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

Fumio S. Ohuchi (PI)* and Rajendra K. Bordia(Co-PI)**

YiHsun Yang (Graduate Student)

Department of Materials Science and Engineering

*University of Washington
Box 352120, Seattle, WA 98195

** Clemson University
Clemson, SC 29634

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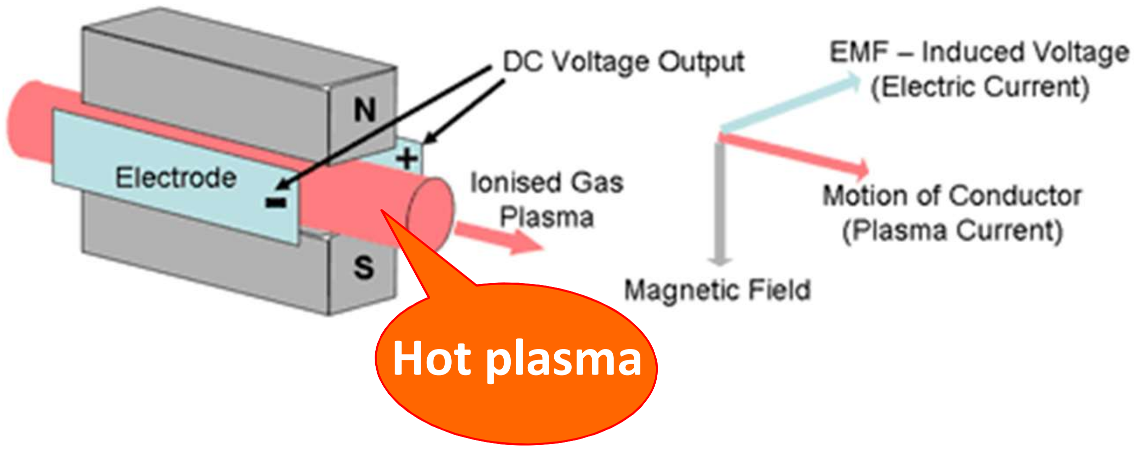
# *MHD Power Generation*




## 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

## *Overall Goal*

Develop a novel class of SiC based ceramic composite materials with tailored compositions for MHD channel applications.

## *Our Focus:*

Control and understand the effect of the nature of the excess carbon of SiC on the structural and electrical properties.

## *Questions to be asked:*

- What is (are) the most appropriate parameter(s) to describe and quantify the nature of these materials?
- How can these parameters be controlled?
- What are their effects on the properties of these materials, especially relevant to targeted MHD channel applications?
- How does the nanostructure and hence the properties evolve under extreme conditions (e.g. temperature and plasma)?

# *Our 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 @ Clemson

**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

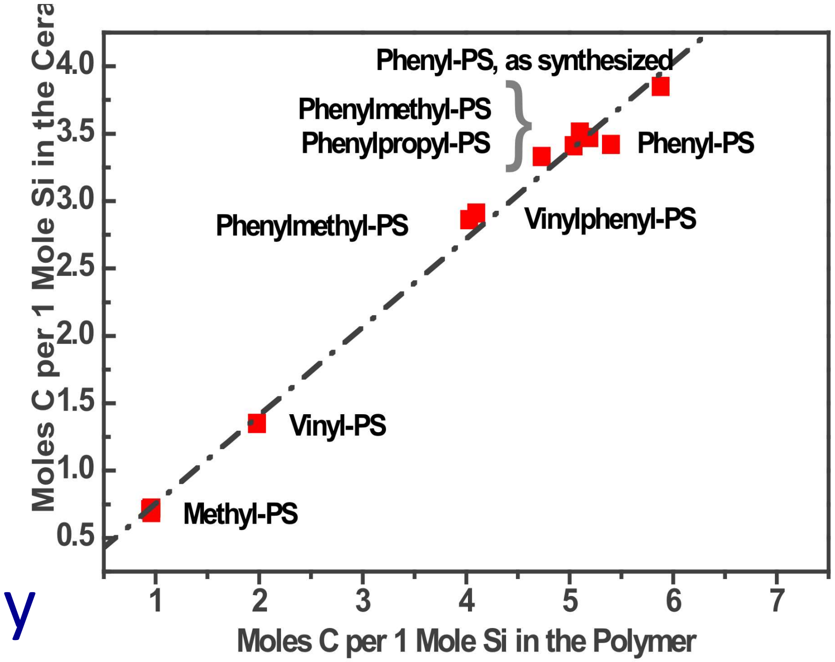
Lead: Prof. F. Ohuchi @ Washington

# TASK 1: PROCESSING OF SI-C-X CERAMICS

## Effect of Stoichiometry and Temperature on the Nanostructure

***Polycarbosilanes***

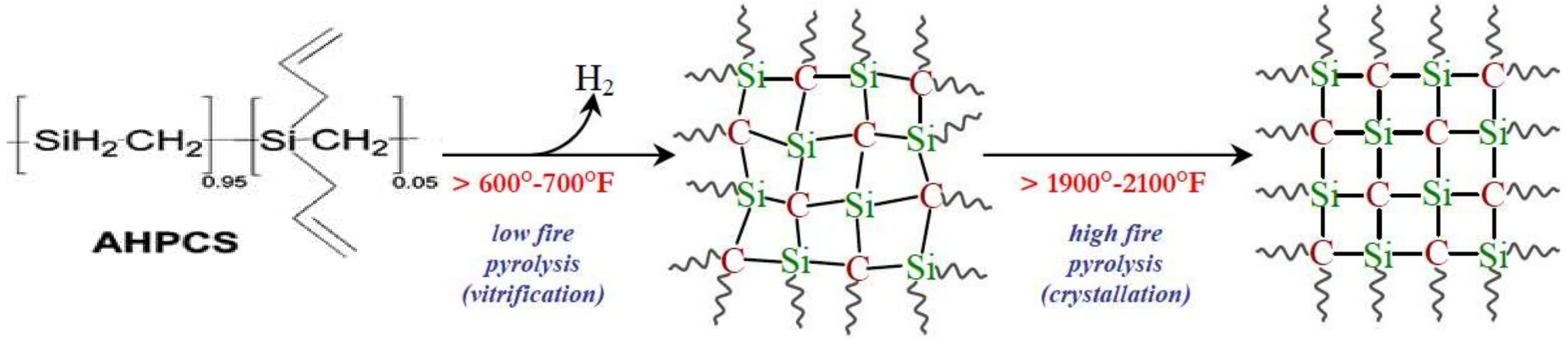
One-to-one correlation between the C/Si ratio in precursor and ceramic.



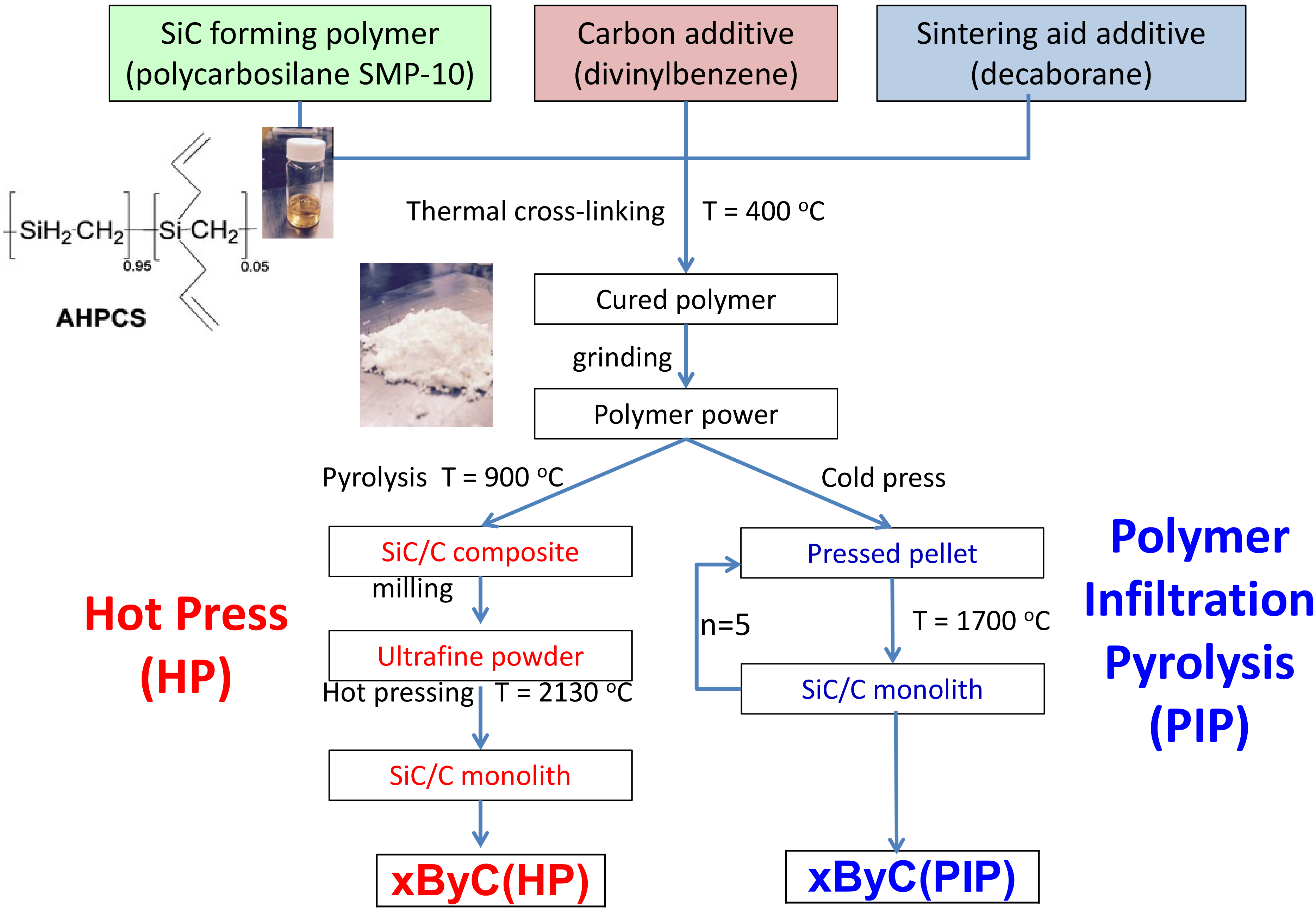

Our choice : ***Polycarbosilane*** family

Precursors: **Starfire® System's SMP series**

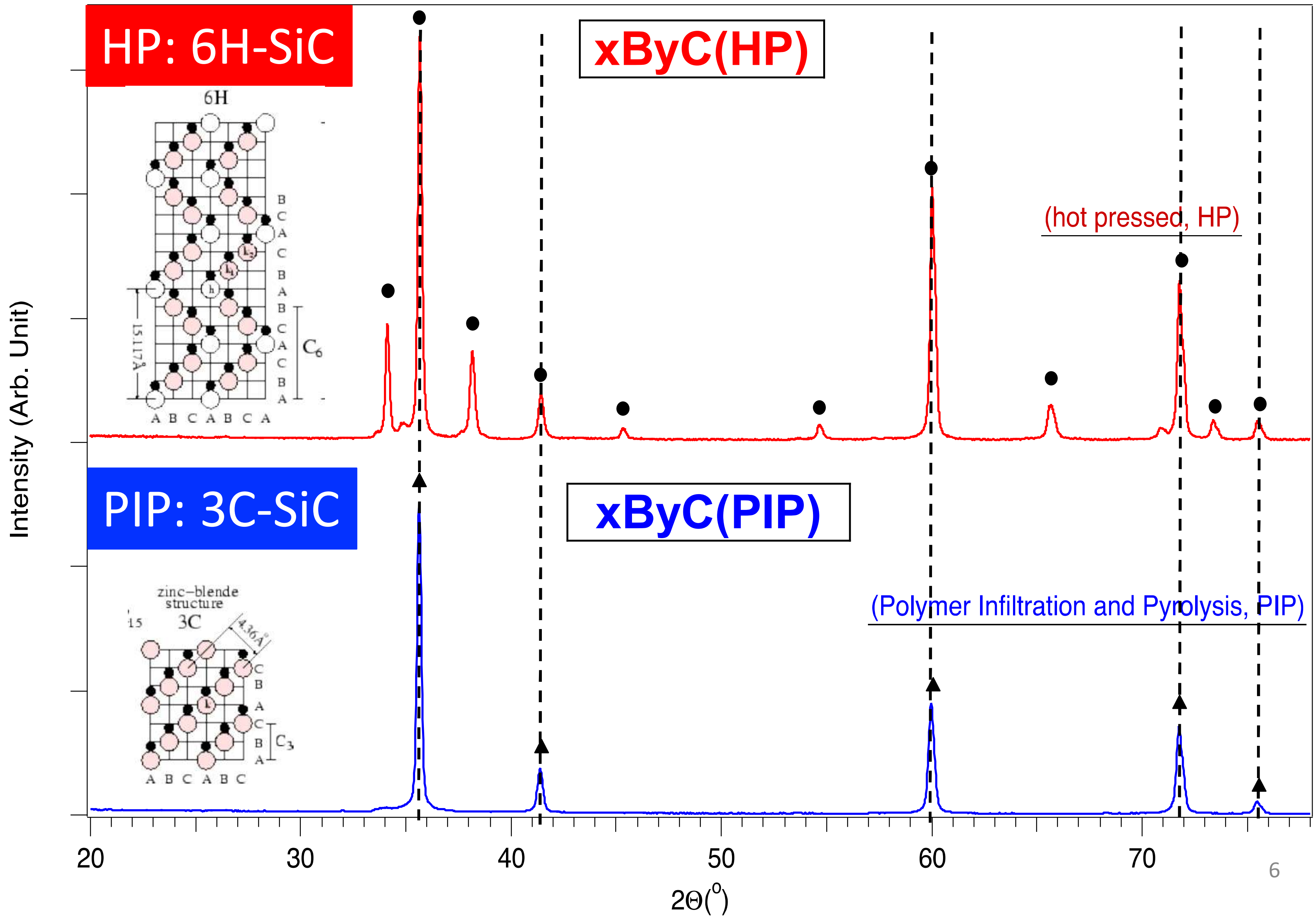
C/Si ratio from 1 to 2.25 (SMP-10, -25 and -75)



# Polymer Derived Si-C-X Ceramic Process



# Bulk Crystalline Structure of Si-C-X

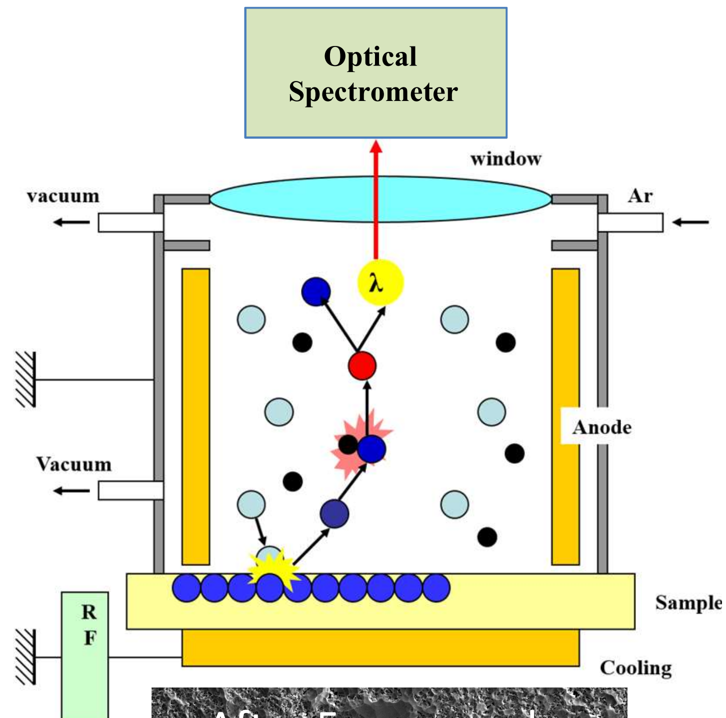


# Bulk C:Si Atomic Ratio of Si-C-X

## Glow Discharge Optical Emission Spectrometer (GDOES)

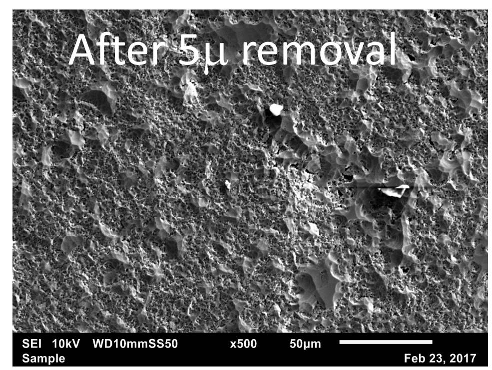
(Horiba GD-Profiler-2)

Ion induced optical emission




- Internal calibration by CVD-SiC (Si:C=1:1)
- Measure C/Si ratio after 250 sec. sputtering (Equivalent to ~5micron removal)
- C/Si Results

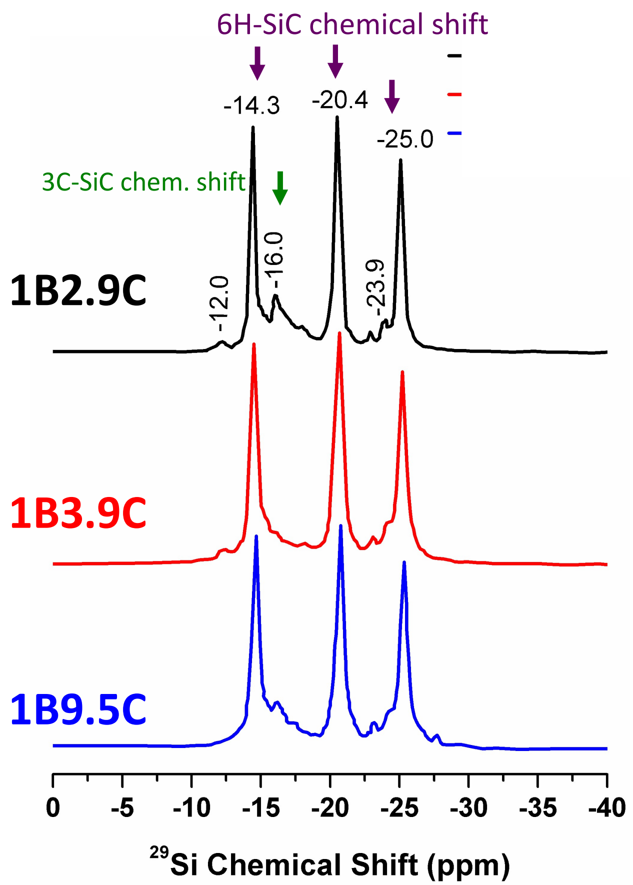
| Composition | xByC (HP) | xByC(PIP) |
|---|---|---|
| 0C | 1/08 | 1.16 |
| 1C | 1.11 | |
| 3C | 1.17 | |
| 5C | 1.20 | 1.34 |
| 10C | | 1.50 |
| 15C | | 1.62 |




- Excess C in bulk Si-C-X

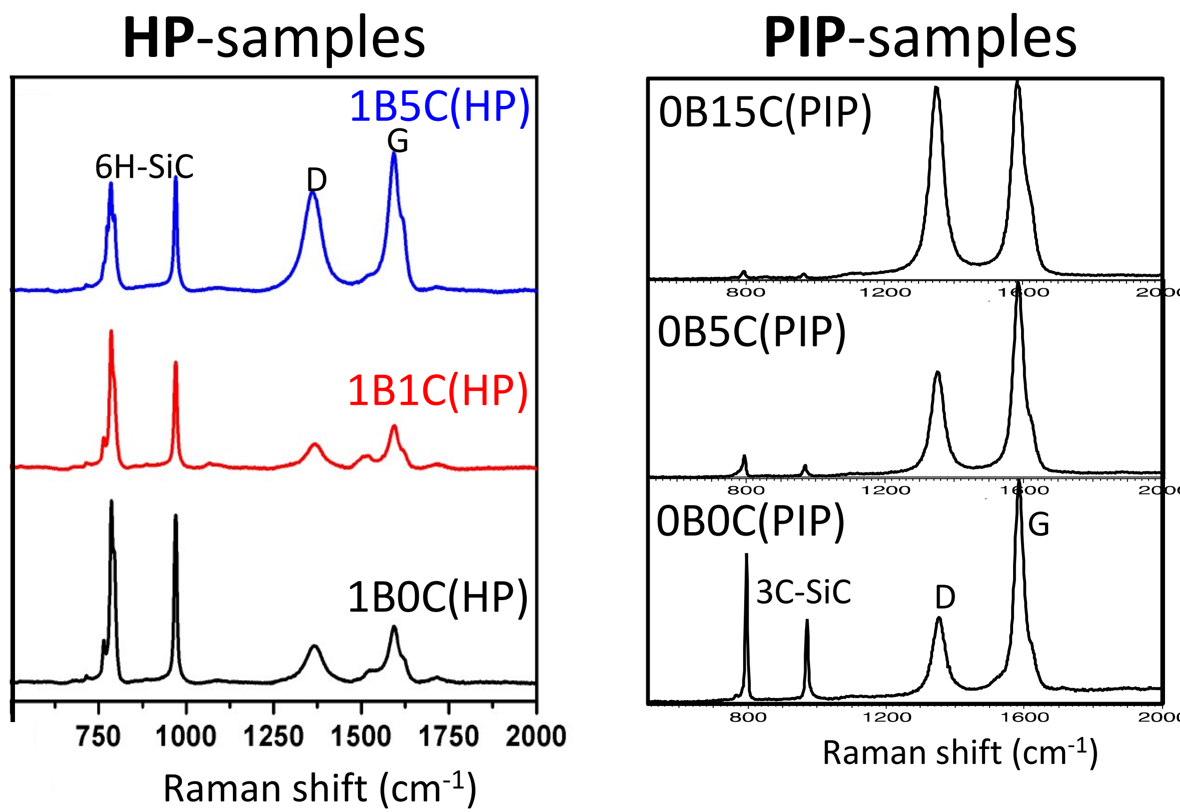
# Chemical and Molecular Structure of Si-C-X

## Bulk Chemical State by Si29 NMR




- No oxygen in bulk Si-C-X

## Surface and Bulk Structure of Carbon by Raman Spectroscopy



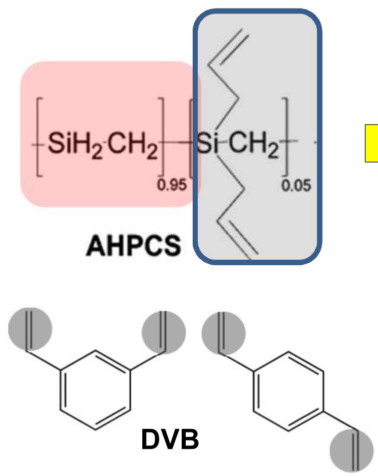

- Probing depth difference by 514nm laser Raman

3C-SiC ~100μ
6H-SiC ~300μ

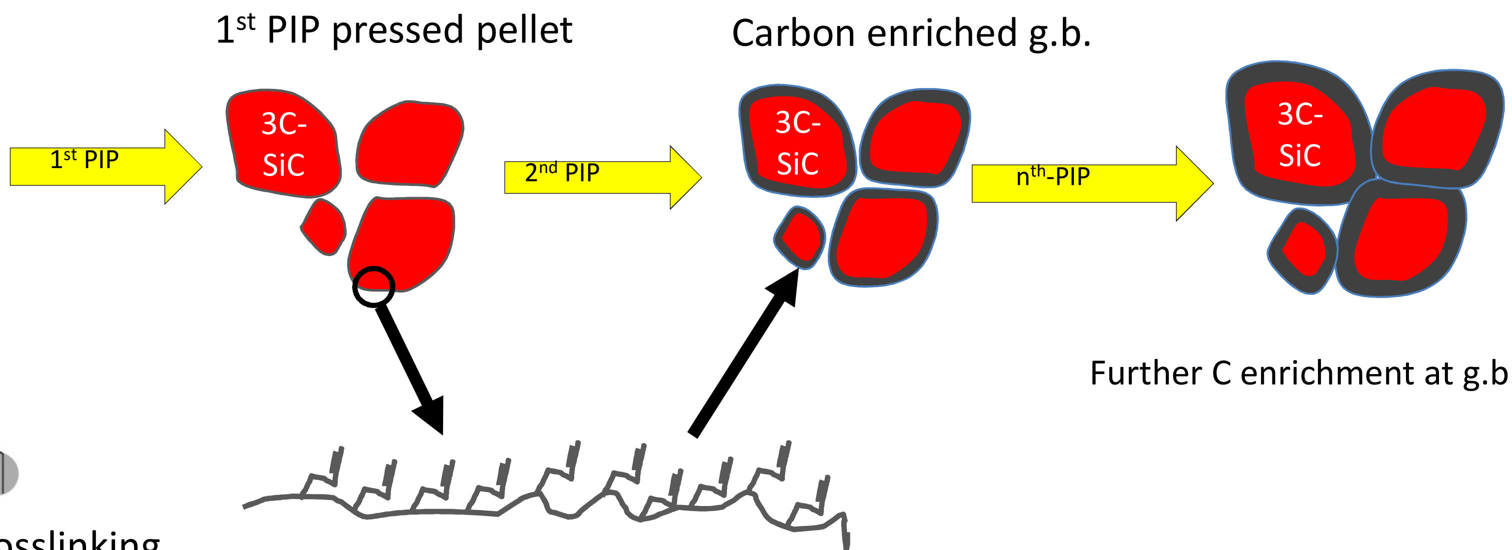
D & G (graphite)~100-200nm

∴ Excess carbon species on surface/grain boundary

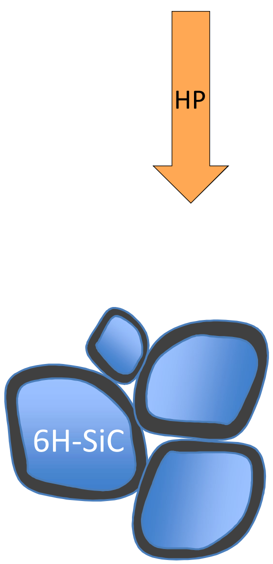
# Process Related Structural Model of Si-C-X



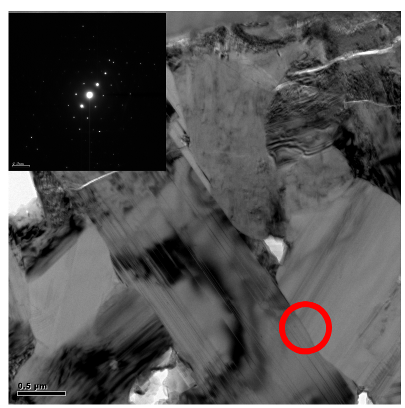

Double bond for crosslinking




Double bonds serve as **reactive functional group**



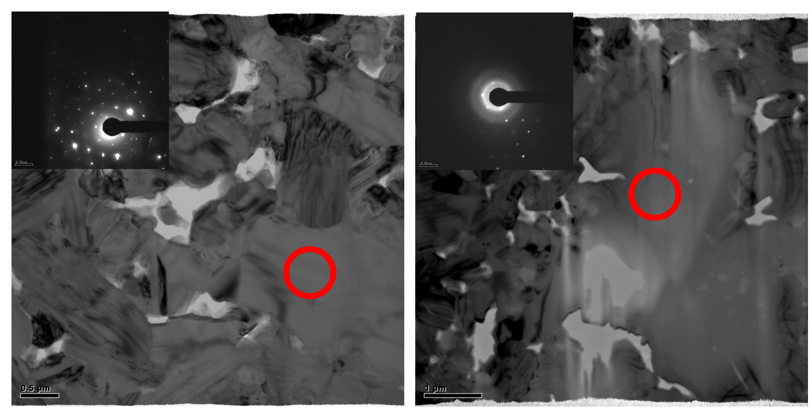

HP(1B0C)



Fully crystallized

vs.

HP(1B5C)

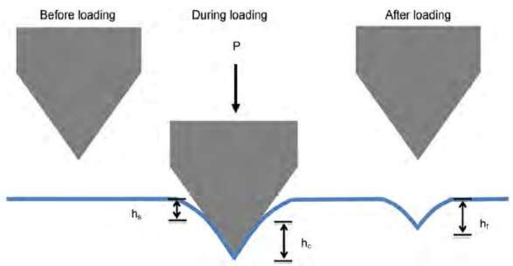


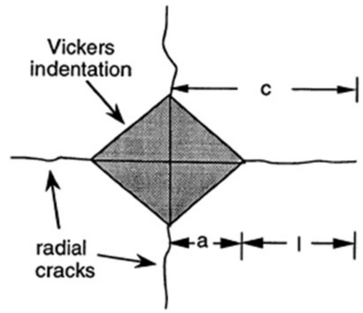
Crystalline phase admixed with amorphous phase

# TASK 2: MECHANICAL AND THERMAL PROPERTIES OF Si-C-X CERAMICS

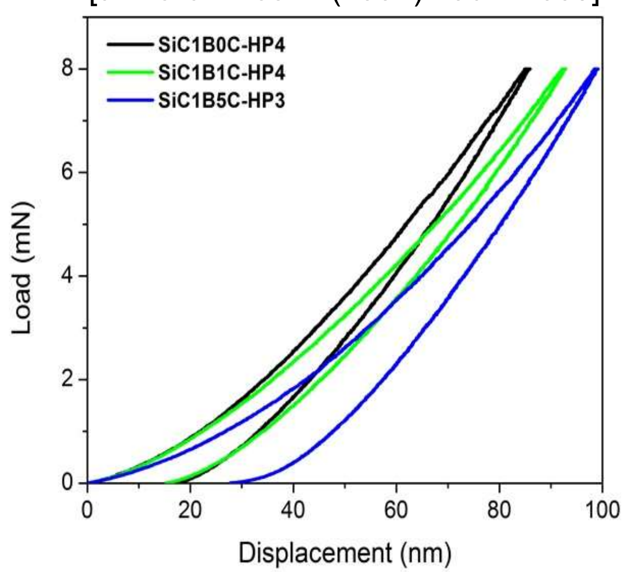
## Modulus, Toughness, Strength and Thermal Diffusivity

### (1) Modulus and Hardness: Indentation

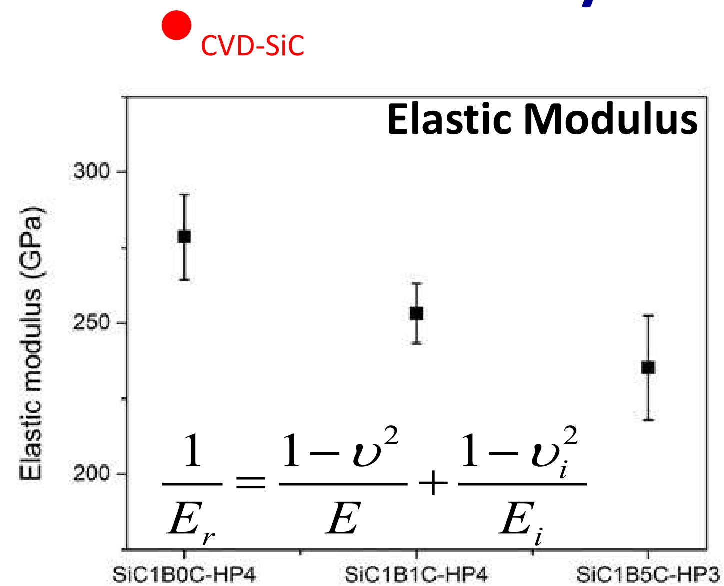


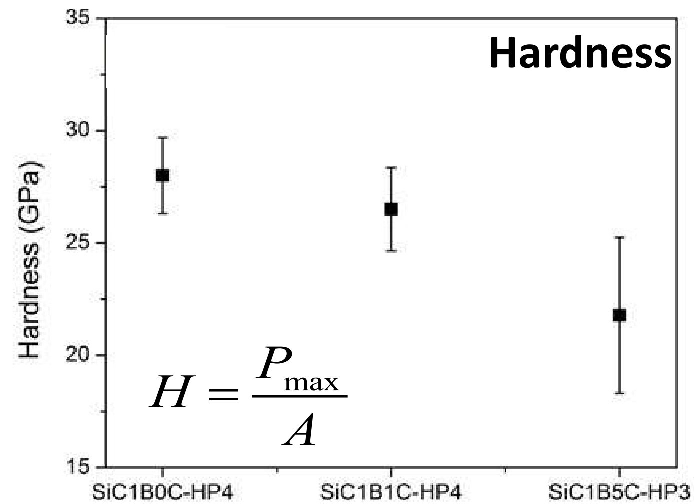




Oliver-Pharr analysis
[J. Mater. Res. 7 (1992) 1564–1583]



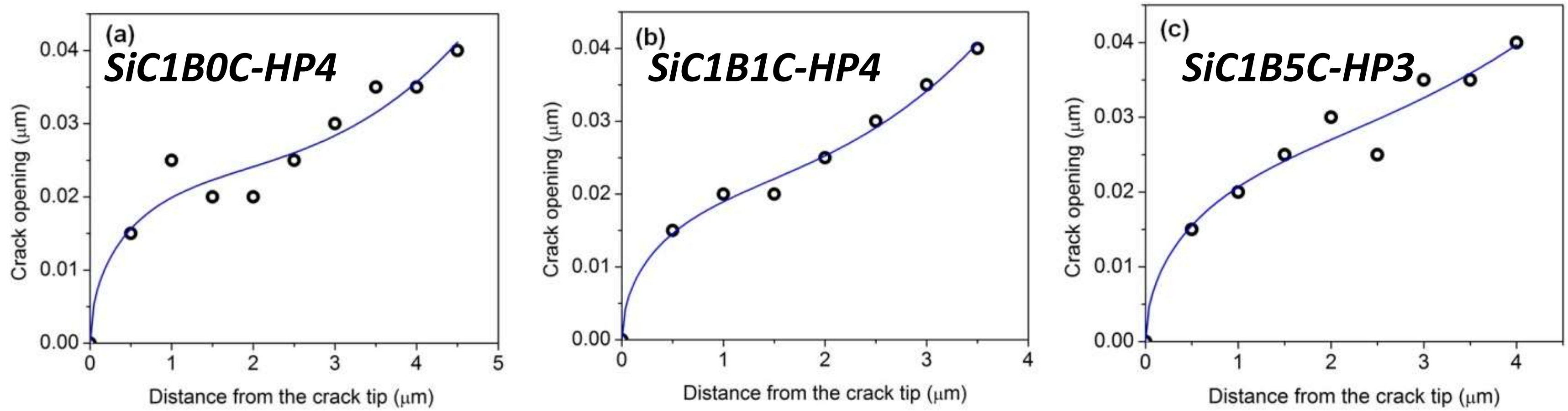


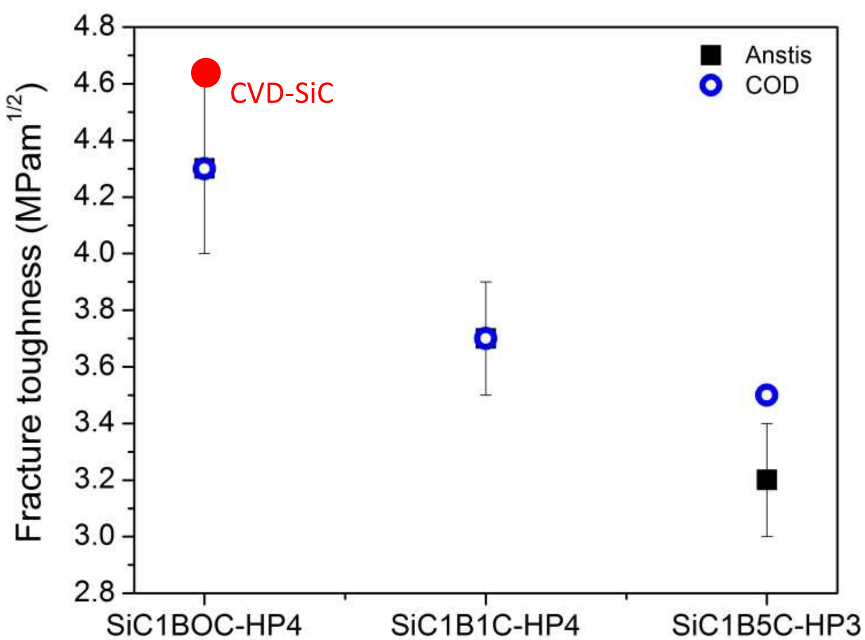


# (2) **Fracture Toughness:** Vicker's indentation

[Lawn, Evans, D.B. Marshall, J. Am. Ceram. Soc. 63 (1980) 574.

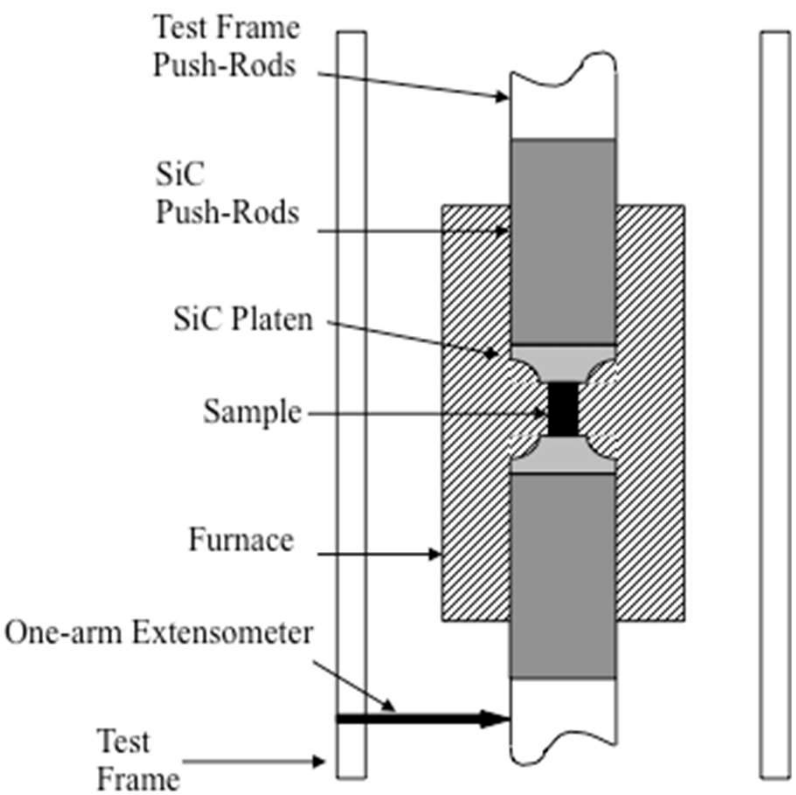


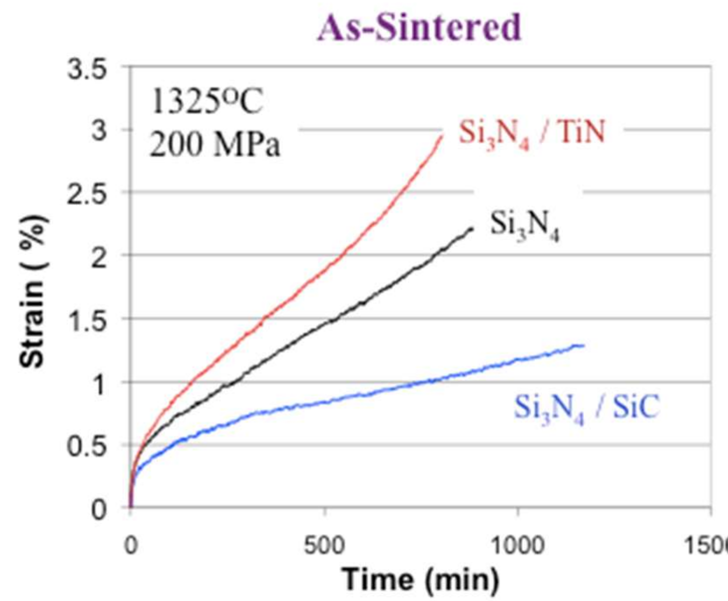



# TASK 2.2: Compressive Creep of Si-C-X Ceramics

**Goal: Effect of temperature and stochiometry on creep resistance of Si-C-X**

Compressive creep




Recent compressive creep results on $Si_3N_4$ matrix composites from our group (unpublished)

**To be completed**

# *TASK 3: ELECTRICAL PROPERTIES OF Si-C-X*

## Our Research Focus:

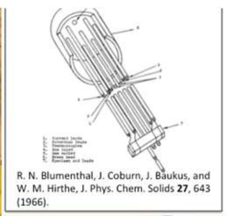
- Conductivity measurements at extreme temperatures.

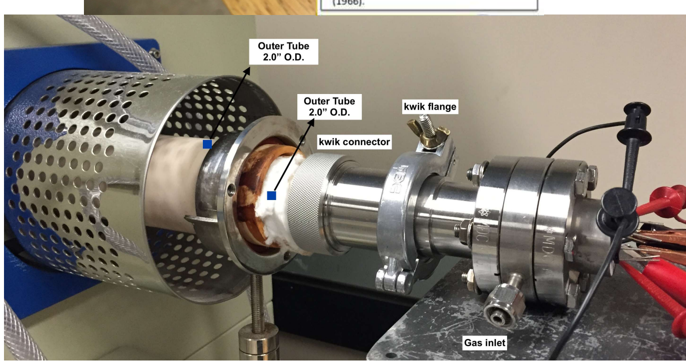
  Development: Pt lead-graphite contact, Kelvin probe method,
  Alternative polarity to avoid capacitance effect.

- Effect of C/Si ratio on the electrical conductivity

  Evaluate whether electrical conductivity of SiC-PDCs is dominated by precipitation of excessive carbon at elevated temperatures

- Create data-base for dc-electrical conductivity of PDC Si-C-X at a wide range of high temperature (RT~1700˚C)



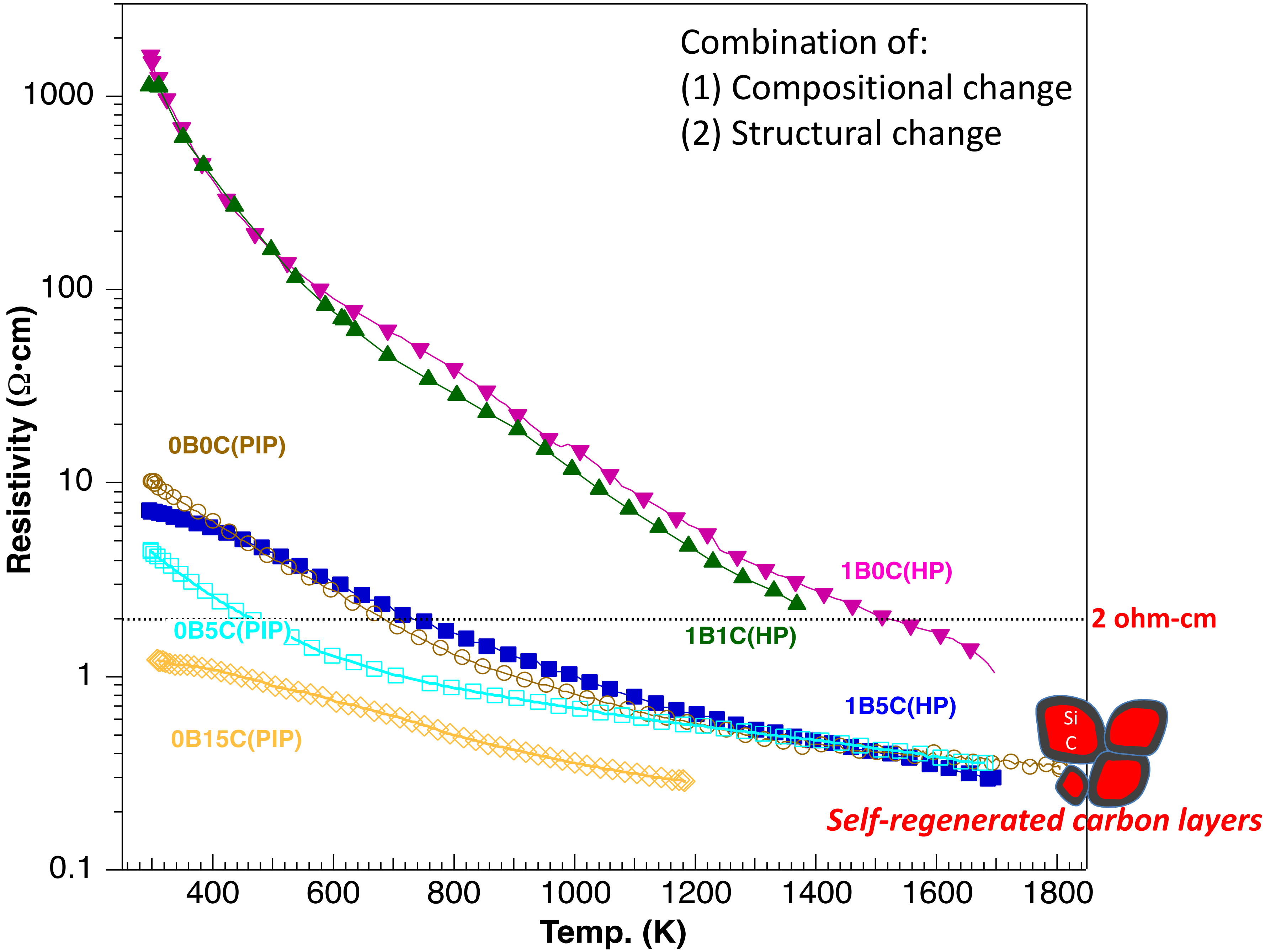




1700°C Tube furnace

Electrometer and current source

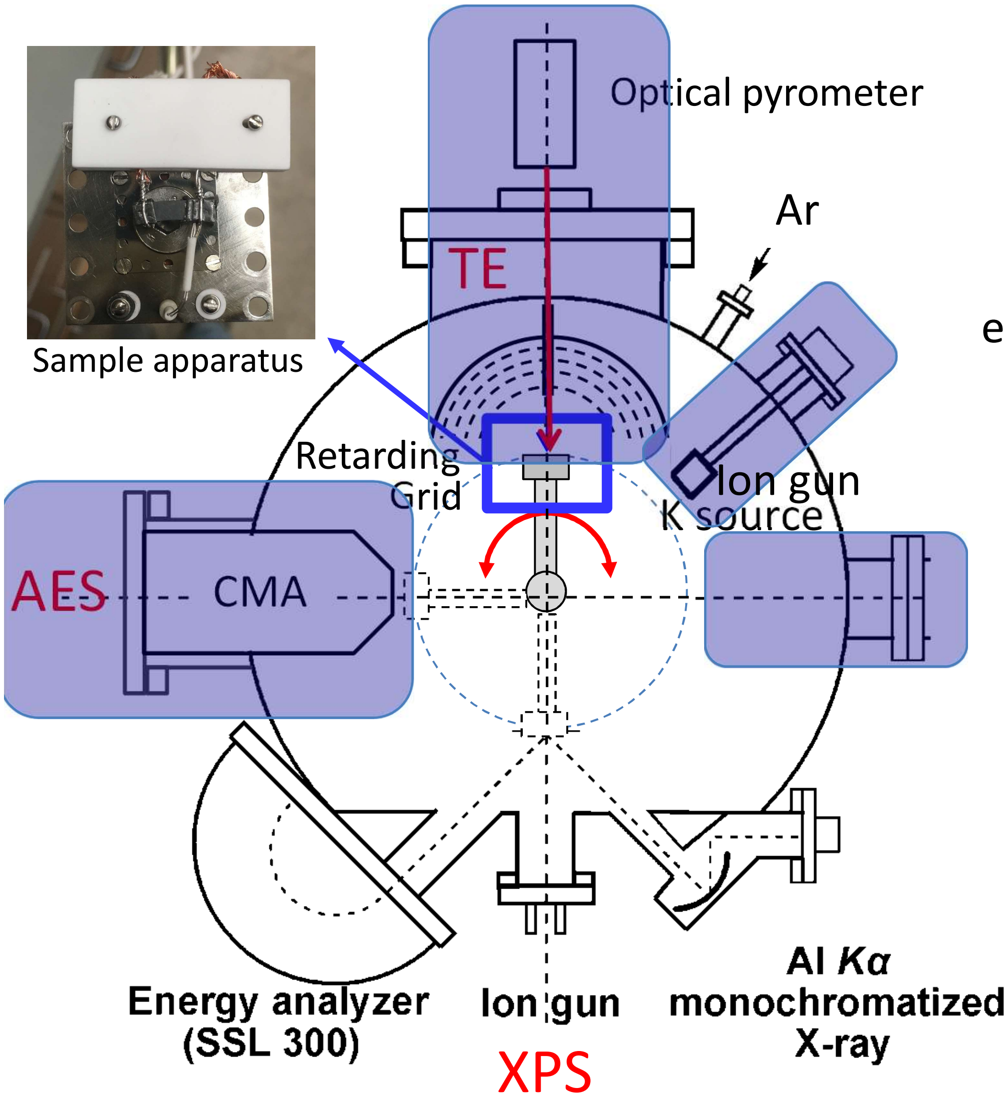
LabVIEW Work station

# Electrical Resistivity Change with T for HP and PIP samples



# TASK 4: SURFACE ENGINEERING OF SI-C-X

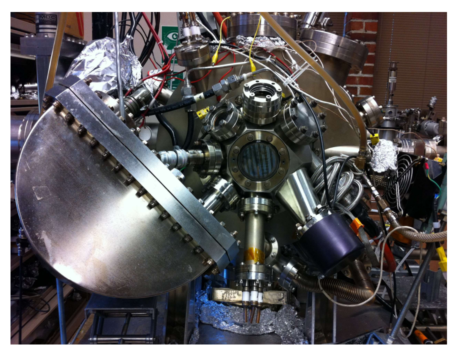
## Integrated Experimental System:

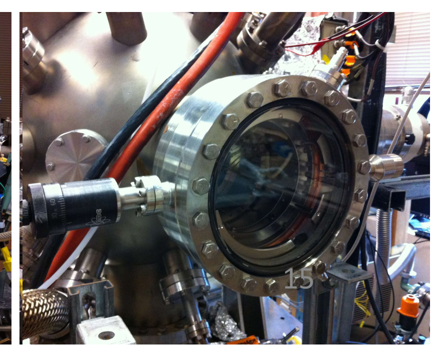



- Retarding grid spectroscopy to measure thermionic emission (**TE**)
- X-ray photoelectron spectroscopy (**XPS**)
- Auger electron spectroscopy (**AES**)
- K deposition for work function engineering
- R-type TC and optical pyrometer for temperature measurement
- Ion gun for surface cleaning

## Capable of measuring:

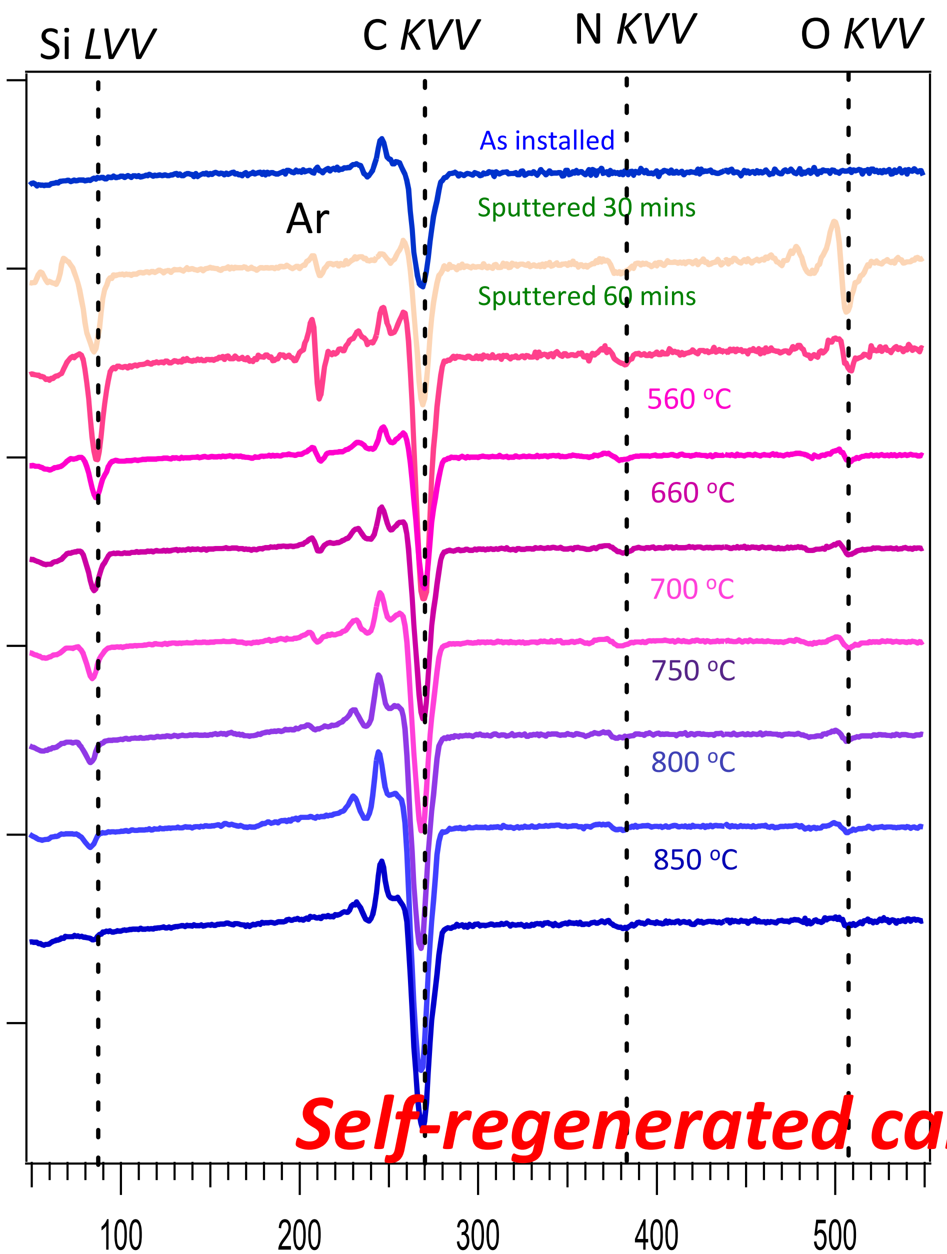
- Surface composition at elevated temp.
- Total current and kinetic energy distribution of thermionic emission.

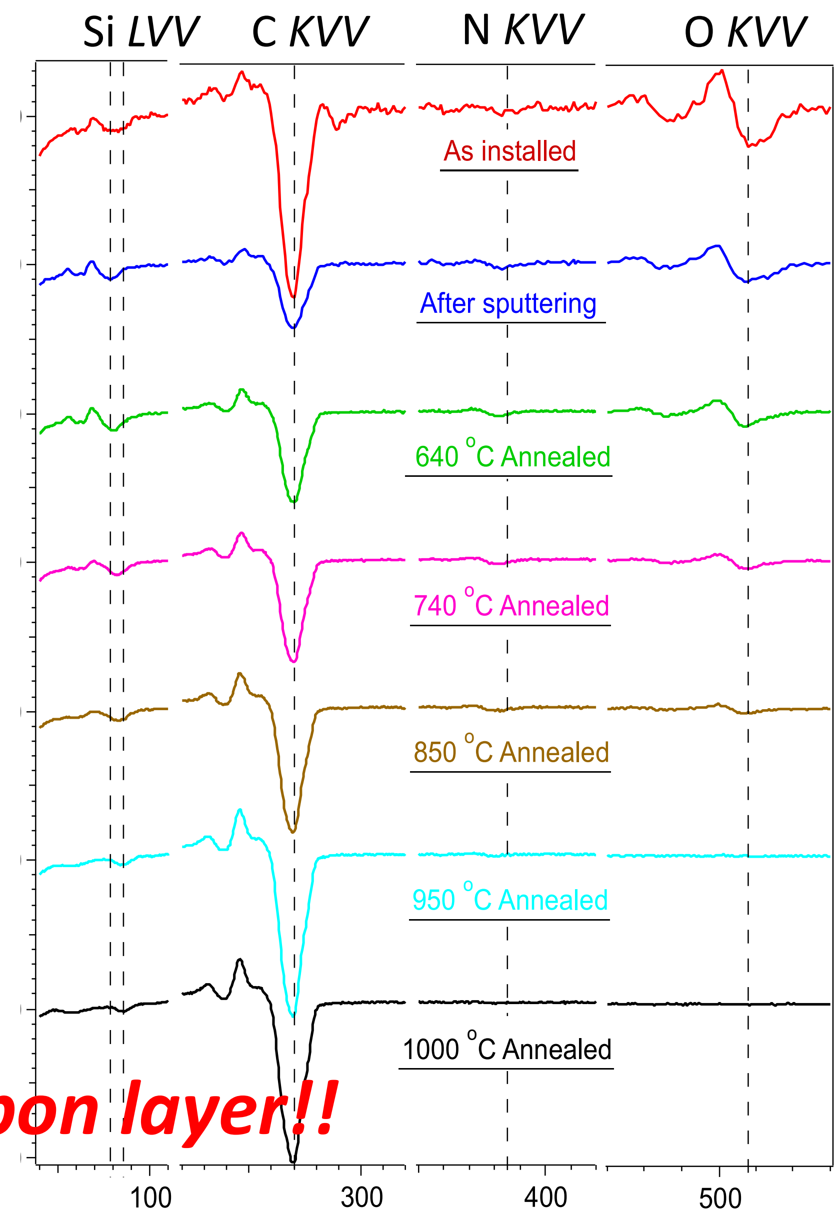




# Dynamic Changes of the Surface Composition with T

**Sample: 1B5C(HP)** | **Sample: 0B0C(PIP)**

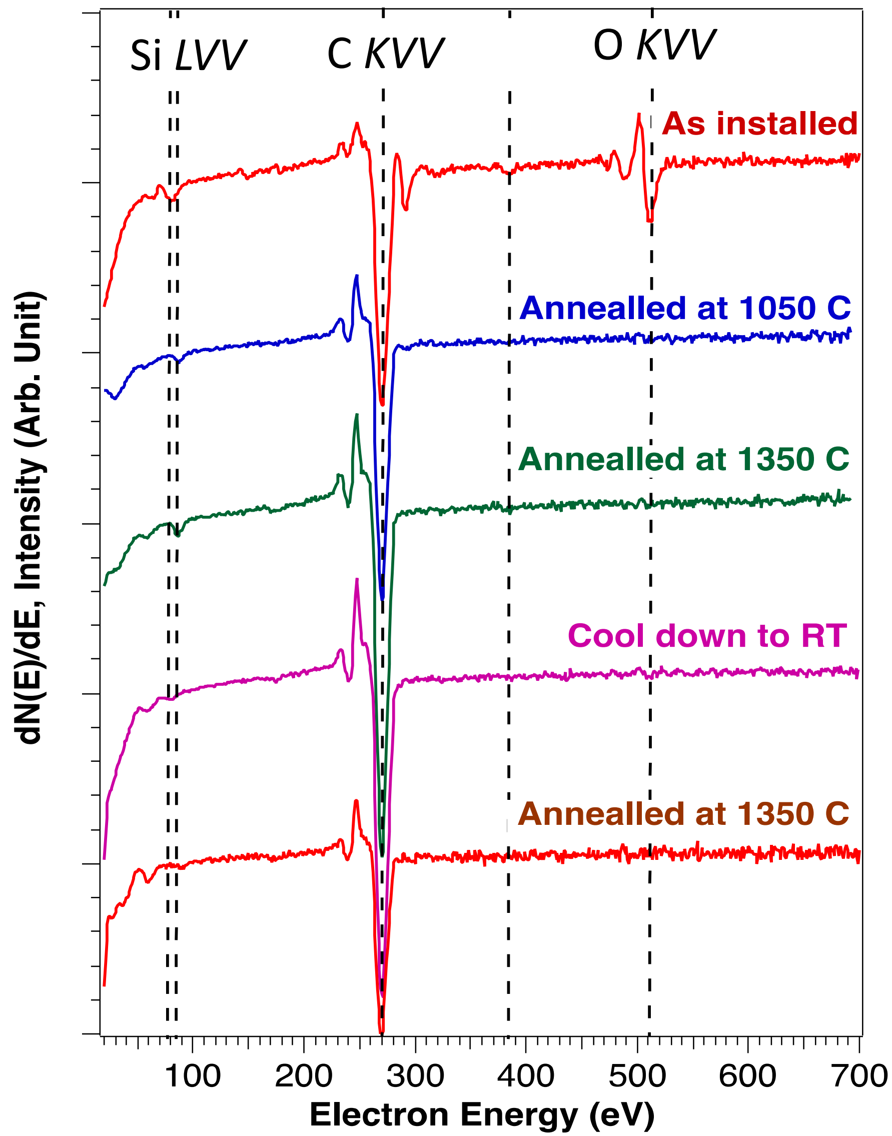


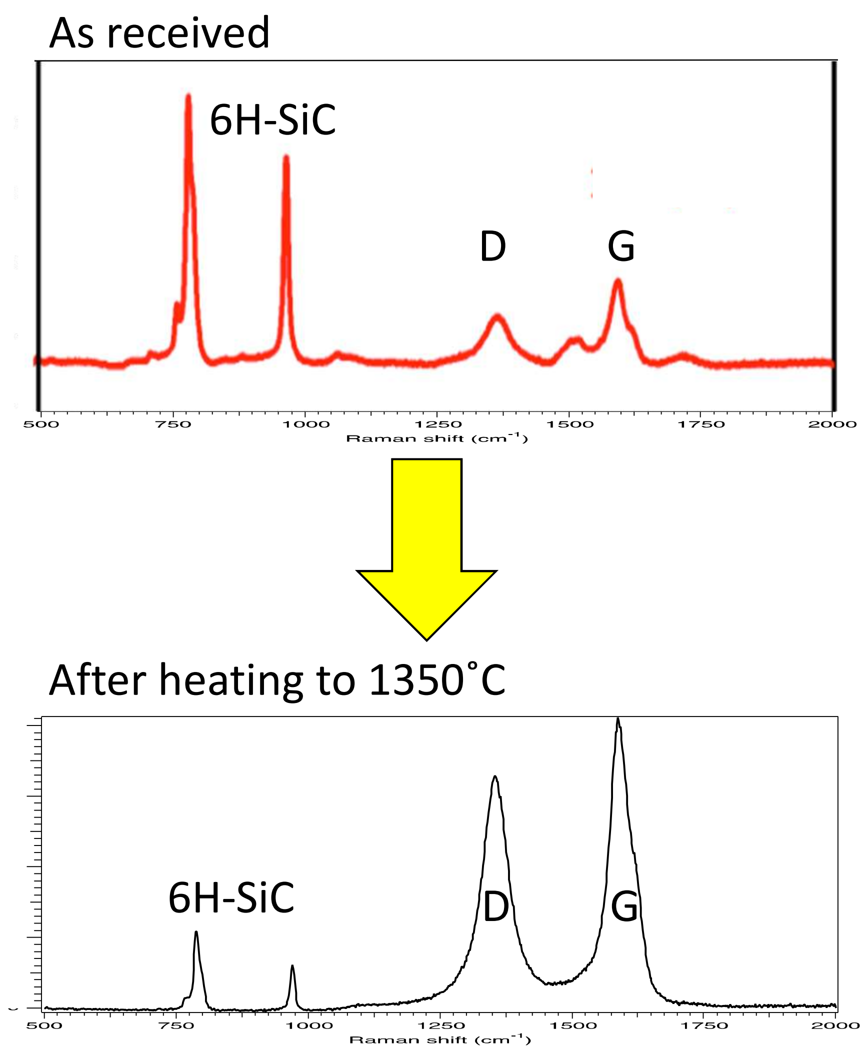

**Self-regenerated carbon layer!!**

# Dynamic changes of the Surface Structure with T

Auger Surface Composition with T



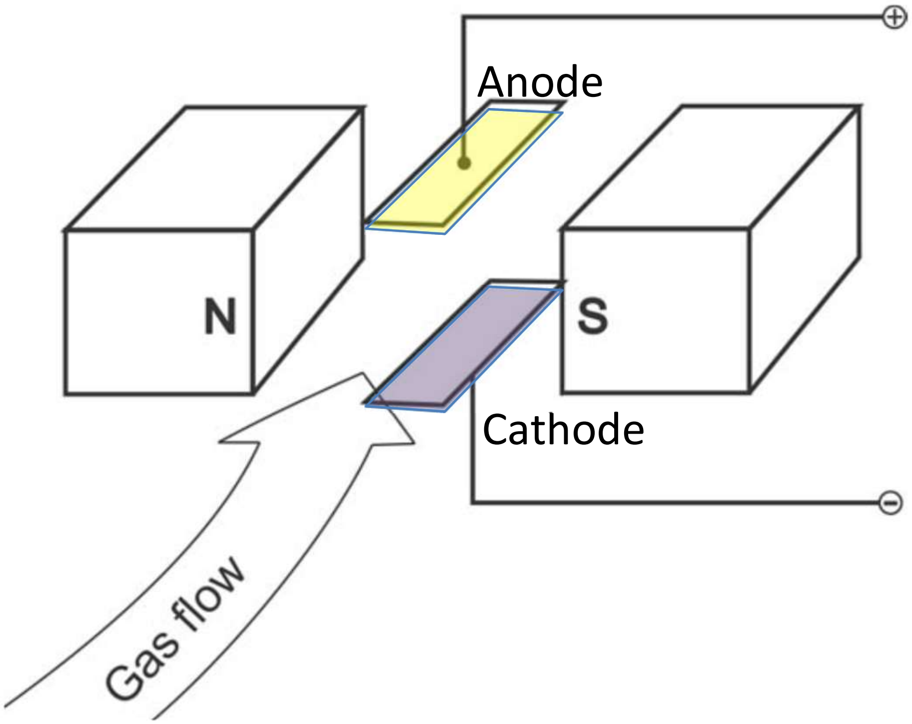

Raman Molecular Structure

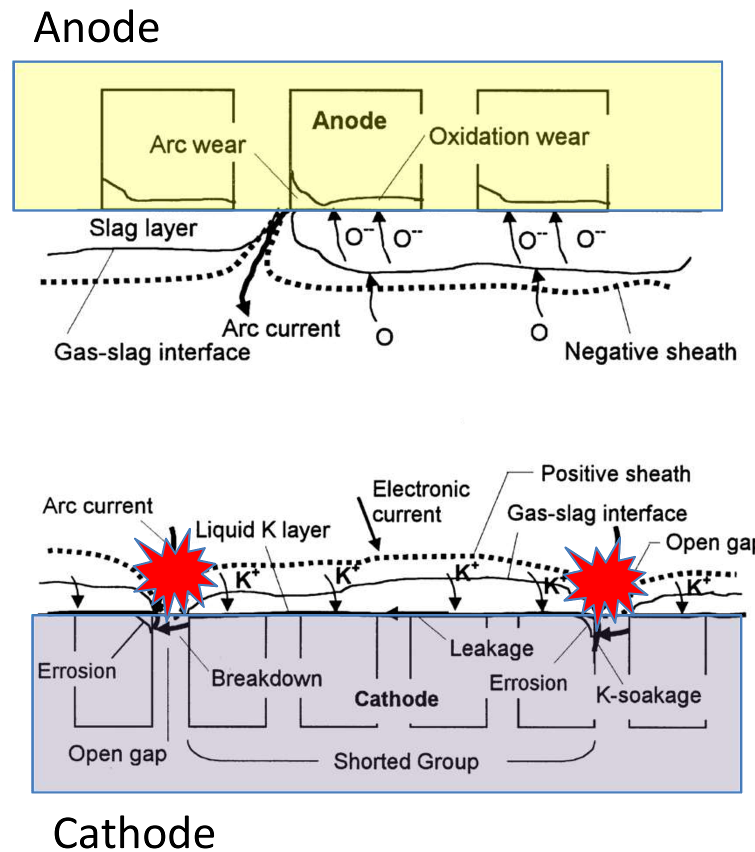



**Sample: 1B1C (HP)**

# *A common failure reason for MHD channel electrodes*

## *Electrical Arcing  or Electrical Discharge*



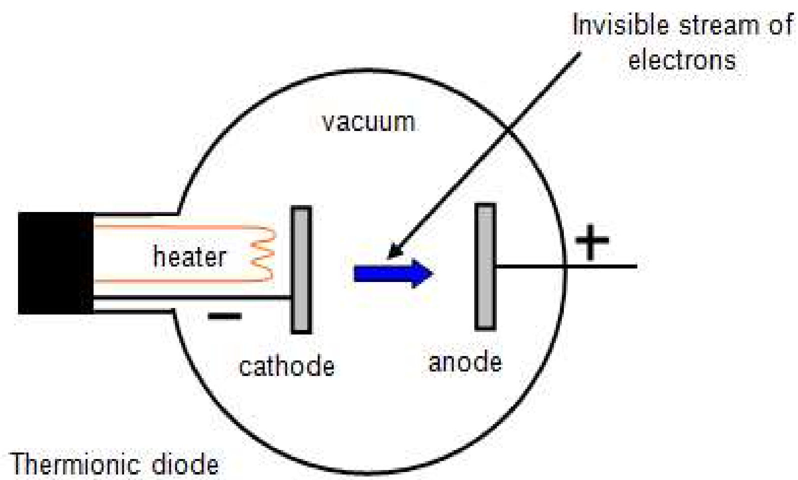



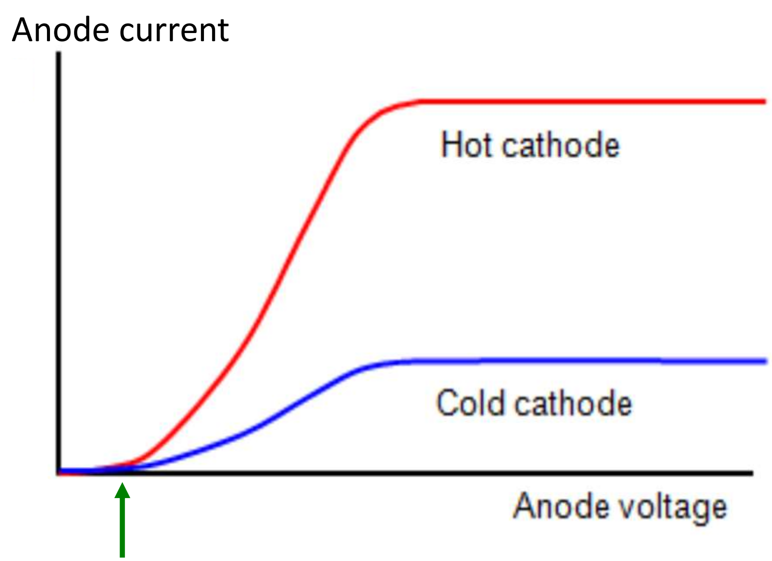

**Solution**: Thermally emit accumulated charge

- Workfunction determines thermionic emission.

# *Thermionic emission (TE) Properties*

## Principle of Thermionic Emission

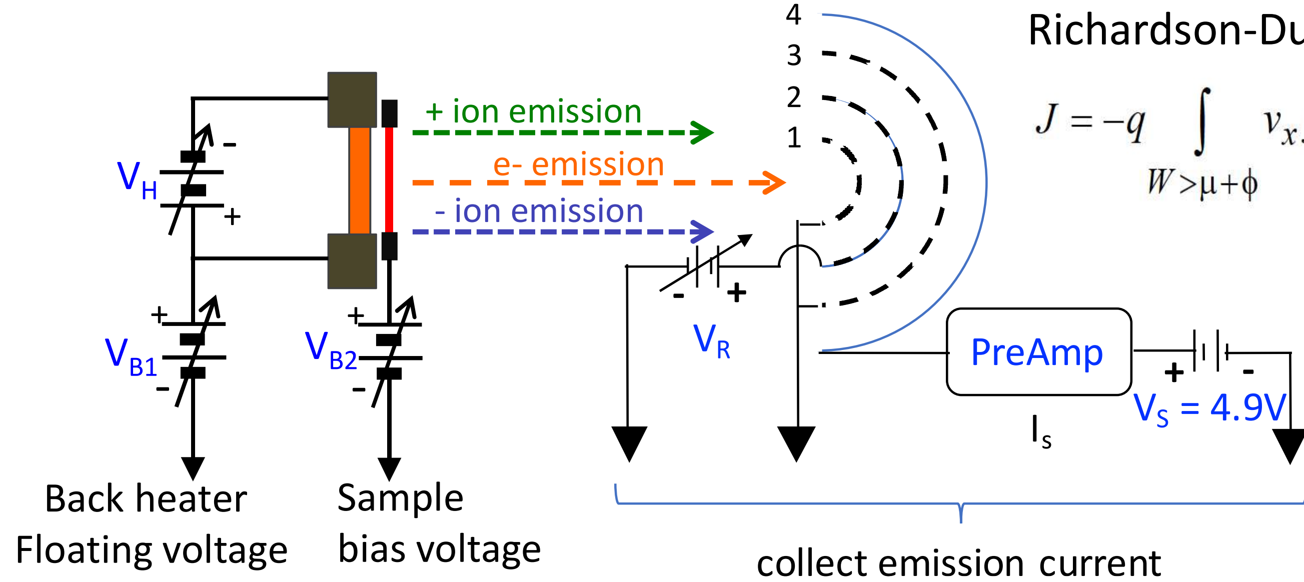



## Experimental challenge:

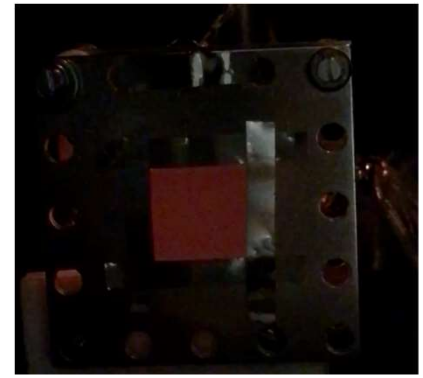
- Emission consists of thermionic emission of electrons, positive/ negative ions at elevated temperatures.
- How do you separate contribution of each emission?
- How do you count the change of the surface composition at elevated temperatures?

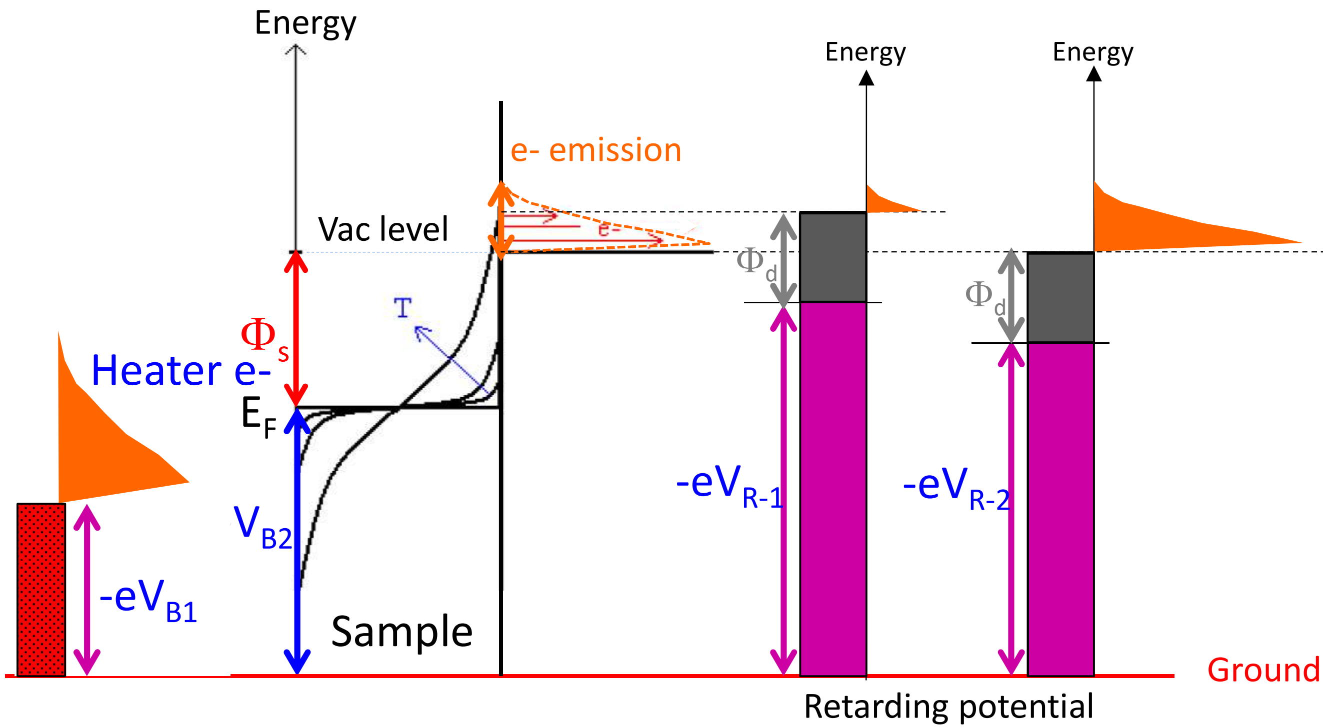
# *Physics of Thermionic Emission Measurement*

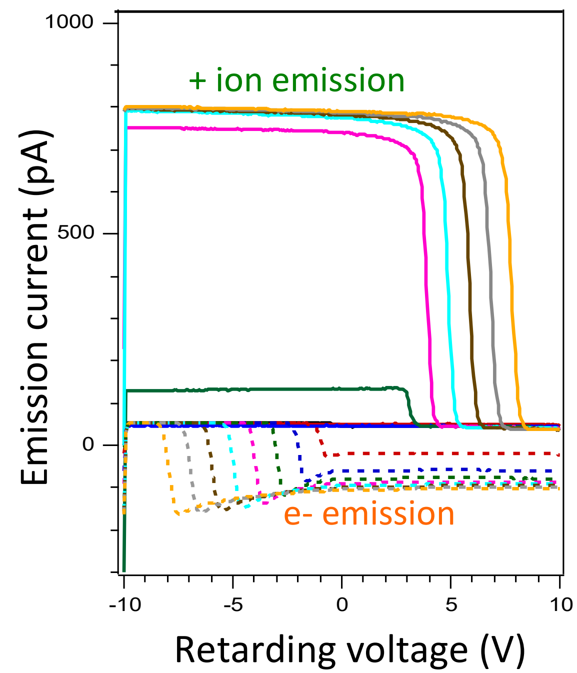



Richardson-Dushmann's TE formula

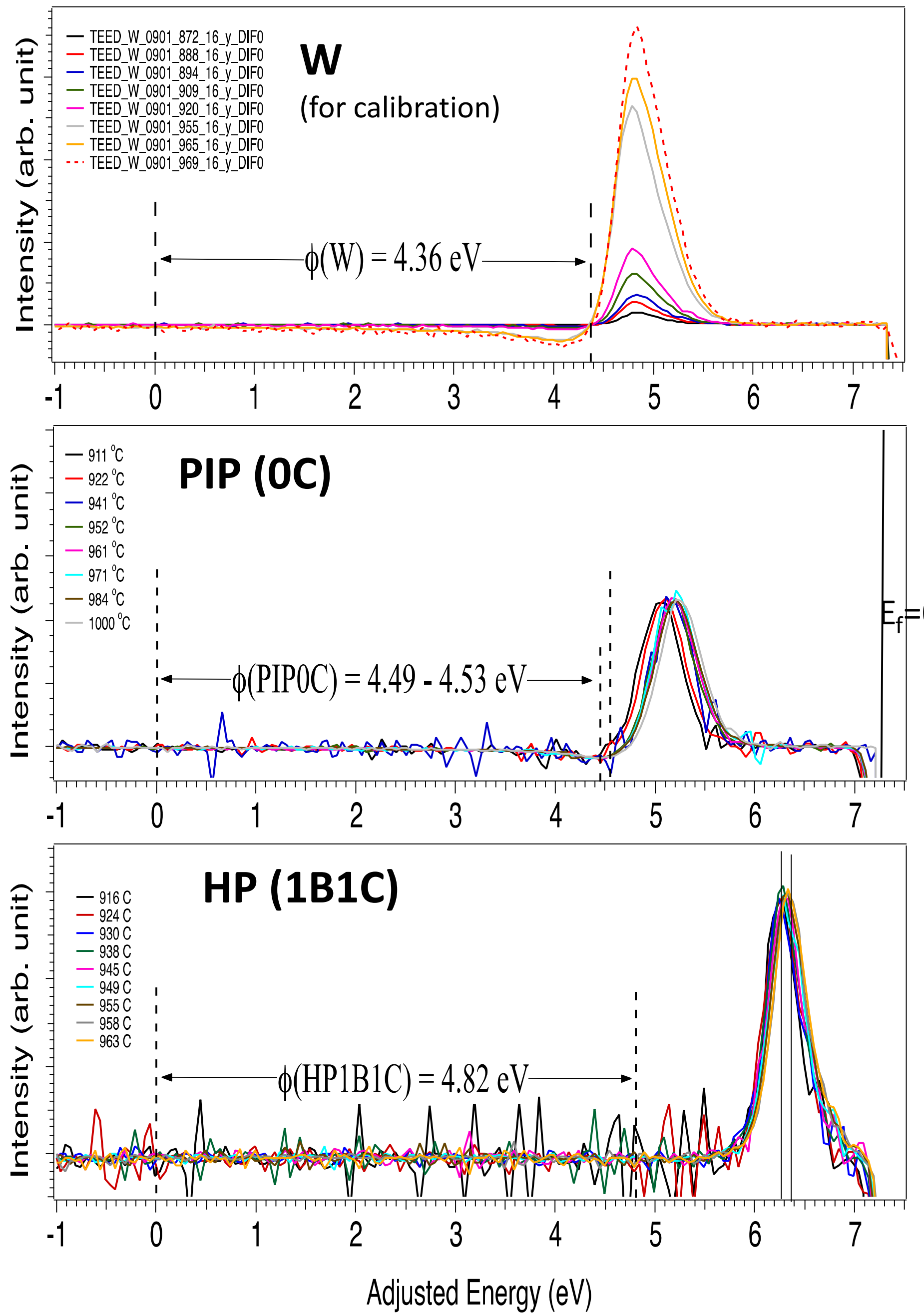
$$J = -q \int_{W>\mu+\phi} v_x f(k) \frac{d\mathbf{k}}{4\pi^3} = \frac{m k_B^2 q}{2\pi^2 \hbar^3} T^2 \exp\left\{\frac{-\phi}{k_B T}\right\}$$

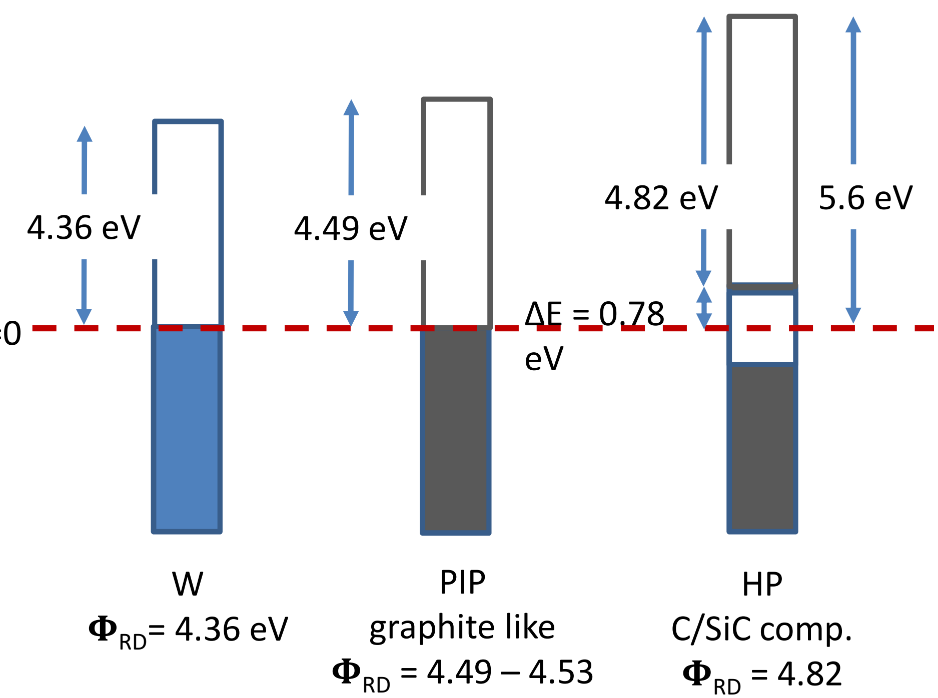




# *Thermionic Emission of Si-C-X*



# *Summary of this project*

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

  Two routes: Hot-pressed and Polymer Infiltration
- Thermo-mechanical properties decrease with C content
- 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.
- Comprehensive understanding of polymer derived Si-C-X on high-temperature thermo-mechanical-structural-electrical-surface properties through this project.

Thanks to DOE for financial support.