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

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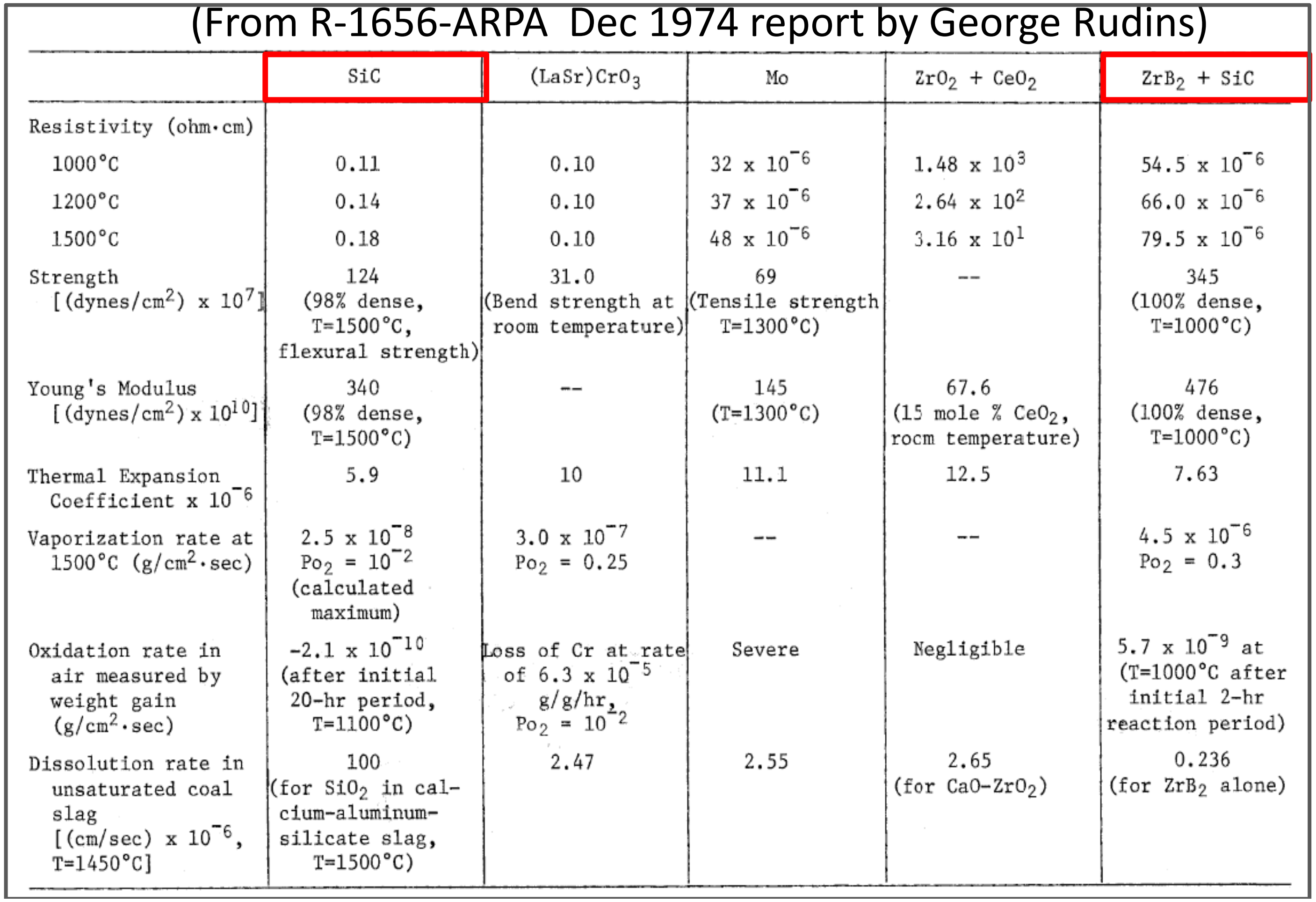
Rationale/Introduction

- Limited choice of electrode materials in contact with the high temperature plasma and harsh environment in MHD.
- These materials are subjected to stresses of mechanical, thermal chemical and electromagnetic nature.

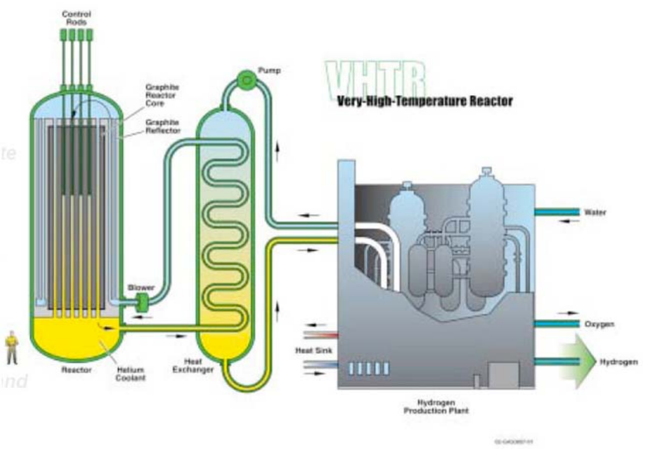


(From R-1656-ARPA Dec 1974 report by George Rudins)

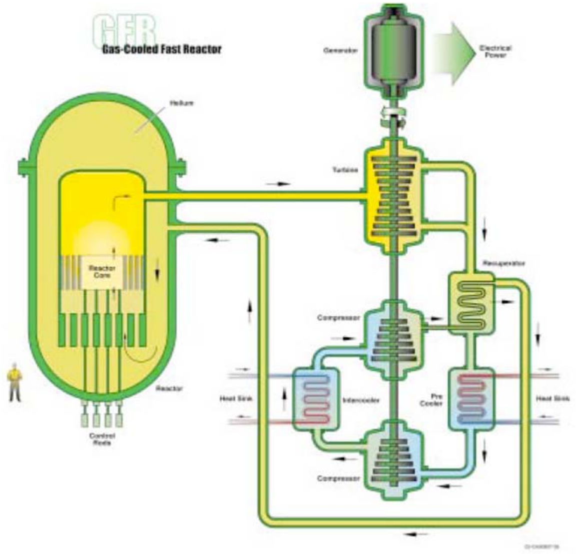
	SiC	(LaSr)CrO_3	Mo	ZrO_2 + CeO_2	ZrB_2 + SiC
Resistivity (ohm·cm)					
1000°C	0.11	0.10	32×10^{-6}	1.48×10^{3}	54.5×10^{-6}
1200°C	0.14	0.10	37×10^{-6}	2.64×10^{2}	66.0×10^{-6}
1500°C	0.18	0.10	48×10^{-6}	3.16×10^{1}	79.5×10^{-6}
Strength [(dynes/cm^2) x 10^7]	124 (98% dense, T=1500°C, flexural strength)	31.0 (Bend strength at room temperature)	69 (Tensile strength T=1300°C)	--	345 (100% dense, T=1000°C)
Young's Modulus [(dynes/cm^2) x 10^{10}]	340 (98% dense, T=1500°C)	--	145 (T=1300°C)	67.6 (15 mole % CeO_2, rocm temperature)	476 (100% dense, T=1000°C)
Thermal Expansion Coefficient x 10^{-6}	5.9	10	11.1	12.5	7.63
Vaporization rate at 1500°C (g/cm^2·sec)	2.5×10^{-8} $Po_2 = 10^{-2}$ (calculated maximum)	3.0×10^{-7} $Po_2 = 0.25$	--	--	4.5×10^{-6} $Po_2 = 0.3$
Oxidation rate in air measured by weight gain (g/cm^2·sec)	-2.1×10^{-10} (after initial 20-hr period, T=1100°C)	Loss of Cr at rate of 6.3×10^{-5} g/g/hr, $Po_2 = 10^{-2}$	Severe	Negligible	5.7×10^{-9} at (T=1000°C after initial 2-hr reaction period)
Dissolution rate in unsaturated coal slag [(cm/sec) x 10^{-6}, T=1450°C]	100 (for SiO_2 in calcium-aluminum-silicate slag, T=1500°C)	2.47	2.55	2.65 (for CaO-ZrO_2)	0.236 (for ZrB_2 alone)

SiC and SiC-composites

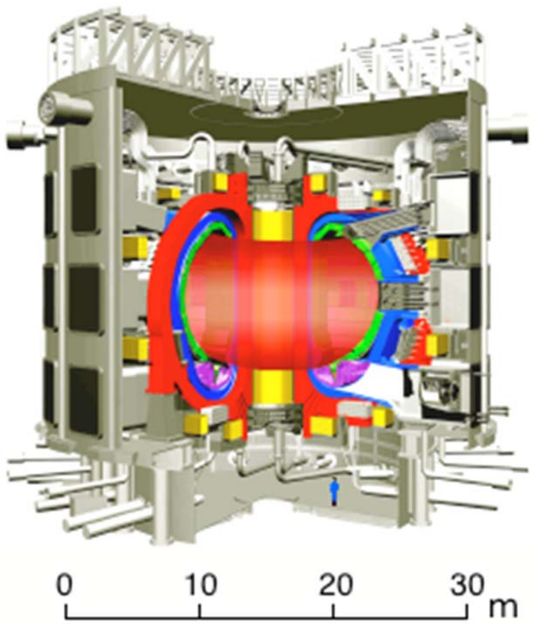
Advanced structural and functional materials
that are used in extreme conditions.



VHTR
(Very High Temp Reactor)
- Control rods
- Control rod supports



GFR
(Gas-cooled Fast Reactor)
- Core structures
- Fuel pins



Fusion
- Blanket structures
- Blanket channel liners

SiC-composites (Si-C-X form) as a new class of materials for MHD electrode applications

Overall 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.

Questions to be asked:

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

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.

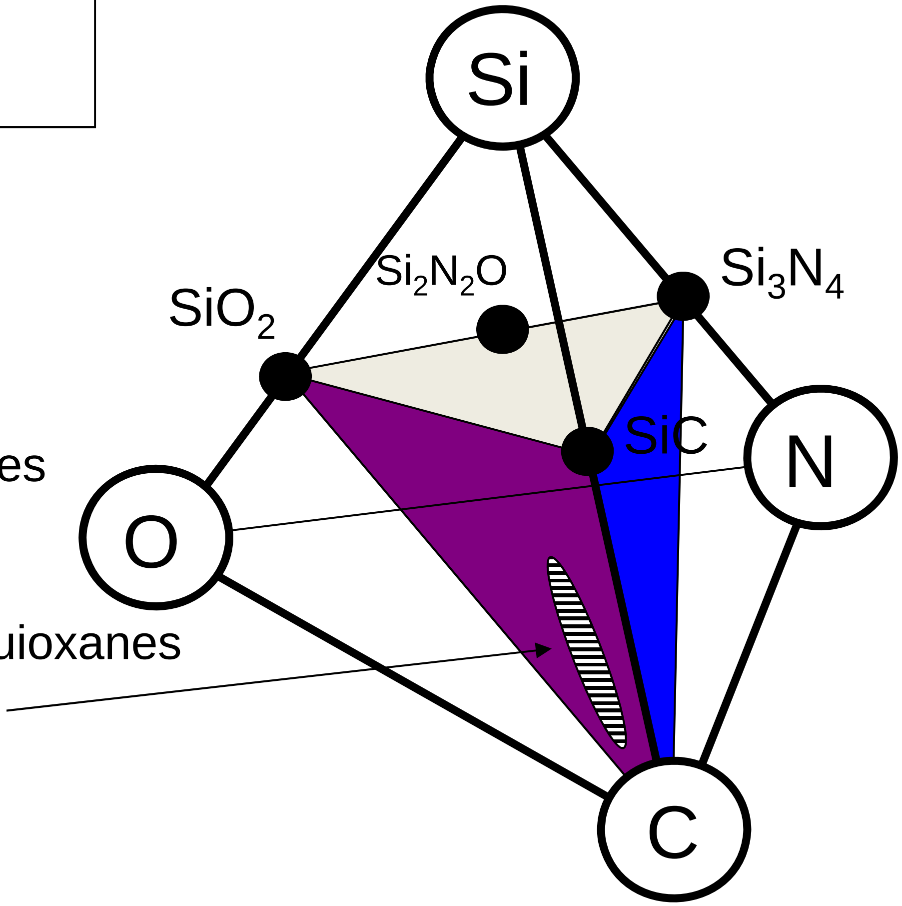
Lead: Prof. F. Ohuchi

Sub-Task 4.3: Simulation of plasma interactions

Si-Based Polymeric Precursors for Ceramics

R: $-CH_3$,
$-C_6H_5$,
$-CH=CH_2$
....

Polysilanes
$[-R_2Si-]$



Polysiloxanes
$[-R_2SiO-]$

Polysilsesquioxanes
$[-RSiO_{1.5}-]$

Polysilazanes
$[-R_2SiNH-]$

Polysilsesquiazanes
$[-RSi(NH)_{1.5}-]$

Polysilylcarbodiimides
$[-R_2Si(N=C=N)-]$

Polysilsesquicarbodiimides
$[-RSi(N=C=N)_{1.5}-]$

Polycarbosilanes
$[-R_2SiCH_2-]$, $[-R_2SiC\equiv C-]$

Polymer Derived Ceramics

Advantages over traditional methods

- Liquid state polymers--ease of processing
- High purity and well mixed reactants
- Relatively low processing temperature (800-1500C)
- Unusual nanostructures: amorphous and nano-domains
- Ability to make metabstable compositions (ceramic alloys)
- Broad range of polymers commercially available
- Tailorable composition, microstructure and properties

Limitations

- Shrinkage upon pyrolysis
- Pore formation
- Defects and cracks

X

Fillers to occupy the space
Near net shape fabrication

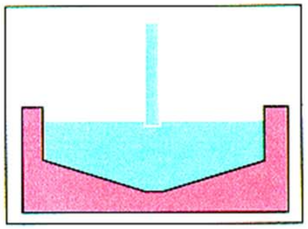
Si-C-X

Polymer Derived Ceramics

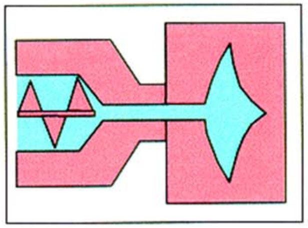
The PDC Society

•Community •Technology •Science

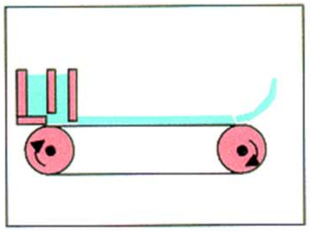
Casting



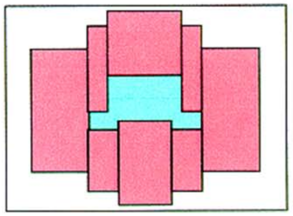
Injection Molding



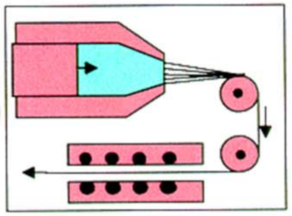
Tape Casting



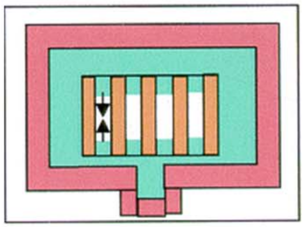
Pressing



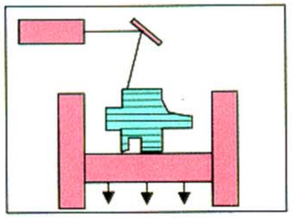
Fiber Drawing



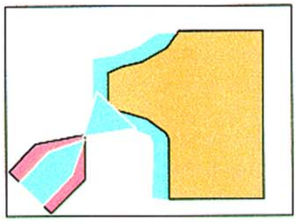
Impregnation



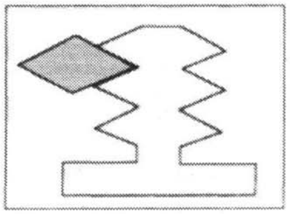
Rapid Prototyping



Coating

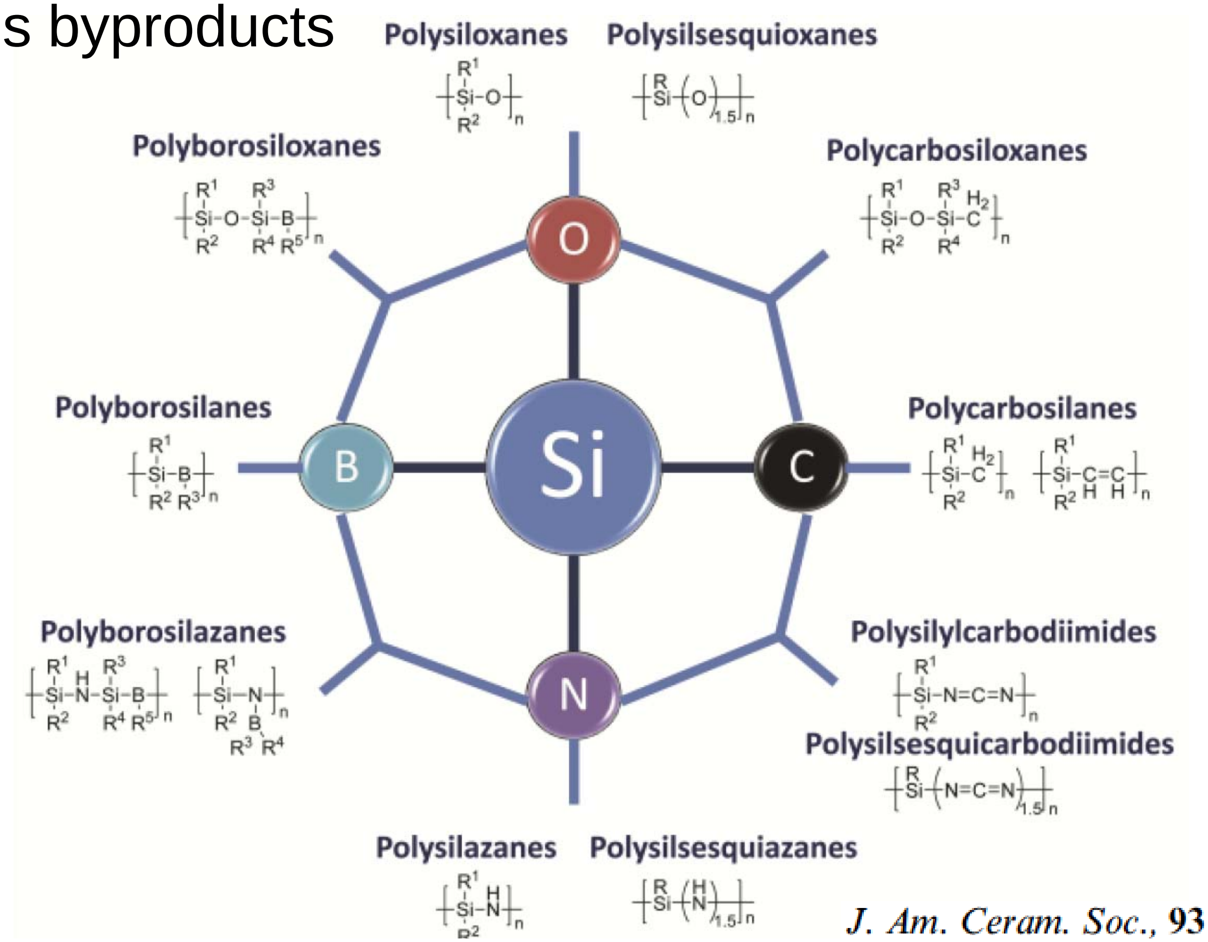


Machining



Criteria for Selection of Si-based Preceramic Polymers

- High ceramic yield on pyrolysis
- Relatively low pyrolysis temperature
- Polymer must be soluble or liquid
- Phase formed upon pyrolysis
- Pyrolysis byproducts

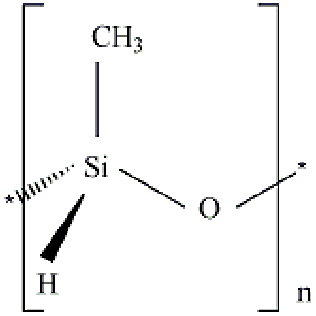


J. Am. Ceram. Soc., **93** [7] 1805–1837 (2010)

Polymers Investigated in Our Group

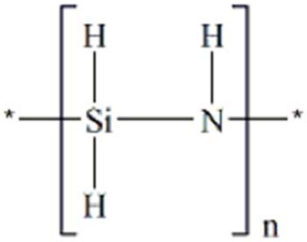
Polymer I: Poly(hydromethylsiloxane) (PHMS)

- High ceramic yield: >85% when pyrolyzed <800C
- Liquid form: viscosity ~1.2 cP, ideal for coating processing
- In-situ crosslinking: @150C in humid air



Polymer II: Perhydropolysilazane (PHPS)

- Liquid form: low viscosity ~1.0 cP, ideal for coating processing
- Crosslinking: @170C in air
- Conversion to ceramic at low temperature (400 – 1000 C)

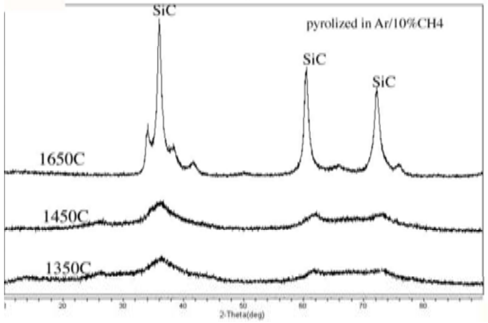


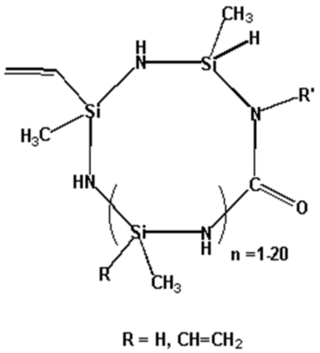
Polymer III: Polysilazanes (Ceraset^{SN})

- Low viscosity thermoset liquid polymer
- Low oxygen content
- Pyrolysis in N_2/NH_3 Si_3N_4

  in Ar/CH_4 SiC

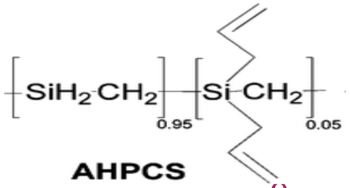
  in air $SiC_xN_yO_z$





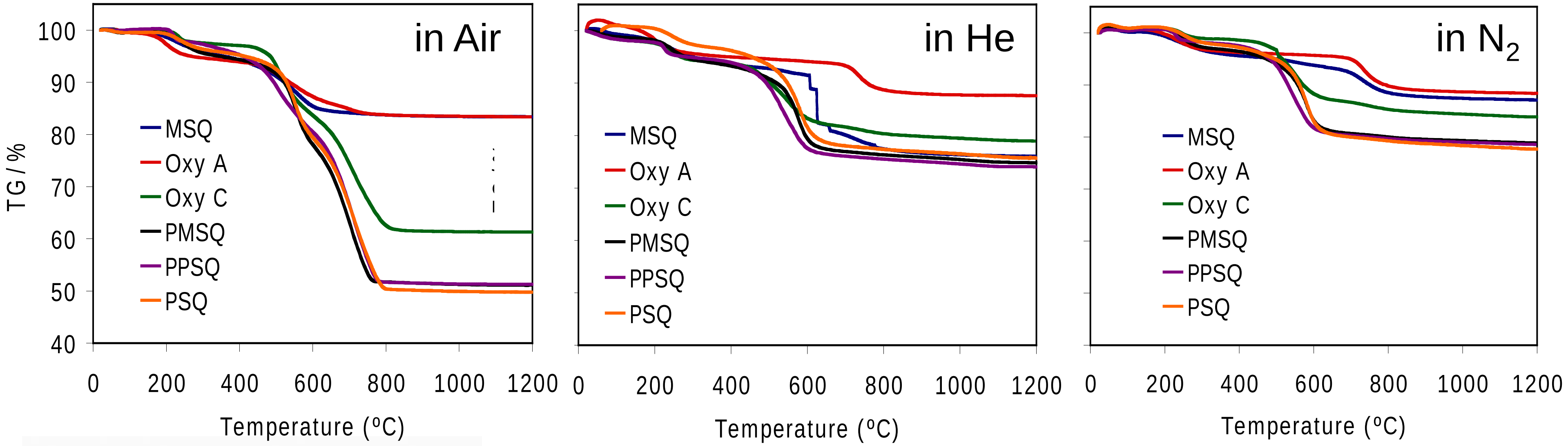
Polymer IV: Polycarbosilane (Starfires SMP-10)

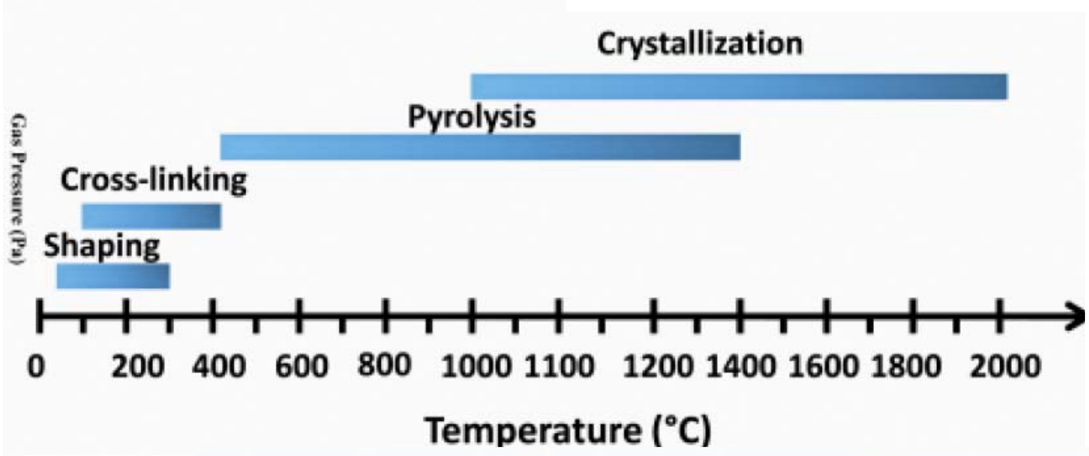
- Precursor for Si:C=1:1



Polymer to Ceramic Conversion

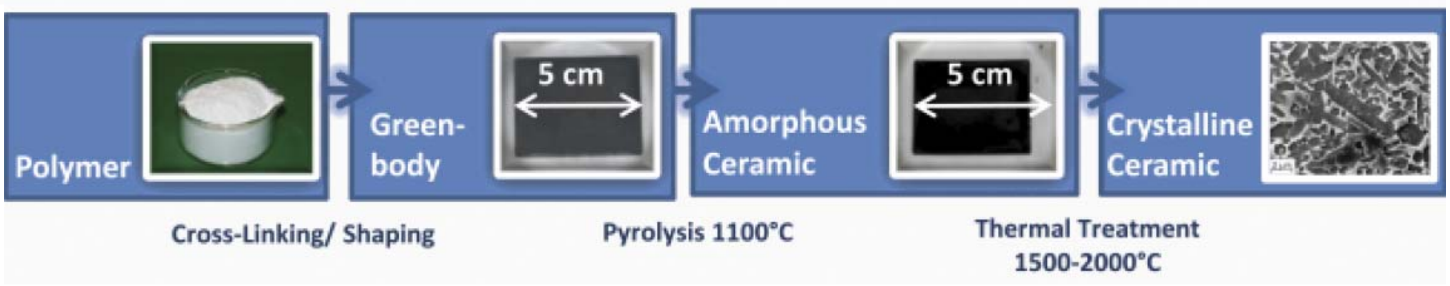
(Data from Thermo-Gravimetric Analysis)





Ceramic Yield:

$$\alpha^P = \frac{mass_{pyrolyzed\ ceramic}}{mass_{polymer\ precursor}}$$

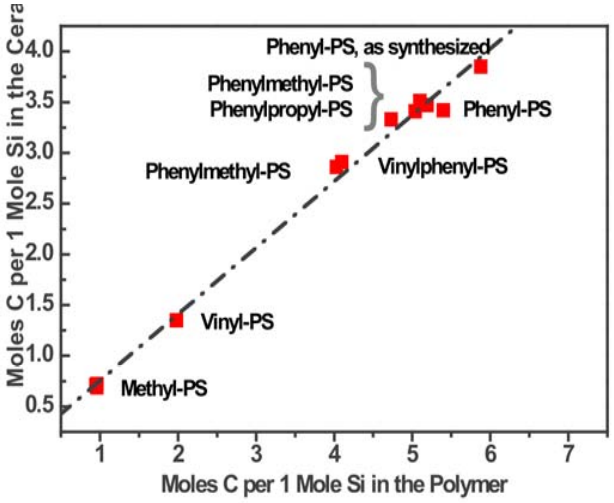


TASK 1: PROCESSING OF SI-C-X CERAMICS

Task 1.1: Effect of Stoichiometry and Temperature on the Nanostructure

Poly(silsesquioxanes) family $[RSiO_{1.5}]_n$

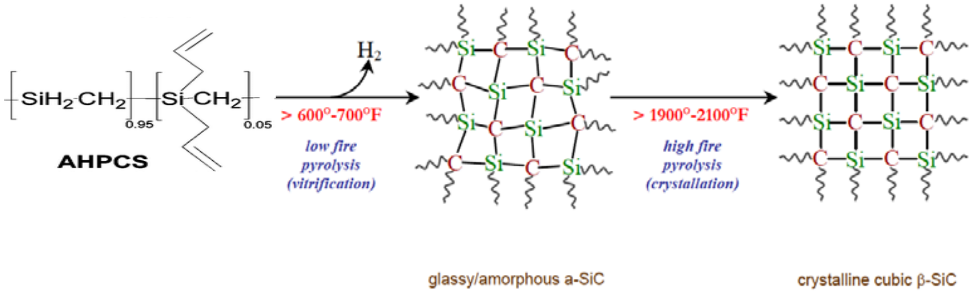
One-to-one correlation between the C/Si ratio in precursor and ceramic.



Will look at ***Polycarbosilane*** family in this project

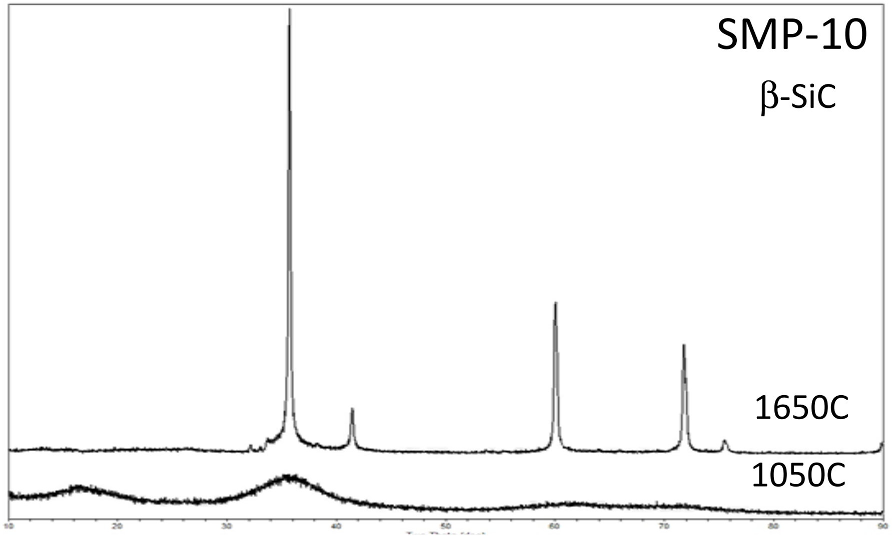
Precursors: Starfire® System's SMP series

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



Preliminary result

Polymer (SMP-10) to β-SiC conversion



Specific Research Plan for Processing of Precursor Derived SiC_{1+x}

Step-1: Modification of the precursor

- A common sintering aid for SiC is Boron: Molecularly add B to the SMP-10 polymer using Deca-borane ($B_{10}H_{14}$)
- Molecularly add excess carbons using Divinylbenzene (DVB)

Step-2: Generation of the powders

- Cross link the modified precursors (with varying C and B contest), and convert to a ceramic powder by heat treatment in inert environment to 1000 ^{0}C

Step-3: Processing of Dense Ceramics

- Three different approaches to make dense ceramics
  - Pressure-less sintering
  - Hot pressing
  - Field assisted sintering

Modification of Polymer
SMP-10 with $B_{10}H_{14}$ and DVB

⇩

Crosslinking
Precursor in furnace to 400˚C

⇩

Milling
in glove box for 30 min.

⇩

Pyrolysis
in controlled environment
to 1000˚C

⇩

Attrition Milling
400 rpm, 2 hours with hexane

⇩

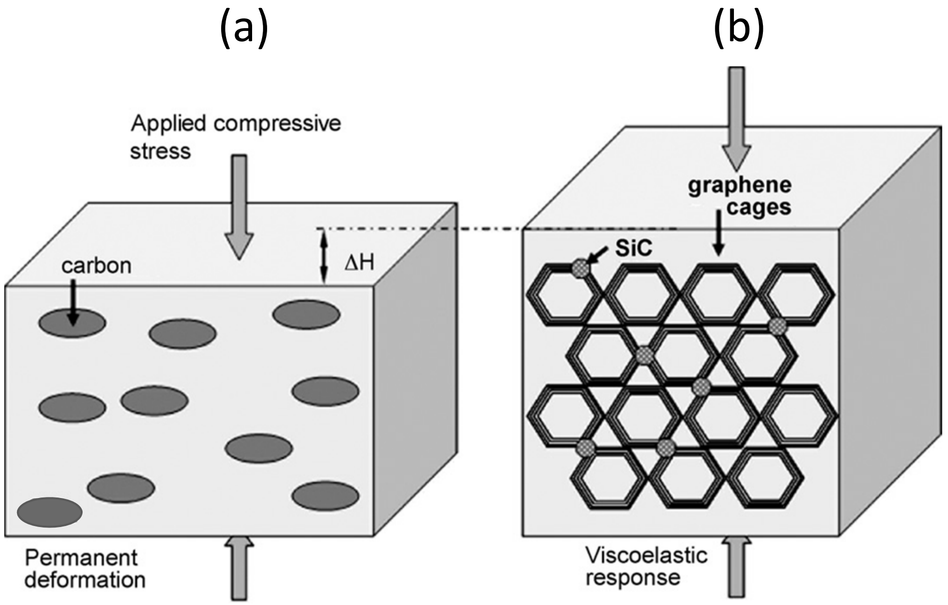
Hot Pressing
Result in different microstructure

Task 1.2: Effect of Temperature and Stress on the Stability of the Nanostructure

Two potential models of the carbon dispersion within the SiC bulk

(a) Isolated carbon clusters embedded in the remaining phase

(b) Graphene cages encapsulating the remaining phase



Experimental conditions and questions to be addressed in this project:

- Compressive tests at temperatures as high as 1800 ^{0}C and stresses in the range of 50 to 200 MPa in inert environment
- Effect of stochiometry, (excess carbon), temperature and stress on stability of carbon phase and nanodomains.

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

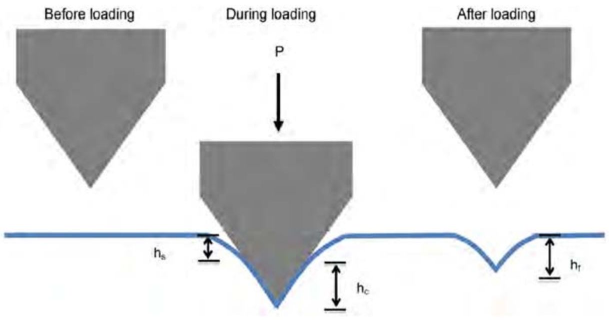
TASK 2.1: Modulus, Toughness, Strength and Thermal Diffusivity

Questions to be asked:

- Effect of stochiometry (excess carbon), temperature and stress on modulus, hardness, toughness strength and thermal diffusivity of carbon phase and nanodomains.
- What are the roles of excess carbon in the structure on the mechanical and thermal properties?
- What is (are) the most appropriate processing condition(s) for these materials to be withstood under the MHD conditions?
- How does the nanostructure and hence these properties evolve under extreme conditions (e.g. temperature and plasma)?
- There are numerous research activities on C-fiber/SiC composites, but little is known about mechano-thermal properties for C (graphene form)/SiC → Set-up data-base

Experimental plans

(1) Modulus and Hardness: Indentation

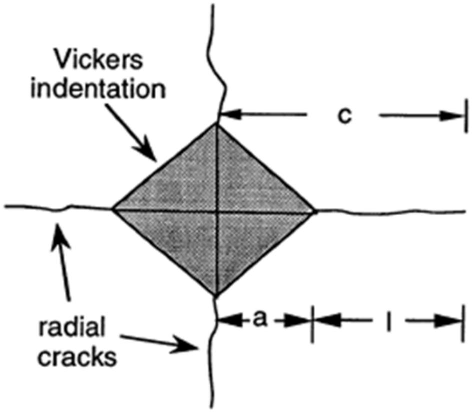


Using instrumented indenter that measures load and displacement, the elastic modulus and the hardness can be obtained using Oliver-Pharr analysis

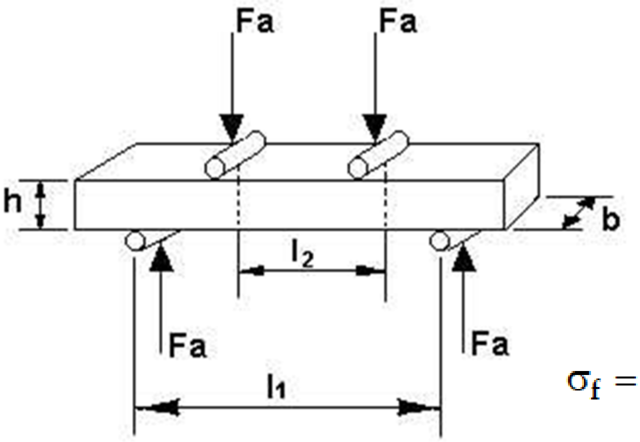
[Oliver, Pharr, J. Mater. Res. 7 (1992) 1564–1583]

(2) Fracture Toughness: Vicker's indentation

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

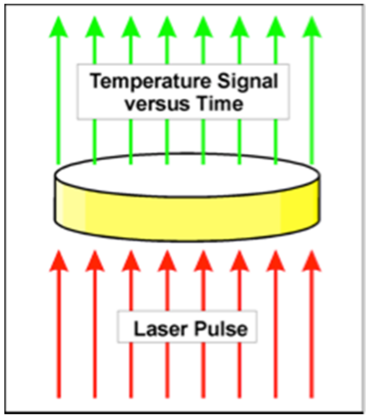


(3) Strength: Four-point flexure



$$\sigma_f = \frac{3}{2} F_A \times \frac{(I_1 - I_2)}{b \times h^2}$$

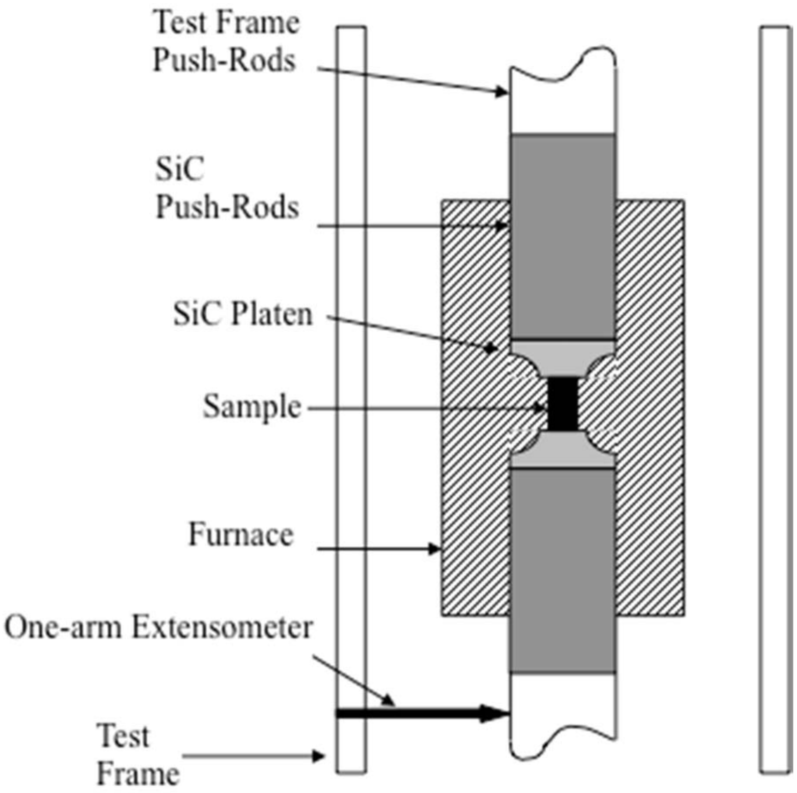
(4) Thermal Diffusivity: Laser Flash

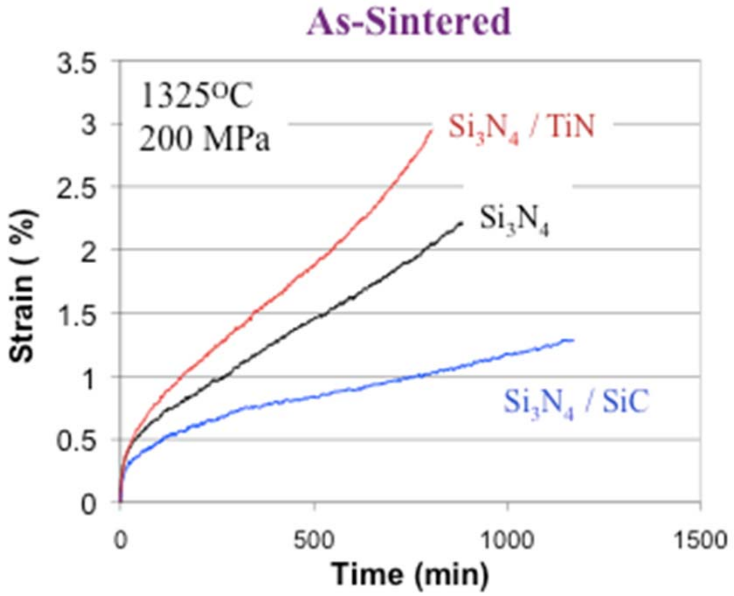


TASK 2.2: Compressive Creep of Si-C-X Ceramics

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)

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

Our Research Focus:

- Effect of C/Si ratio and the nanostructure on the electrical conductivity
- Evaluate whether electrical conductivity of SiC-PDCs is dominated by the precipitation of excessive carbon at elevated temperatures
- Evaluate how percolation or interconnection of the excess carbons limits the electrical conduction.

T < 1000˚C

Variable range hopping

$$\sigma(T) \approx \exp\left(-\frac{T_0}{T^{\frac{1}{4}}}\right)$$

T > 1000˚C

Tunneling of charge carriers between excited states, and excitation into the conduction band.

$$\sigma_{dc}(T) \approx \exp\left(-\frac{E^*}{kT}\right)$$

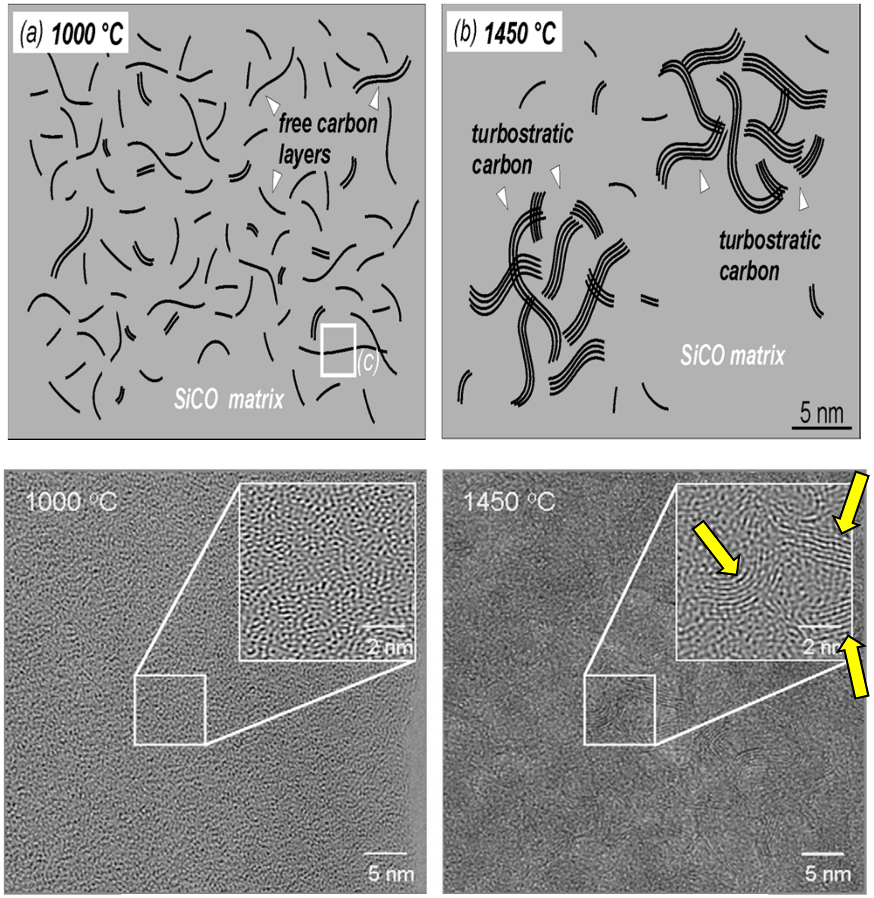
- Create data-base for the dc-electrical conductivity of PDC Si-C-X at a wide range of high temperature (RT~1700˚C)

Unique Nanostructures for C/Si>1

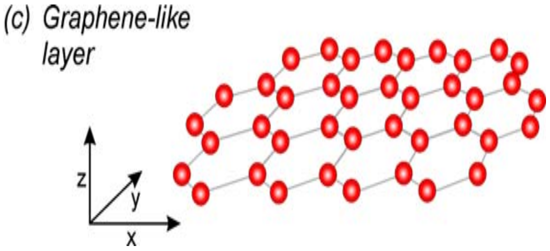
PHMS +
60wt% DVB

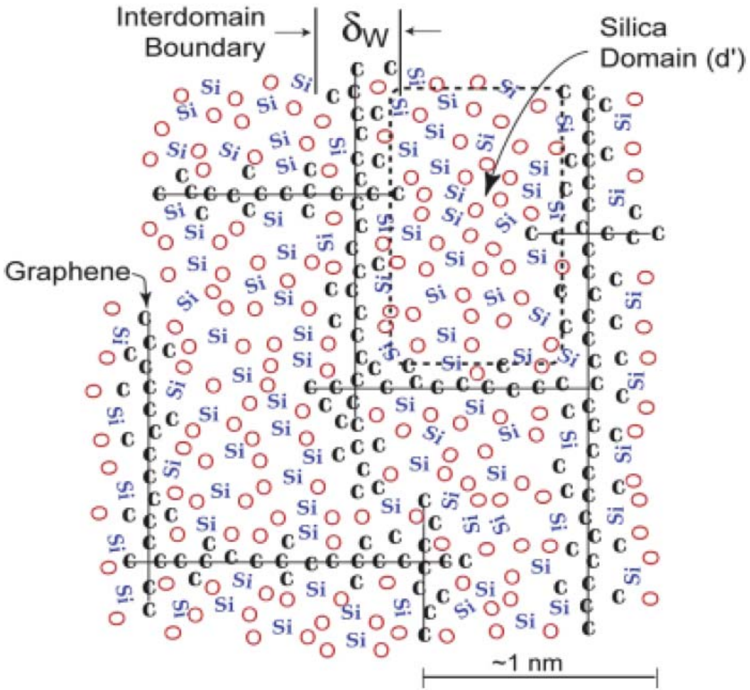
Poly-Hydrido-Methyl-Siloxane (SiOC)

Di-Vinyl-Benzene



Journal of the European Ceramic Society 28 (2008) 1037–1042





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

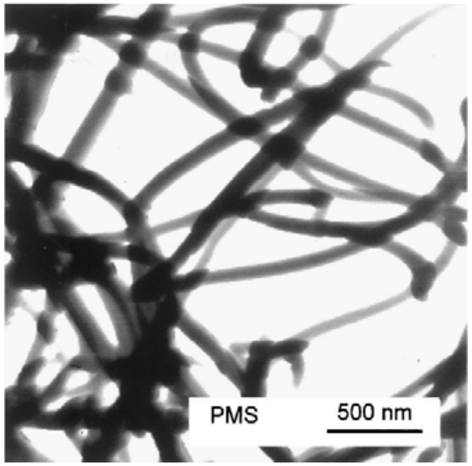
- Evolution of free carbon in polymer derived ceramics
- Free carbon clusters in single graphene-like sheets (Raman Spectroscopy)
- Volume fraction of graphene can be controlled

Will look at ***Polycarbosilane*** family with C/Si>1

Turbostratic carbon network

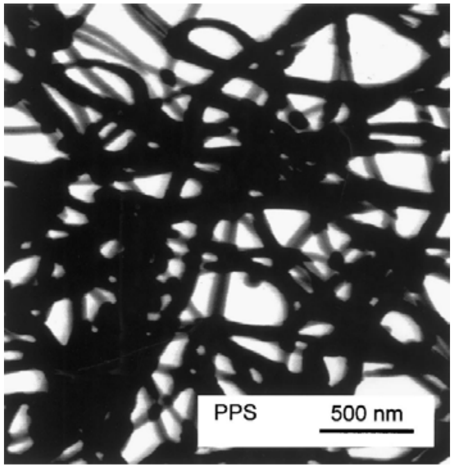
PMS:

Poly(methylhydrogensiloxane)
$RSiO_{1,5}$
$R=[(CH_3)]$
Liquid form



Below percolation limit

$$\sigma(T) \approx \exp\left(-\frac{T_0}{T^{\frac{1}{4}}}\right)$$

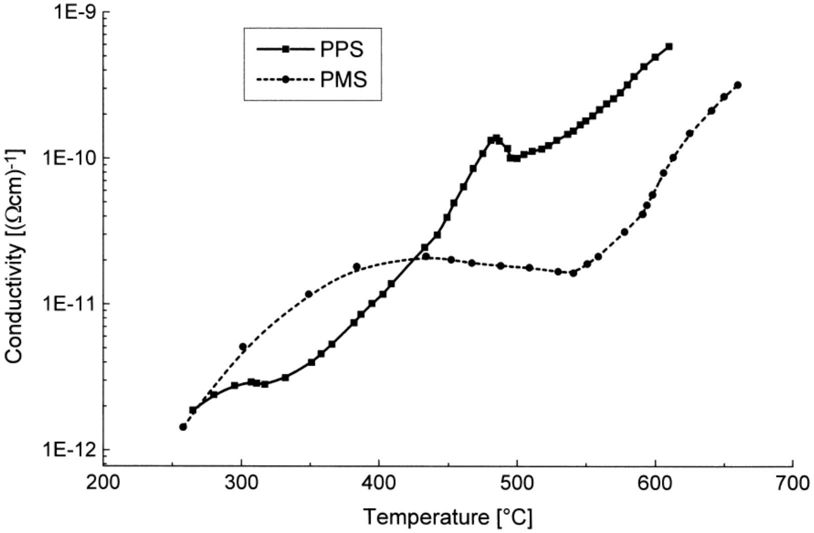


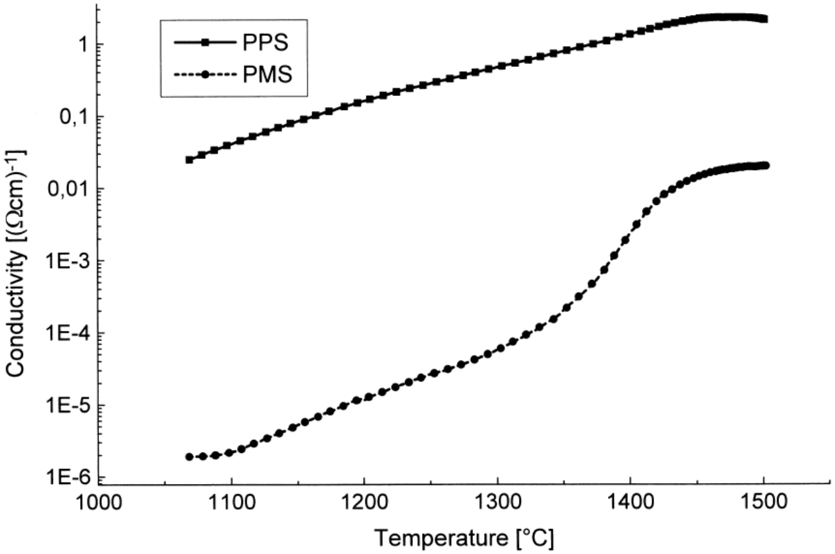
Interconnection

$$\sigma_{dc}(T) \approx \exp\left(-\frac{E^*}{kT}\right)$$

PPS:

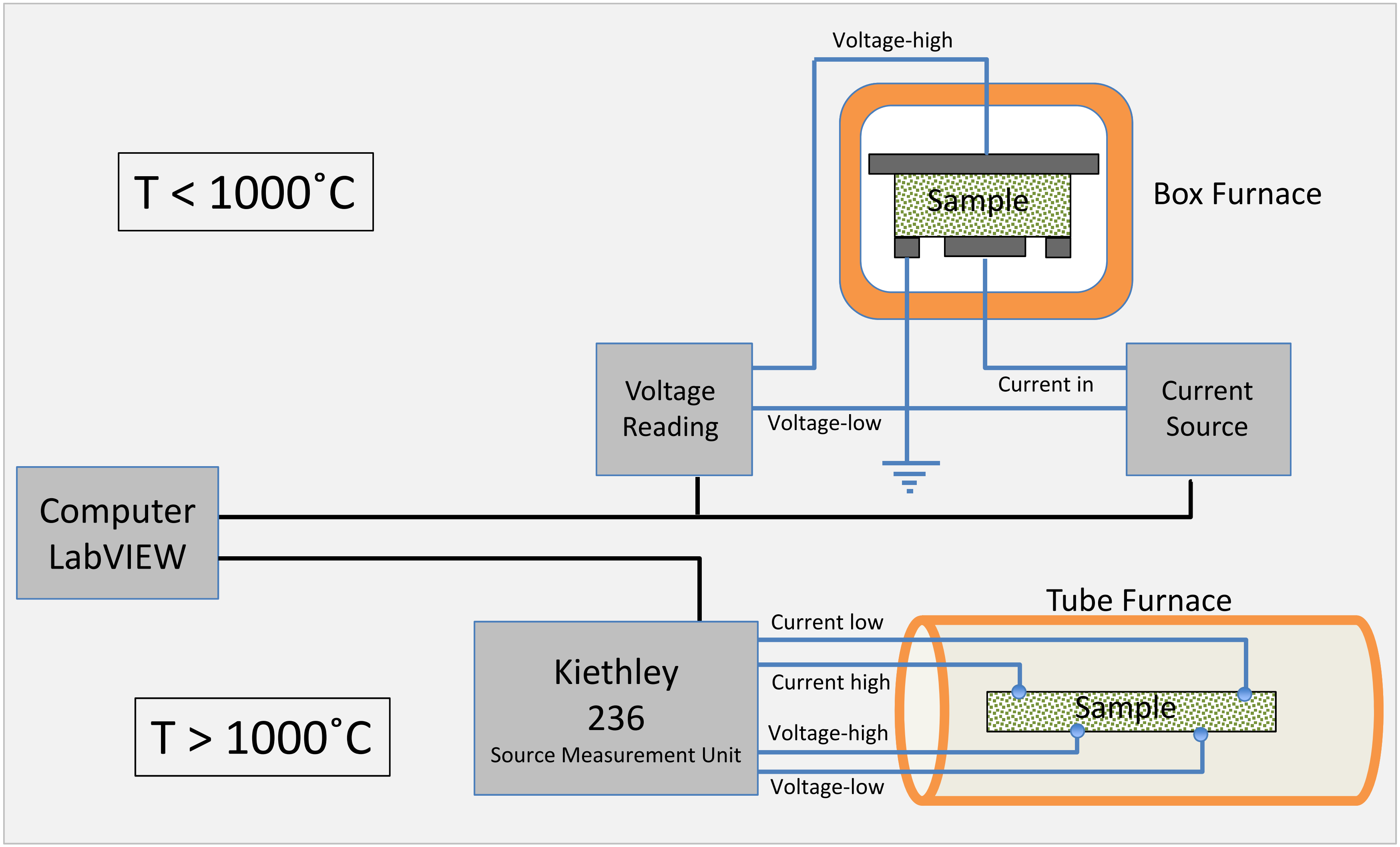
Poly(phenylmethylvinylhydrogen-siloane)
$RSiO_{1,5}$
$R=[(C_6H_5)_{2,8}, (CH_3)_{1,5}, (CH_2{=}CH),(H)]$
Powder form



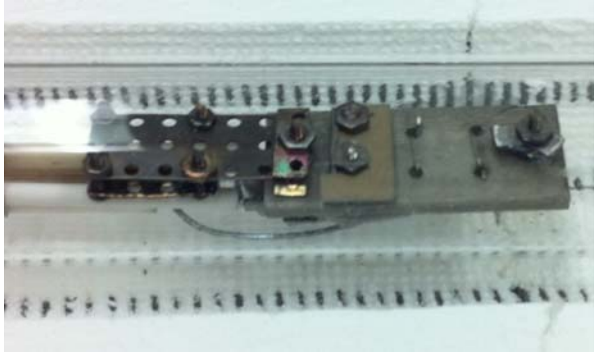


Journal of the European Ceramic Society 20 (2000) 1947–1957

Develop an “in-situ” measurement technique of dc-conductivity during the pyrolytic conversion from polymer to ceramic phase.



High T prototype device (Oct 2014)

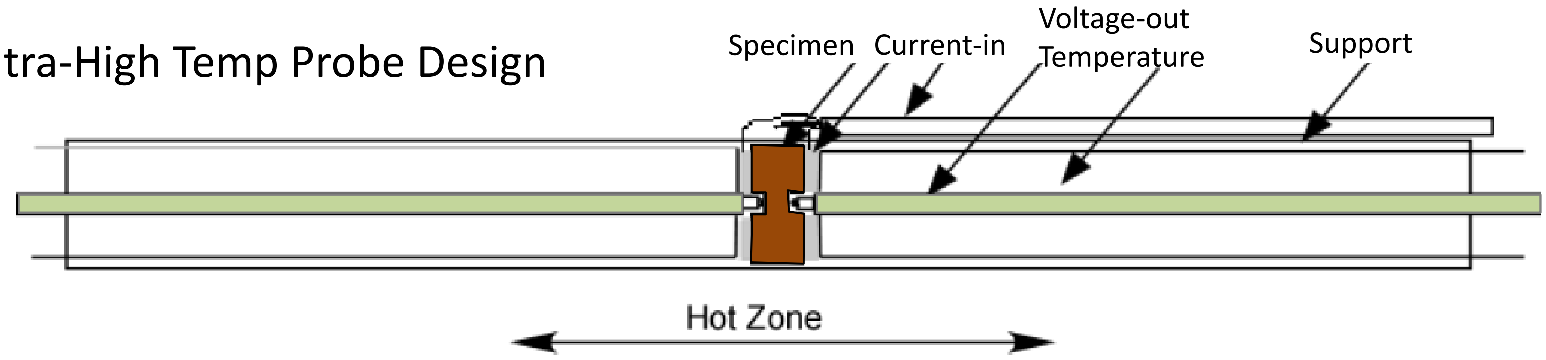


Newly Installed High Temperature Tube Furnaces

1400˚C max

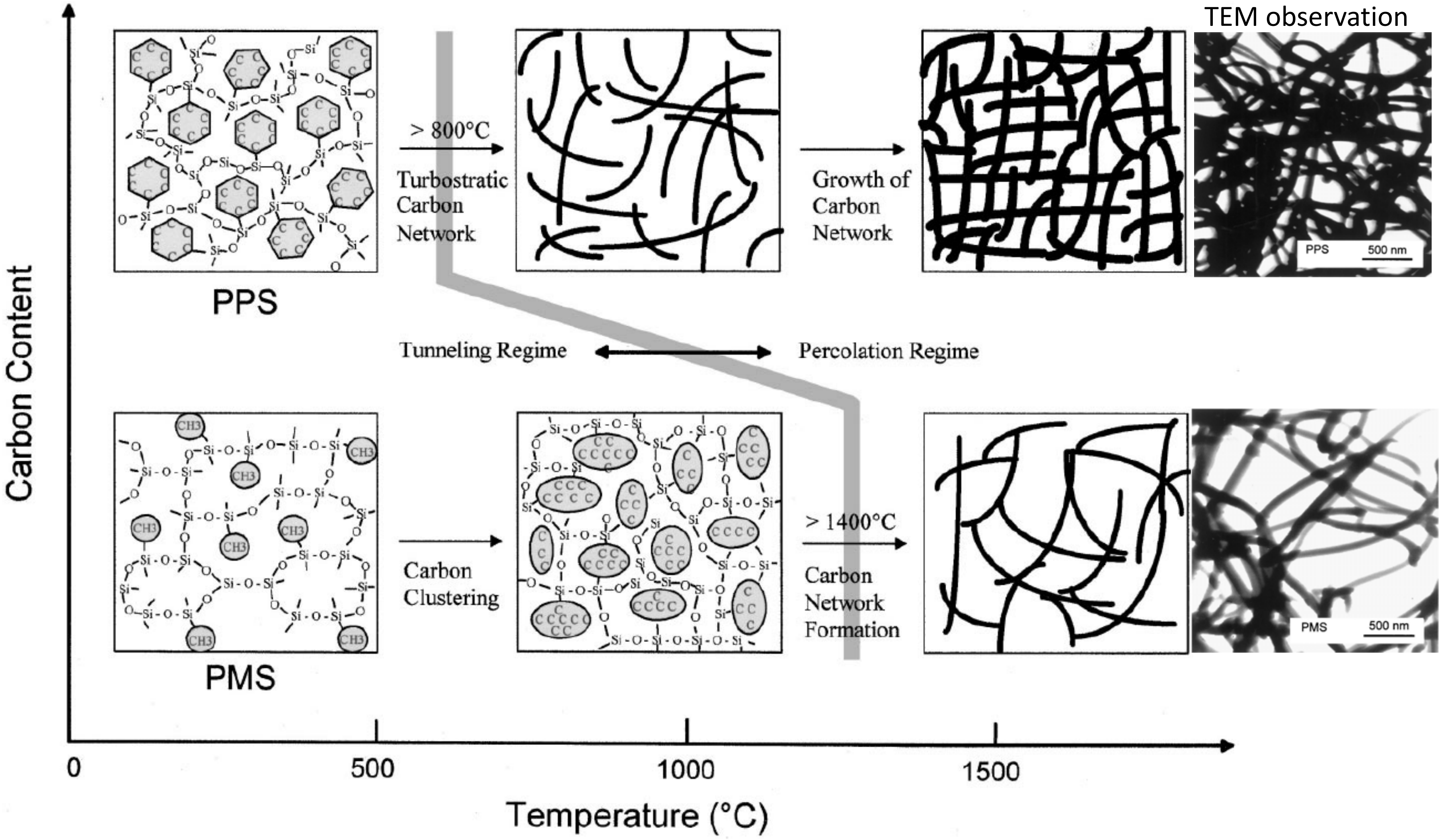
1700˚C max

Ultra-High Temp Probe Design



Model of carbon redistribution reactions during pyrolysis

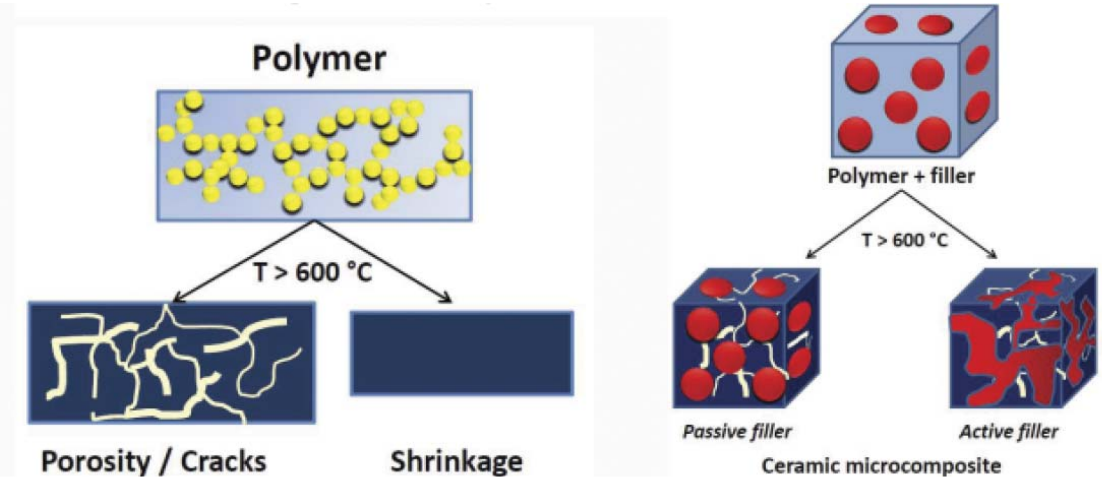
From Journal of the European Ceramic Society 20 (2000) 1947–1957



Will look at ***Polycarbosilane*** family with C/Si>1

Control of Shrinkage for Bulk Component

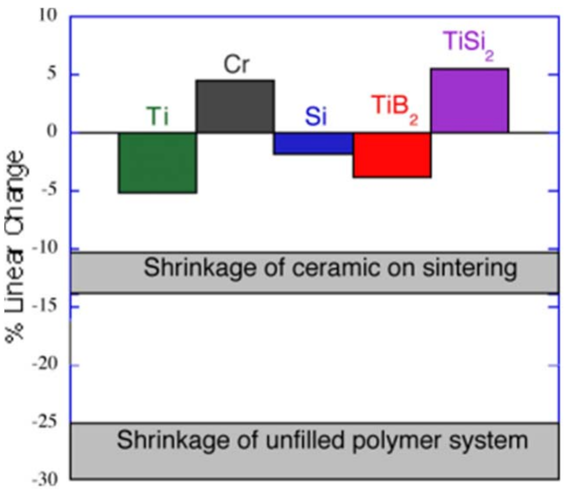
Active Filler Controlled Pyrolysis (AFCOP)

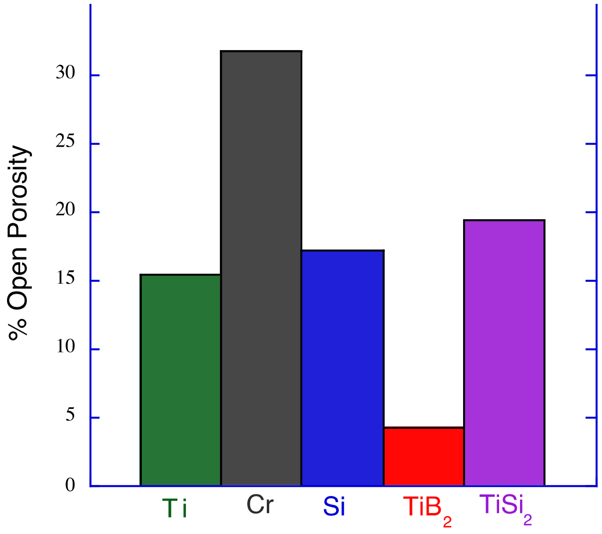


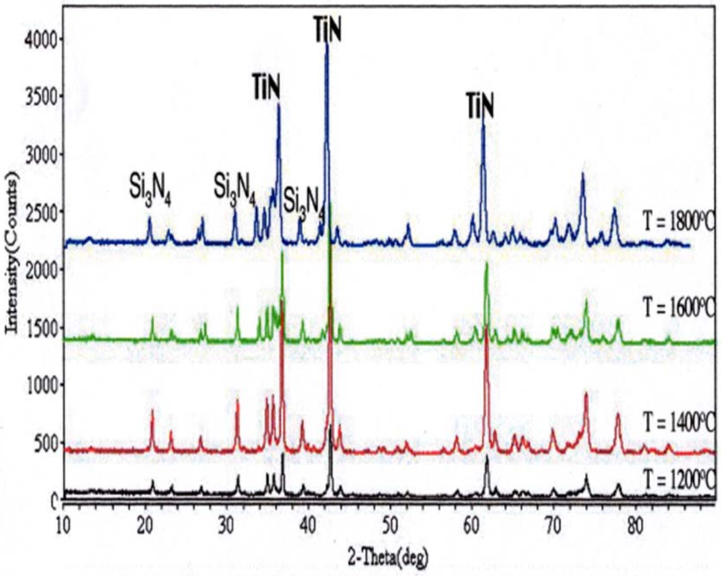
P. Greil, *J. Am. Cer. Soc.*, 78 [4], 1995, p835-848

Example: Polysilazanes (Ceraset^{SN})

Processing temperature 1400˚C in N_2 at p=2MPa







Proposed fillers for PDC Shrinkage / Porosity

Multipurpose Fillers

- Control the shrinkage
- *In-situ* reactions to control the composite phases
- Control and tailoring of properties

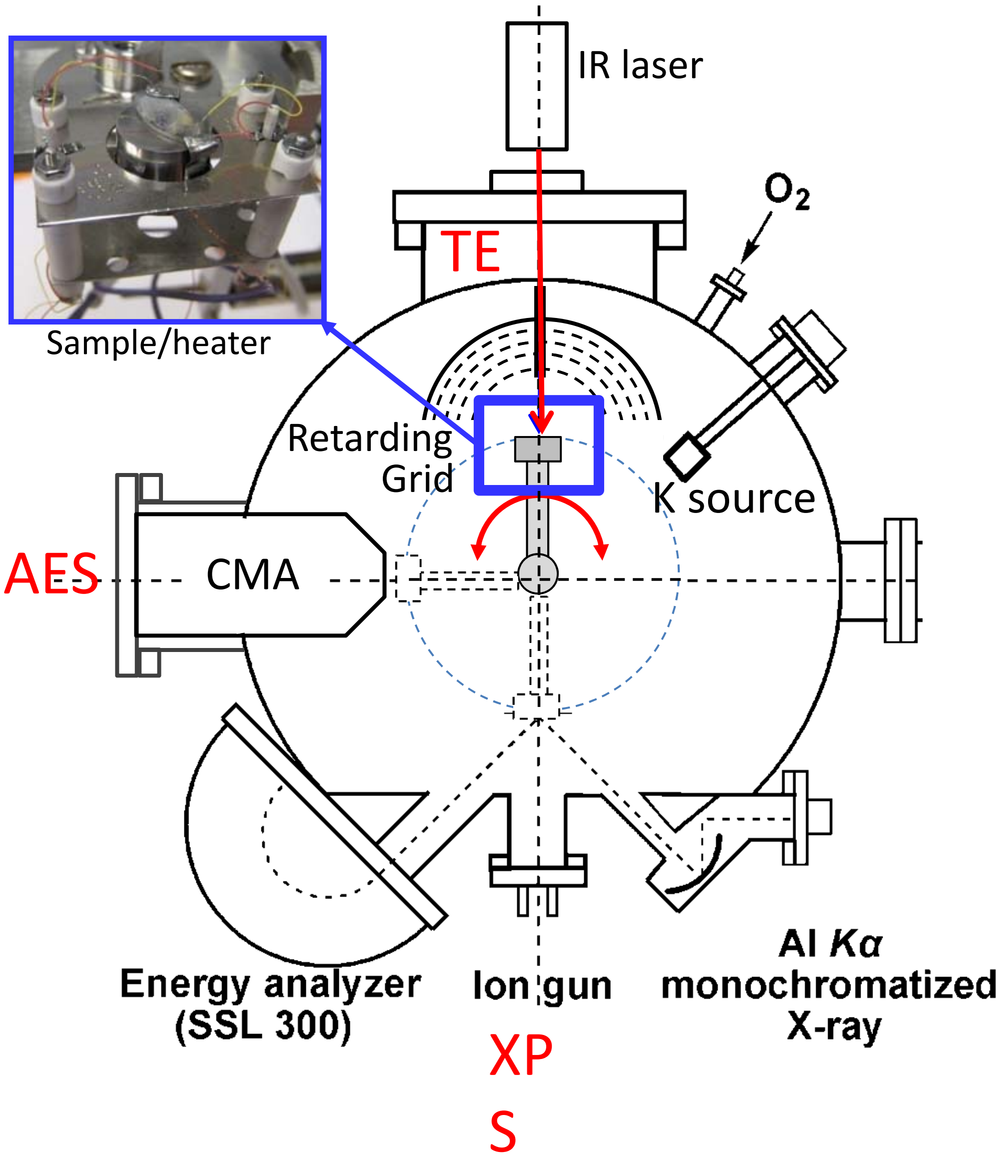
Planned Fillers

- SiC particles – reduce shrinkage during pyrolysis without changing compositions
- Si, Mo and Ti particles for *in-situ reactions* to make corresponding silicides
- High electrical conductivity fillers like $MoSi_2$ and ZrB_2 to improve high temperature electrical conductivity

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

- The thermionic emission characteristics of the electrode materials play a significant role to determine the mode of current transfer (diffuse versus arcing) at near electrode region in the MHD channels
- Essential to characterize the thermionic emission of materials under consideration
- Specific tasks:
  1. Modify surface of the electrode by “in-situ” deposition of potassium and other elements that lower the work function
  2. Measure the surface composition
  3. Measure the work function values -before and after the deposition
  4. Measure the total thermionic emission from the sample
  5. Spectroscopically determine the kinetic energy distribution of thermionic emission of electrons from the surface.
  6. Investigate plasma interactions with materials

Experimental Setup



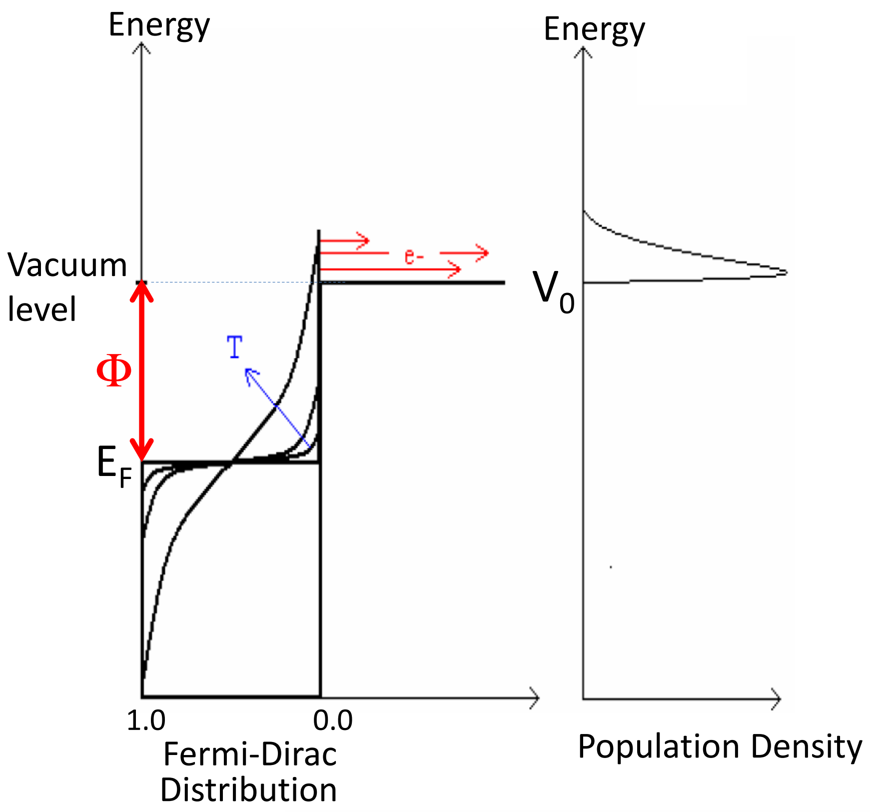
Integrated UHV system:

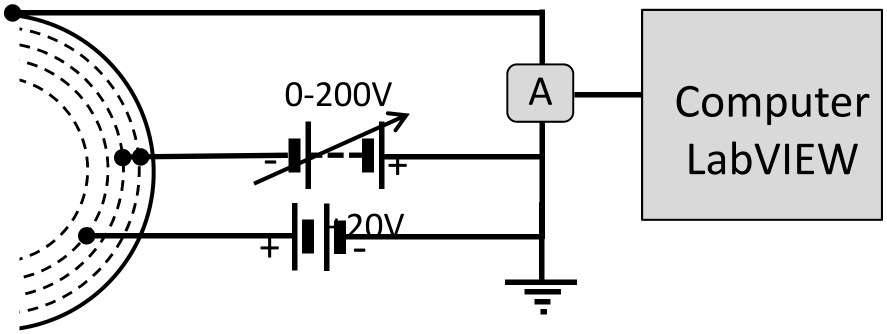
- Retarding grid spectroscopy to measure thermionic emission from the sample
- X-ray photoelectron spectroscopy (XPS)
- Auger electron spectroscopy (AES)
- K deposition and O_2 source
- IR laser for additional heating
- Ion gun for surface cleaning

Capable of measuring:

- Surface composition and states
- Heating to >3000˚C by IR laser
- Total current and kinetic energy distribution of thermionic emission.
- Workfunction

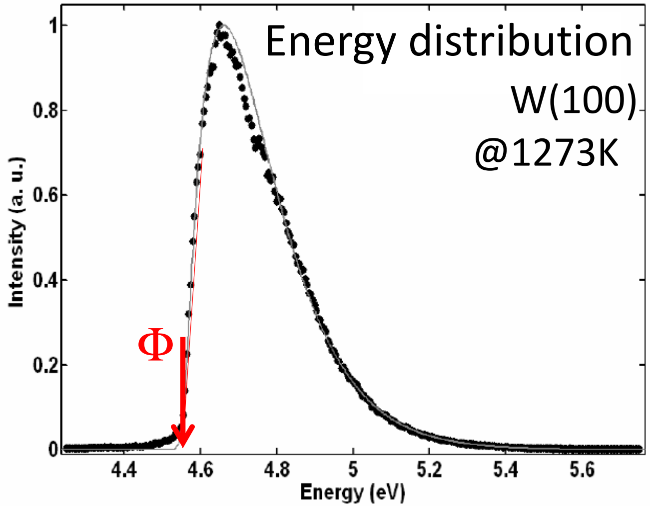
Thermionic Current and Energy Distribution

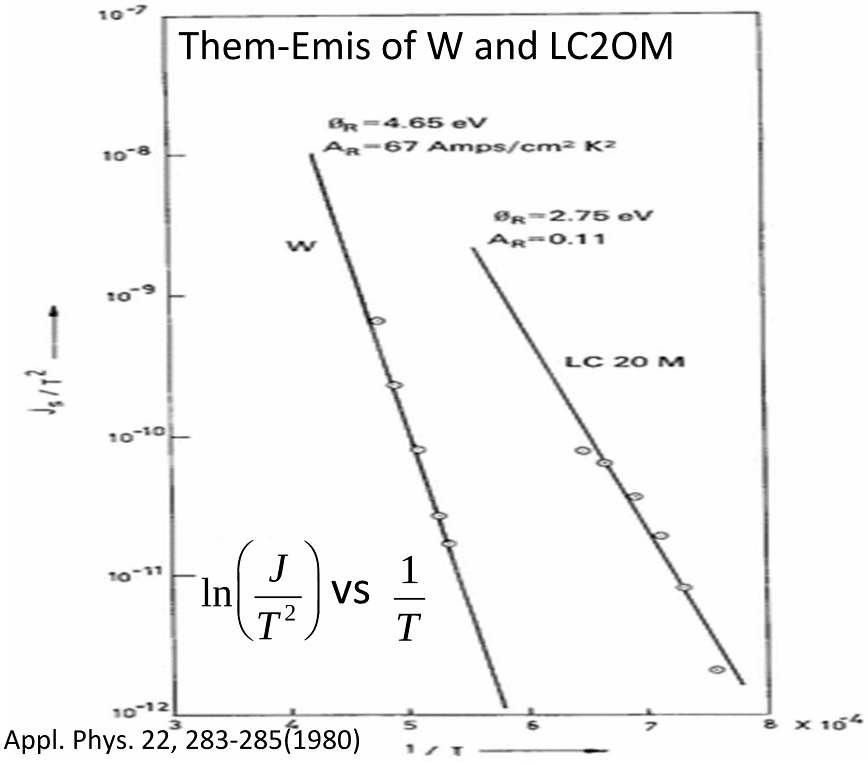




$$J = -q \int_{W>\mu+\phi} v_x f(k) \frac{d\mathbf{k}}{4\pi^3} = \frac{m k_B^2 q}{2\pi^2 \hbar^3} T^2 \exp\left\{ \frac{-\phi}{k_B T} \right\}$$

Example



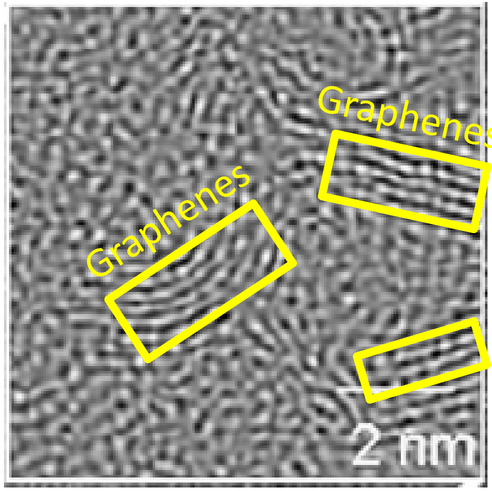


$$\ln\left(\frac{J}{T^2}\right) \text{ vs } \frac{1}{T}$$

Appl. Phys. 22, 283-285(1980)

Turbostratic carbons and SiC Interdomains

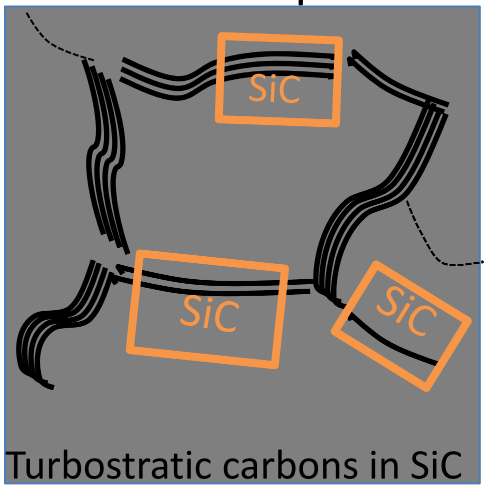
SiOC + Graphens



PHMS+60%DVB Pyrolysis at 1000˚C,
followed by annealing at 1450˚C

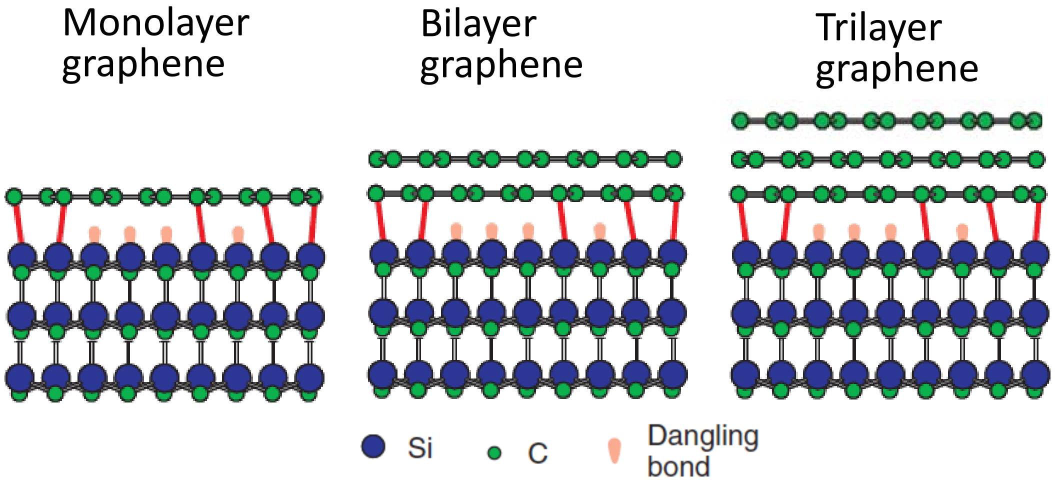
Journal of the European Ceramic Society 28 (2008) 1037–1042

SiC + Graphens

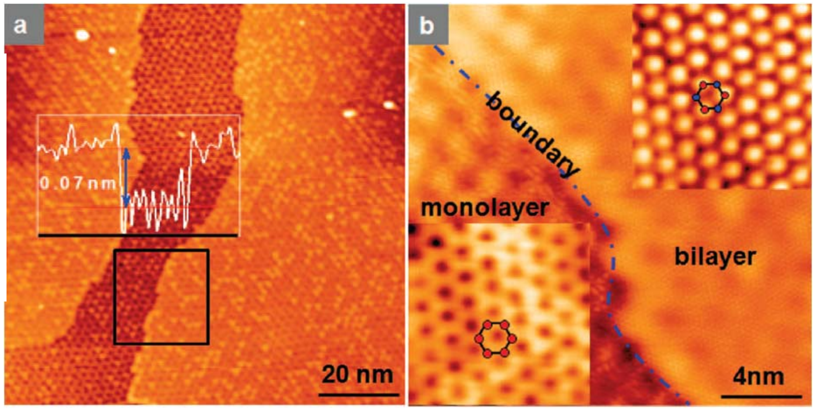


Our proposal

State of the Art Knowledge about Graphene/SiC interfaces



PRL **103**, 246804 (2009)

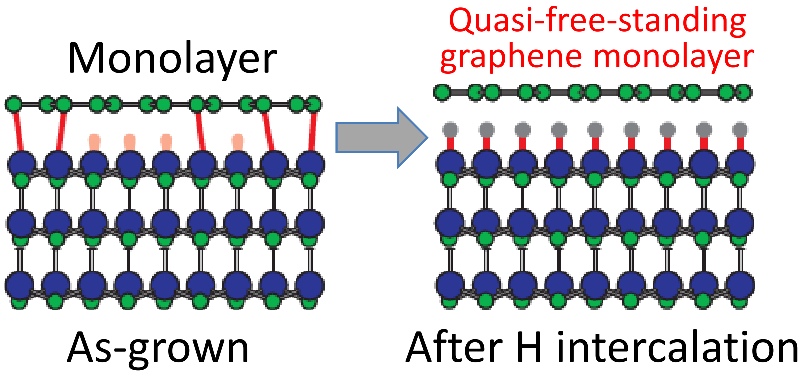


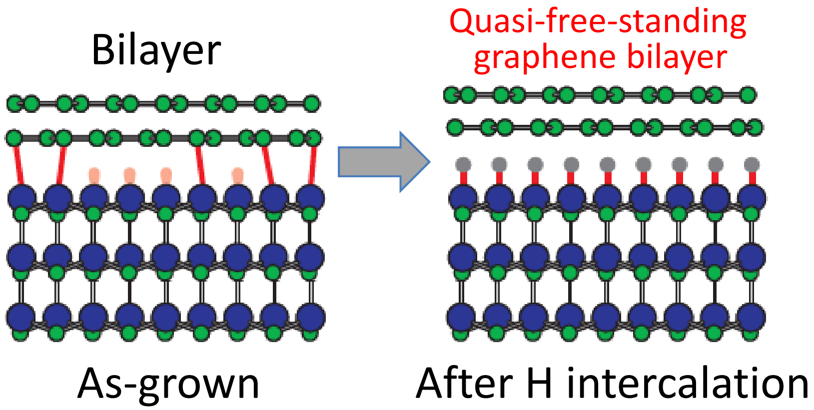
ACSNANO VOL. 2 ▪ NO. 12 ▪ 2513–2518 ▪ 2008

Effect of Hydrogen at the Graphen/SiC Interface

Hydrogen Intercalation forms Quasi-Free-Standing Graphen

PRL **103**, 246804 (2009)





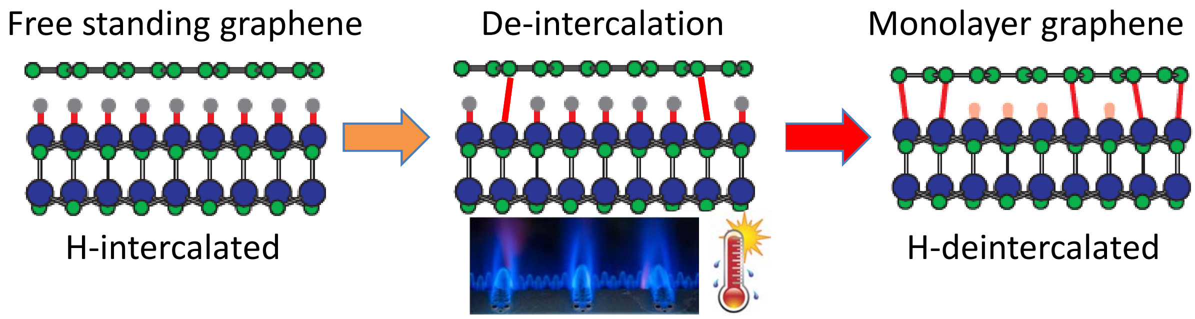
- Hydrogen is a common constituent in the environment
- H moves between the reconstructed initial carbon layers and SiC
- Topmost Si atoms are satulated by H bonds, removing Si-C bonds
- Quasi-free-standing graphene layers are formed.

How do the quasi-free-standing graphene layers influence on the electronic properties, in particular, thermionic emission?

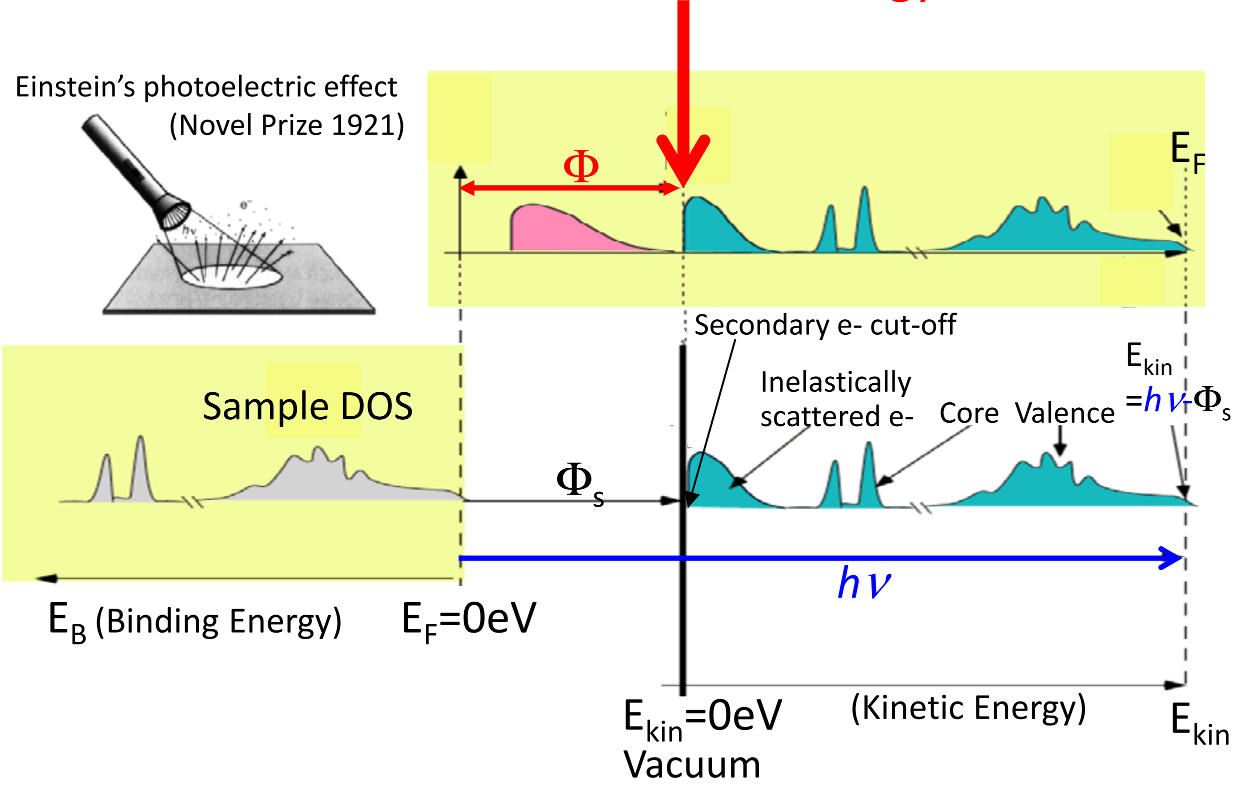
Variation of workfuction in pure and H-intercated graphene on SiC

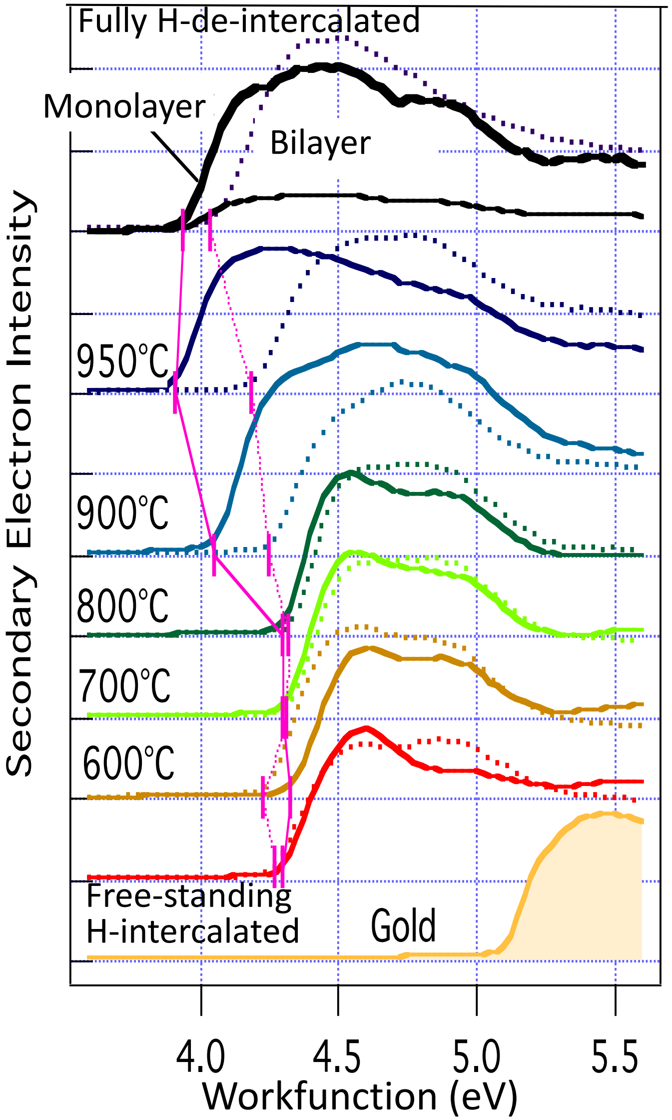
From Our Previously Conducted Experiments

Monitor variation of "workfunction" measured by the Al-Kα X-ray induced secondary electron cut-off energy as a function of Hydrogen "**de-intercalation**" in XPS



Watch how this cut-off energy shifts.

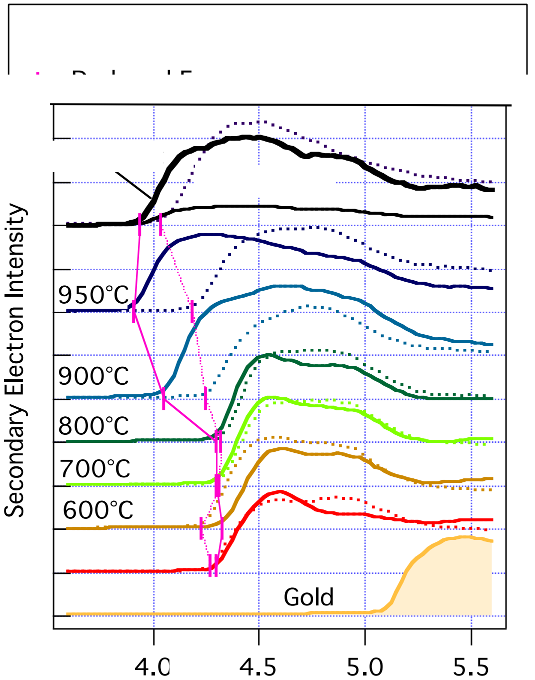




Unpublished work: B.Kruger, T. Ohta, M. Olmstead and F. Ohuchi

Our Strategy:

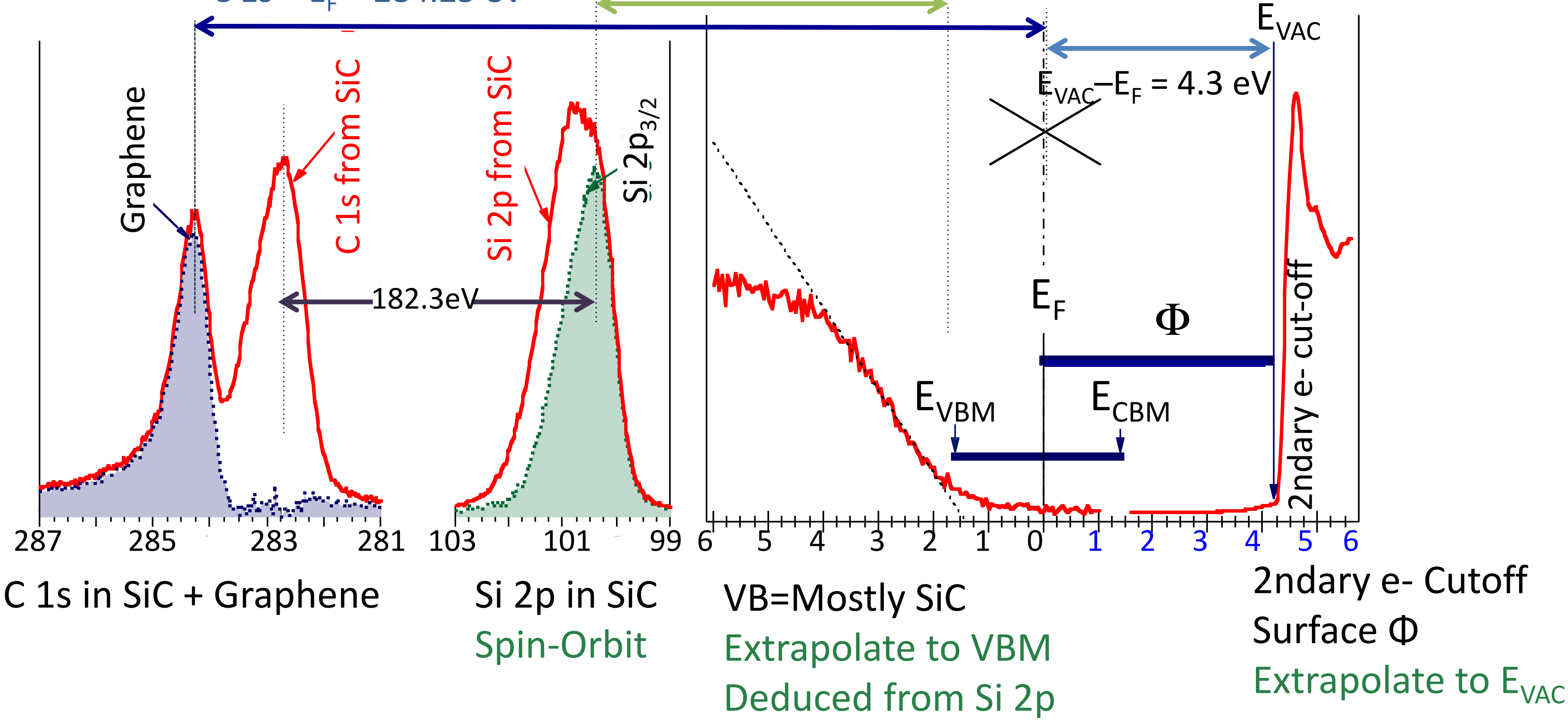
Complete measurements of the core and valence energy levels together with the workfunction allow to deduce electronic structures of the Si-C-X system, from which nature of the thermionic emission will be investigated in this project.



Si 2p – VBM = 98.9 eV

Then E_F - VBM = 1.6 eV

C 1s – E_F = 284.25 eV



C 1s in SiC + Graphene

Si 2p in SiC

Spin-Orbit

VB=Mostly SiC

Extrapolate to VBM

Deduced from Si 2p

2ndary e- Cutoff

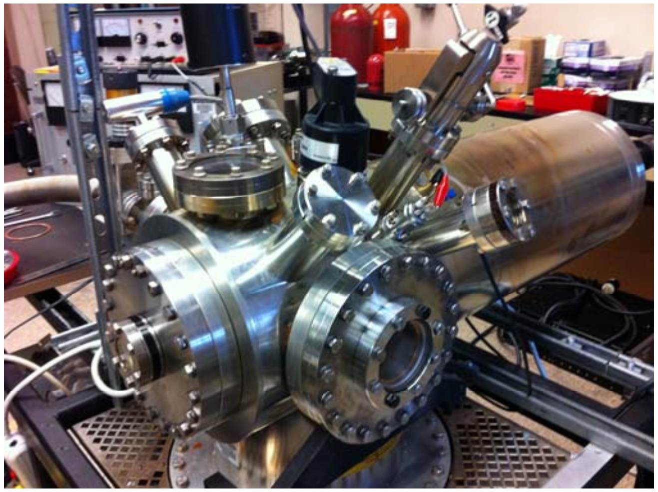
Surface Φ

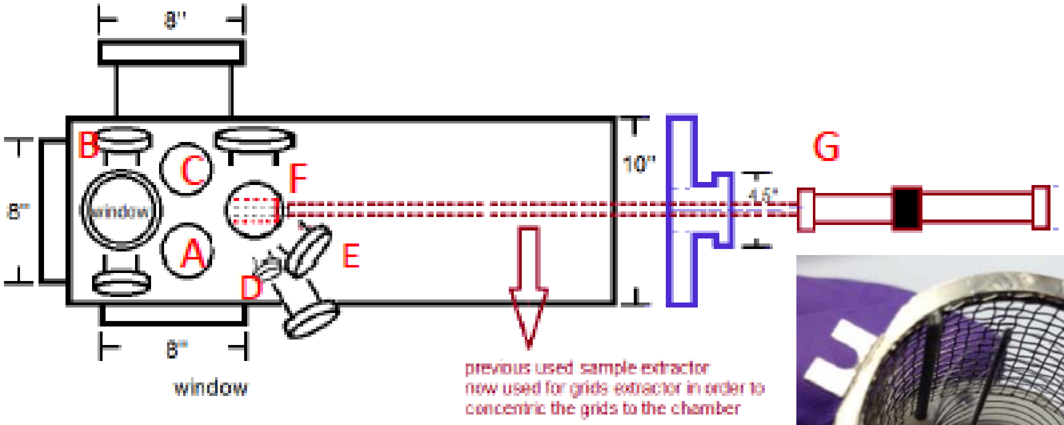
Extrapolate to E_{VAC}

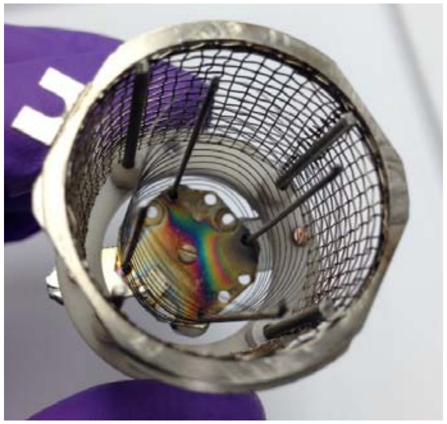
Task 4.2: Changes of Surface/Sub-Surface Structure and Chemistry

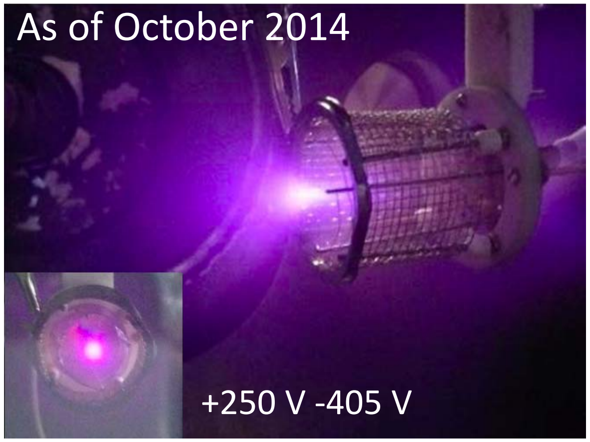
Inertial-Electrostatic-Confinement (IEC) of Plasma

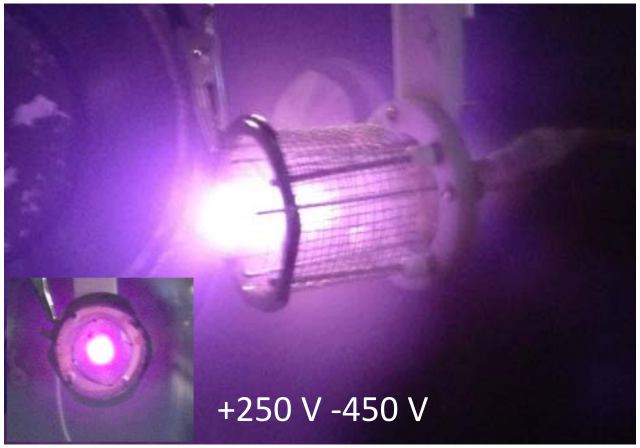
- Independently developed in our laboratory (2014)
- Simple and versatile design for high density plasma
- Well confined plasma in the center of the grid structure
- Use this source to investigate surface damages

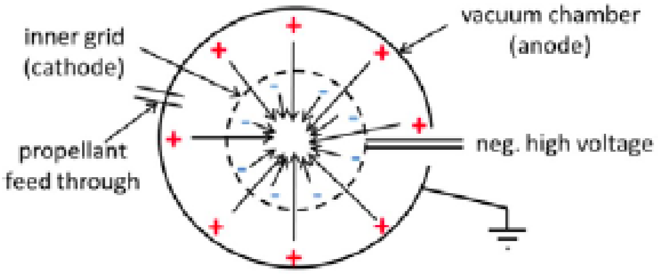




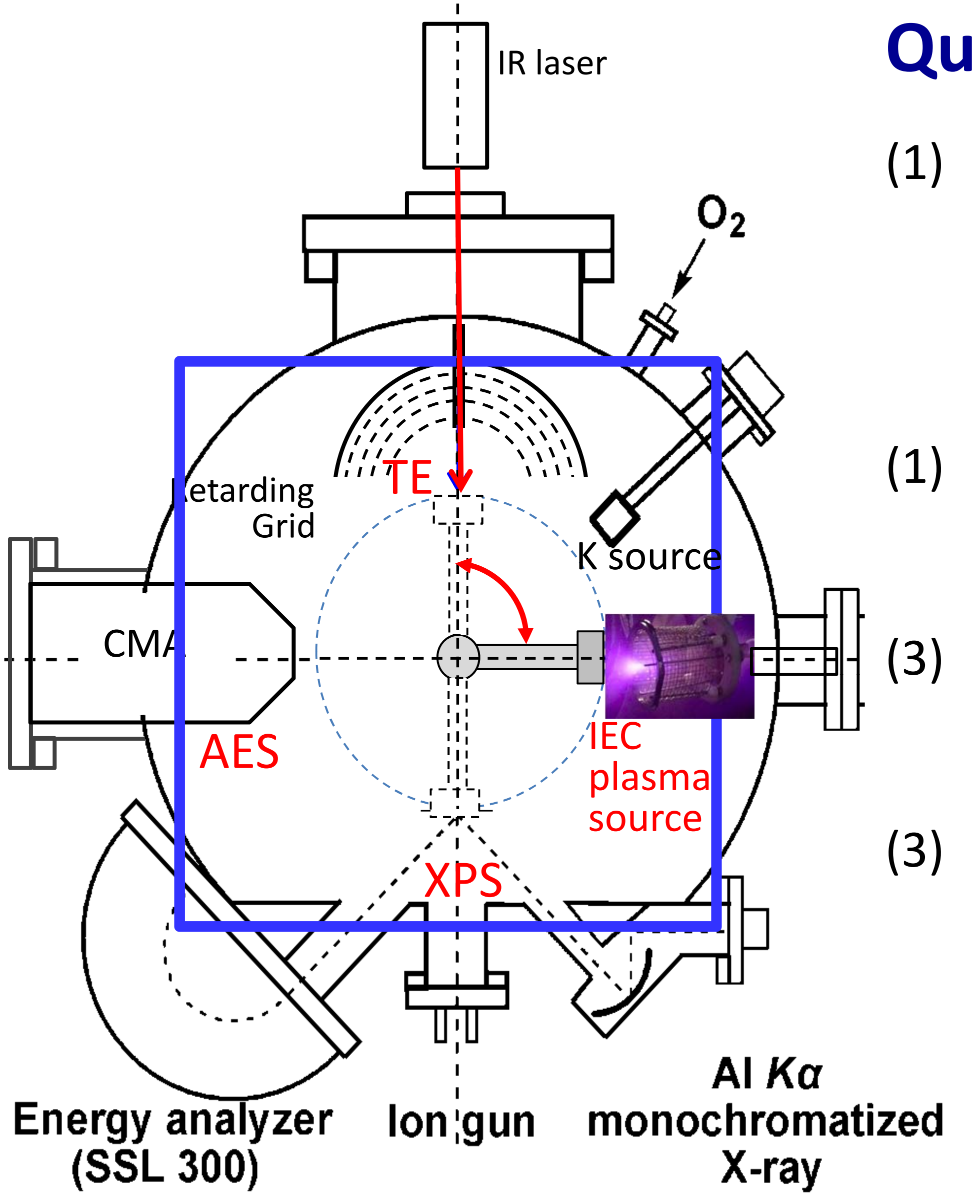








Incorporation of the plasma source



Questions to be asked:

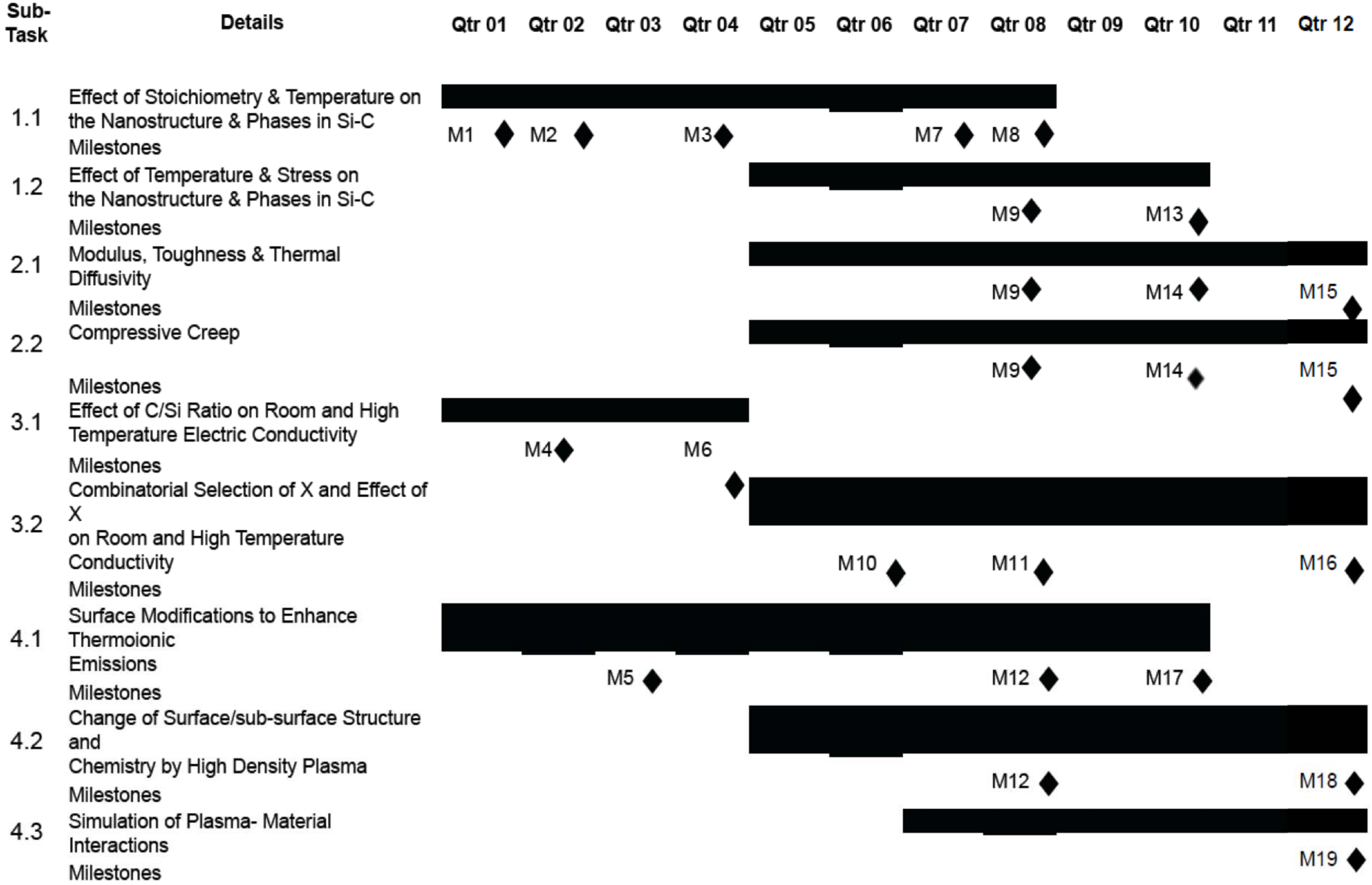
(1) How are the surface and sub-surface chemistry altered by chemical and physical sputtering, re-deposition, and evaporation of materials?

(1) How does the microstructure of the surface evolve with plasma exposure?

(3) How does plasma exposure alter the structure of the materials?

(3) How do plasma-material interactions extend in all three dimensions for each material system?

Precursor Derived Nanostructured Si-C-X Materials MHD Electrode Applications



Summary of this project

- This project is to develop a novel class of SiC based ceramic composite materials with tailored compositions through a precursor derived synthesis route for electrode applications in MHD generators.
- A unique feature of the precursor-derived materials is the presence of nanostructured crystalline SiC domains separated by nanoscale carbon.
- We postulate that by making Si-C based materials with nano-structured features and by tailoring the composition, the high temperature resistance, the electrical properties and plasma resistance of SiC will improve relative to that for SiC produced by conventional powder processing approaches using solid state sintering.
- Successful outcome of this research will results in the emergence of reliable and affordable designed materials for MHD applications.

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Thank you!

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