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

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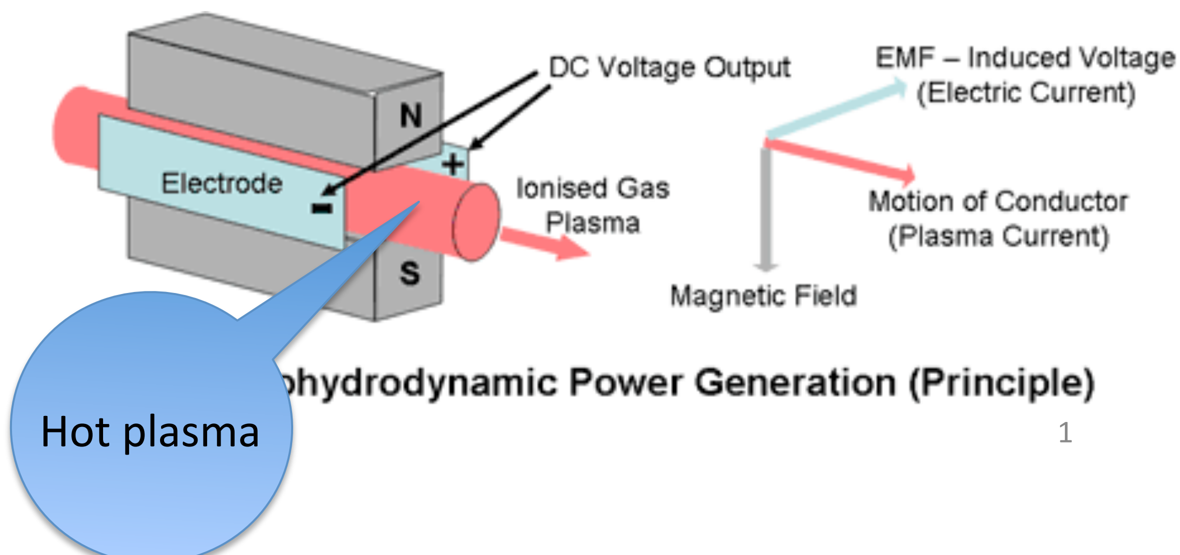
Major Obstacle in MHD Power Generation

Issues in electrode materials

- Must withstand in harsh MHD environments
  - Extremely high temperature
  - Exposure to hot plasma
  - Severe ion bombardment
  - Mechanical stress via thermal expansion
  - Thermal, electrical, mechanical and chemical stability of materials for all above.

- Conformal process

- Low resistivity



…hydrodynamic Power Generation (Principle)

Long Term Goal

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

Our Focus

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

Role of excess carbon

- ✓ Polymer based synthesis
- ✓ Structural information
- ✓ Electrical resistivity
- ✓ Work function from thermionic emission

Process of Making Silicon Carbide

- Conventional method (Acheson method):

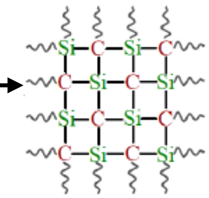
$$SiO_2 + 2C \xrightarrow{2500^{o}C} CO_2 + SiC$$

  - High processing T
  - Difficult to dope uniformly

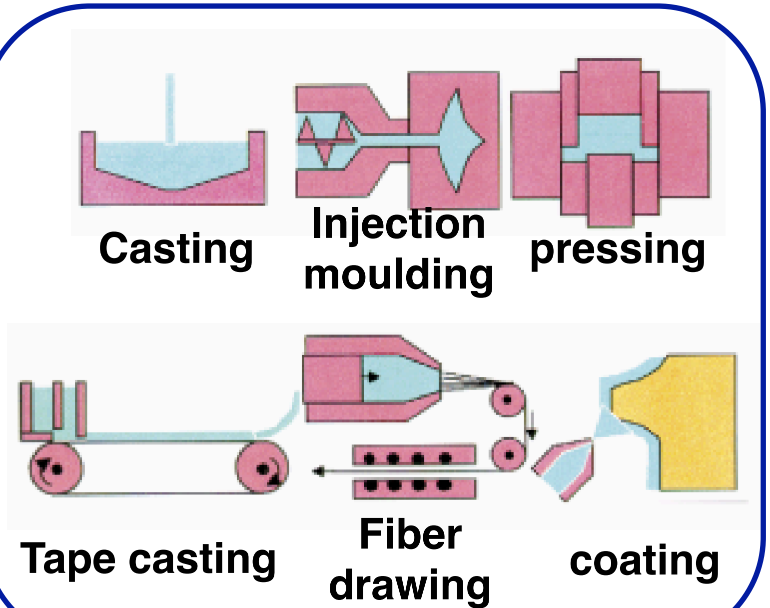
- Chemical Vapor Deposition

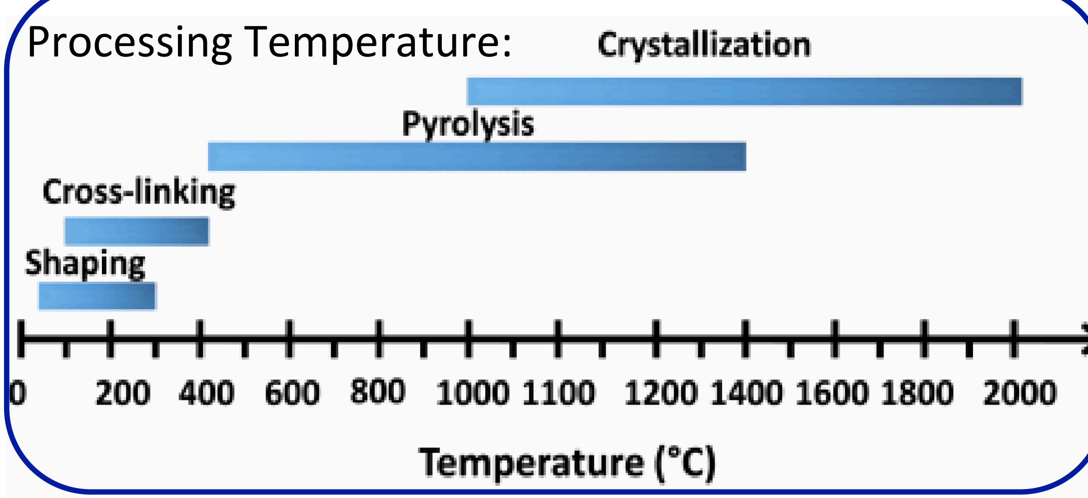
- Polymer Derived Process:

Polymer Precursor → Crosslinked Product → Amorphous ceramic →



1. Conformal process
2. Possible low processing temperature
3. Uniform composition
4. Versatile choice of dopant

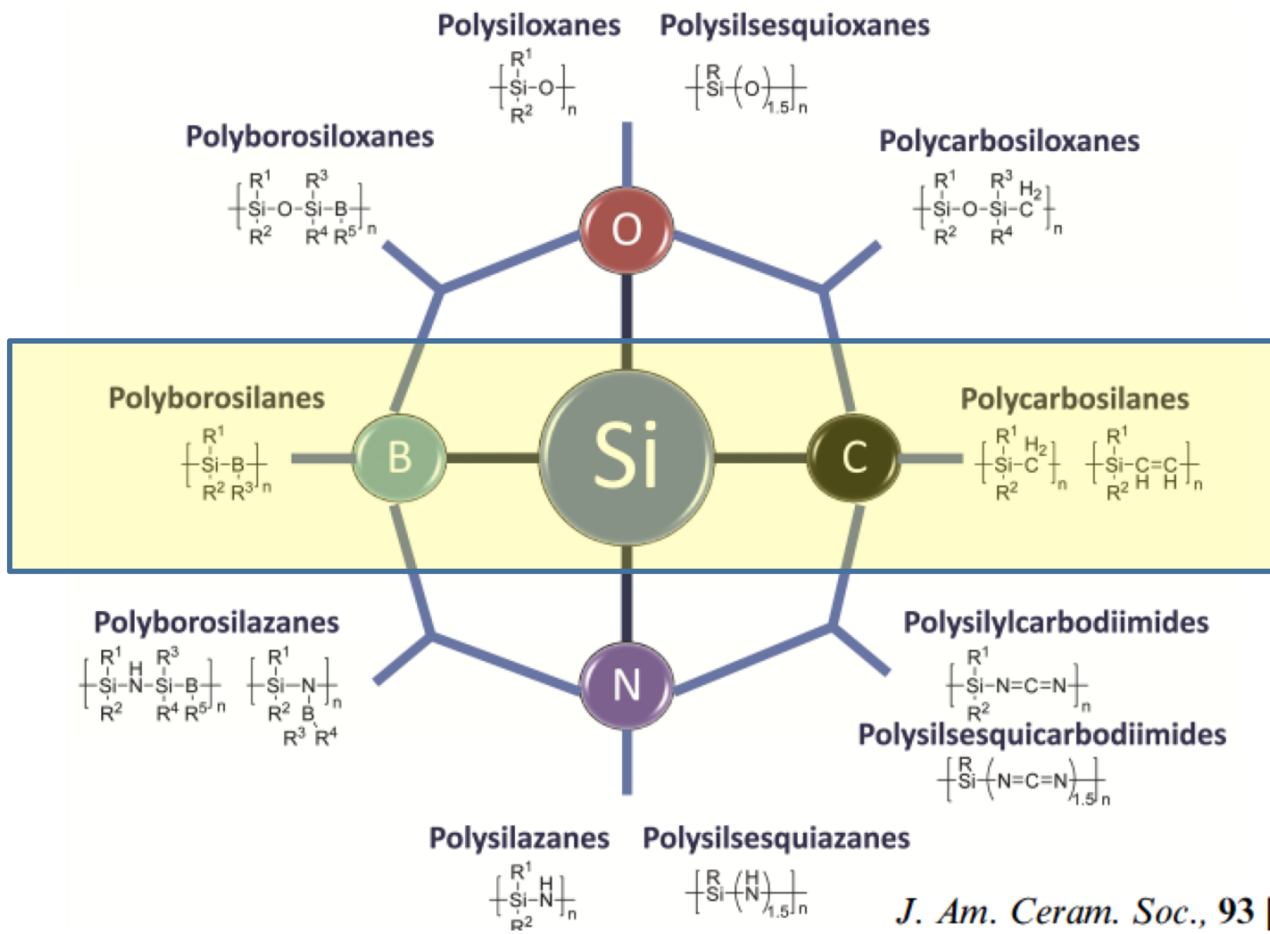




P. Colombo, G. Mera, R. Riedel, and G. D. Sorarù, J. Am. Ceram. Soc. **93**, 1805 (2010)

Diversity of Silicon Based Precursors

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



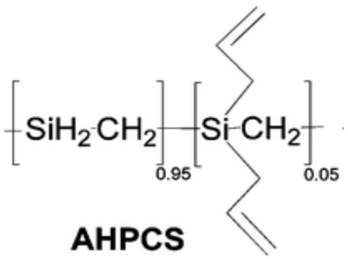
J. Am. Ceram. Soc., **93** [7] 1805–1837 (2010)

Selection of Polymer and Processing

SiC forming polymer (polycarbosilane SMP-10)

Carbon additive (divinylbenzene)

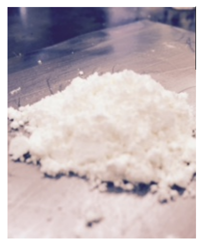
Sintering aid additive (decaborane)



AHPCS

Thermal cross-linking T = 400 °C

Cured polymer



grinding

Polymer power

Pyrolysis T = 900 °C

Cold press

Hot Press (HP)

SiC/C composite

milling

Ultrafine powder

Hot pressing T = 2130 °C

SiC/C monolith

Polymer Infiltration Pyrolysis (PIP)

Pressed pellet

T = 1700 °C

n=5

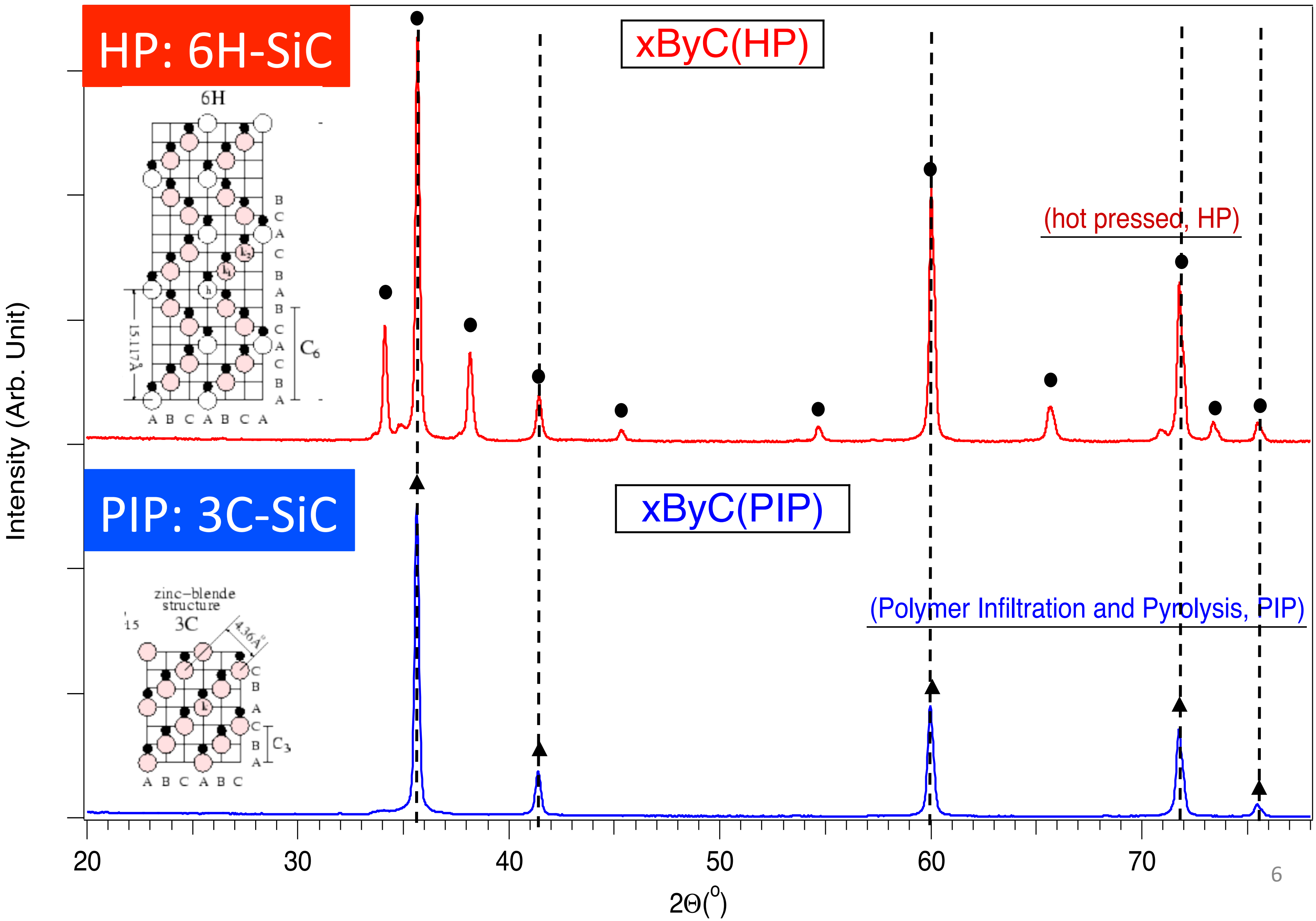
SiC/C monolith

Sample designation

xByC(HP)

xByC(PIP)

Overall XRD Bulk Structural Analysis



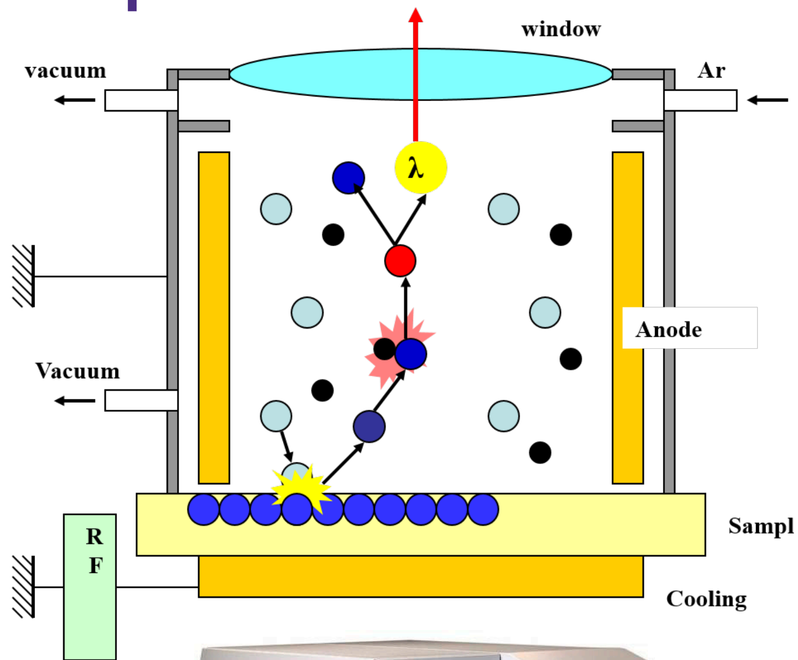
C:Si Atomic Ratio for SiC-C

xByC(HP) vs xByC(PIP)

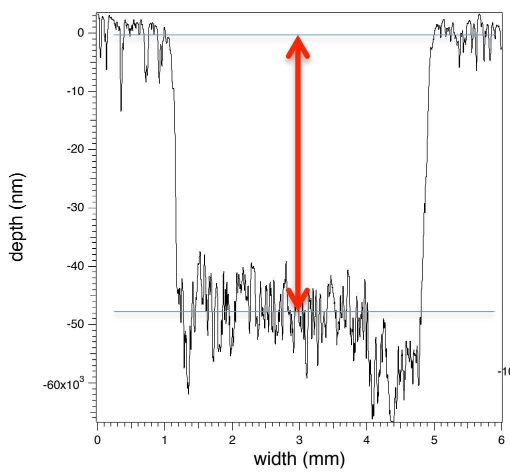
Glow Discharge Optical Emission Spectrometer

Horiba GD-Profiler-2

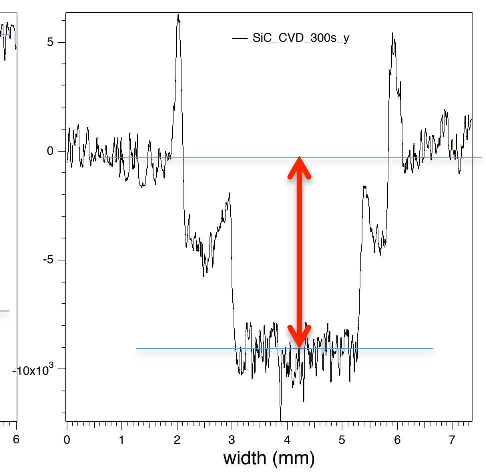
- Depth-resolved elemental analysis
- with ~10 nm depth resolution
- Semi-quantitative analysis



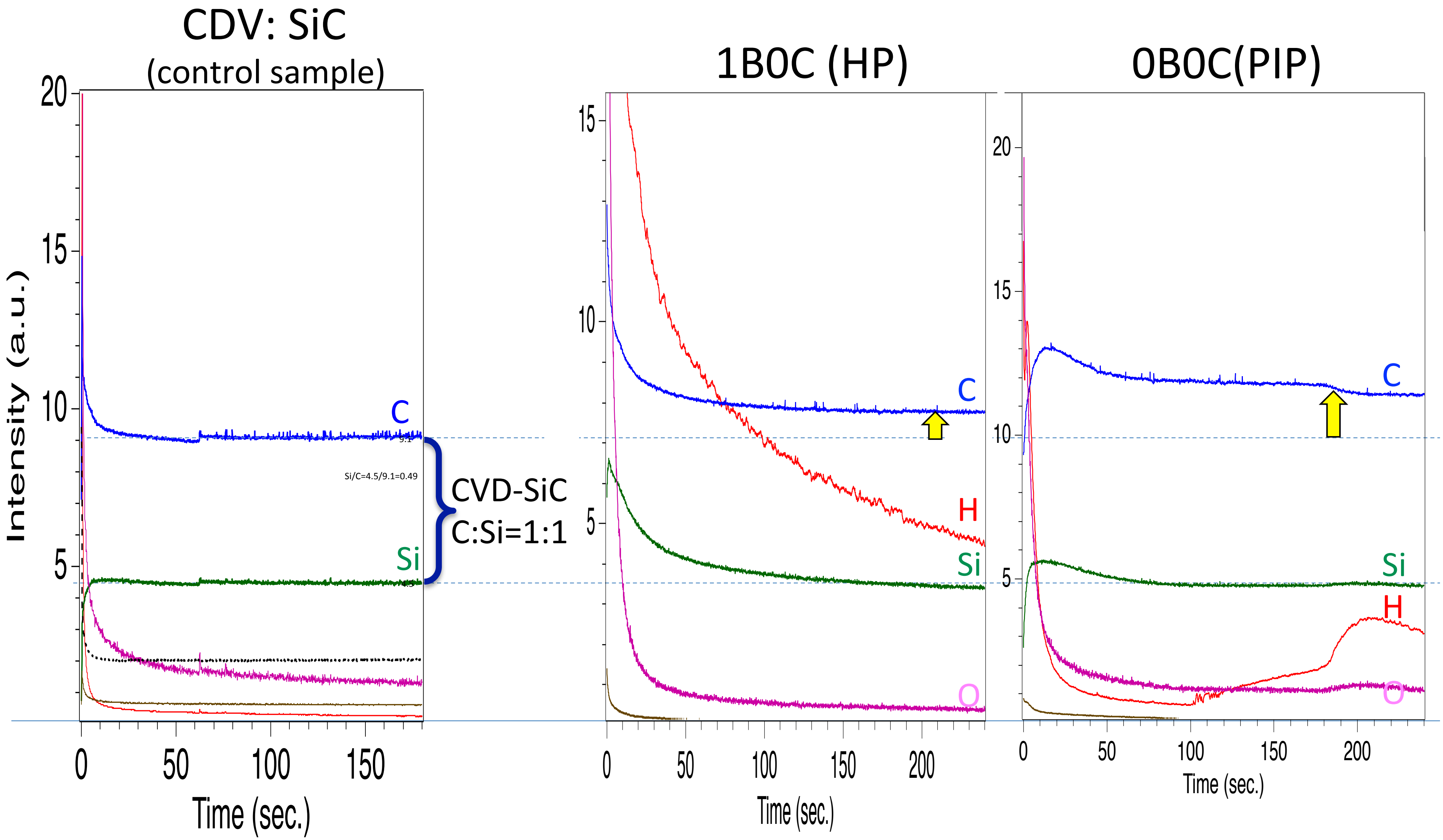
Sputter-Depth Calibration nm/sec

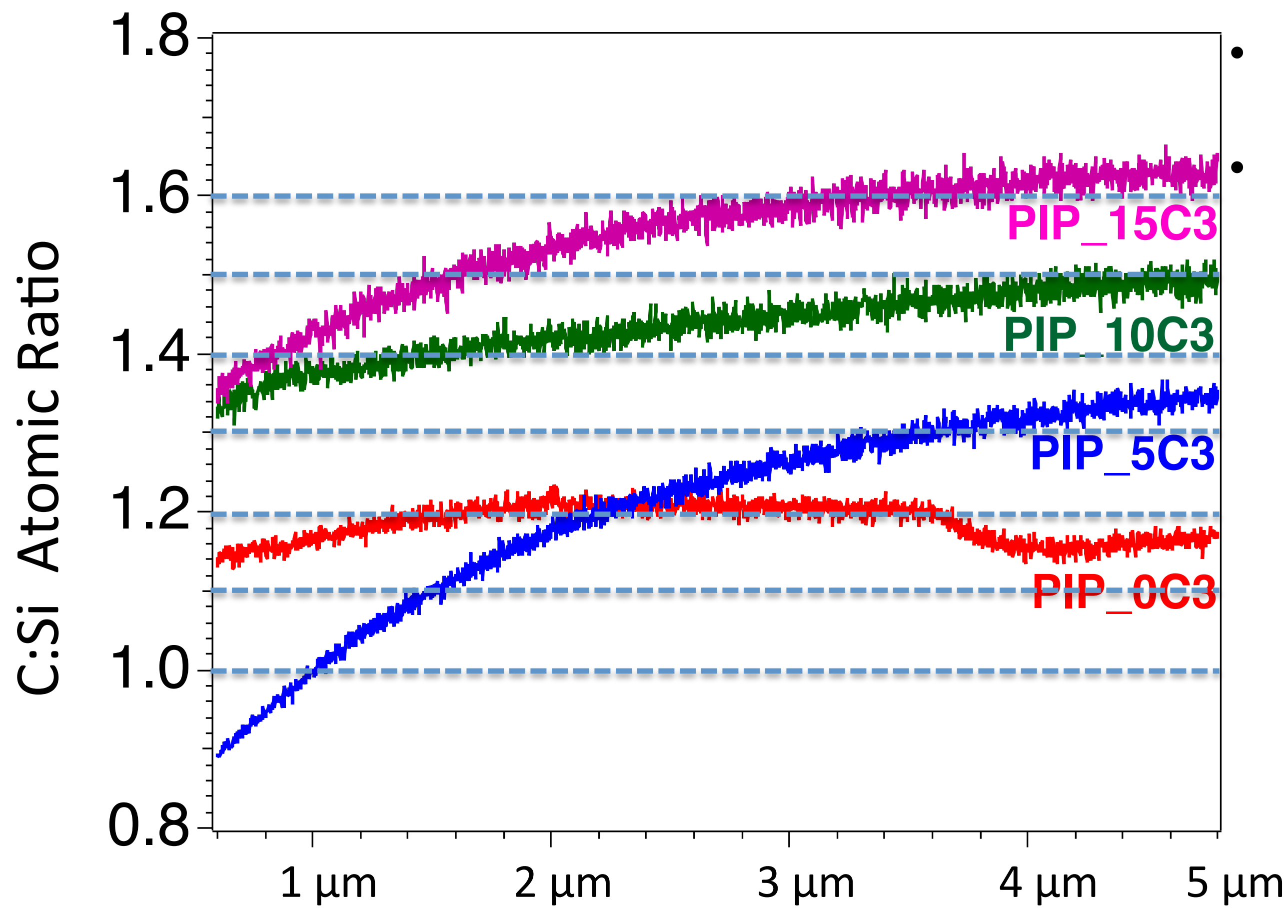


Graphite, 300s, ~50μm

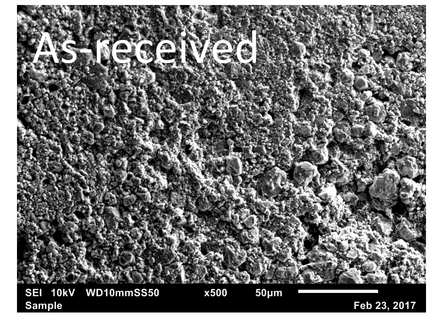


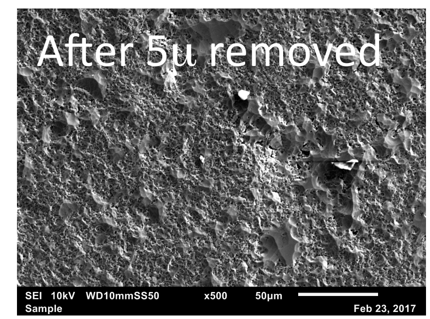
CVD-SiC, 300s, ~5 μm

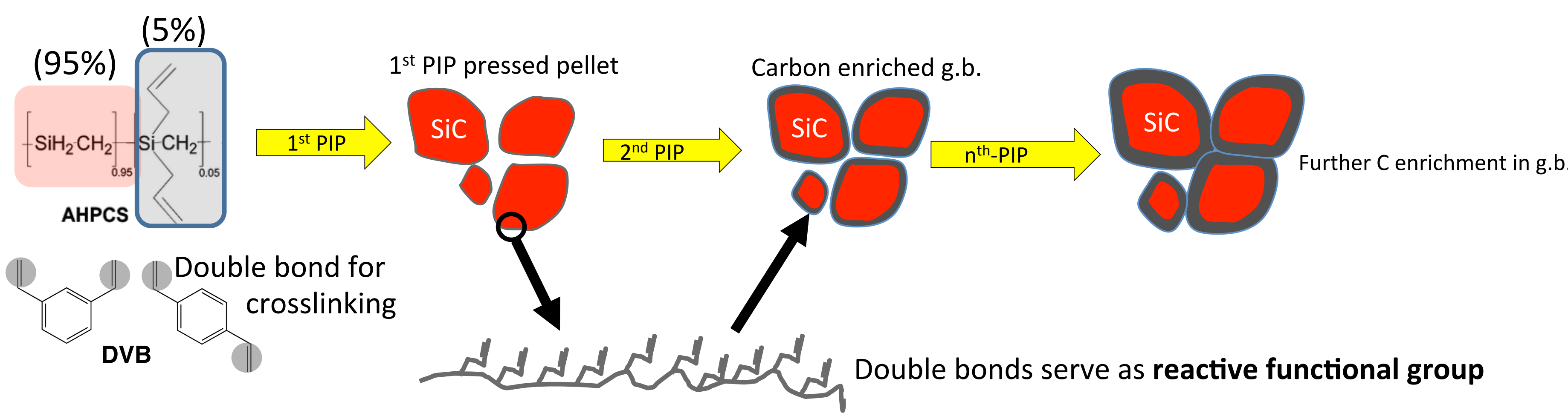

CDV: SiC
(control sample)
1BOC (HP)
0BOC(PIP)
Intensity (a.u.)
Time (sec.)
Time (sec.)
Time (sec.)
C
Si
Si/C=4.5/9.1=0.49
CVD-SiC
C:Si=1:1
C
H
Si
O
C
Si
H
O



- Excess amount of carbon layers created by PIP
- Sputtering rate for C(graphite) ~ 10 times higher than SiC(3C)

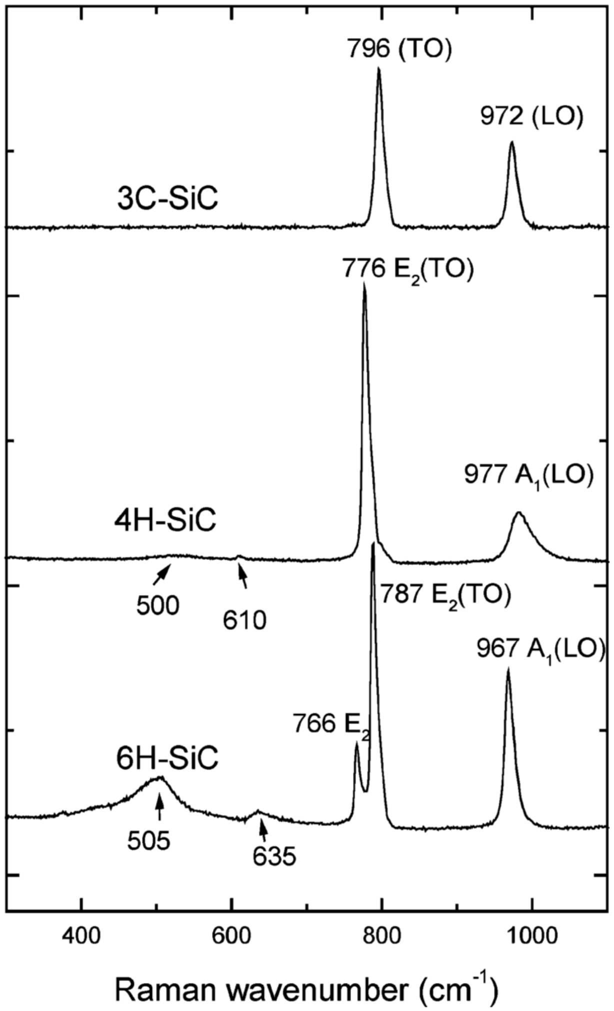




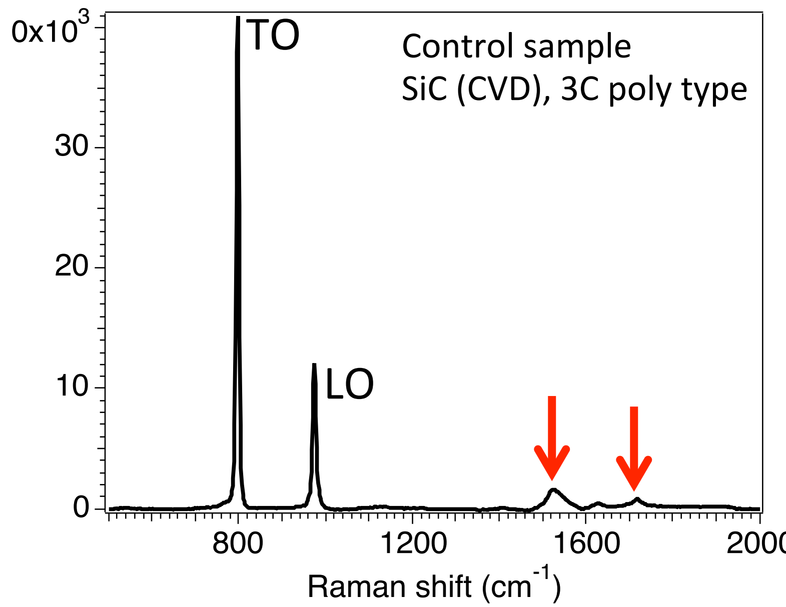


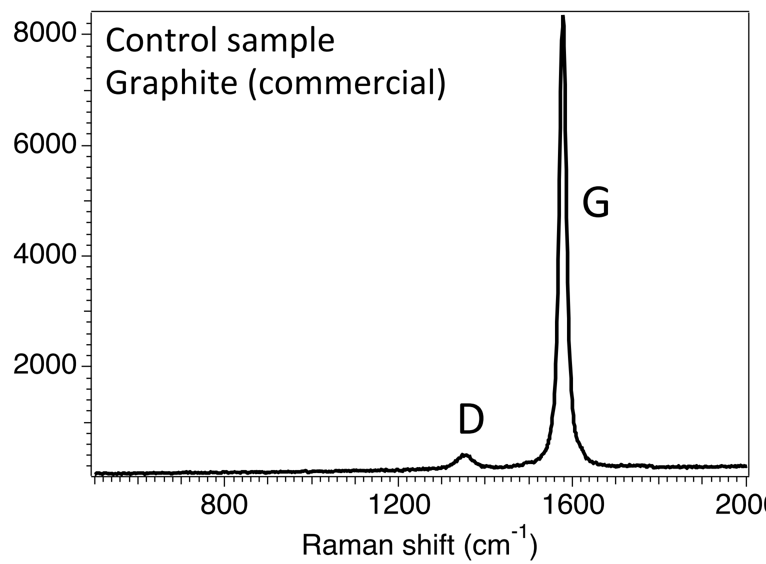
Molecular Structure of SiC-C by Raman

Excitation: Ar laser (514nm)



Y. Ward, R. J. Young, and R. A. Shatwell, J. Mater. Sci. **39**, 6781 (2004).





Penetration depth of **514nm** laser light

SiC(3C)~100μ

SiC(6H)~300μ

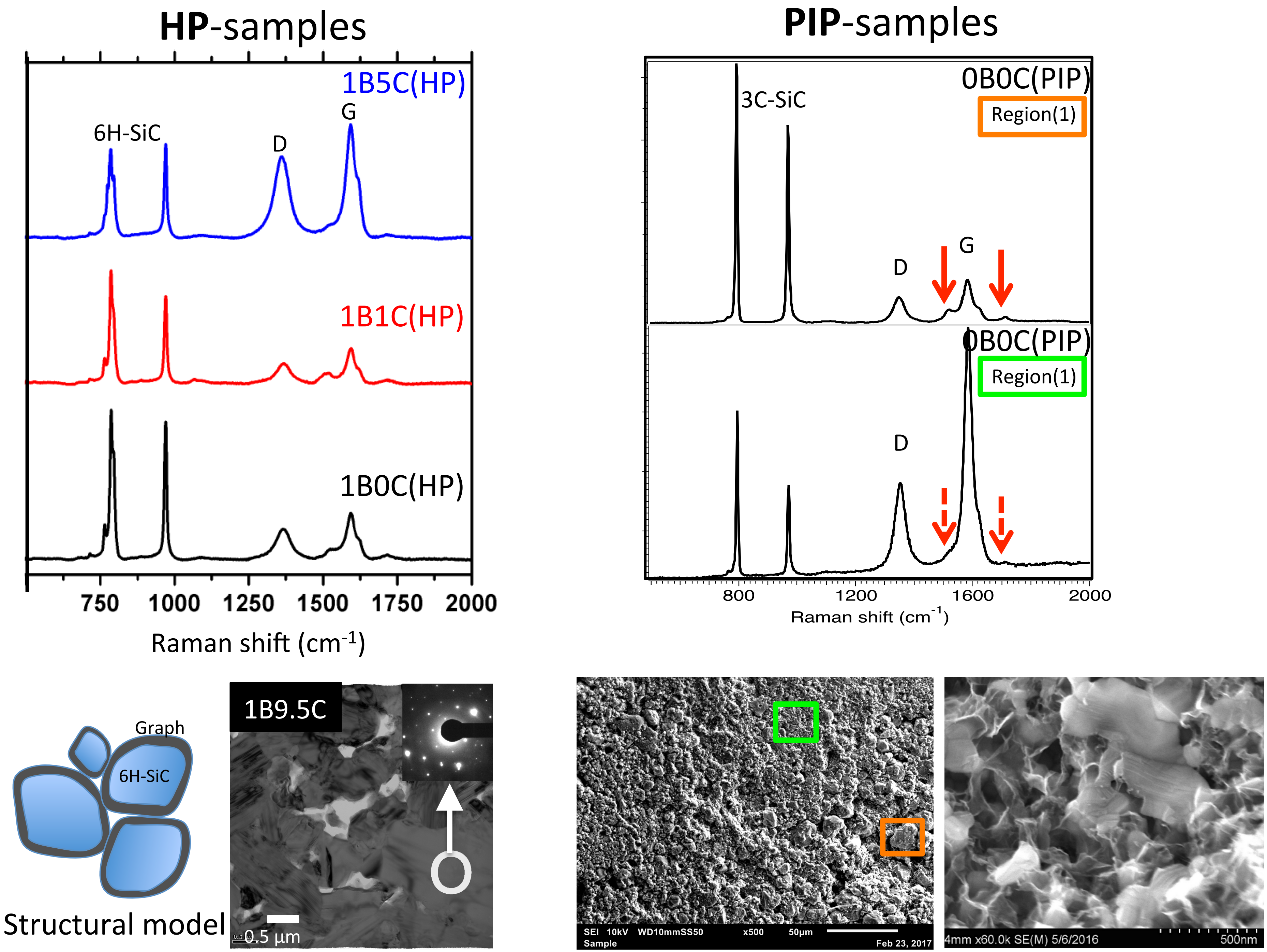
Probing bulk

V

V

C(graph)~100-200nm

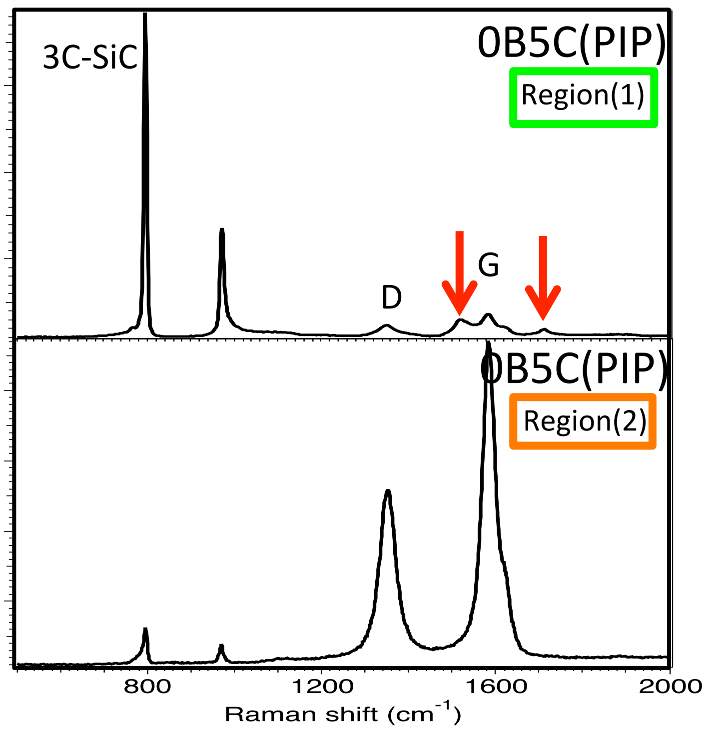
Probing surface



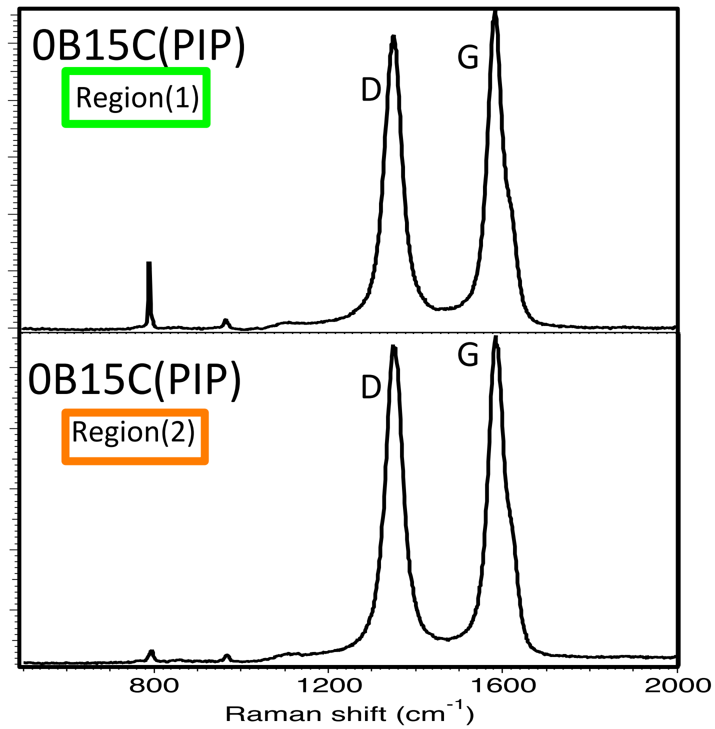
HP-samples
1B5C(HP)
6H-SiC
D
G
1B1C(HP)
1B0C(HP)
750
1000
1250
1500
1750
2000
Raman shift (cm-1)
PIP-samples
0B0C(PIP)
Region(1)
3C-SiC
D
G
0B0C(PIP)
Region(1)
D
800
1200
1600
2000
Raman shift (cm-1)
Graph
6H-SiC
Structural model
1B9.5C
0.5 µm
SEI 10kV WD10mmSS50 x500 50µm
Sample
Feb 23, 2017
4mm x60.0k SE(M) 5/6/2016
500nm

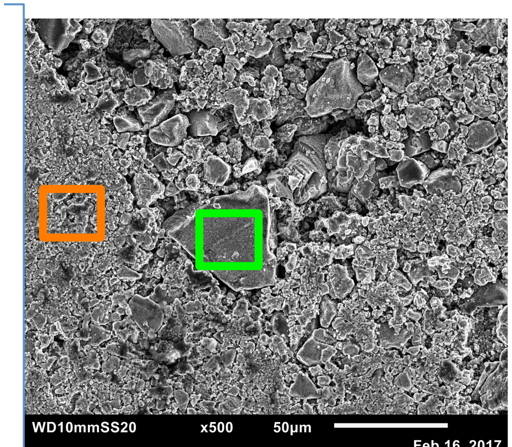
PIP-samples (cont'd)

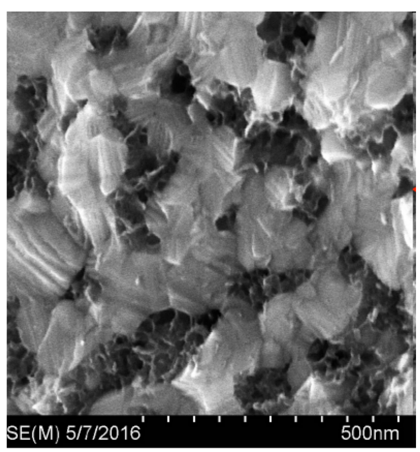
0B5C(PIP)

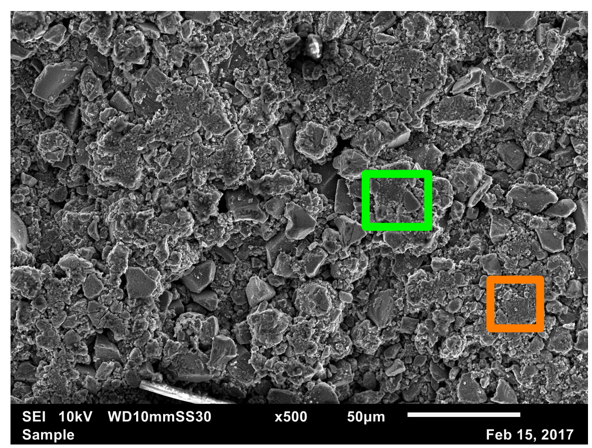


0B15C(PIP)



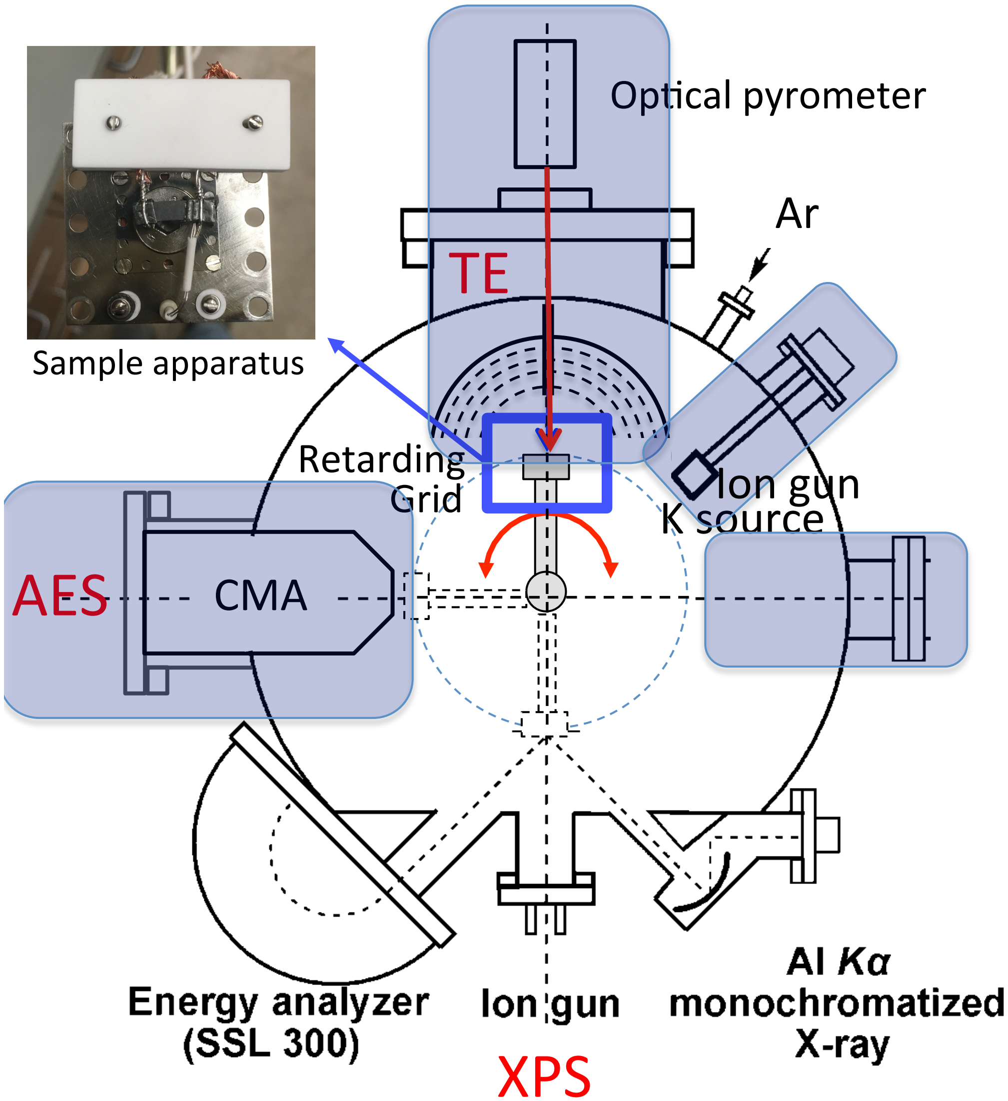






Temperature Induced Surface Change of SiC-C

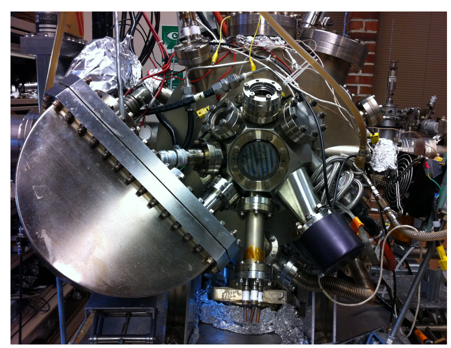
Integrated Experimental System:

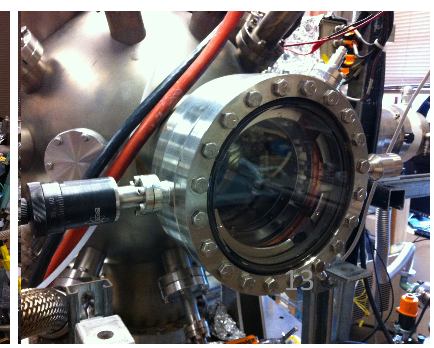


- Retarding grid spectroscopy to measure thermionic emission (**TE**)
- X-ray photoelectron spectroscopy (**XPS**)
- Auger electron spectroscopy (**AES**)
- K deposition for work function engineering
- R-type TC and optical pyrometer for temperature measurement
- Ion gun for surface cleaning

Capable of measuring:

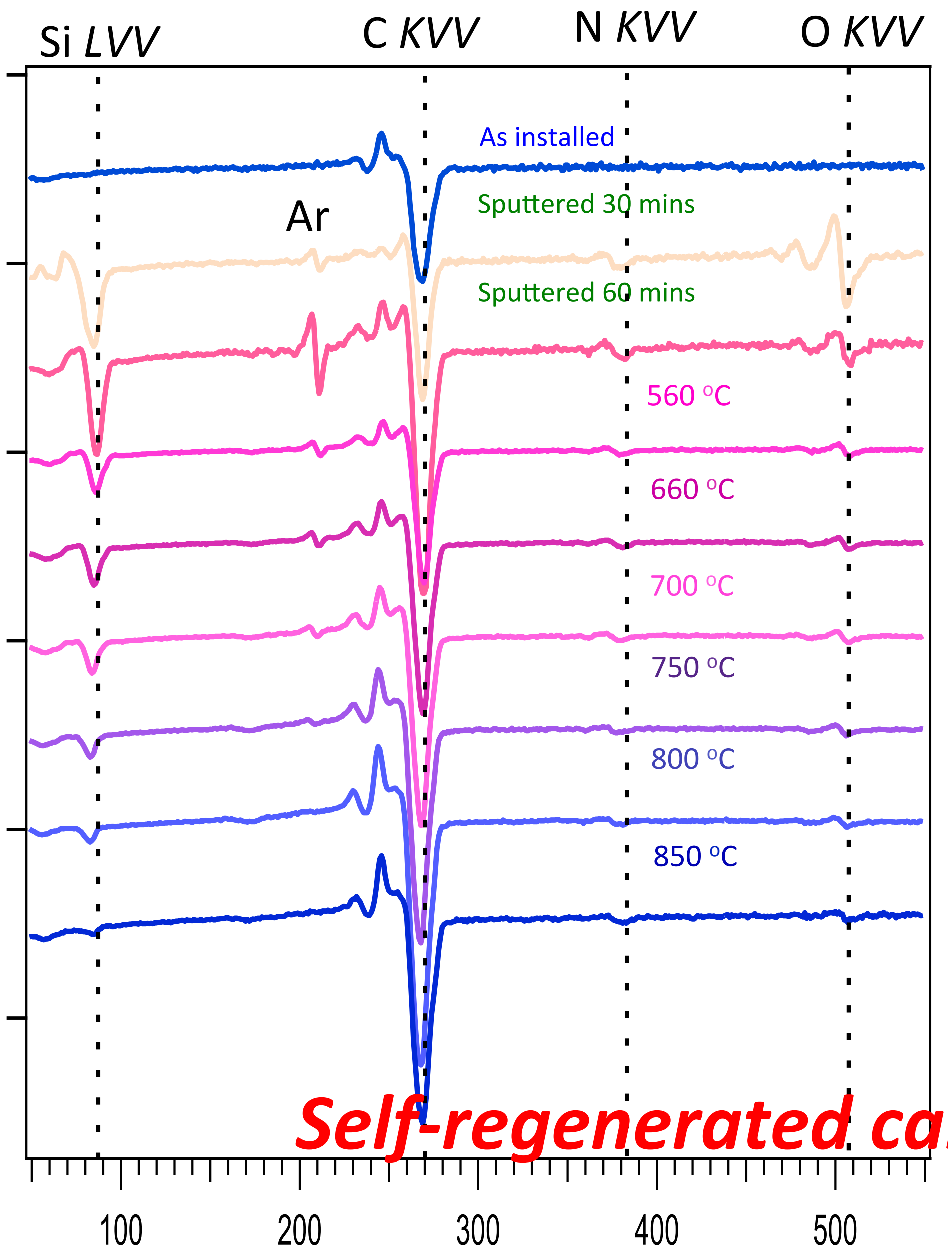
- Surface composition at elevated temp.
- Total current and kinetic energy distribution of thermionic emission.
- Work function



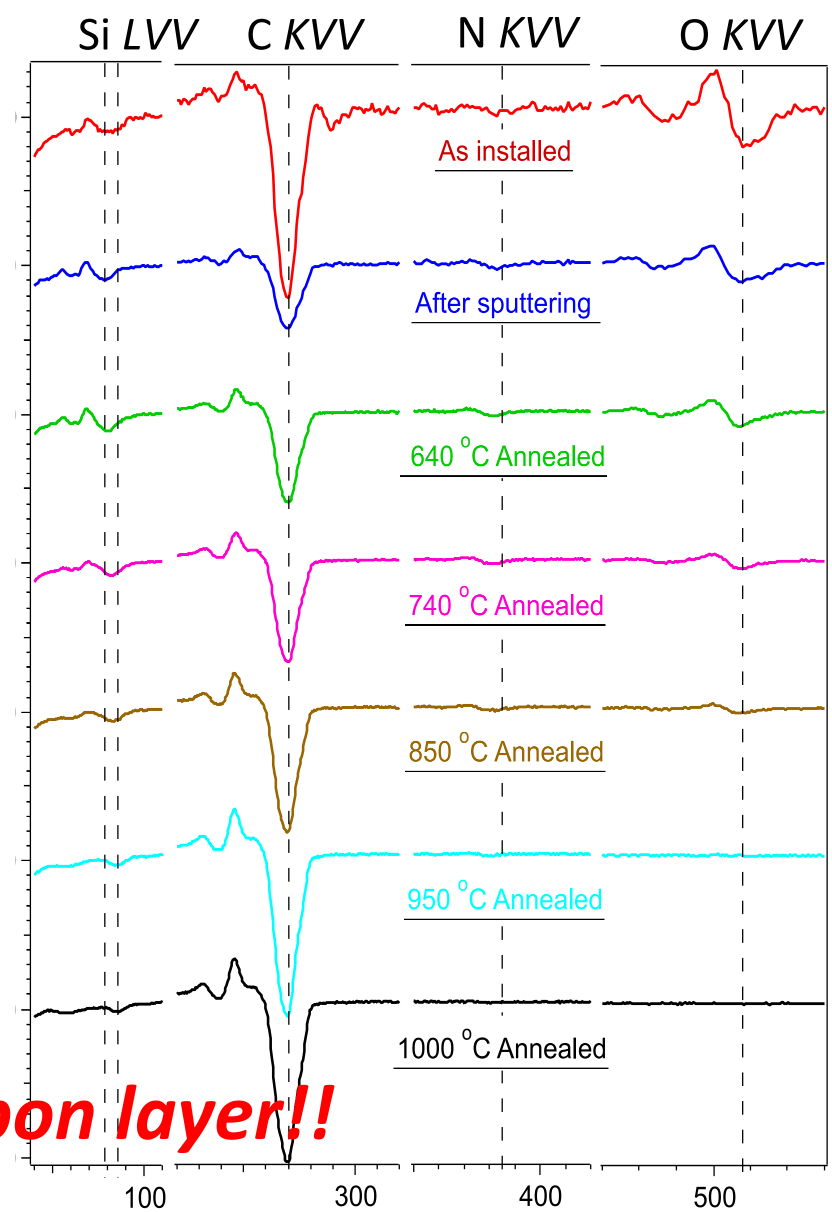


Dynamic Changes of the Surface Composition with T

Sample: 1B5C(HP)



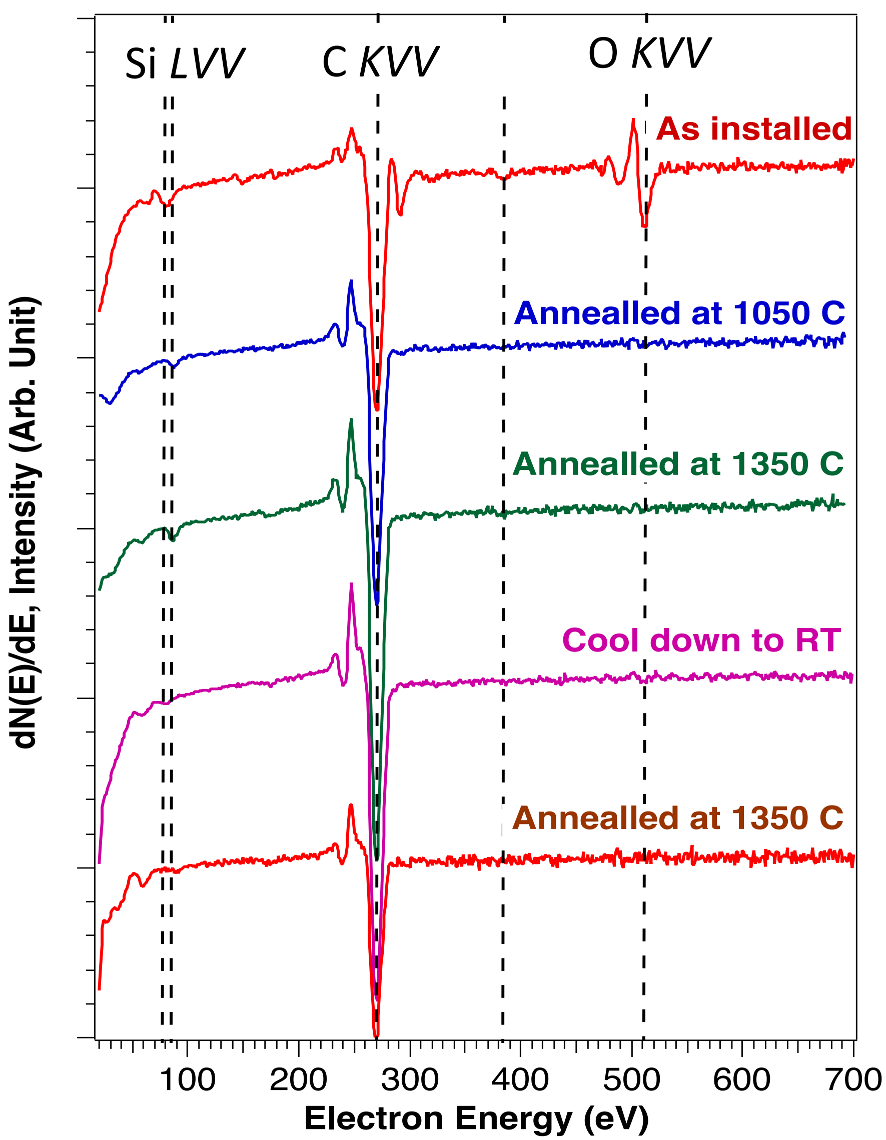
Sample: 0B0C(PIP)



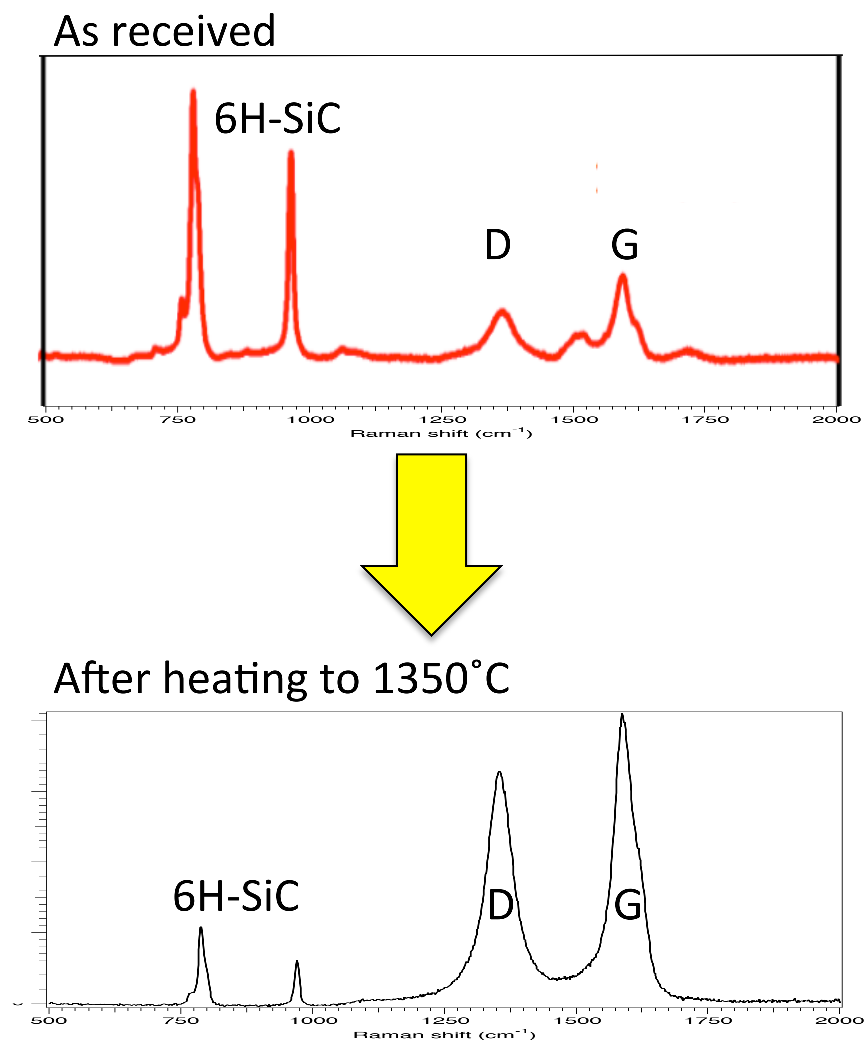
Self-regenerated carbon layer!!

Dynamic changes of the Surface Structure with T

Auger Surface Composition with T



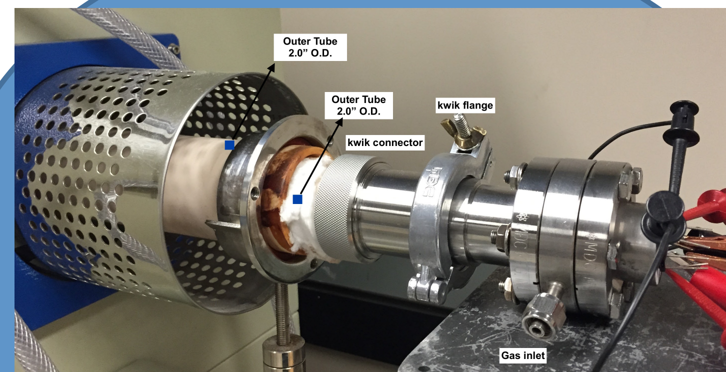
Raman Molecular Structure

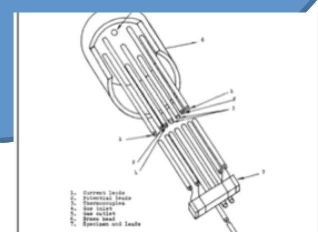


Sample: 1B1C (HP)

Resistivity Measurements

- ✔ Solutions:
  - ➢ Platinum lead, graphite contact and alumina support
  - ➢ Wrapping mechanism
- ✔ Pseudo-four-point probe (Kelvin probe)
- ✔ Alternative polarity to avoid capacity effect



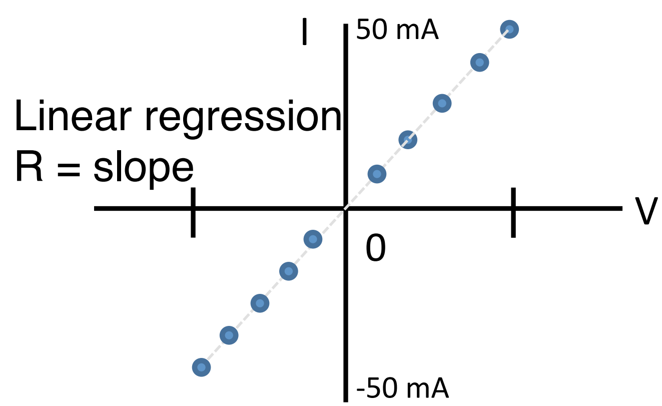


R. N. Blumenthal, J. Coburn, J. Baukus, and W. M. Hirthe, J. Phys. Chem. Solids **27**, 643 (1966).

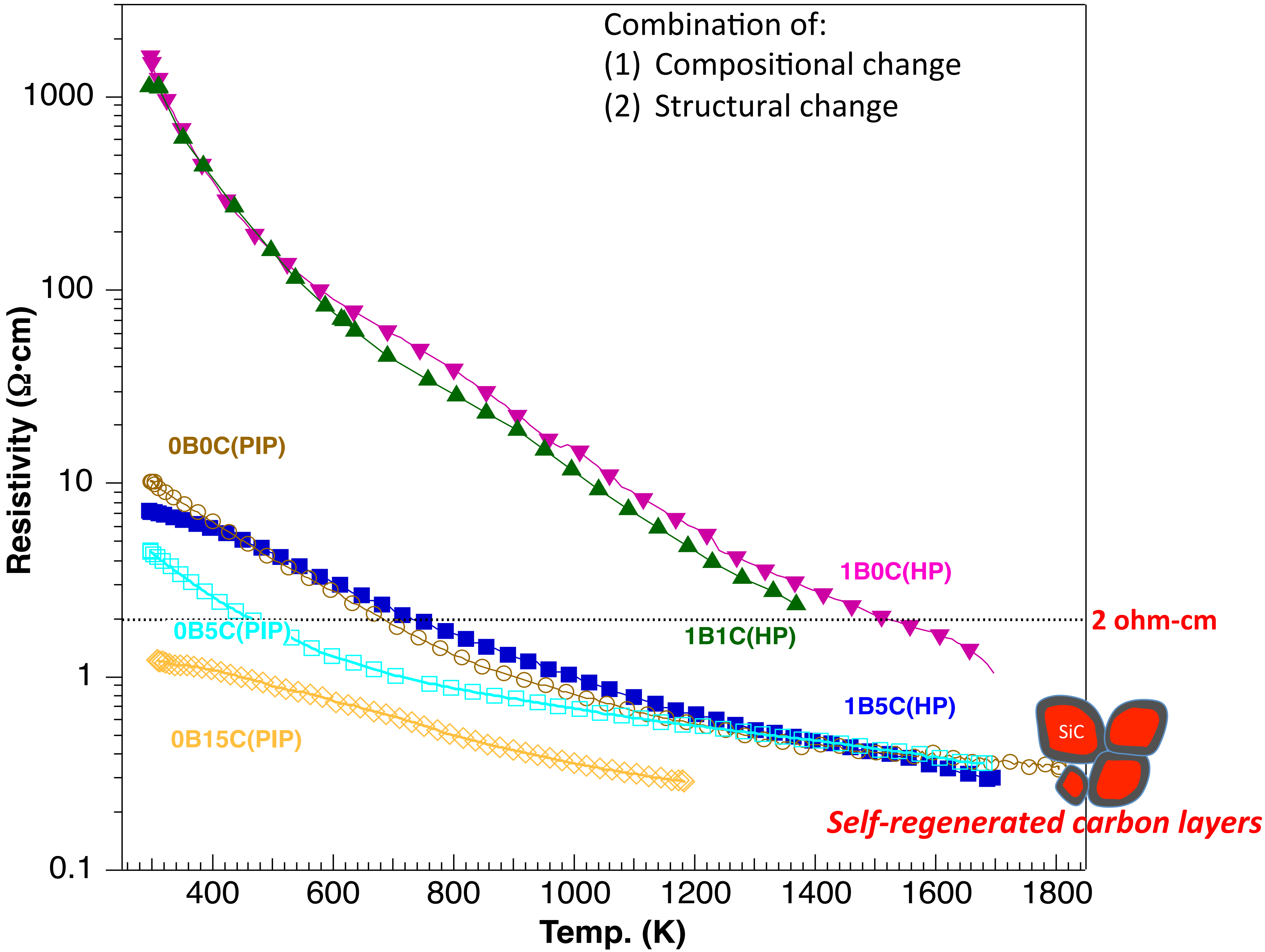
2000°K Tube furnace

Electrometer and current source

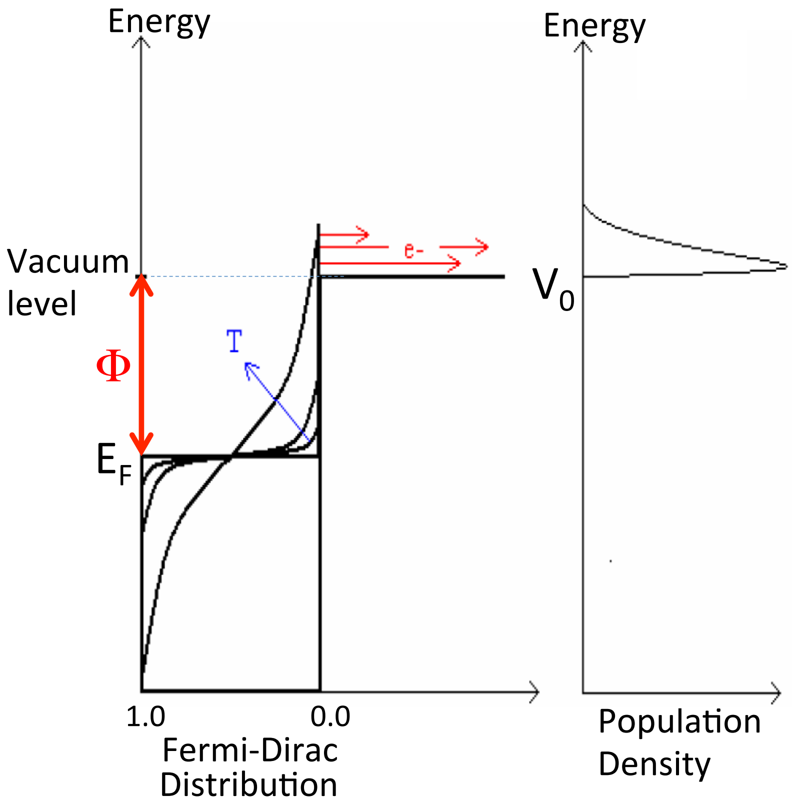
LabVIEW Work station



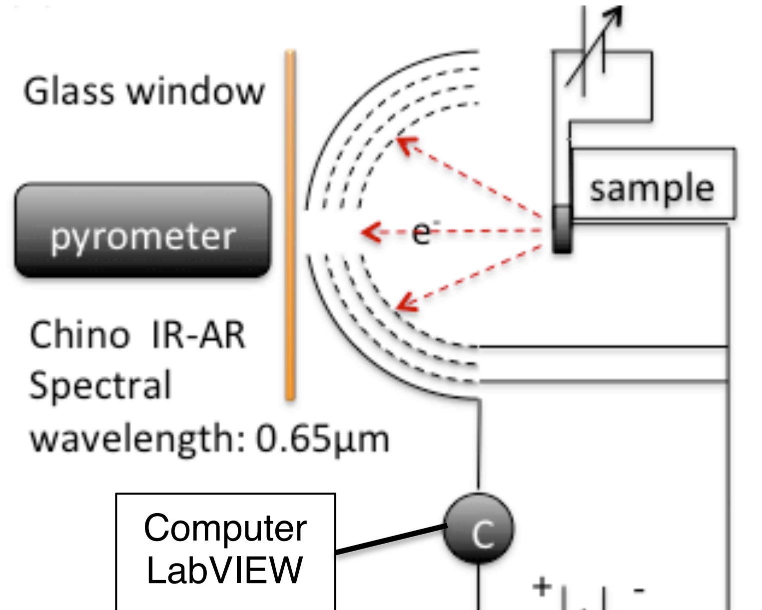
Electrical Resistivity Change with T for HP and PIP samples

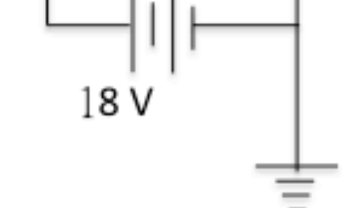


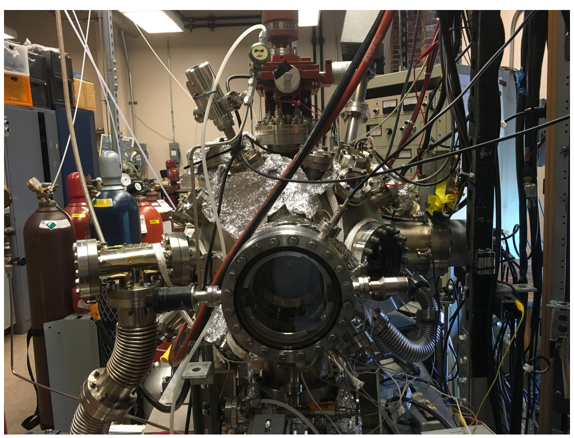
Thermionic emission (TE) Properties



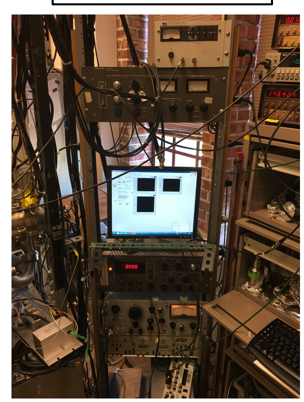
$$J = -q \int_{W>\mu+\phi} v_x f(k) \frac{d\mathbf{k}}{4\pi^3} = \frac{m k_B^2 q}{2\pi^2 \hbar^3} T^2 \exp\left\{\frac{-\phi}{k_B T}\right\}$$







Front view of electron grid



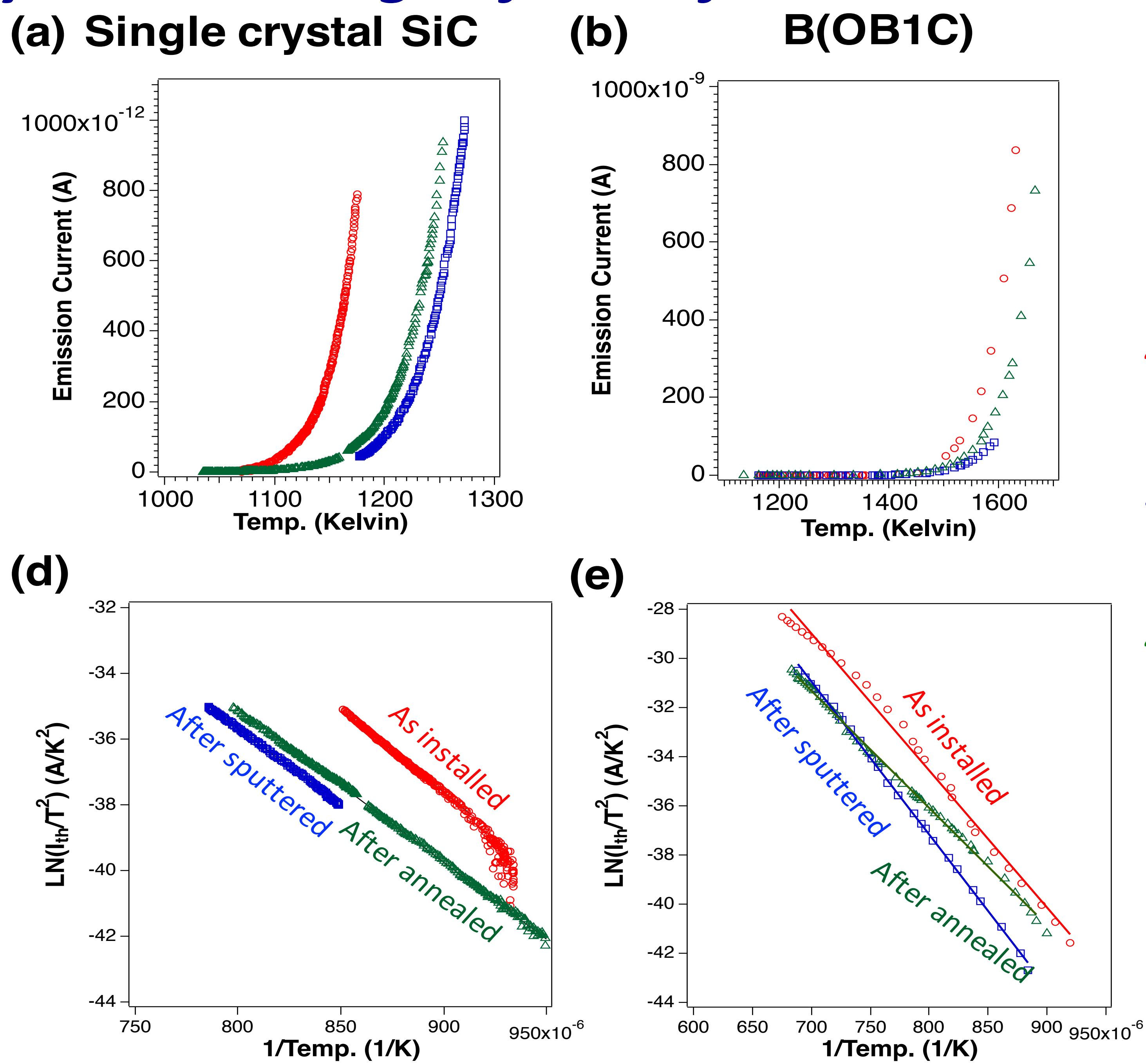
Workstation for data acquisition

Dynamic Change of Workfunction Values

4.39 eV

4.00 eV

4.02 eV



4.8 eV

5.36 eV

4.09 eV

Summary of this project

- A new type of silicon carbide / carbon composite synthesized from polymer derived synthesis:

  Two routes: Hot-pressed and Polymer Infiltration
- Electrical properties of PDC SiC/C tailored by different carbon concentration.
- Self-regenerated surface is unique to the SiC/C composites
- Work function controlled by the self-regenerated carbon.
- K incorporation to SiC at the polymer precursor stage is planned to largely lower the workfunction of SiC-C composites.

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.
Sub-Task 4.3: Simulation of plasma interactions

Lead: Prof. F. Ohuchi

Thank you!