMAL PROPERTIES OF NANOSTRUCTURED SI-C-X CERAMICS

Sub-Task 2.1: Modulus, strength toughness, and thermal diffusivity

Sub-Task 2.2: Compressive creep

Lead: Prof. R. Bordia

TASK 3: ELECTRICAL PROPERTIES OF NANOSTRUCTURED SI-C-X CERAMICS

Sub-Task 3.1: Effect of C/Si ratio on room and elevated temperature electrical conductivity

Sub-Task 3.2: Combinatorial selection of X and effect of X on room and elevated temperature electrical conductivity

TASK 4: SURFACE ENGINEERING OF NANOSTRUCTURED SI-C-X CERAMICS

Sub-Task 4.1: Surface modification to enhance thermionic emissions

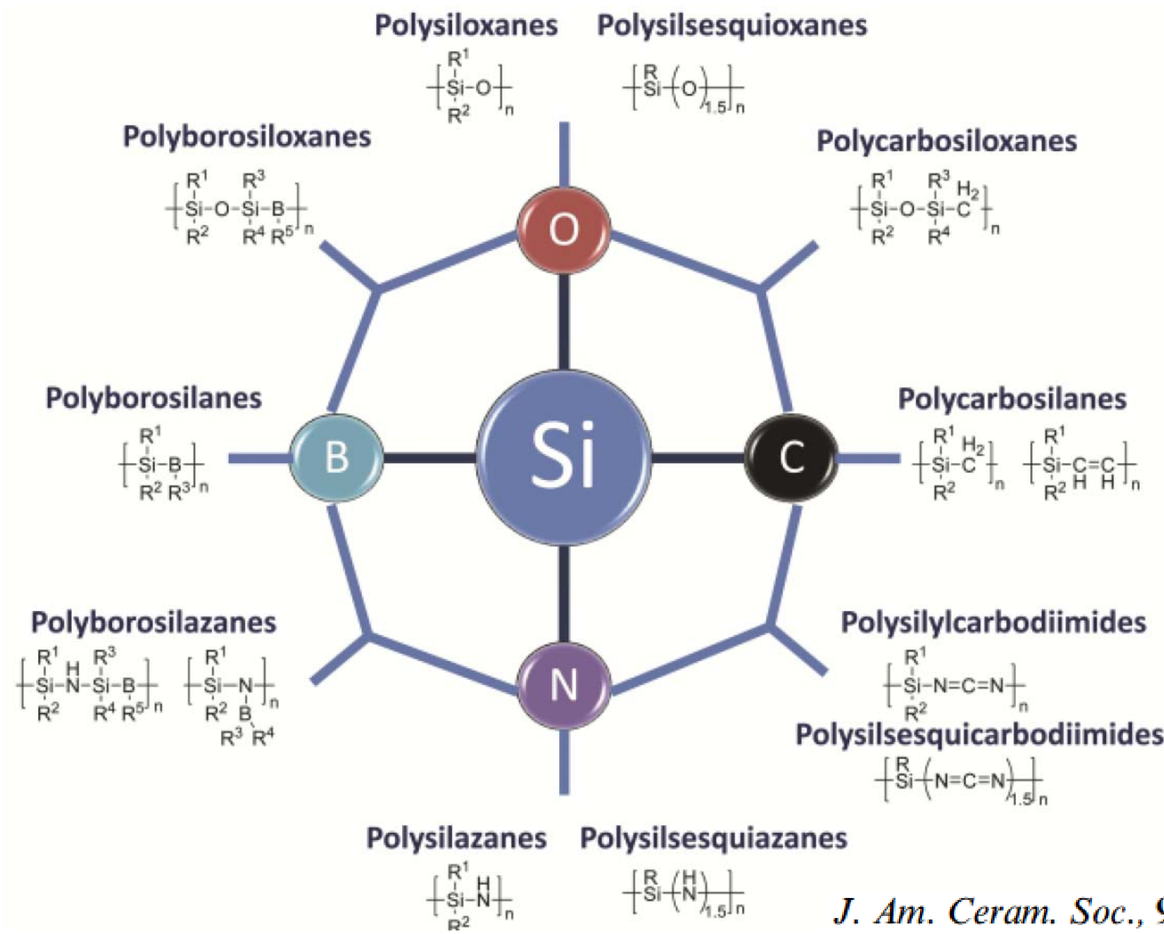
Sub-Task 4.2: Changes of surface/sub-surface structure and chemistry by high density plasma irradiation.

Lead: Prof. F. Ohuchi

Sub-Task 4.3: Simulation of plasma interactions

Diversity of silicon based precursors

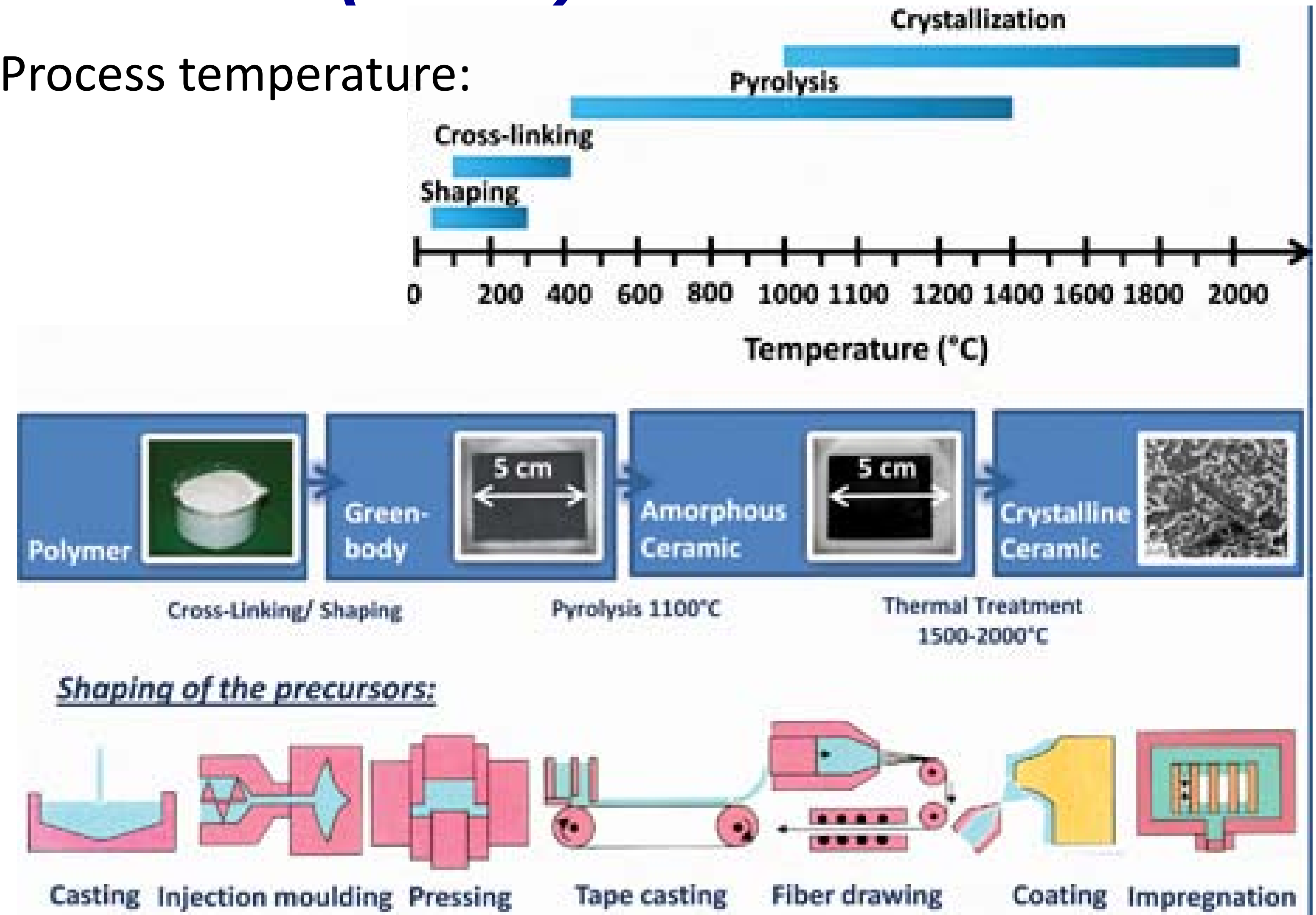
- Liquid form polymer can be mixed homogeneously
- Silicon / carbide ratio could be adjusted through precursors
- Boron, nitrogen and oxygen can be easily incorporated
- Relatively low process temperature



J. Am. Ceram. Soc., **93** [7] 1805–1837 (2010)

Easy of Process for Polymer Derived Ceramics (PDCs)

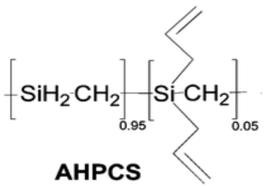
Process temperature:



P. Colombo, G. Mera, R. Riedel, and G. D. Sorarù, J. Am. Ceram. Soc. **93**, 1805 (2010)

Selection of polymer and processing

- ***Precursor: SiC forming Allylhydridopolycarbosilane (Starfire® SMP-10)***
- **Two processes has been developed**



AHPCS

SiC forming polymer (polycarbosilane SMP-10)

Carbon additive (divinylbenzene)

Sintering aid additive (decaborane)

Thermal cross-linking T = 400 °C

Cured polymer

grinding

Polymer power

Carbon additive:
Improve electric conductivity

Boron additive:
densification

Polymer infiltration pyrolysis

Hot press

Pyrolysis T = 900 °C

SiC/C composite

milling

Ultrafine powder

Hot pressing T = 2130 °C

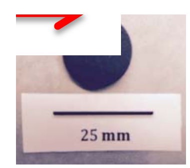
SiC/C monolith

Cold press

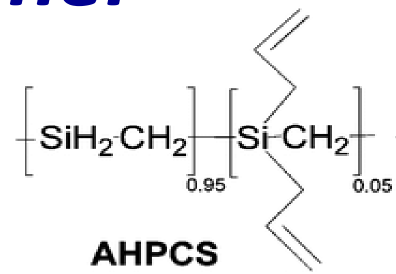
Pressed pellet

Polymer infiltration Pyrolysis (PIP) T = 1700 °C

SiC/C monolith



Effects of different additives for polymer derived ceramics (PDCs)



AHPCS

Effect of dopants on the density of the hot-pressed samples:

Sample ID	Extra carbon		Boron		Bulk Density (g/cm^3)	Relative Density (%)
	nominal	measured	nominal	measured		
0B0C	0		0		1.76	54.8
0B1C	1		0		2.8	87.2
1B2.9C	0	1.7(2.9)*	1	0.4 (0.8)	3.05 ± 0.09	95.9 ± 2.8*
1B3.9C	1	2.2(3.9)	1	0.4 (0.8)	3.15 ± 0.03	99.4 ± 0.9*
1B9.5C	5	5.6(9.5)	1	0.4 (0.8)	2.93 ± 0.06	94.2 ± 1.9*

wt%, mol% in parenthesis. Error is two standard deviation of the mean

*Excess carbon from polymer precursor

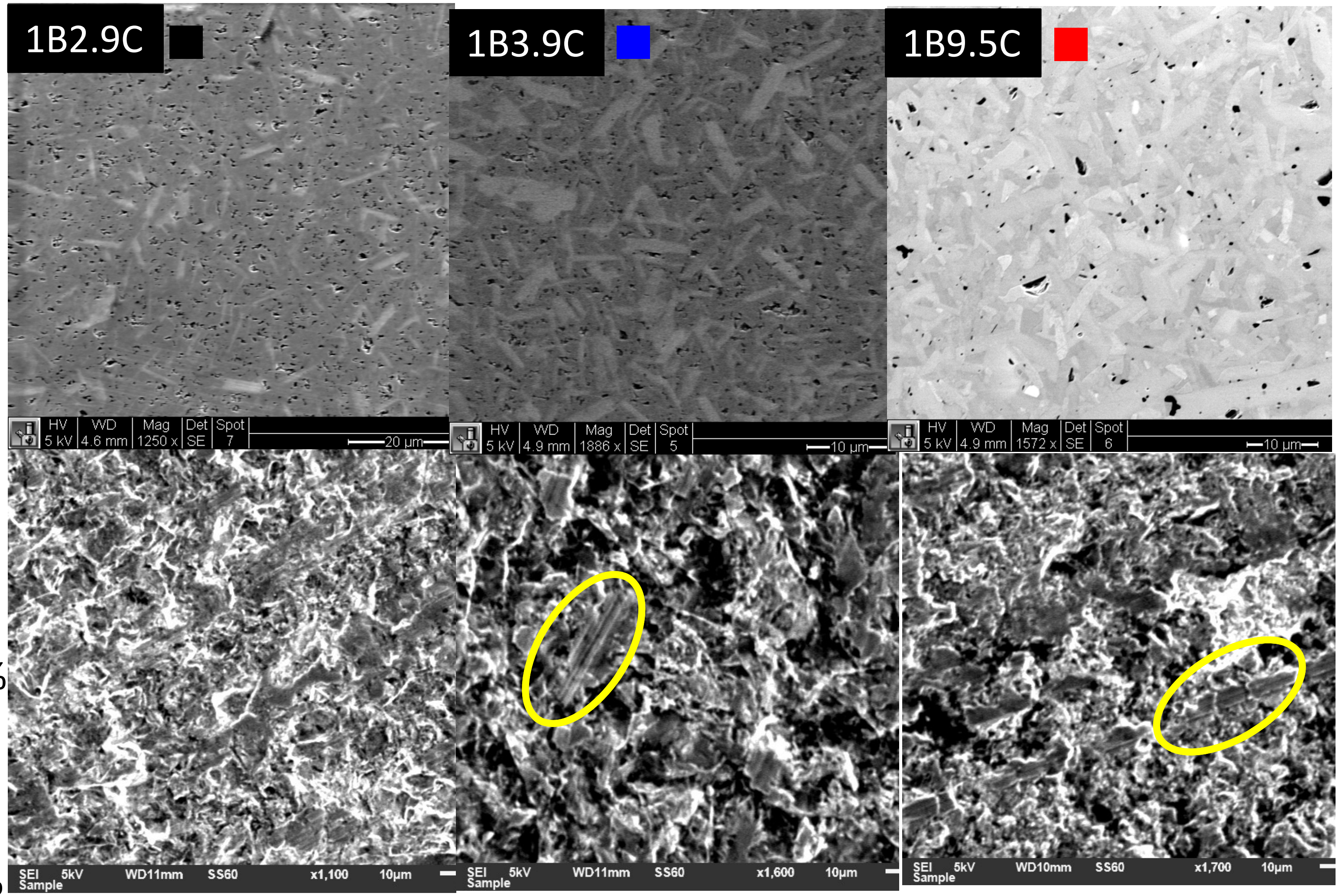
**Density is calculated based on the theoretical density of silicon carbide and graphite

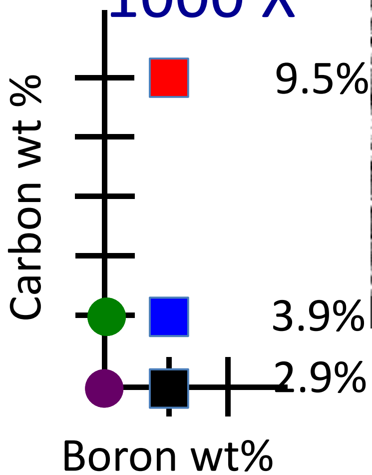
Two phases matrices and elongated grains

by Scanning Electron Microscopy (SEM)

Polished surface ~ 1500 X

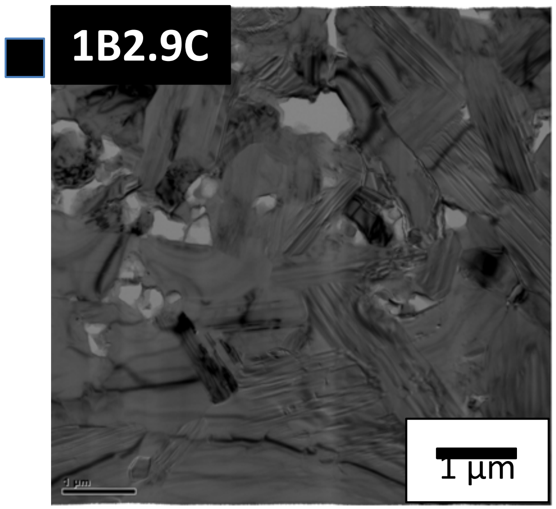
Fractured Surface ~1000 X

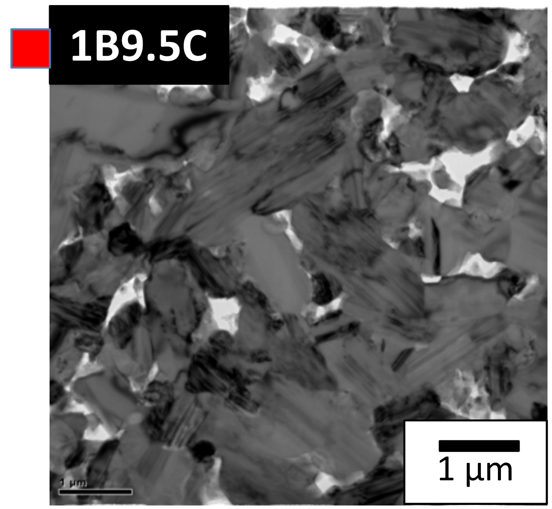


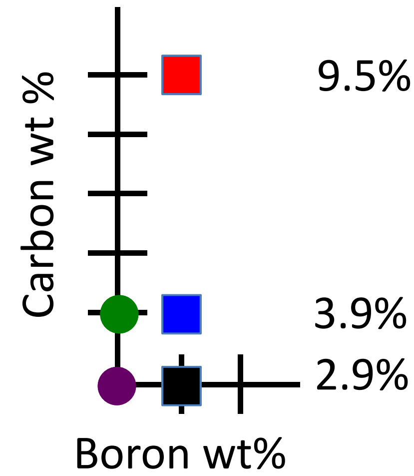


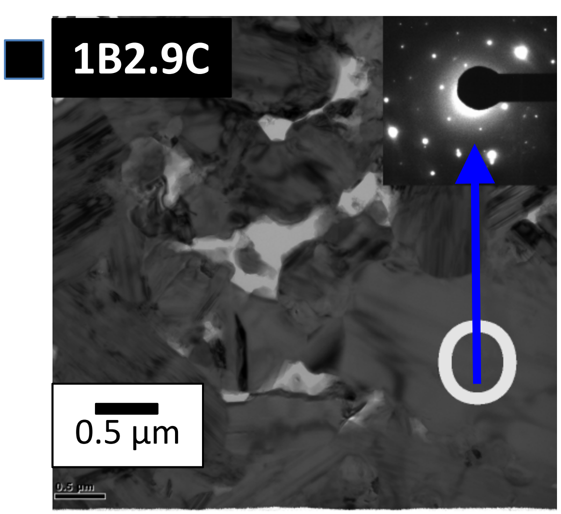
Grain morphology and local crystallinity

by Transmission electron microscopy (TEM)

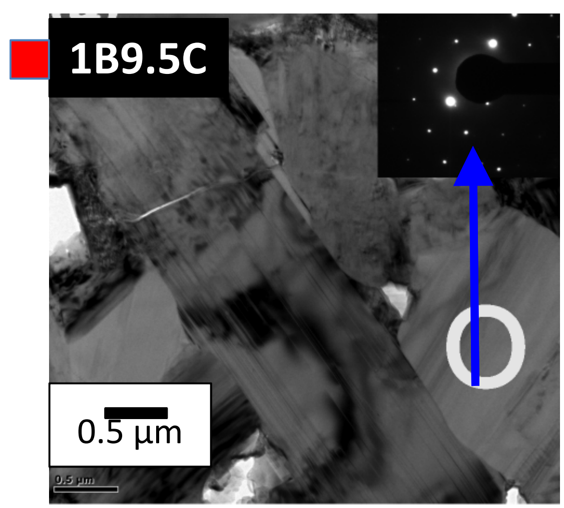




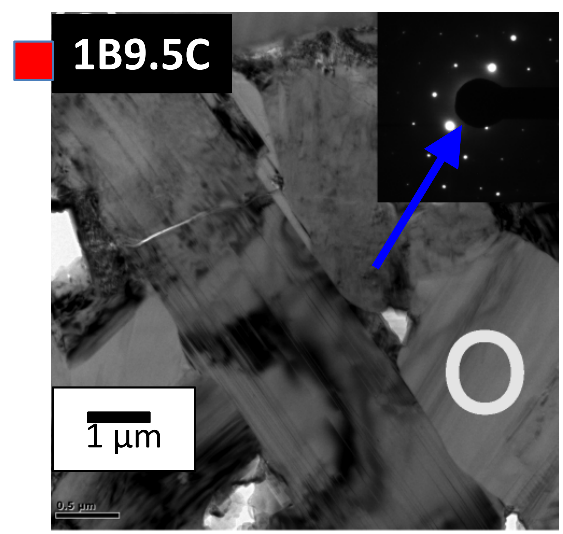




(fully crystalline)



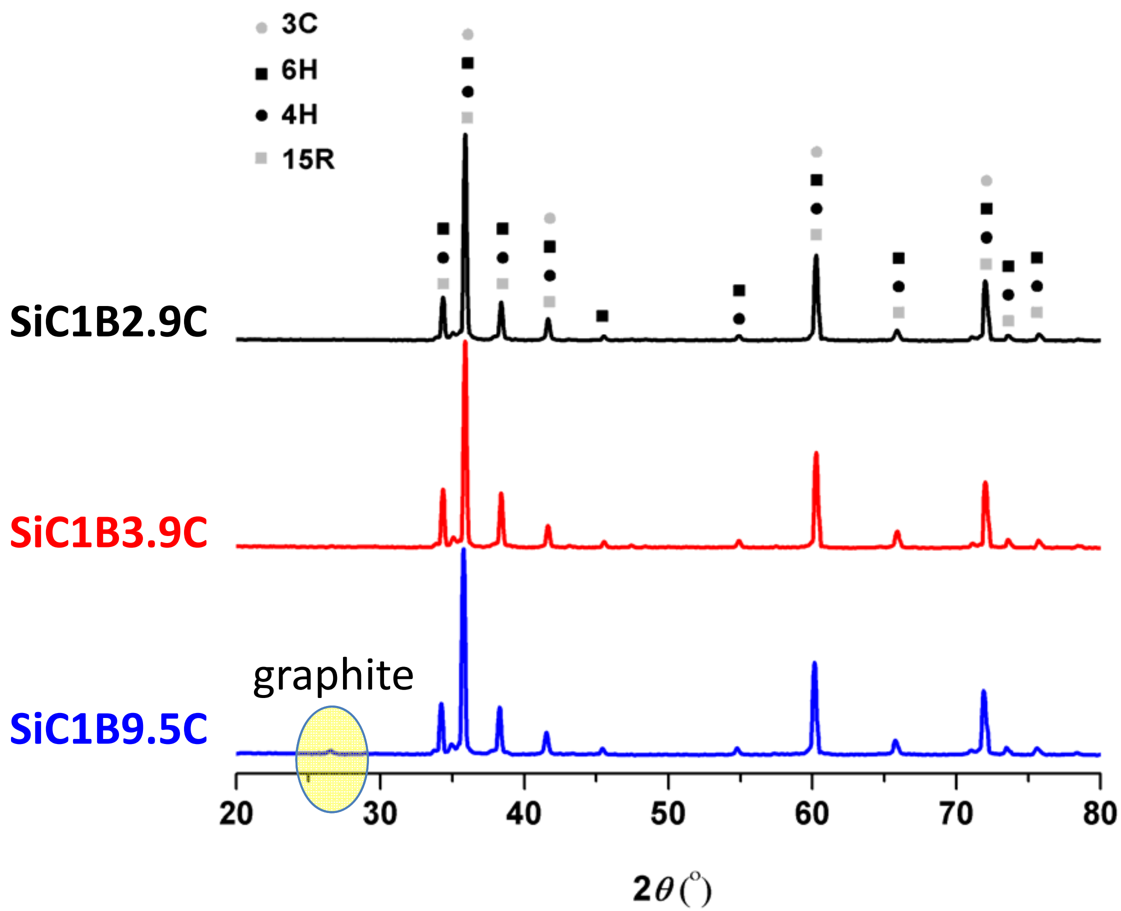
(Mostly crystalline)



(Minor amorphous regions)

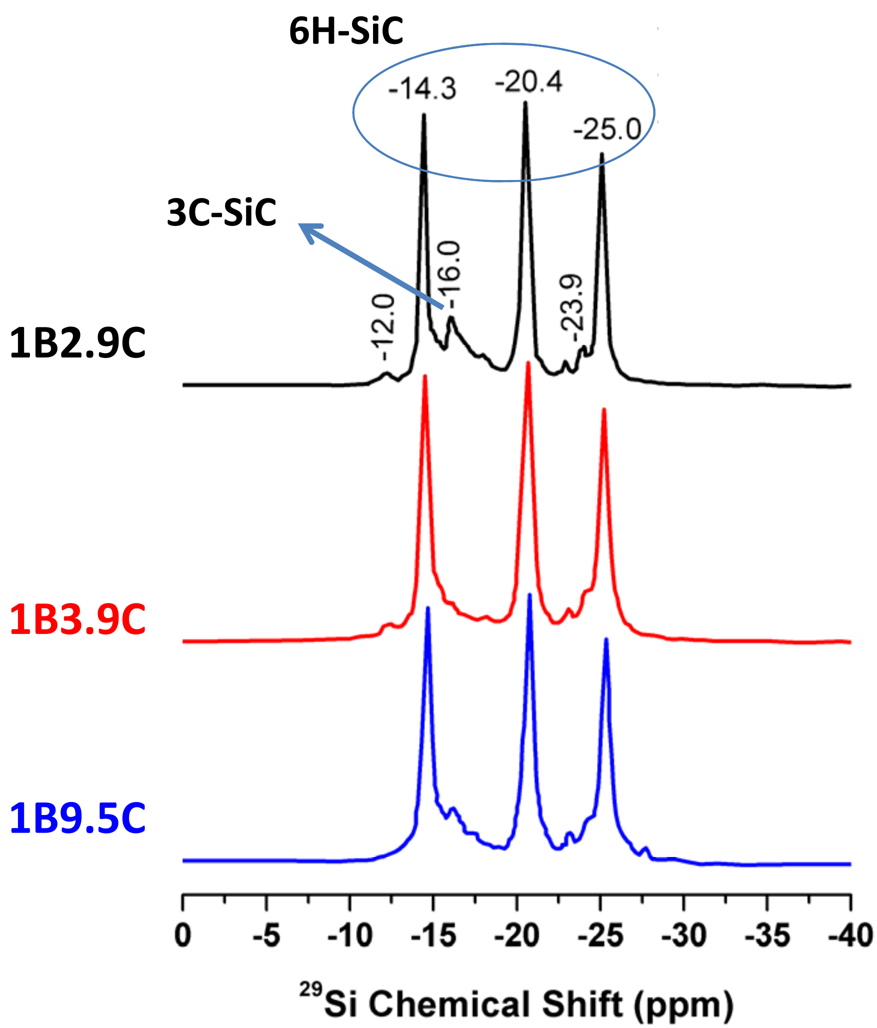
Bulk crystallinity –

X-Ray Diffraction



- ✓ **The XRD analysis confirms the existence of 6H-SiC but is not enough for the complete identification of SiC polytypes.**
- ✓ **Provides information for crystallized part; what if it is not fully crystallize?**

Structural analysis by nuclear magnetic resonance (NMR) spectroscopy



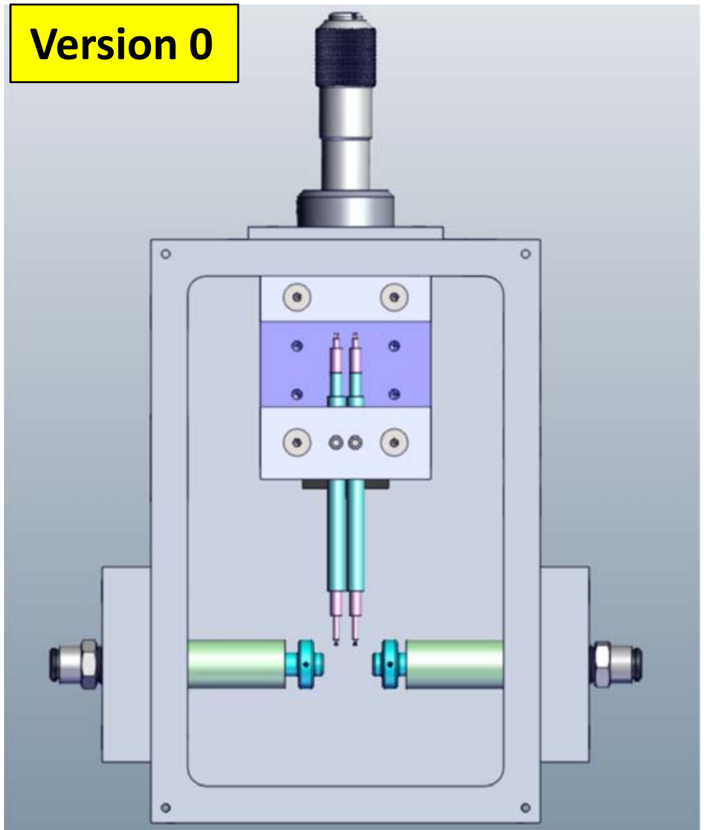
- ✓ Solid state NMR provides bulk information for the chemical environment of the interested element.
- ✓ Three characteristic chemical shift for 6H polytype.
- ✓ Minor 3C polytype was found in some samples.
- ✓ No silicon oxide peak.
- ✓ The NMR characterization confirms the dominance of 6H-SiC for the three samples.

How is the ceramic going to behave above 1000 °C ?

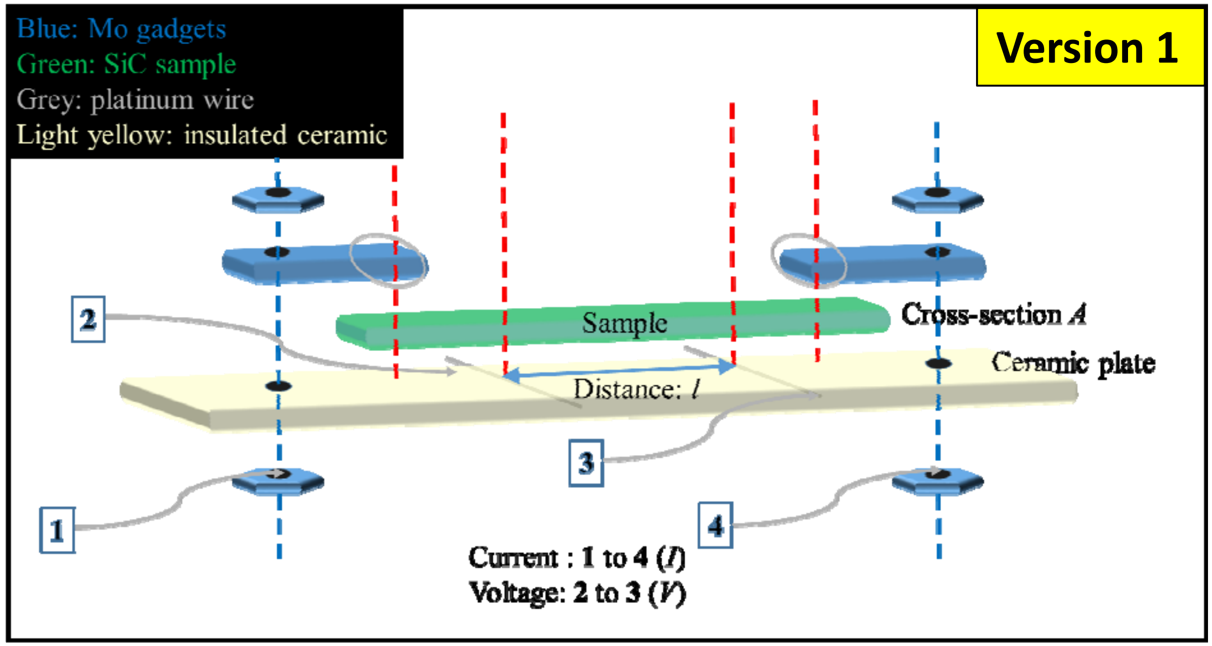
- We need to have the ability to measure the electrical conductivity / resistivity at elevated temperature.
- Standard commercial equipment does not lead us to over 700 °C
  - ZEN-3 Seebeck Coefficient / Electric Resistance Measuring System from ULVAC Technologies, Inc.

We make one on our own!!!

Development of an "in-situ" measurement technique of dc-conductivity



Ma, F. Ph.D. Thesis 2015



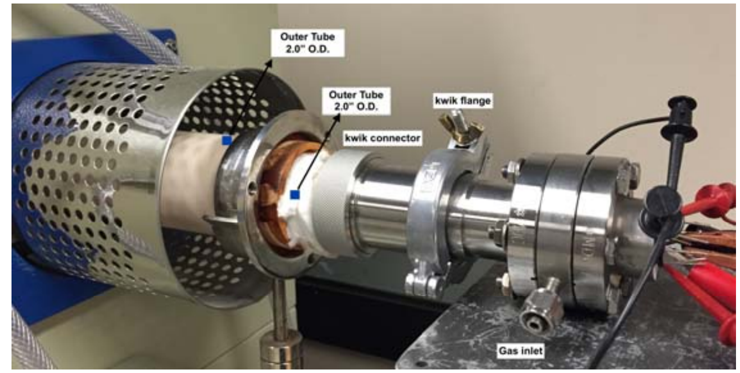
Operation condition:

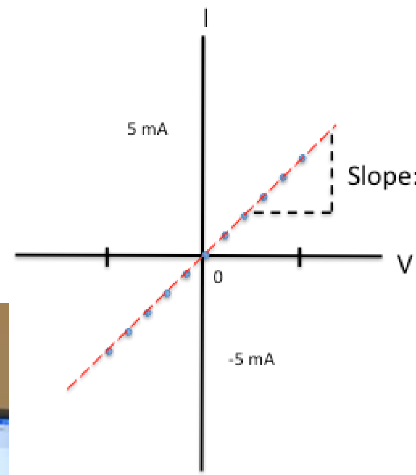
Version 0: Custom made box furnace, made with nichrome heating filament and aluminum cage with active water cooling. Capable up to 700 ^oC.

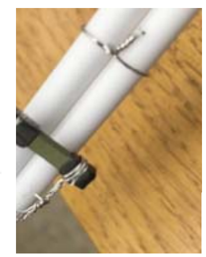
Version 1: Alumina plate, Moly screws and nuts, design for tube furnace. Capable up to 1000 ^oC.

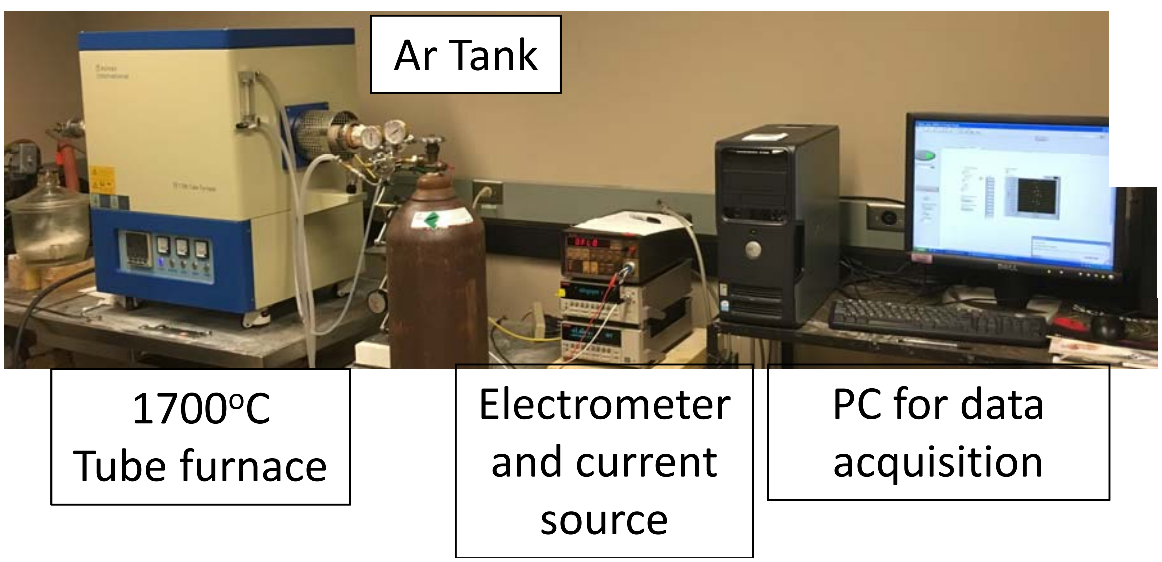
Development of an "in-situ" measurement technique of dc-conductivity

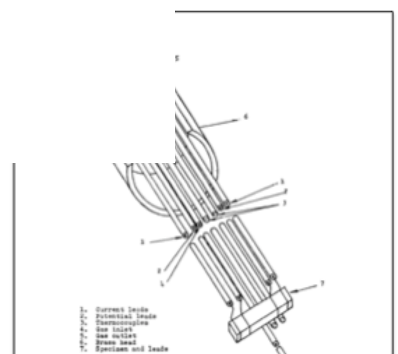
- Commercial 1700 C tube furnace
- Platinum lead, graphite contact and alumina support
- Pseudo-four-point probe (Kelvin probe) technique is applied.
- Control by LabVIEW





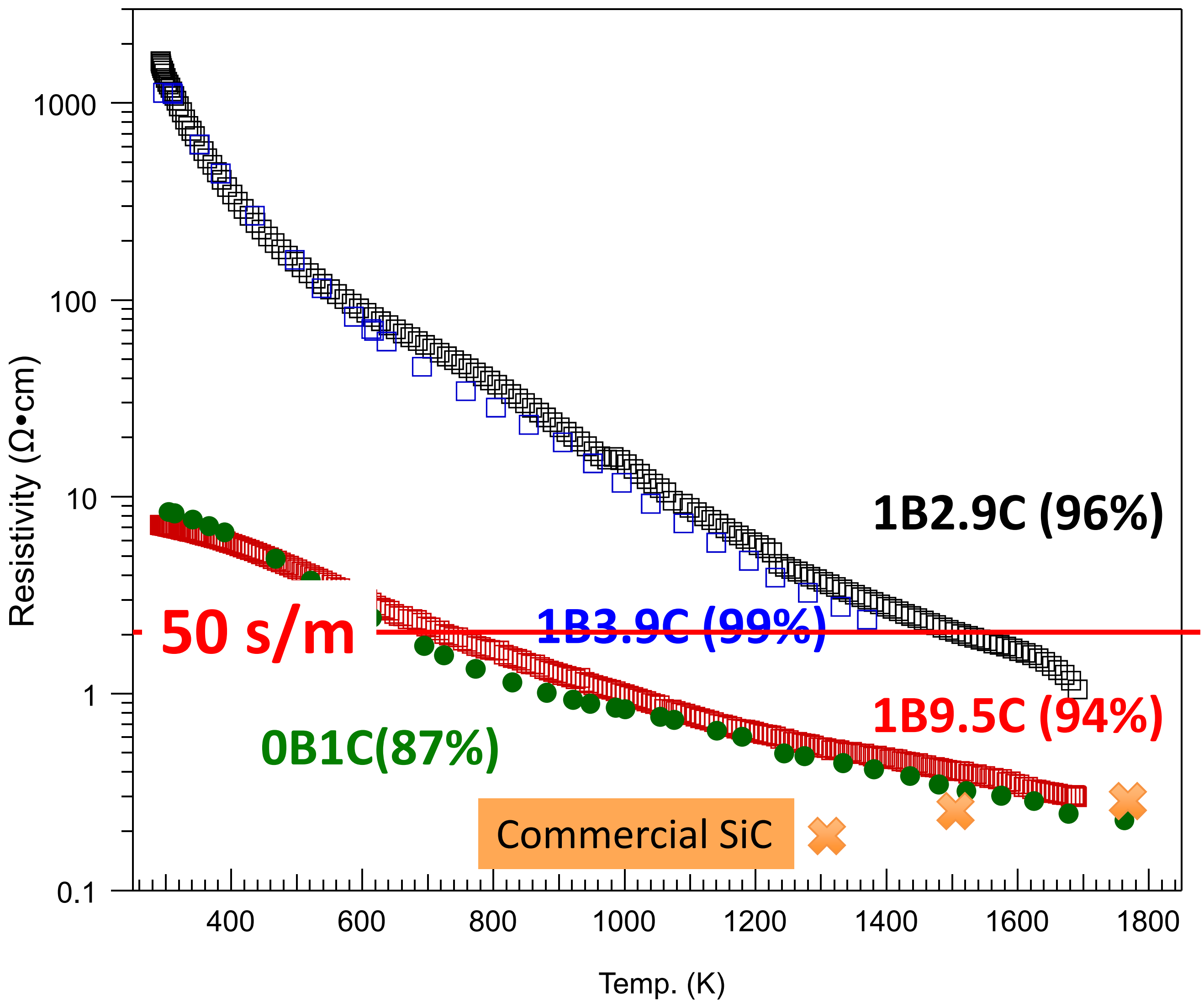






R. N. Blumenthal, J. Coburn, J. Baukus, and W. M. Hirthe, J. Phys. Chem. Solids **27**, 643 (1966).

Effect of boron and carbon additive on electrical resistivity

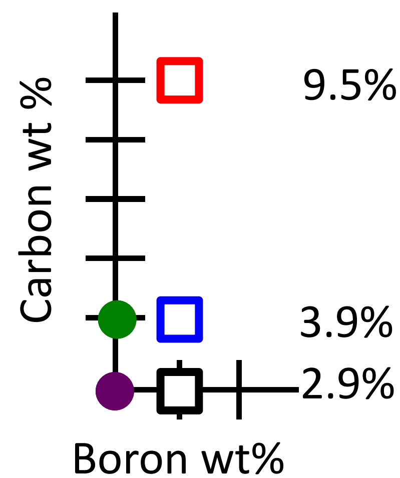


Fact:

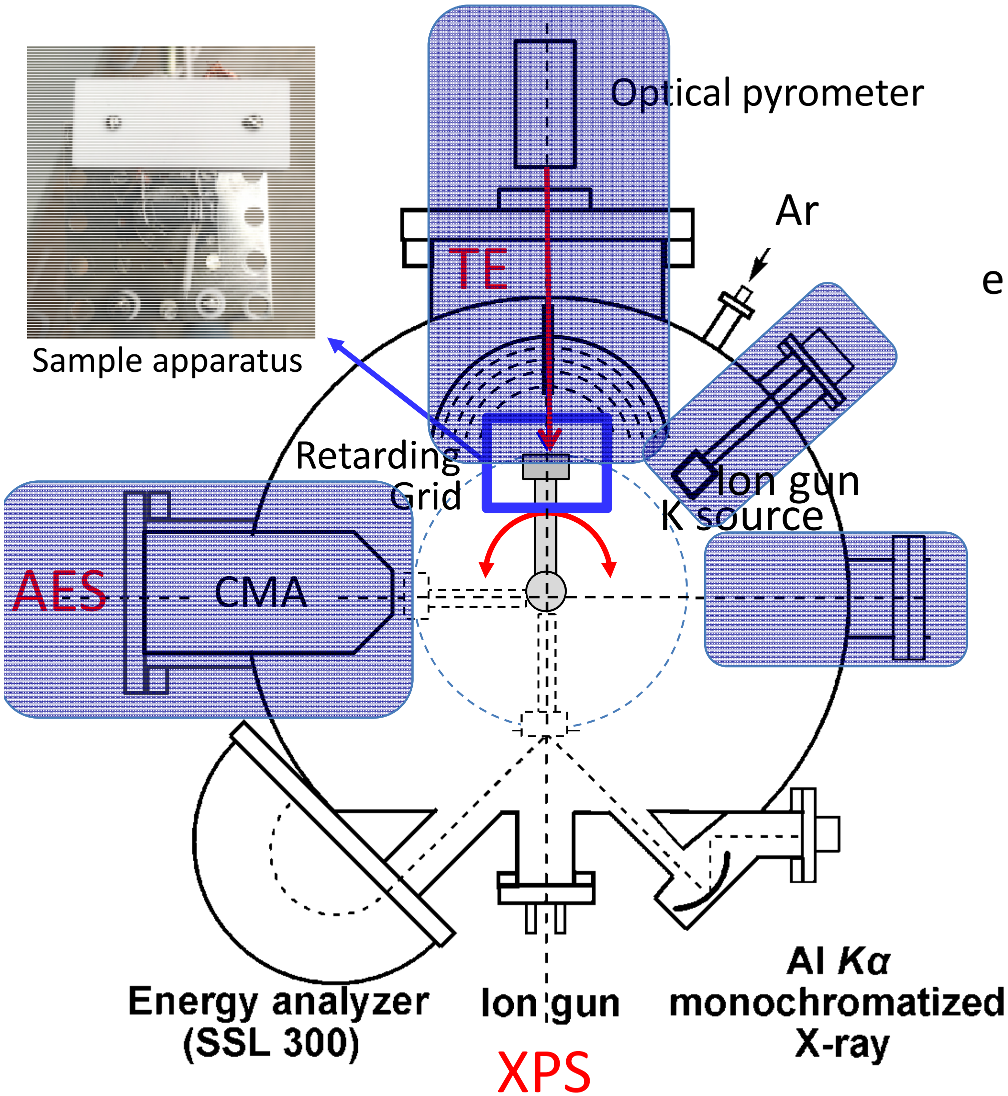
- ➢ Carbon additive lowers resistivity
- ➢ Boron additive helps densification

Finding

- ➢ Boron additive tends to increase resistivity
- ➢ unless huge amount of extra carbon to compensate



Integrated HV chamber for surface modification and analysis

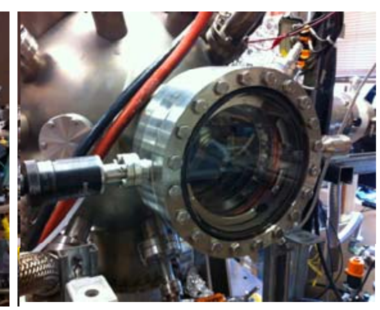


Integrated HV system:

- Retarding grid spectroscopy to measure thermionic emission (**TE**)
- X-ray photoelectron spectroscopy (**XPS**)
- Auger electron spectroscopy (**AES**)
- K deposition for work function engineering
- R-type TC and optical pyrometer for temperature measurement
- Ion gun for surface cleaning

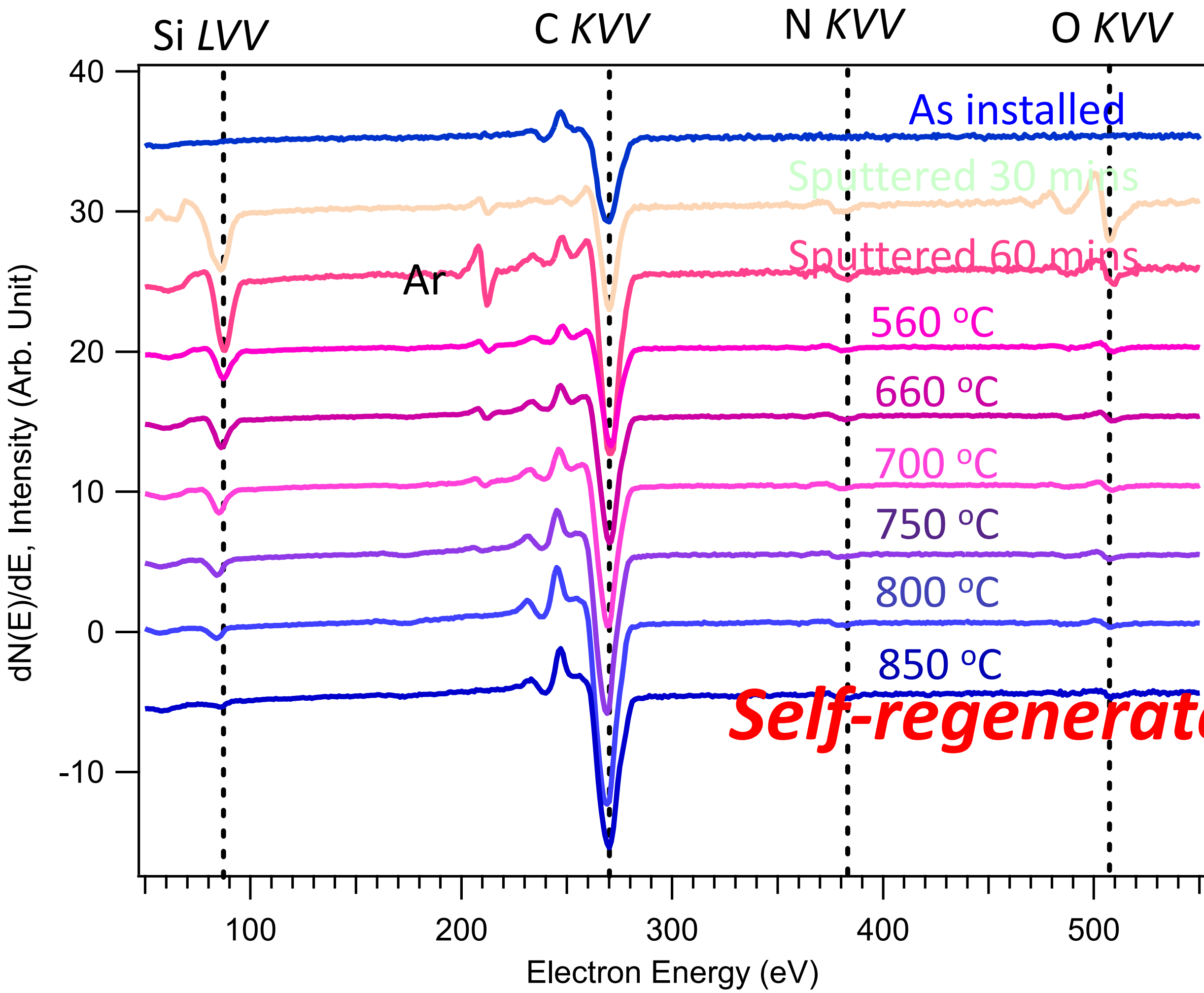
Capable of measuring:

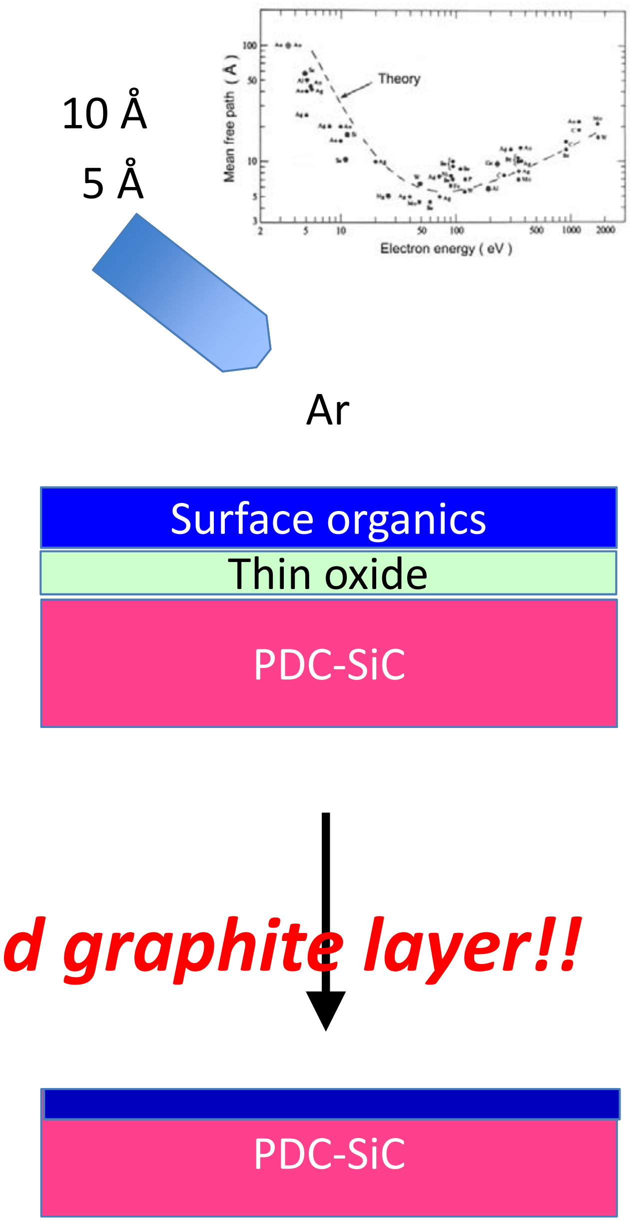
- Surface composition at elevated temp.
- Total current and kinetic energy distribution of thermionic emission.
- Work function



Surface self-regenerate under high temperature annealing

Auger electron spectroscopy for 1B9.5C





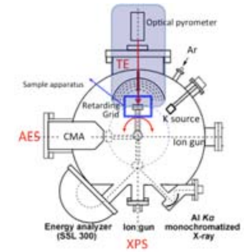
Self-regenerated graphite layer!!

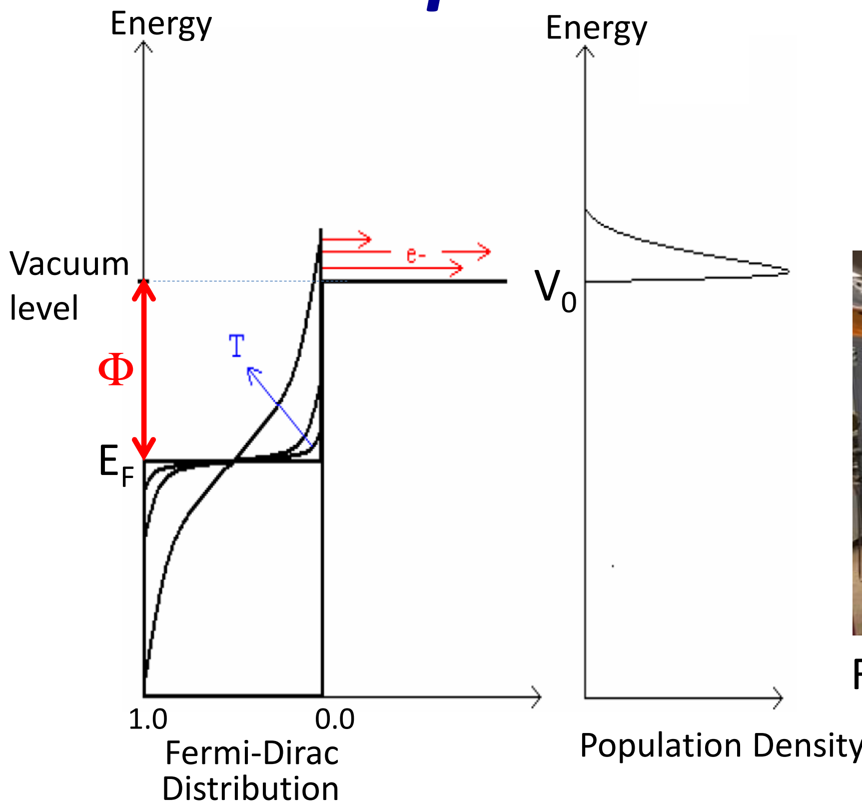
A common failure reason for MHD channel electrodes - Arcing

- Electric arcing or arc discharge: An electrical breakdown of gas.
  - It produces plasma discharge and often damage the surface.
- Thermionic emission: an electron emission due to thermal activation.
  - A physical process that the amount of emitted electron is determined by work function.

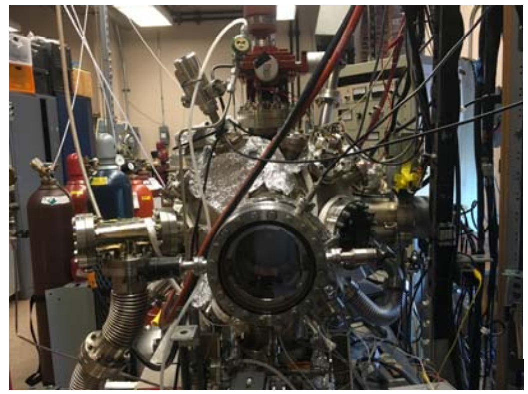
What is work function and how do we measure it experimentally?

Thermionic emission (TE) and Richardson-Dushman eq.



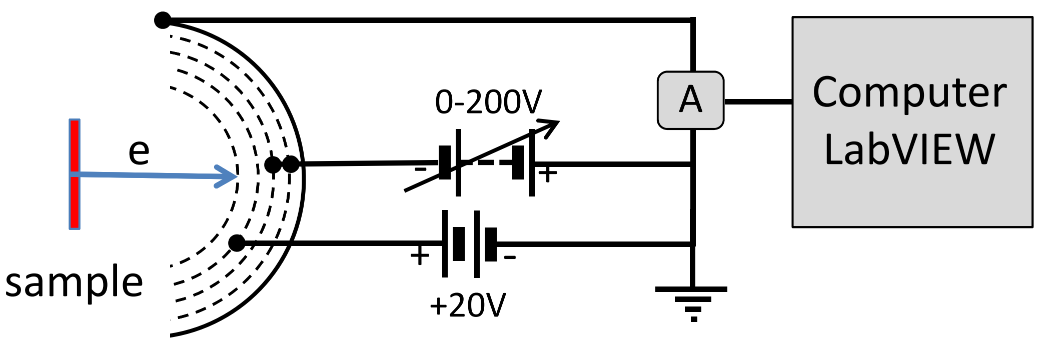


$$J = -q \int_{W>\mu+\phi} v_x f(k) \frac{d\mathbf{k}}{4\pi^3} = \frac{m k_B^2 q}{2\pi^2 \hbar^3} T^2 \exp\left\{\frac{-\phi}{k_B T}\right\}$$



Front view of electron grid

Workstation for data acquisition



Work function converges for all samples after annealing

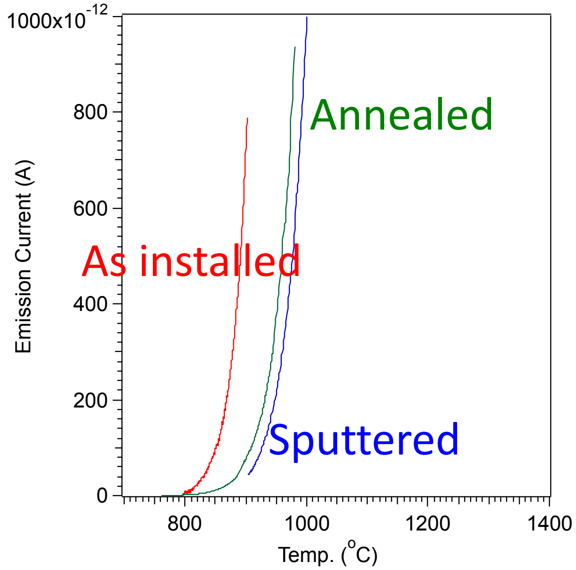
Work function:

4.39 eV

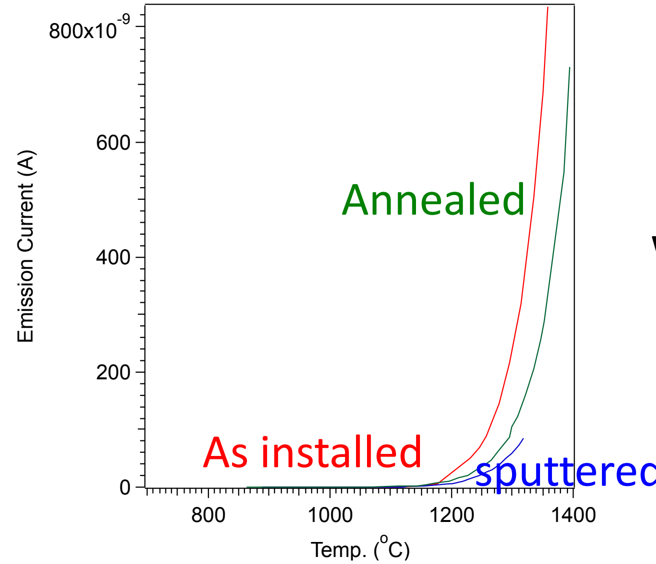
4.00 eV

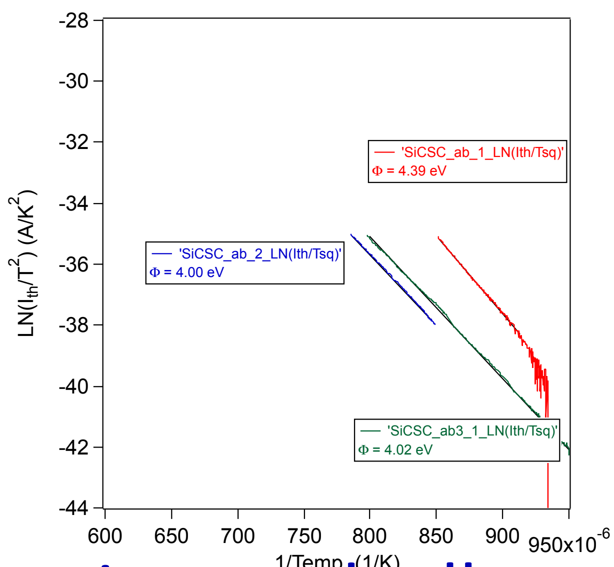
4.02 eV

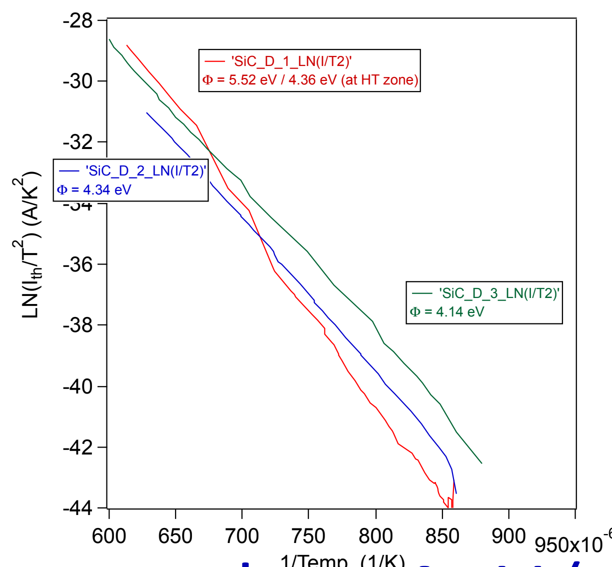
Single crystal SiC



SiC: 1B3.9C







Work function:

5.52 eV

4.34 eV

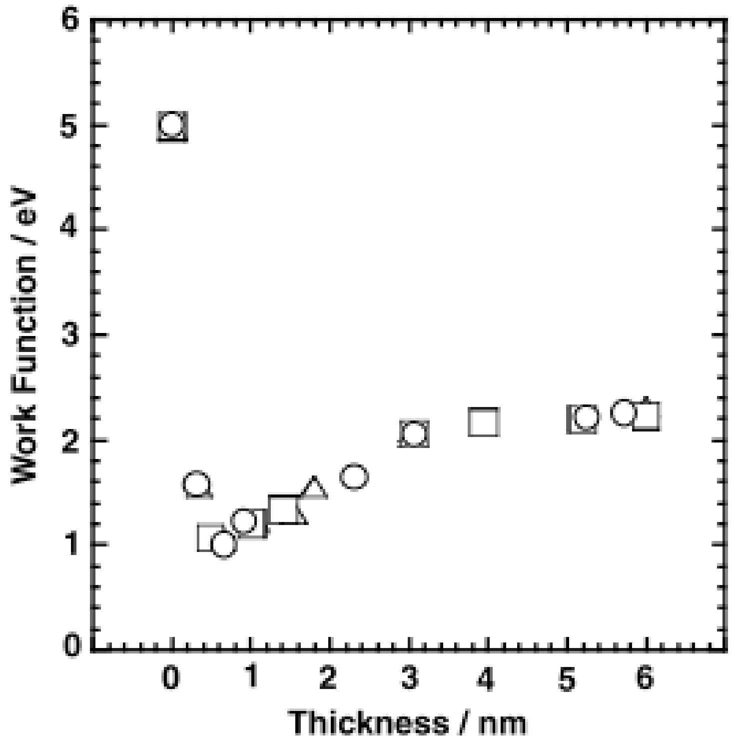
4.14 eV

Work function gradually converged to ~4 eV (graphite)

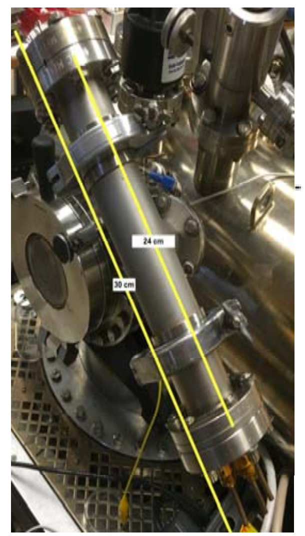
Future plan for further tailoring work function

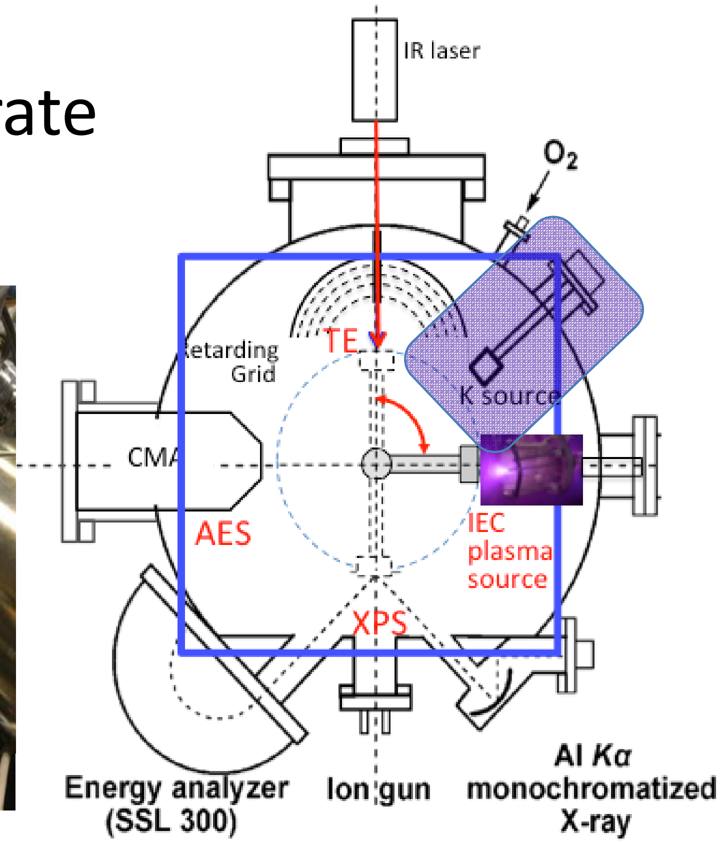
In-situ potassium deposition

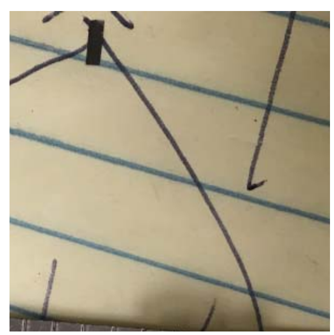
- Potassium deposition on Si substrate

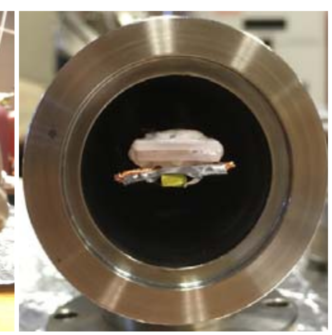


C.-K. Choo, D. Suzawa, and K. Tanaka, Surf. Sci. **600**, 1518 (2006)









Summary of this project

- A new type of silicon carbide / carbon composite synthesized from polymer derived synthesis.
- Electrical resistivity of PDC SiC/C can be tailored by different carbon contain.
- The surface of SiC/C composite has unique property that grows graphite and can be self-regenerated.
- Work function measured through thermionic emission.
- High temperature mechanical properties is on going.
- In-situ alkali metal deposition for work function engineering is on going.
- ICE plasma source has been constructed, ready to be incorporated.

Thank you!