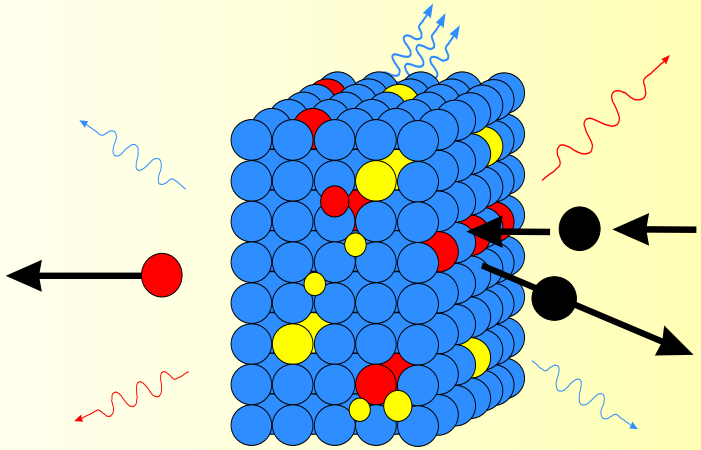
ION BEAM PROCESSING OF POLYMERS AS BIOMATERIAL

Robert L. Zimmerman, Bopha Chhay,
Leslie Evelyn and Daryush ILA



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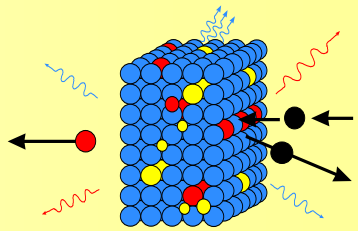
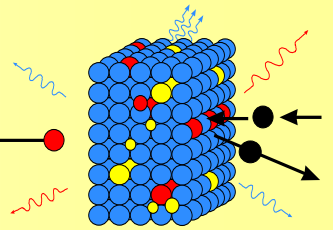
Support in part by AAMU Research Institute, Ctr. for Irrad. of Mat. and National Science Foundation EPSCoR RII program

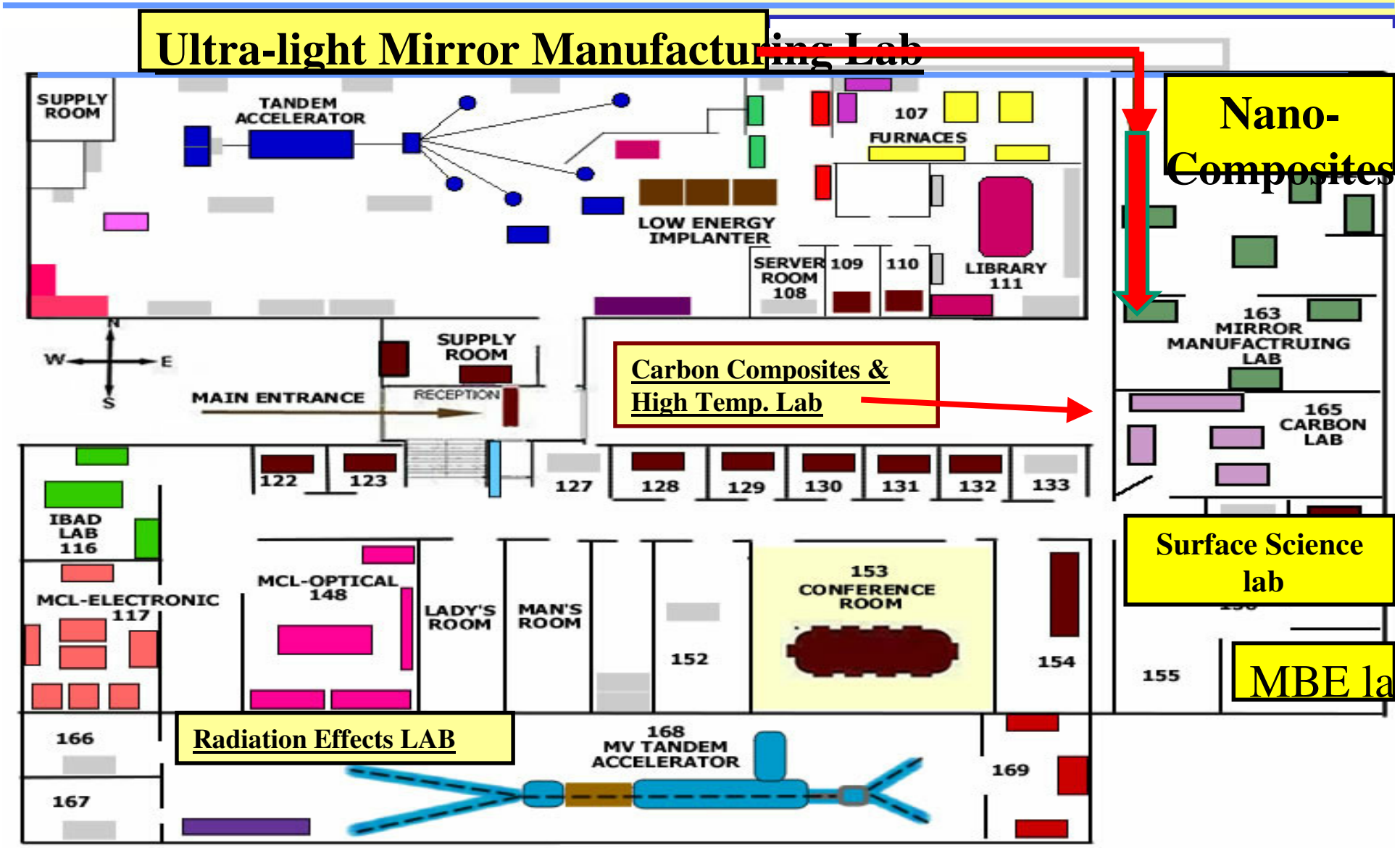
Partners



Ege Univ., USP, ORNL, UAB, TU, Cardio-Carbon, & few other small businesses

Ctr. for Irrad. of Materials

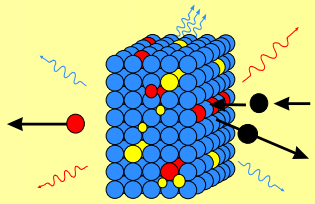




ACKNOWLEDGEMENTS:

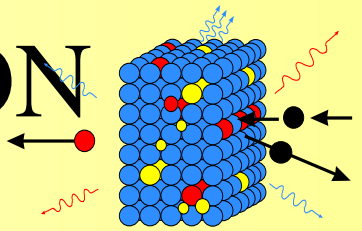
- **Alabama A&M University Research Institute**
- **AAMU Center for Irradiation of Materials**
- **National Science Foundation**
  Grant No. EPS-0447675.
- **Ege University Bioengineering Department**
  for cell adhesion and SEM studies.

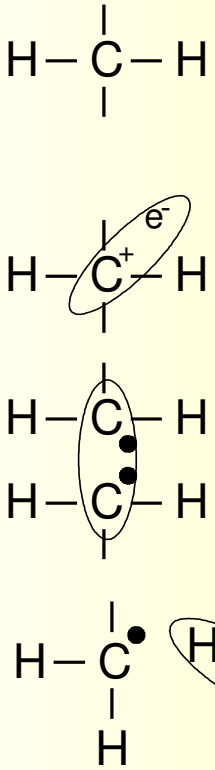
POLYMERS



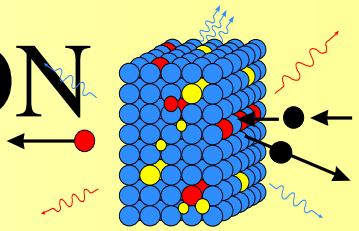
- Biocompatible Polymers
- High Temperature Polymers
- **PE, PTFE, PS, GPC,** PES, PVDC,PVC, PPS, PMMA, ...
- **Fundamental Studies**: OA, FTIR, RAMAN, Electrical Conductivity, Porosity, Surface Roughness, Wetability, Adhesion…

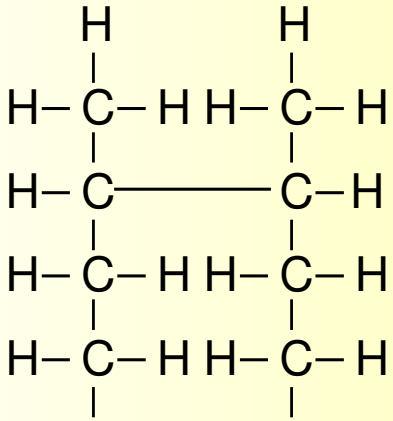
RADIATION EFFECTS ON POLYMERS



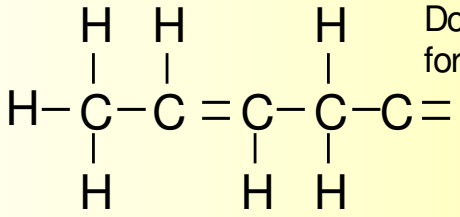


RADIATION EFFECTS ON POLYMERS



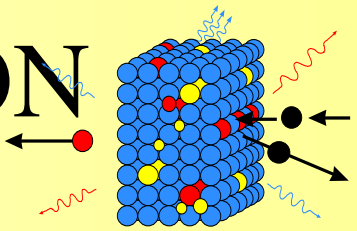


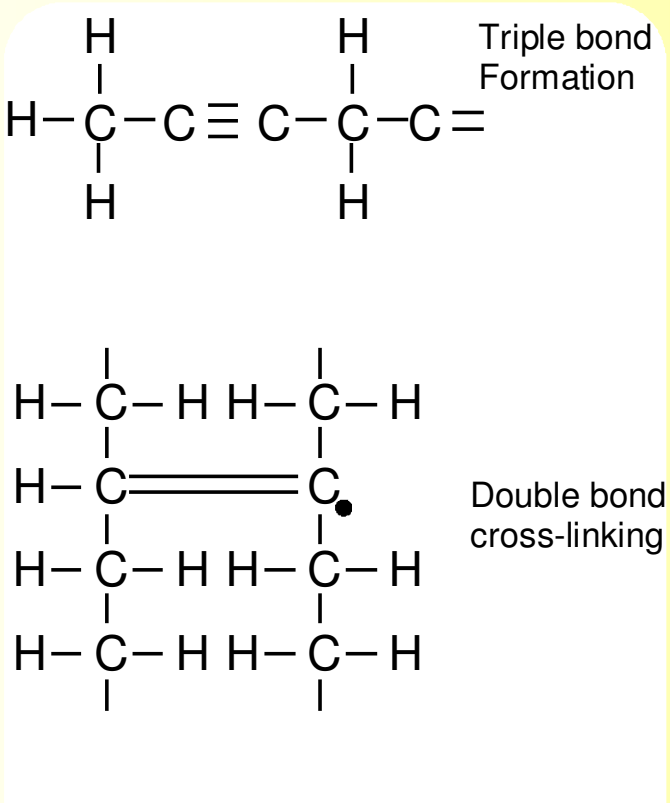
Cross-linking



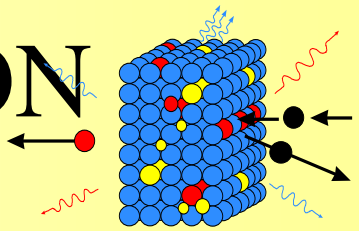
Double bond formation

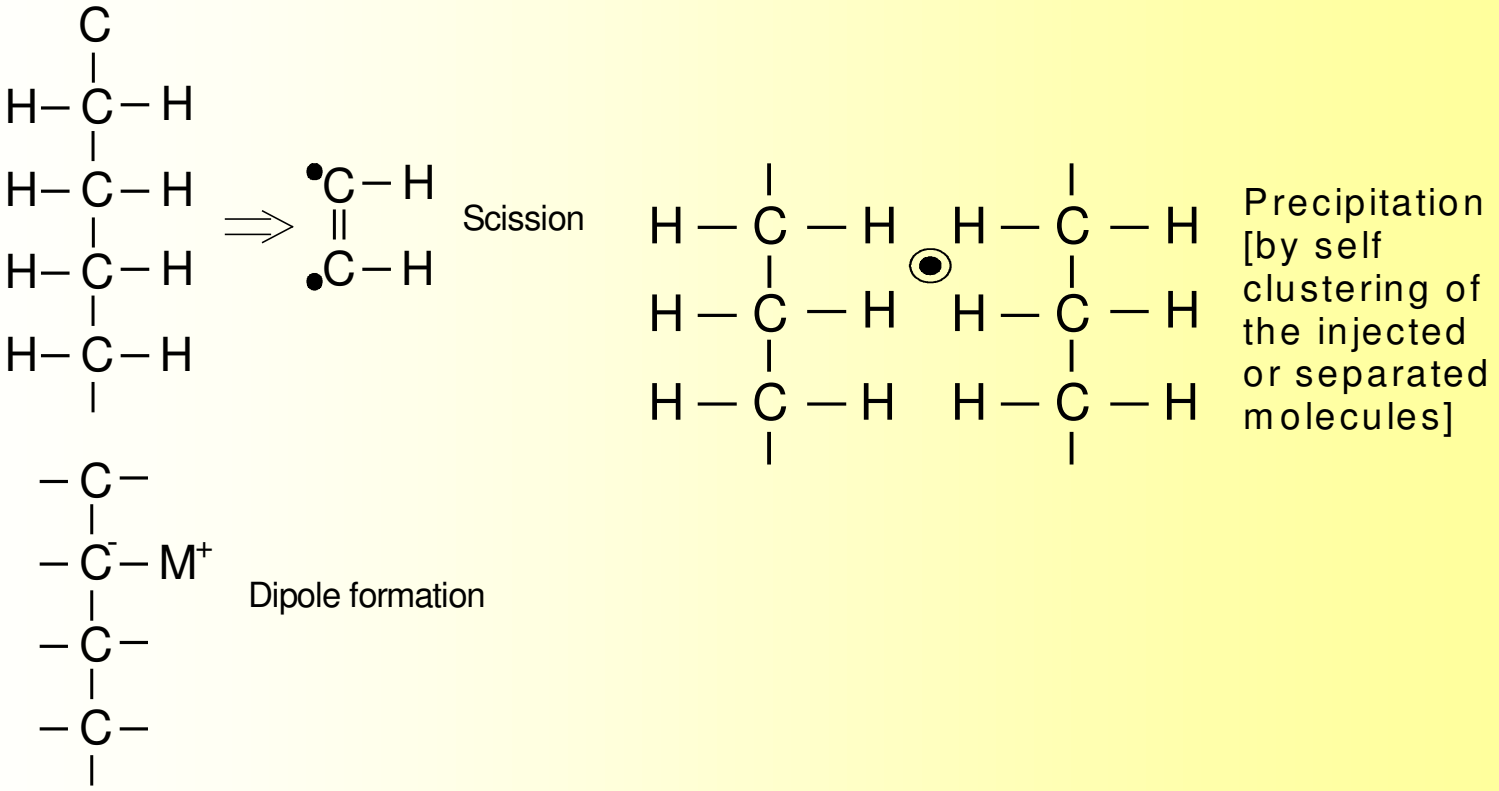
RADIATION EFFECTS ON POLYMERS





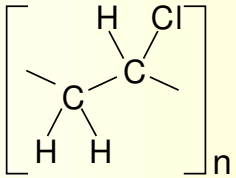
RADIATION EFFECTS ON POLYMERS



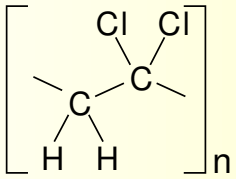


STRUCTURES OF POLYMERIC SYSTEMS

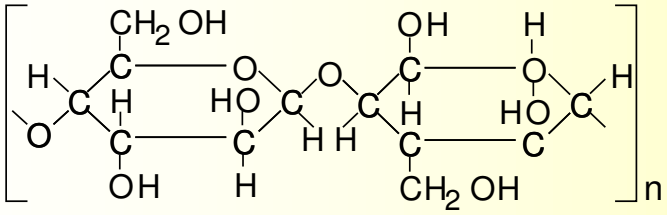
PVC
Polyvinyl chloride
(produces a pitch-coke)



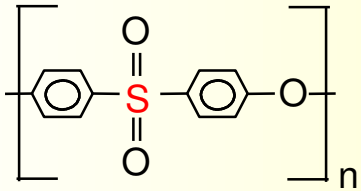
PVDC
Polyvinylidene chloride



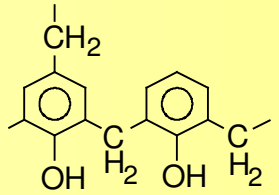
Cellulose



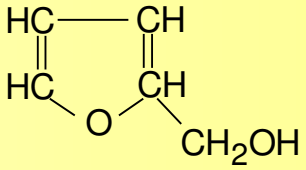
Poly (ether sulfone) (PES)



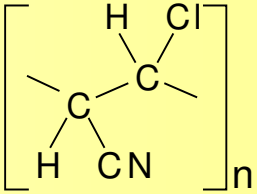
Phenolic resin



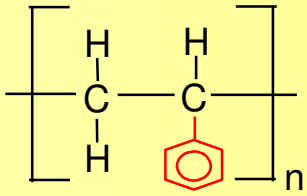
Furfuryl alcohol

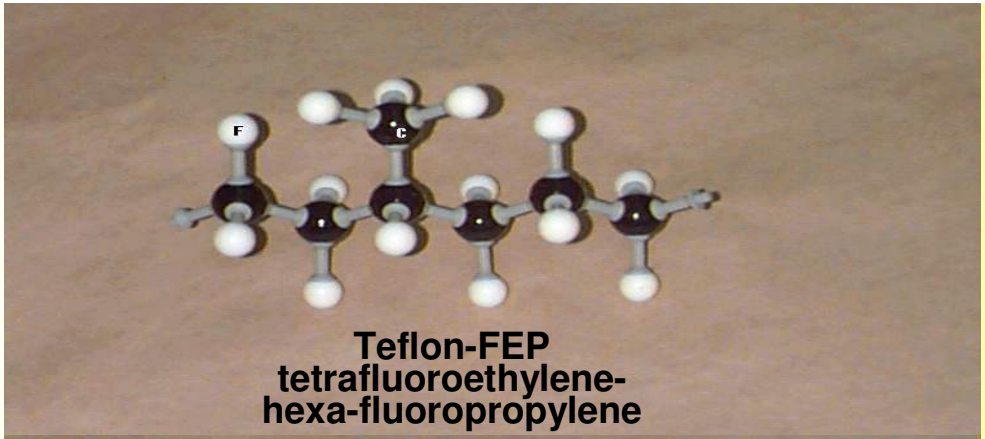


Polyacrylonitrile

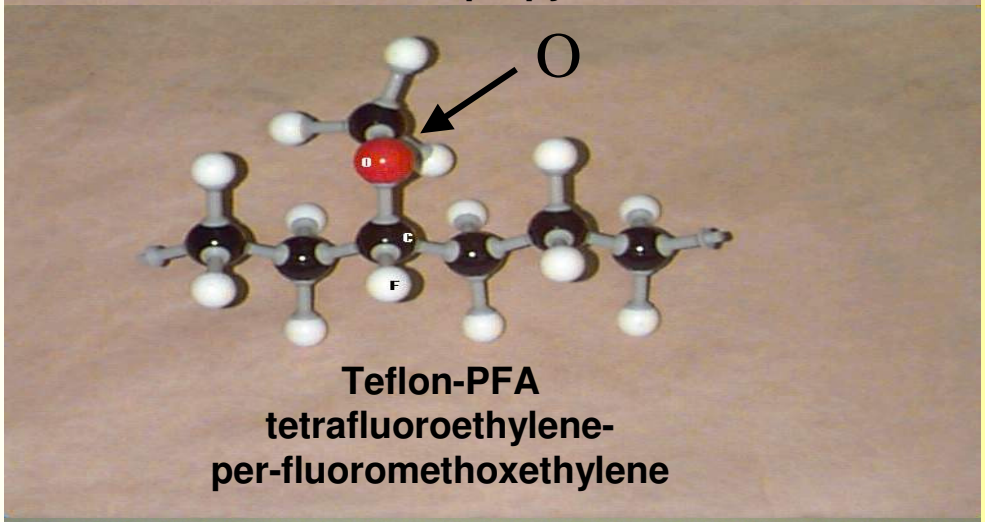


Polystyrene (PS)

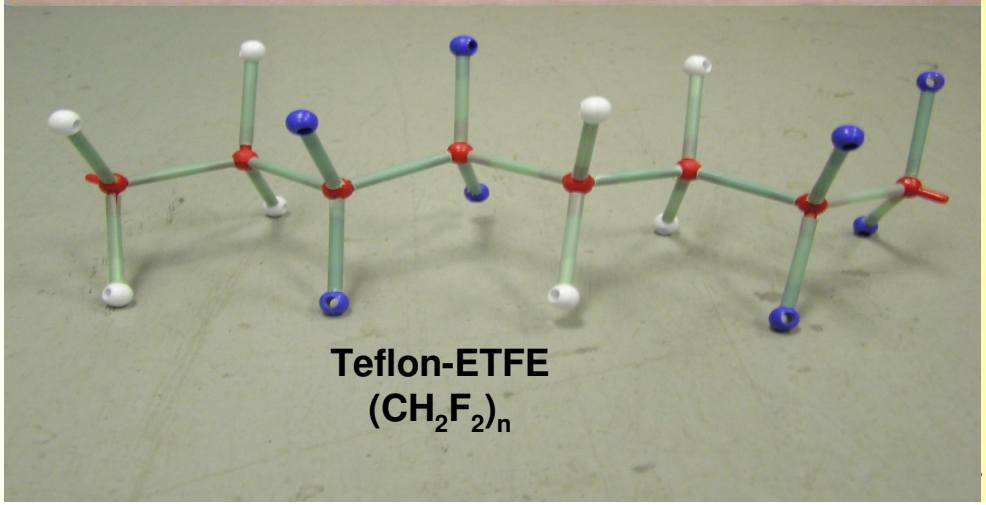




Teflon-FEP
tetrafluoroethylene-
hexa-fluoropropylene

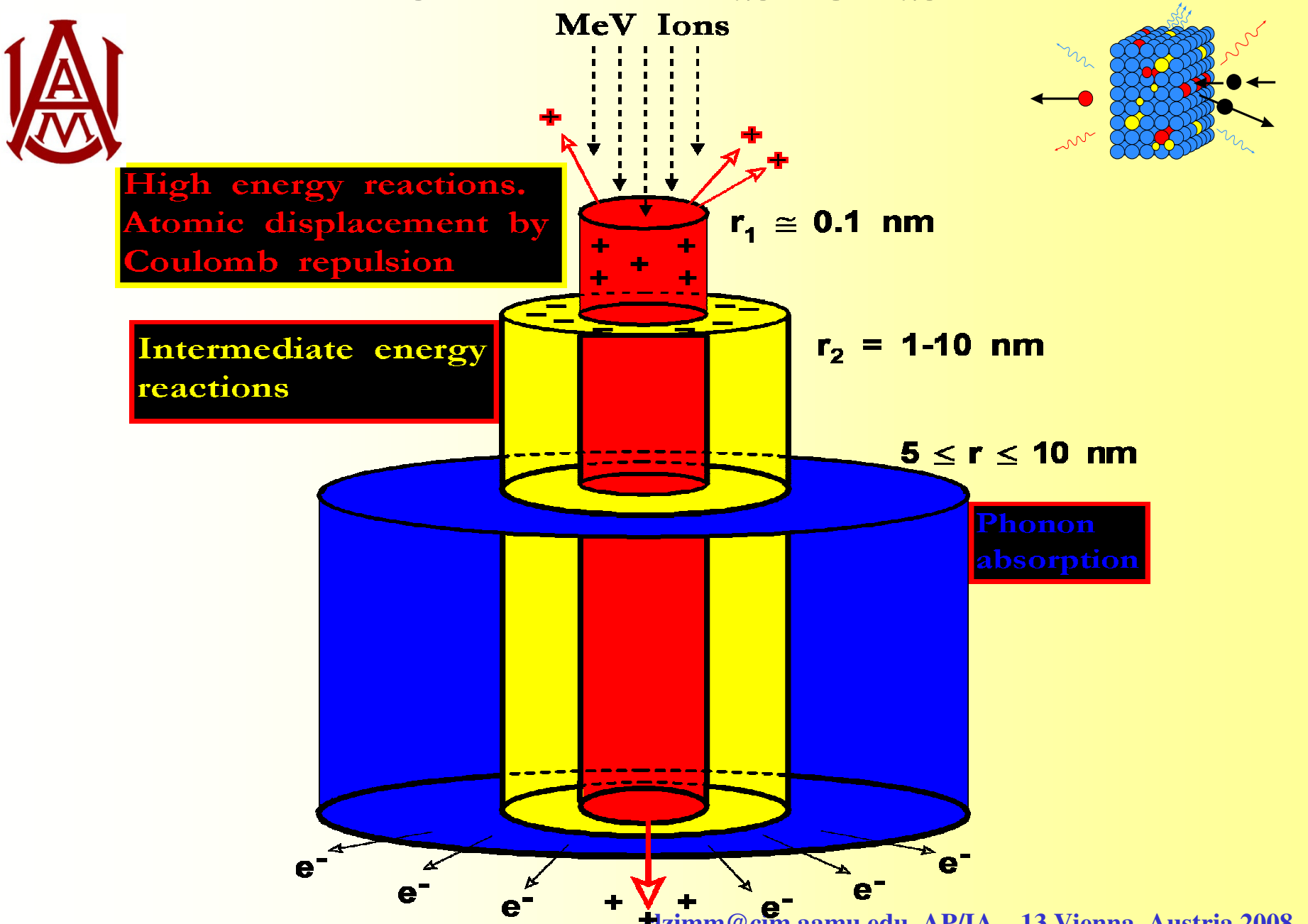


Teflon-PFA
tetrafluoroethylene-
per-fluoromethoxethylene

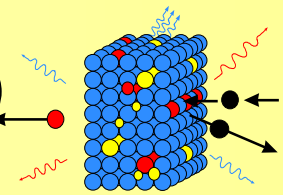


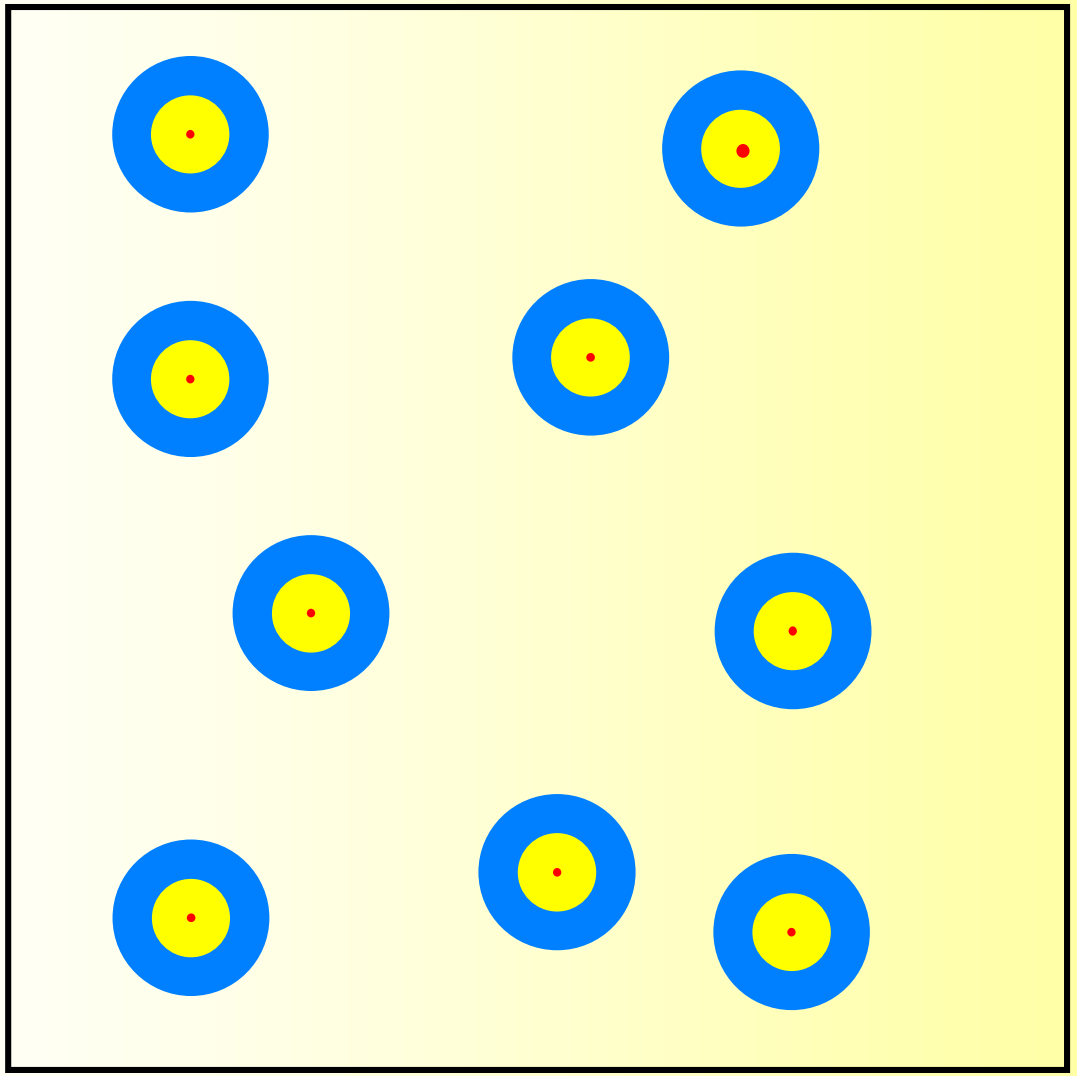
Teflon-ETFE
$(CH_2F_2)_n$

TRACK DIMENSIONS

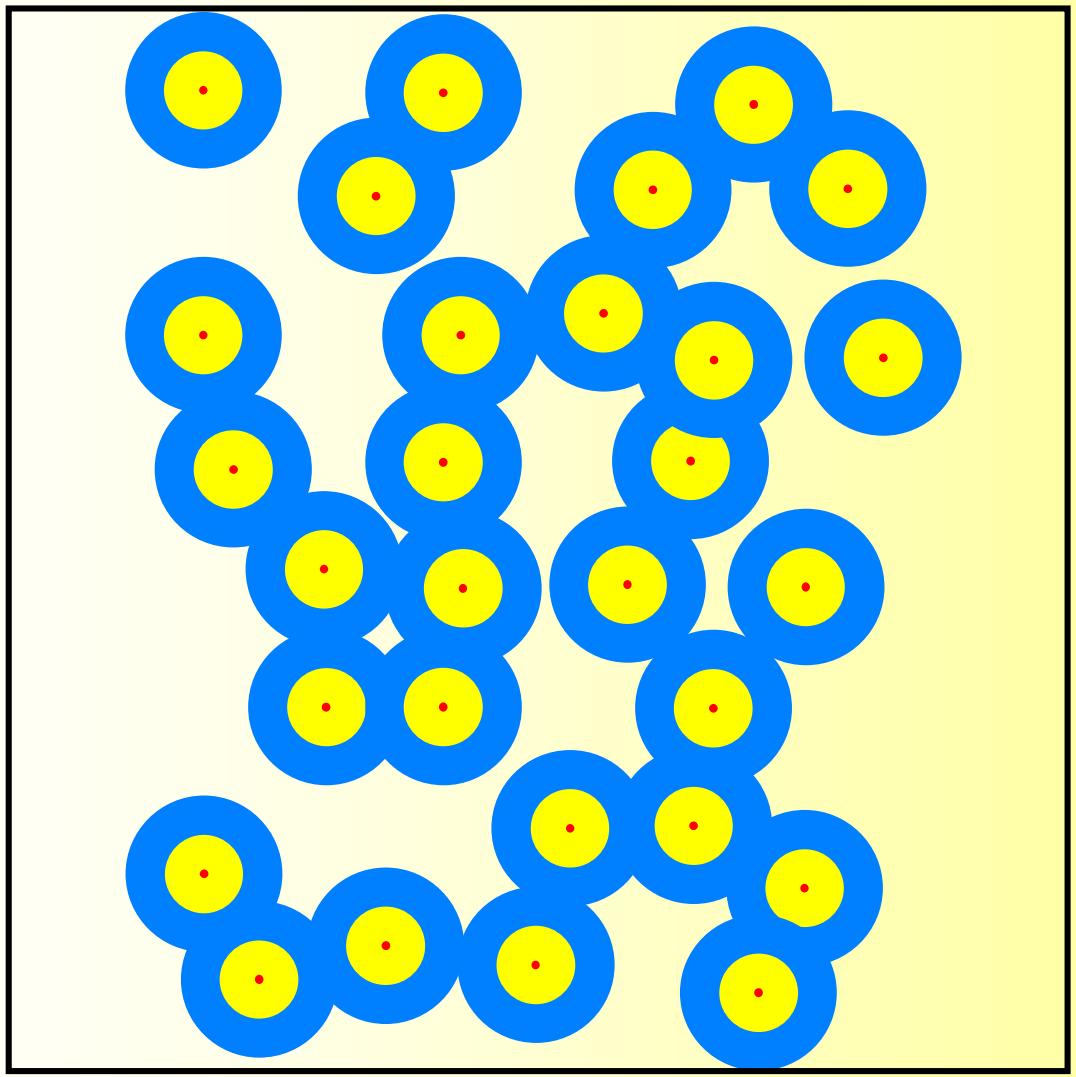


Ion Track Footprints (Low Fluence)

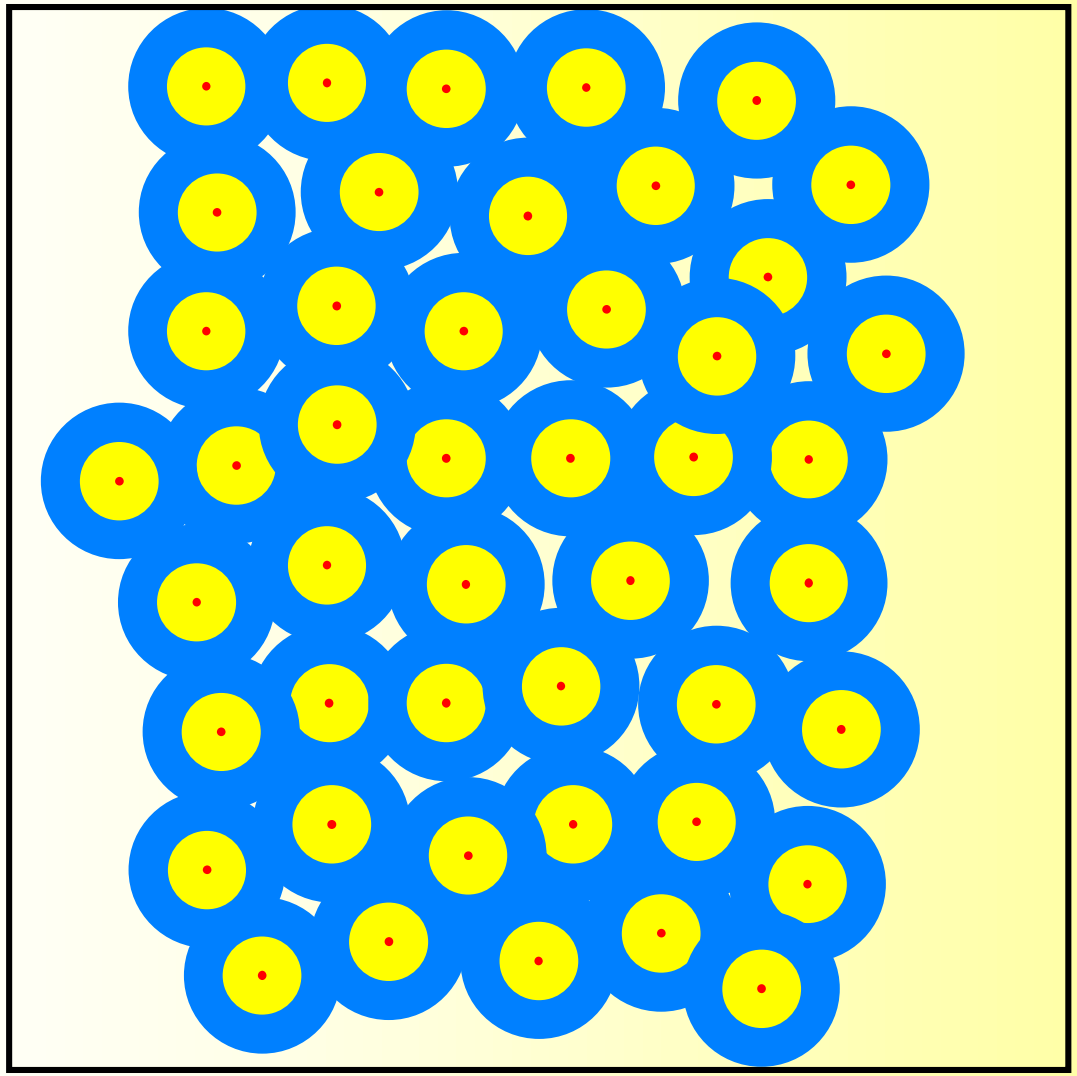




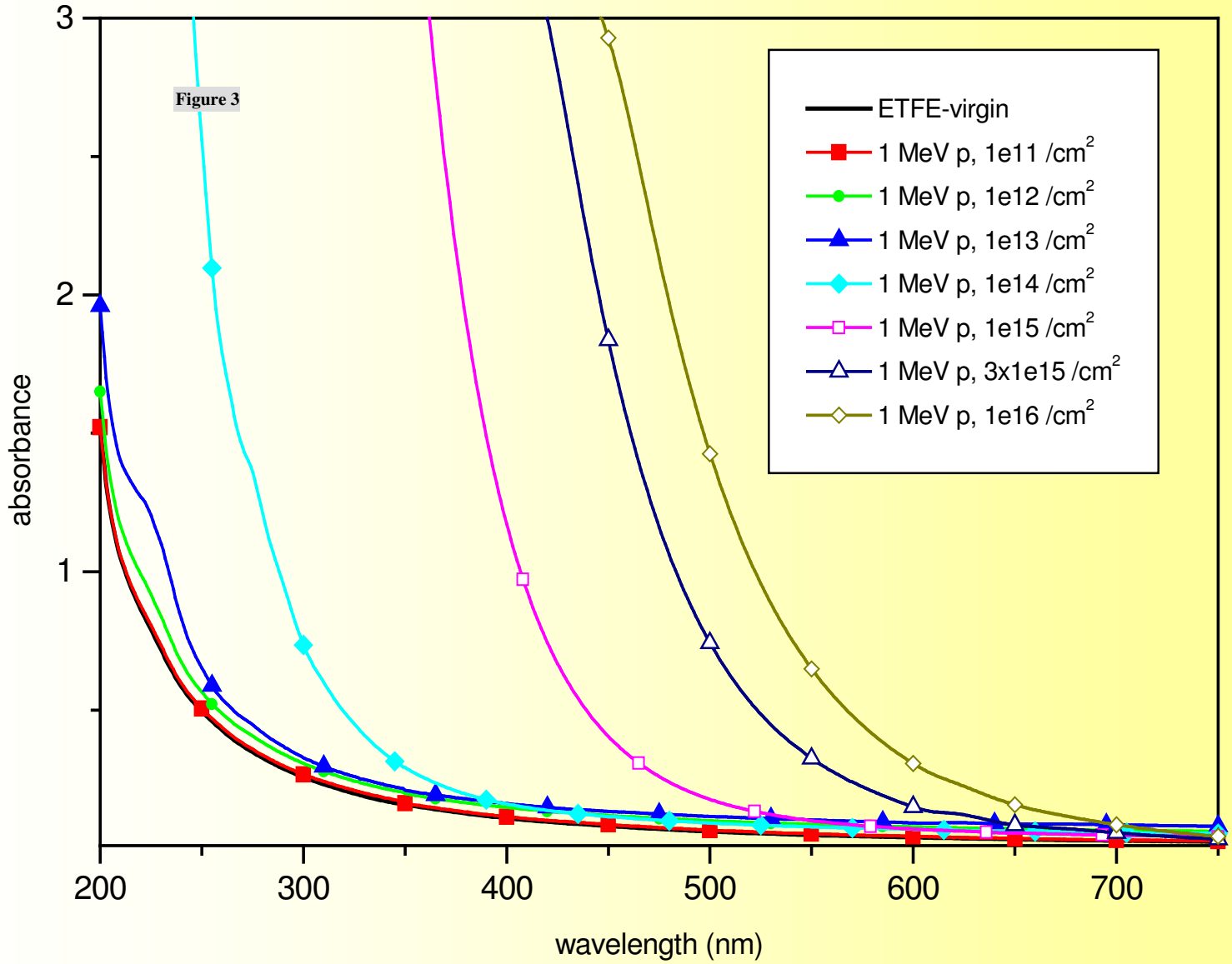
Ion Track Footprints (Intermediate Fluence)

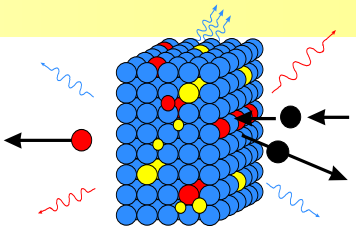


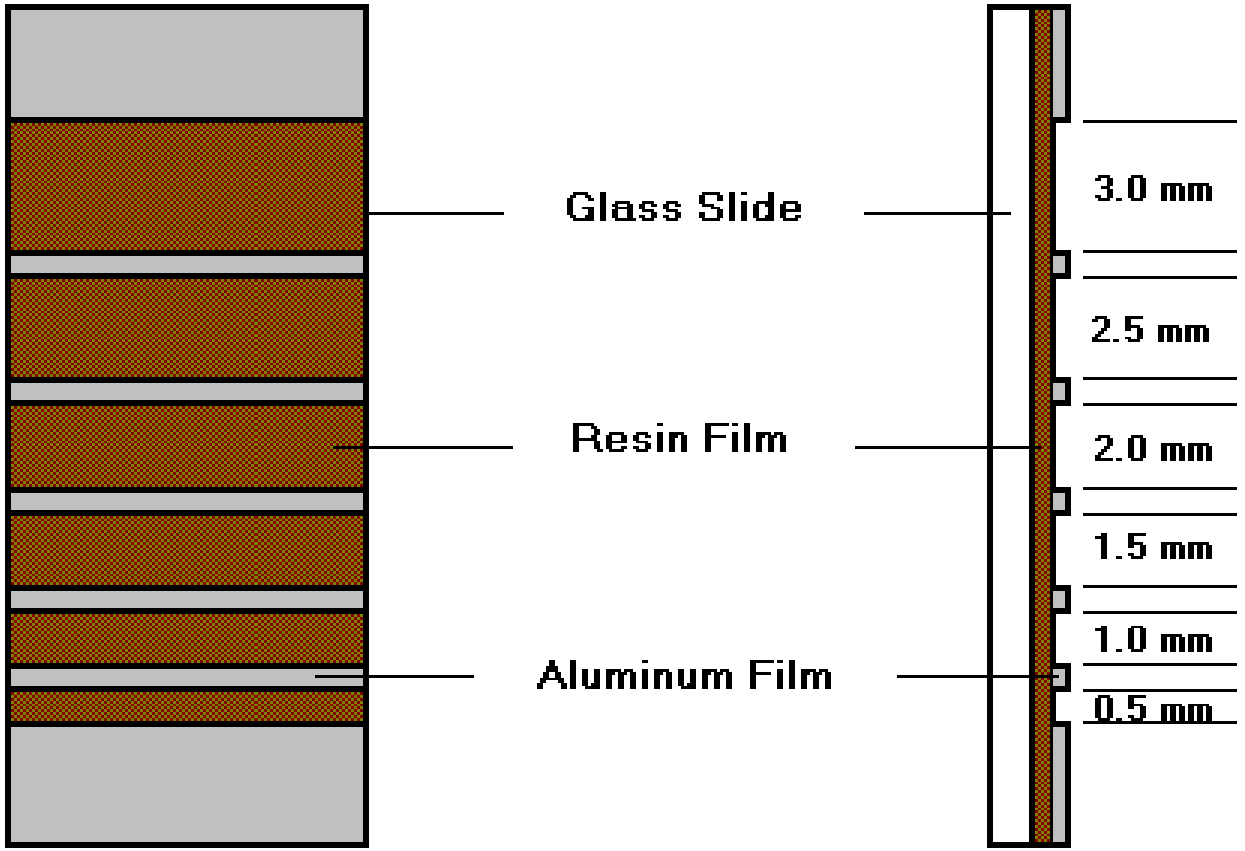
Ion Track Footprints (Hugh Fluence)



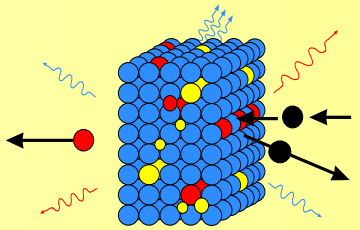
Optical absorption spectra of ETFE after Bombardment by 1 MeV protons.

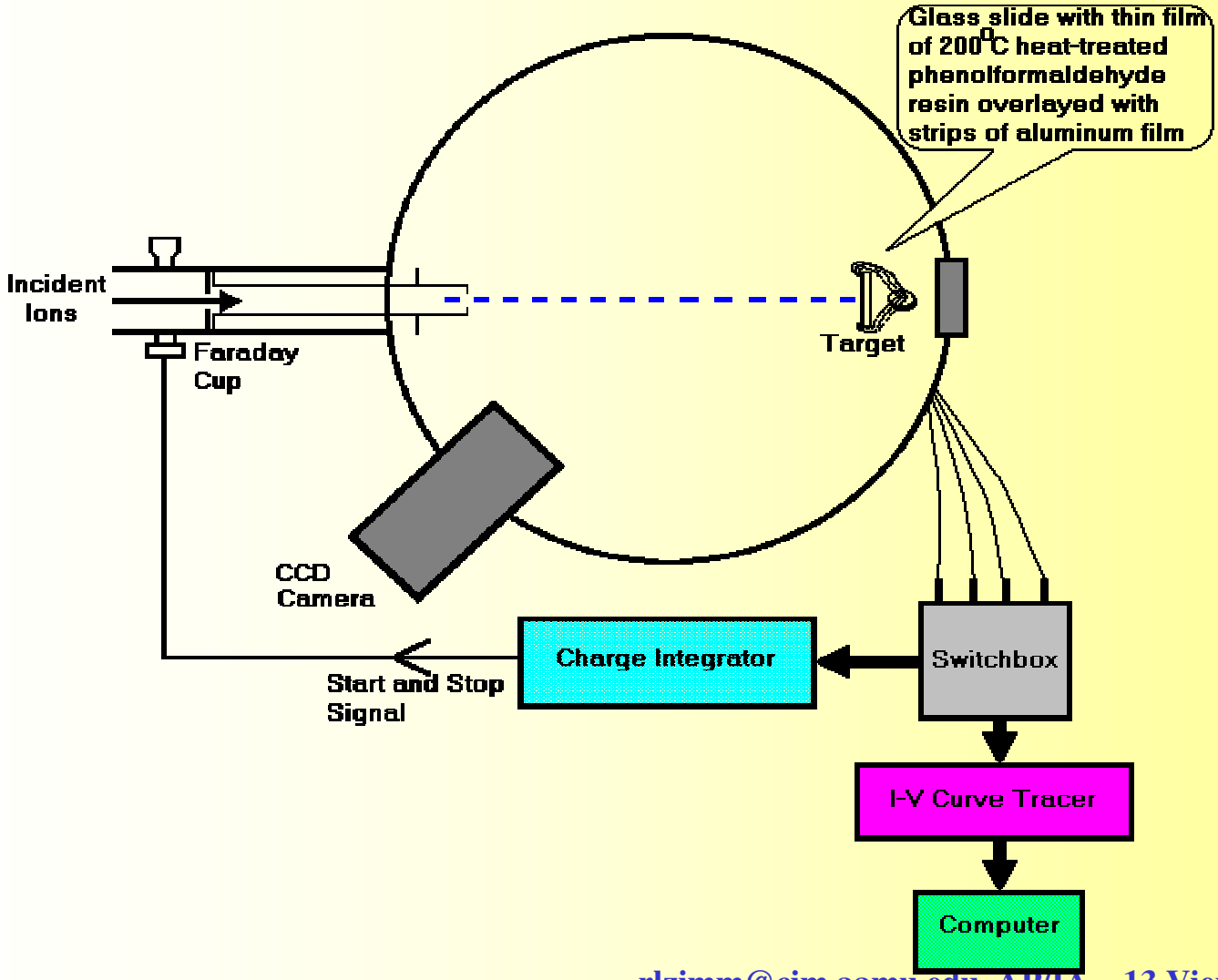





Glass Slide
Resin Film
Aluminum Film
3.0 mm
2.5 mm
2.0 mm
1.5 mm
1.0 mm
0.5 mm
Front View
Side View

Resistivity Measurements





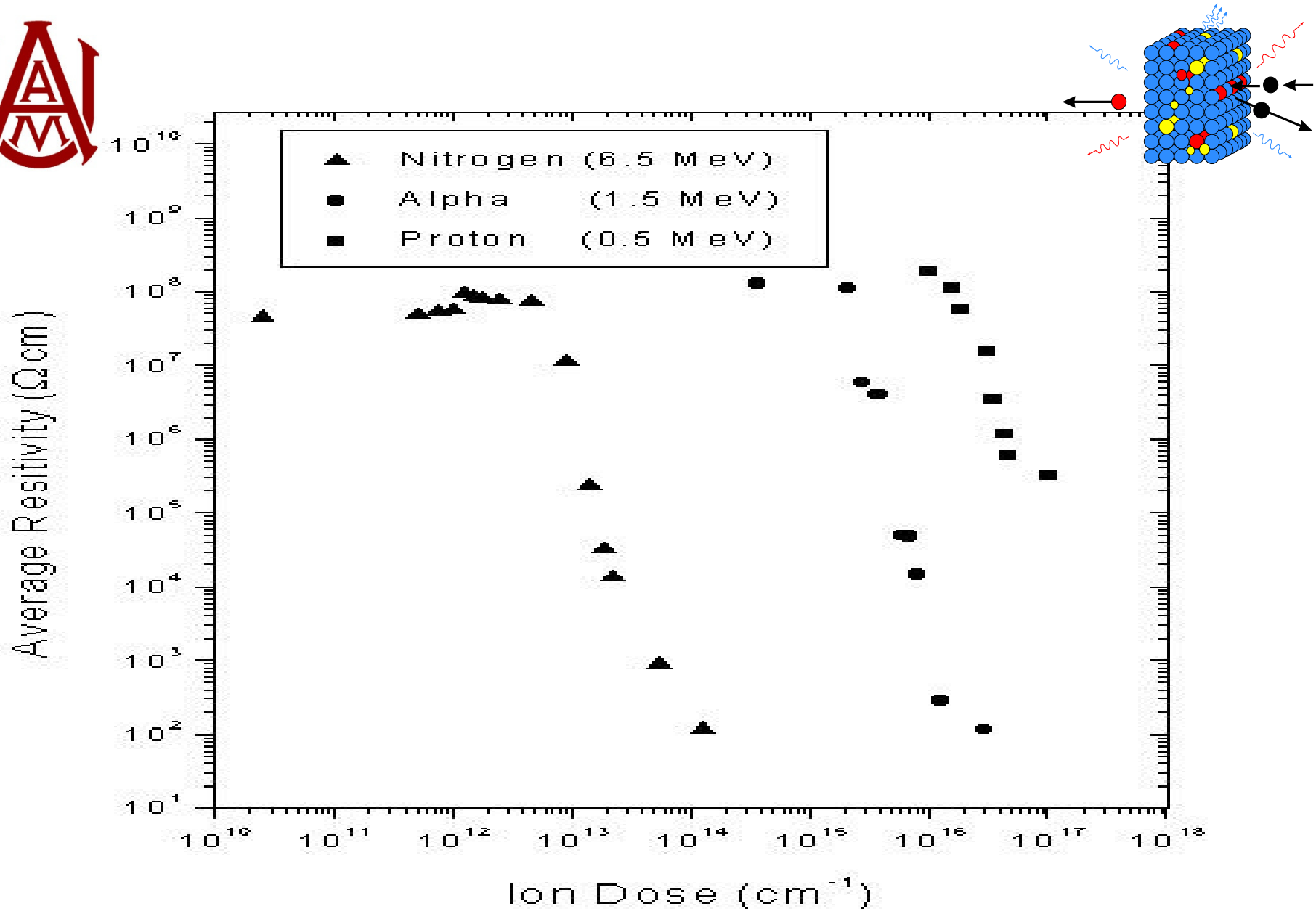
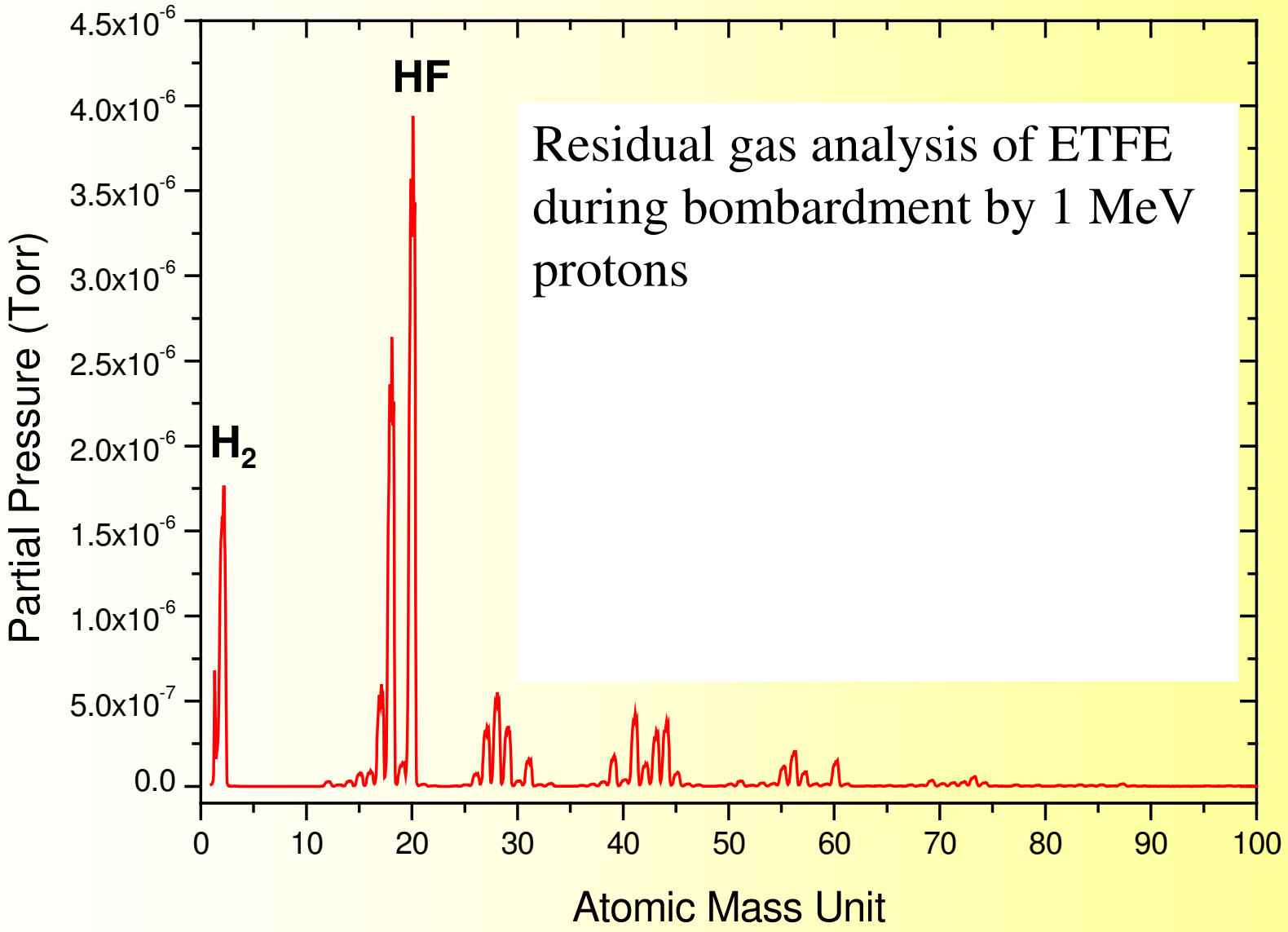
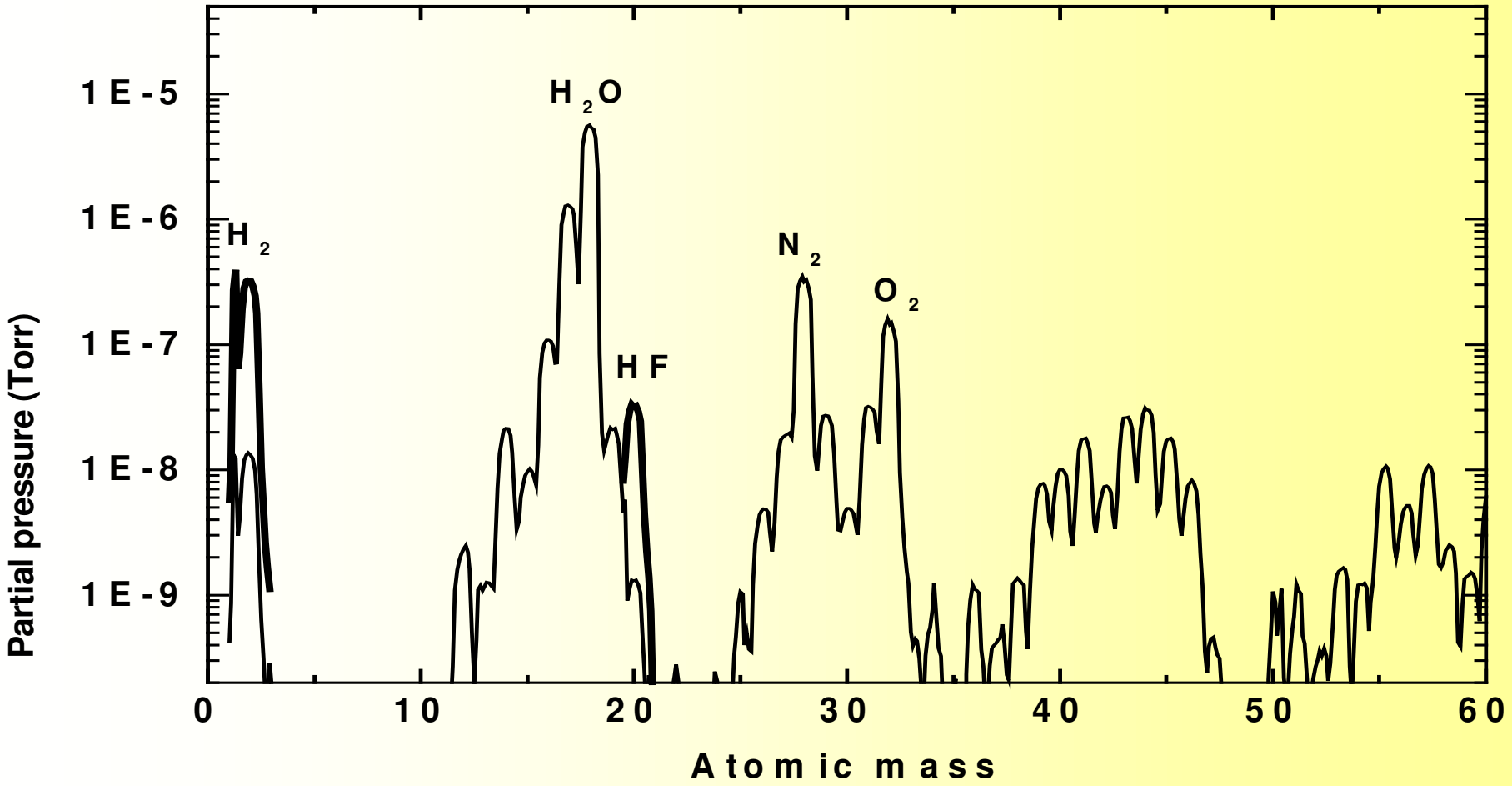
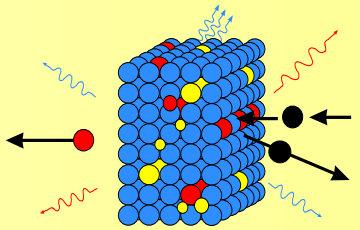

Nitrogen (6.5 MeV)
Alpha (1.5 MeV)
Proton (0.5 MeV)
Average Resitivity (Ωcm)
Ion Dose (cm⁻¹)

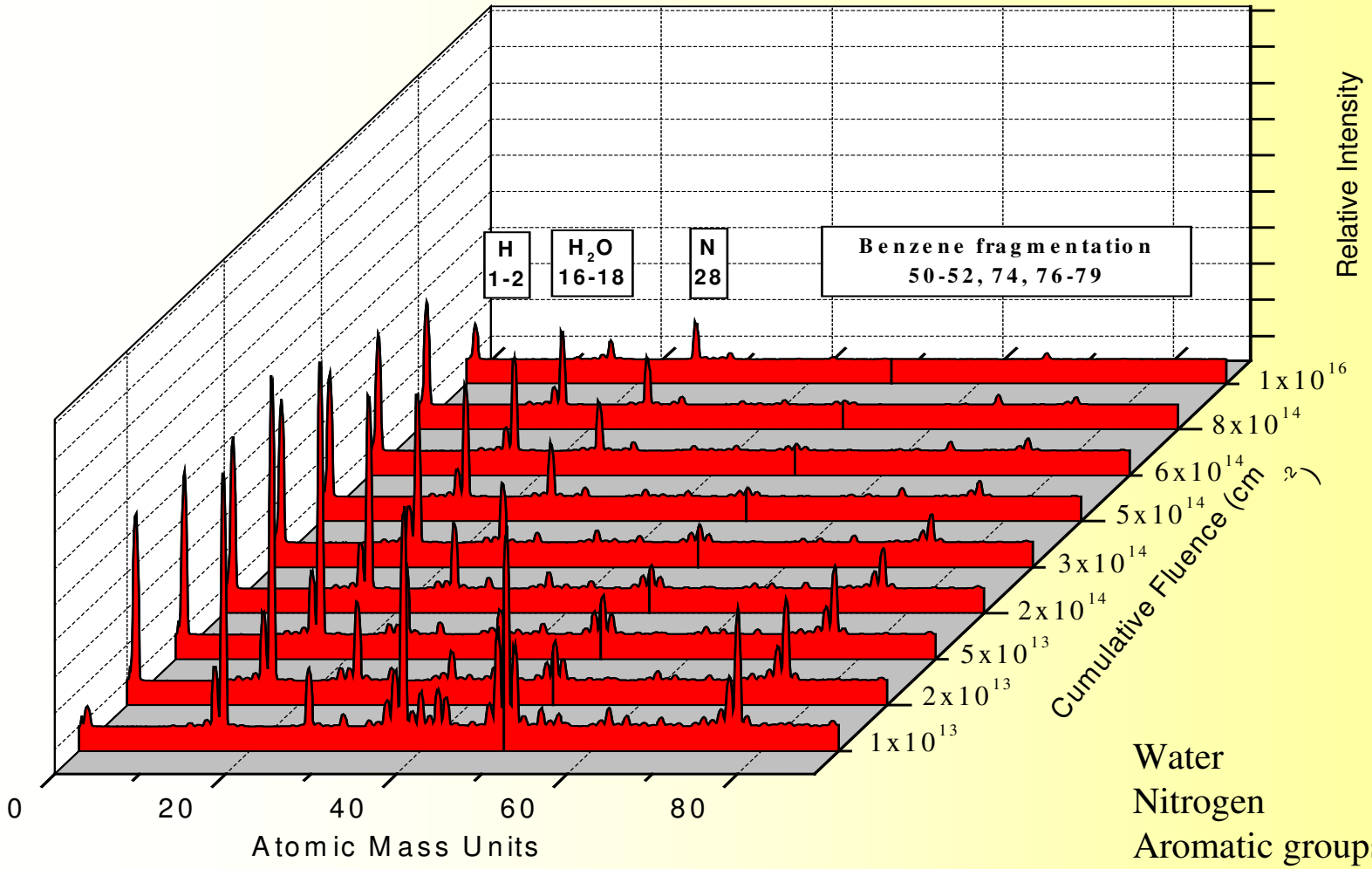
Figure 1


Residual gas analysis of ETFE during bombardment by 1 MeV protons
HF
H2
Partial Pressure (Torr)
4.5x10-6
4.0x10-6
3.5x10-6
3.0x10-6
2.5x10-6
2.0x10-6
1.5x10-6
1.0x10-6
5.0x10-7
0.0
0
10
20
30
40
50
60
70
80
90
100
Atomic Mass Unit


Partial pressure (Torr)
1 E -5
1 E -6
1 E -7
1 E -8
1 E -9
H 2
H 2O
H F
N 2
O 2
0
10
20
30
40
50
60
Atomic mass

RGA SPECTRA FROM 4 MeV α-IRRADIATED PS FILMS: SHOWS POLYMER DEGRADATION OVER TIME





Water	16-18
Nitrogen	28
Aromatic groups (C_6)	74-79

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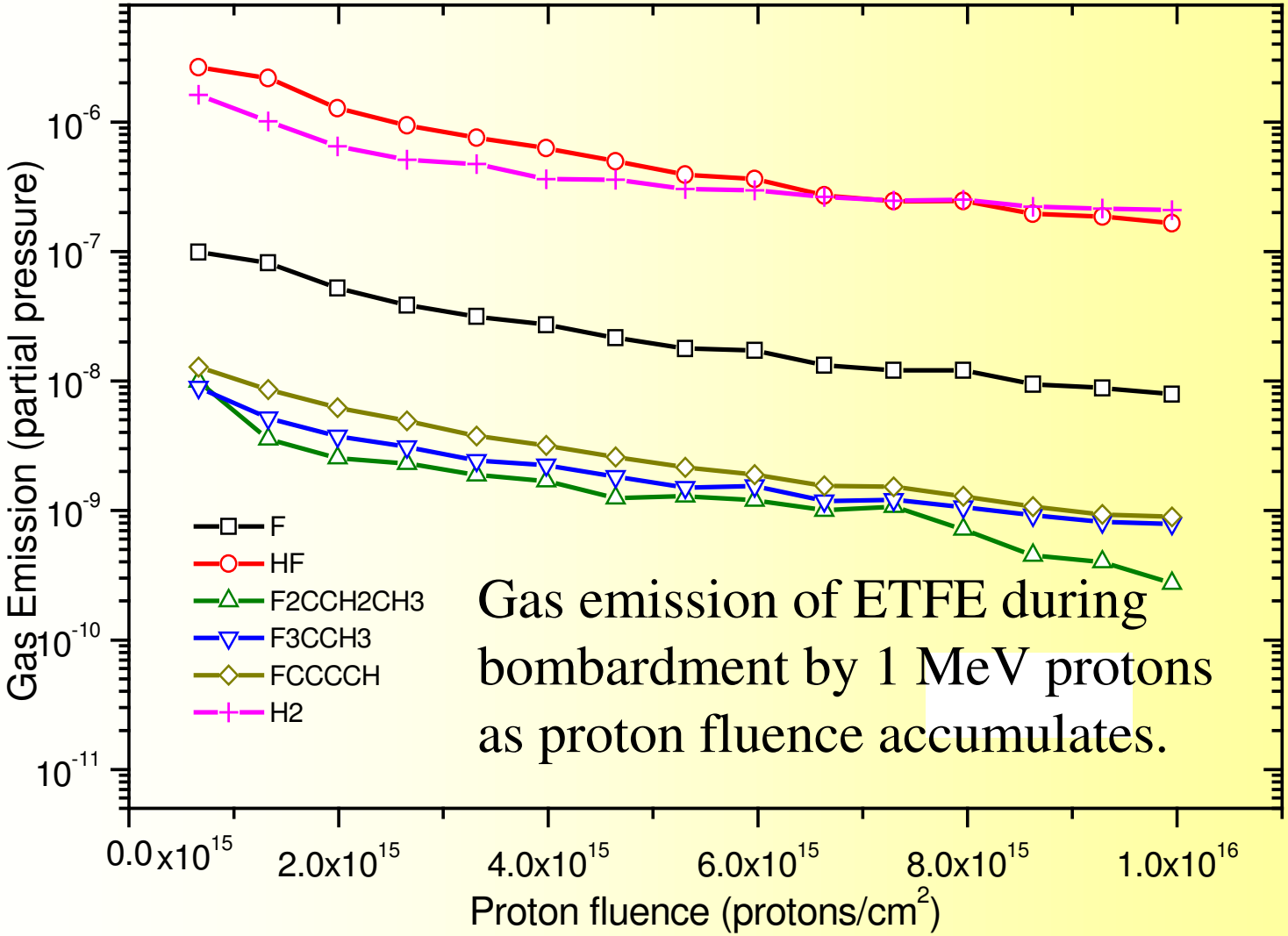
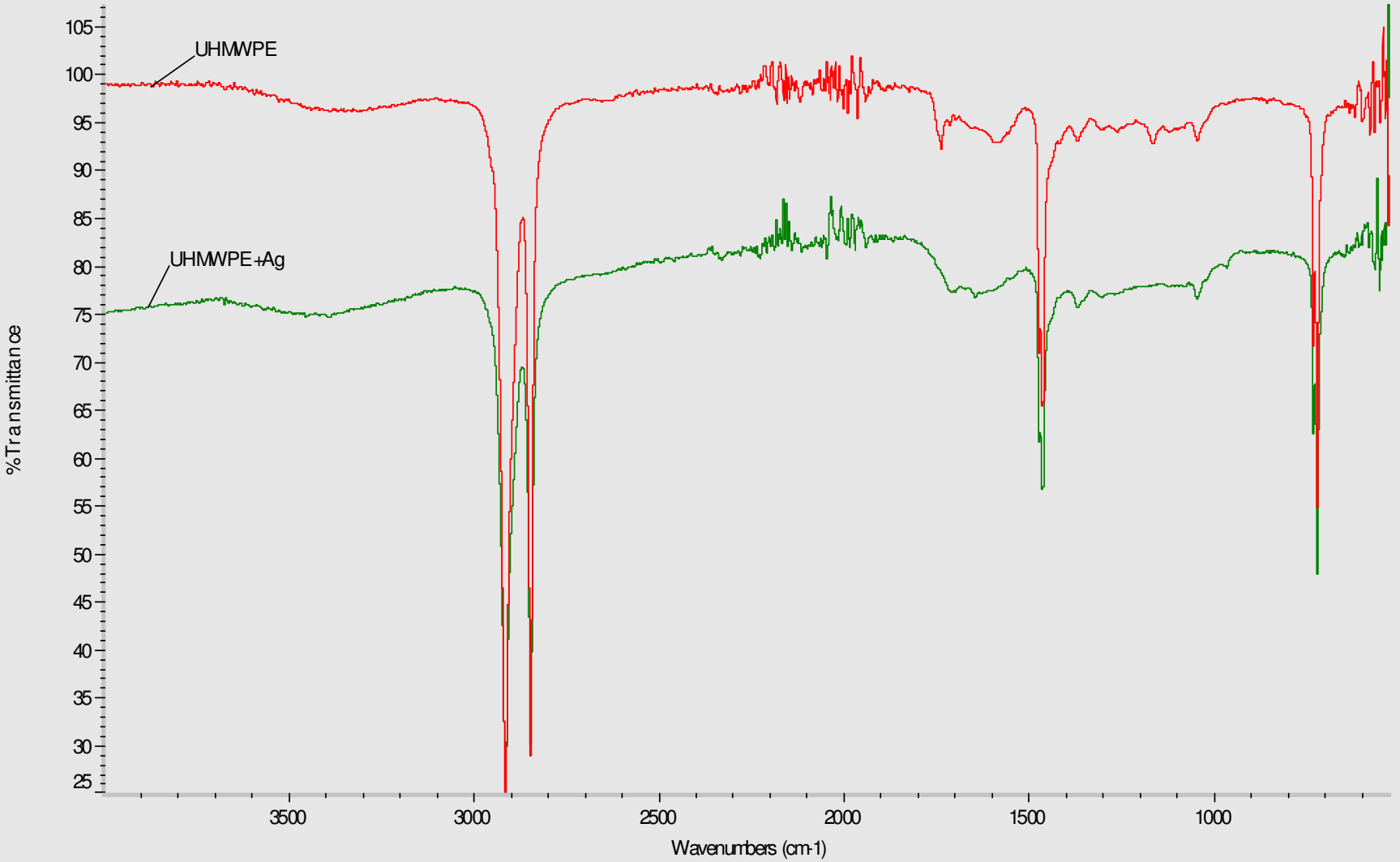
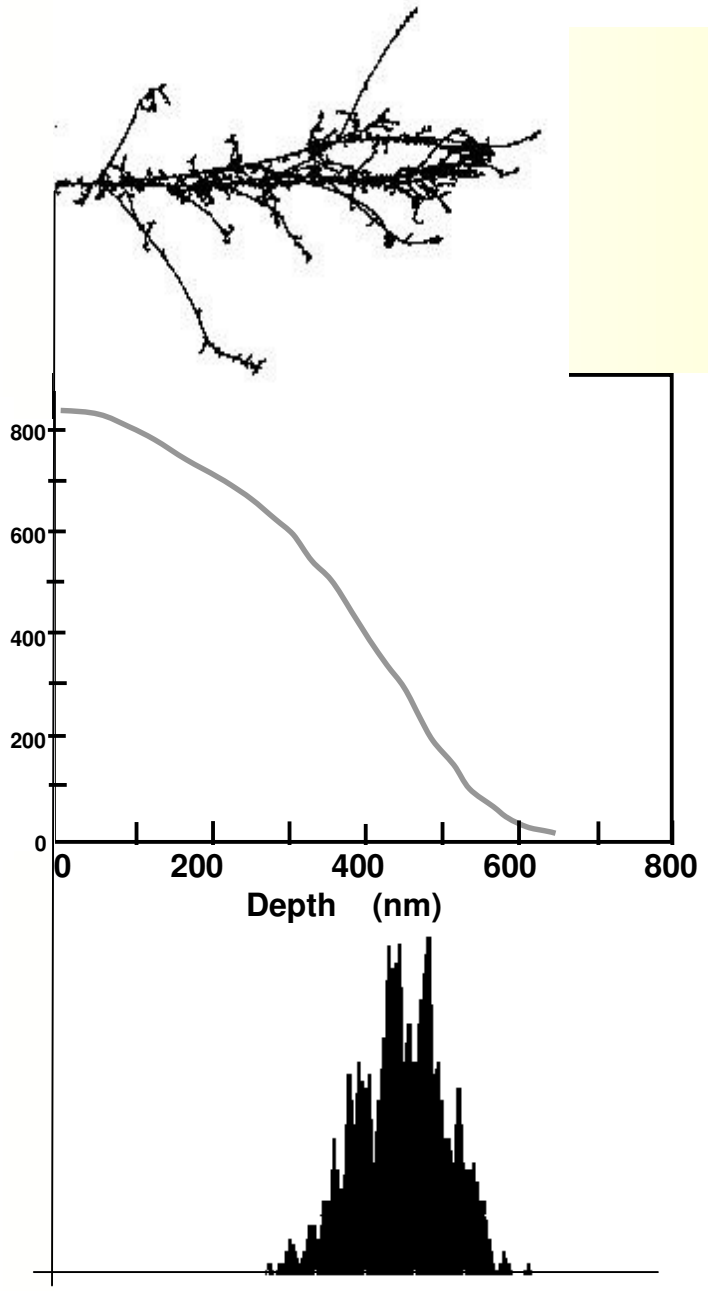


Gas emission of ETFE during bombardment by 1 MeV protons as proton fluence accumulates.



FTIR spectra of UHMWPE implanted with Ag

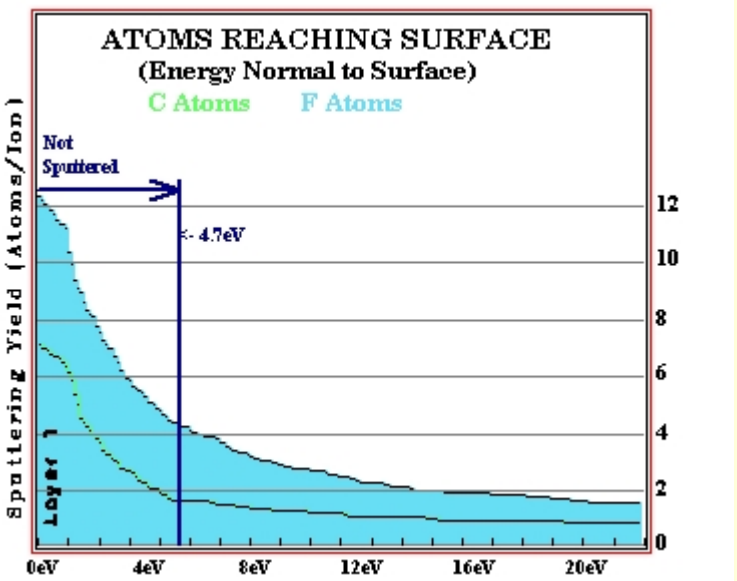
SRIM simulations of the effect of 1 MeV silver ions on GPC.

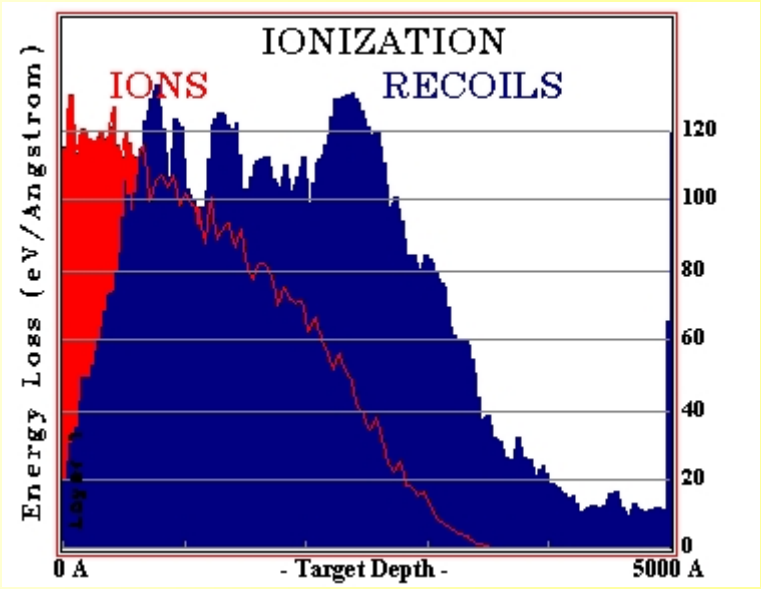


Recoil carbon atoms carry energy laterally hundreds of nm.

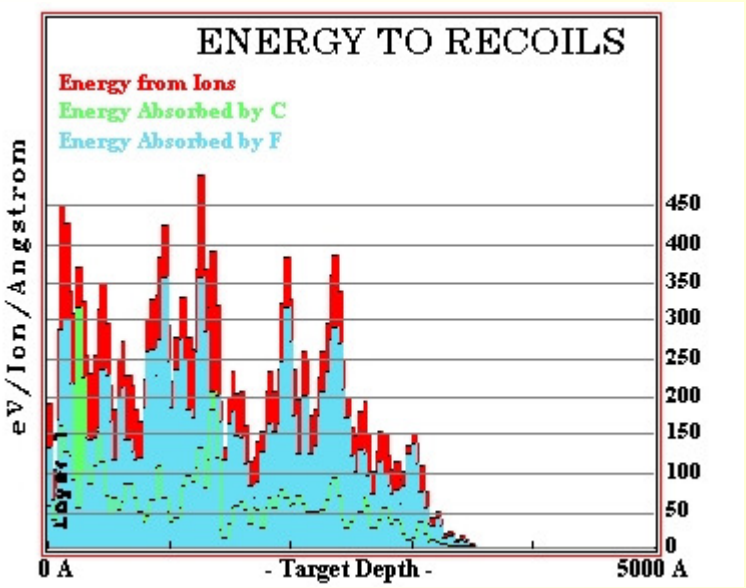
Each incident ion deposits more energy near the surface.

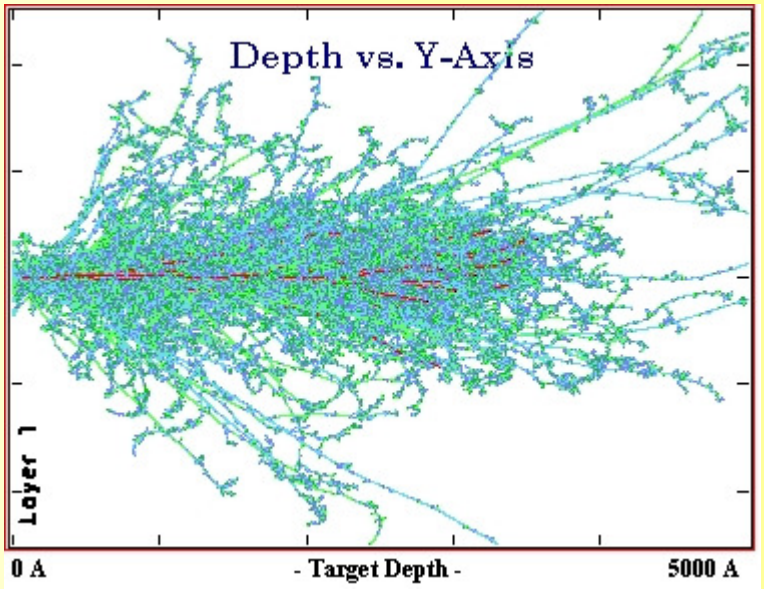
The silver ions are implanted at an average depth of about 450 nm.





1 MeV Au in CF_2





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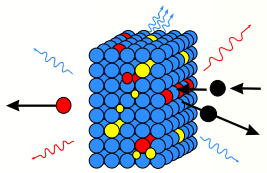
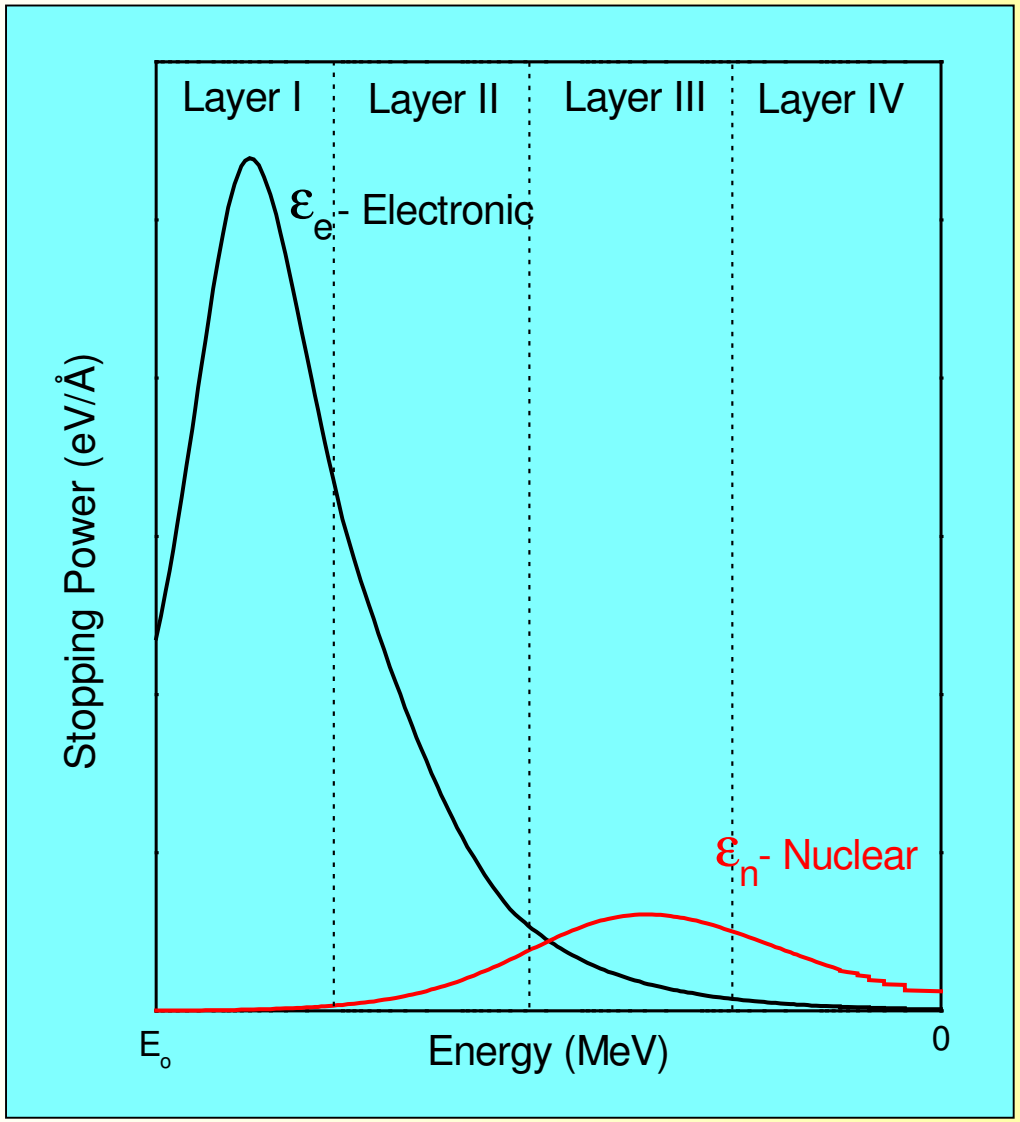
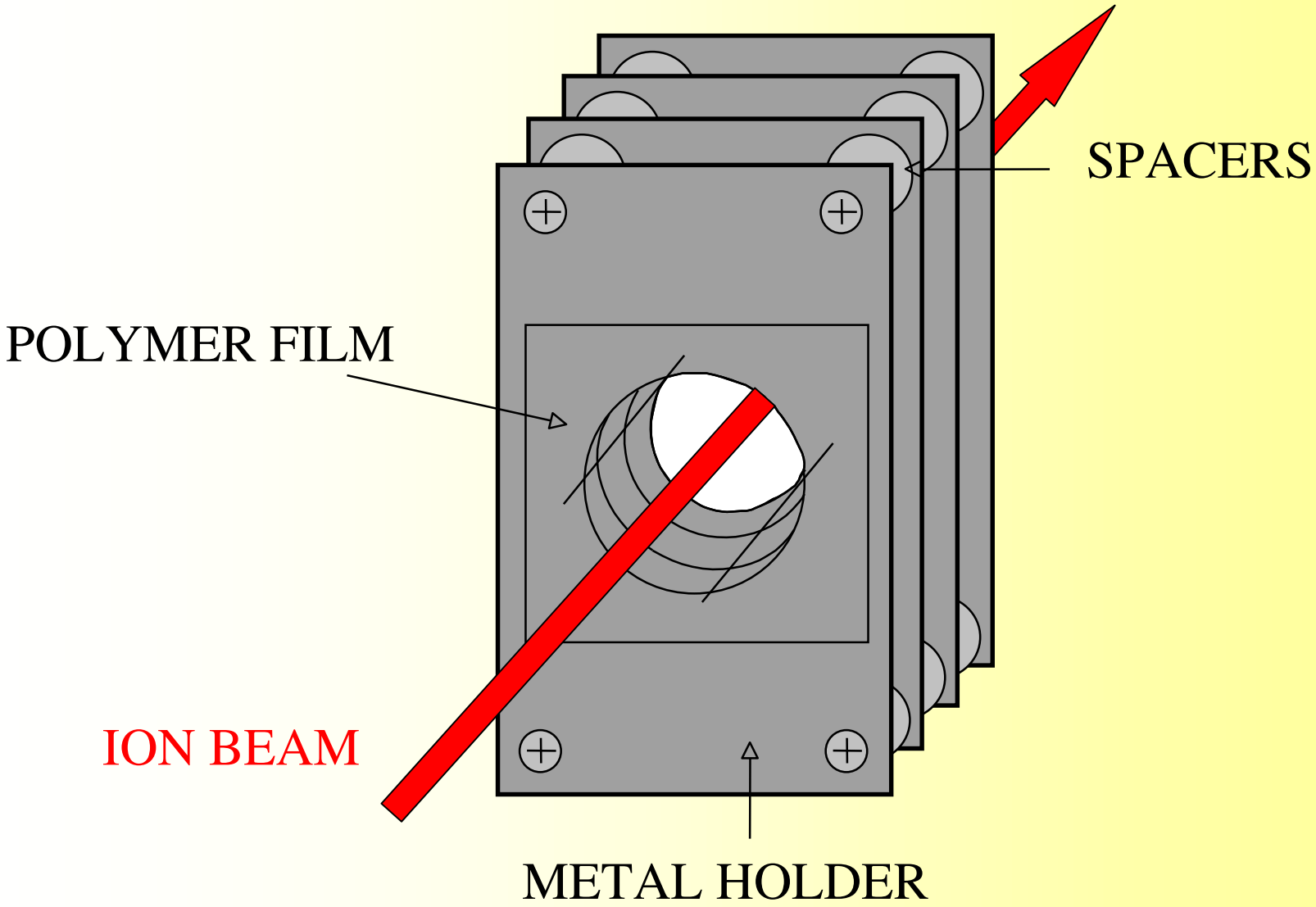


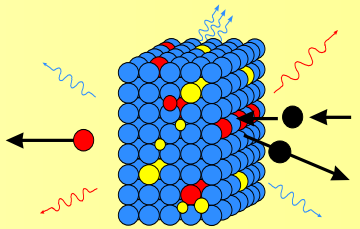
The Stopping Power Profile

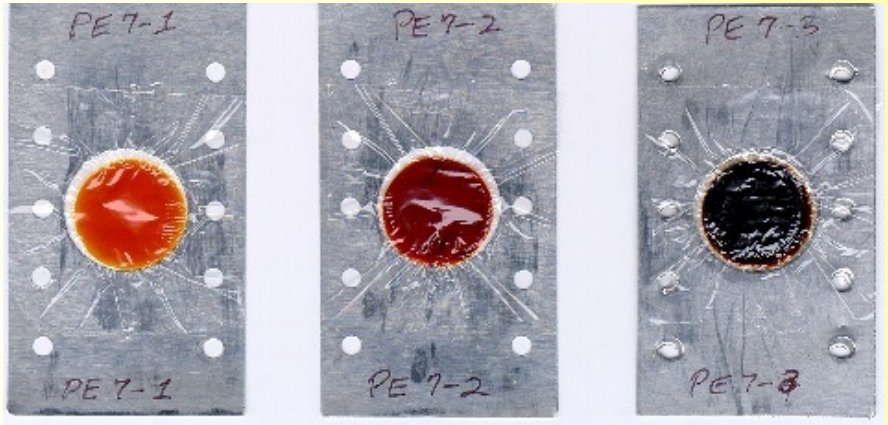


Polymer films are stacked



COLOR CHANGES
in α-IRRADIATED PE FILMS

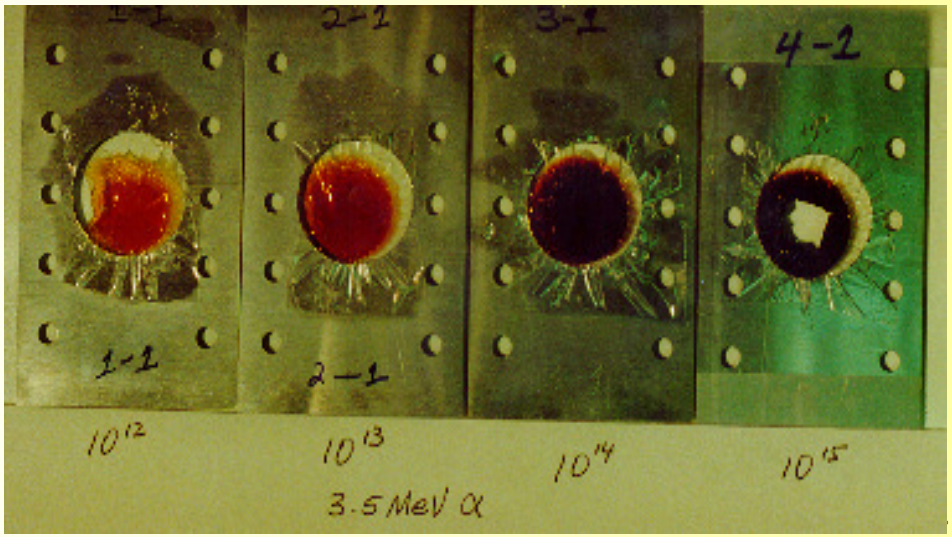


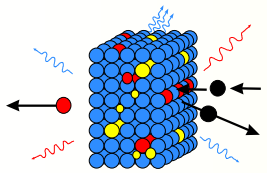


Layer 1
Front

Layer 2
Middle

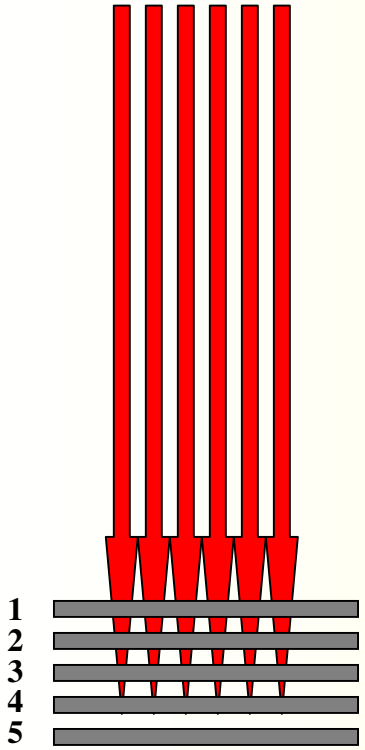
Layer 3
Back

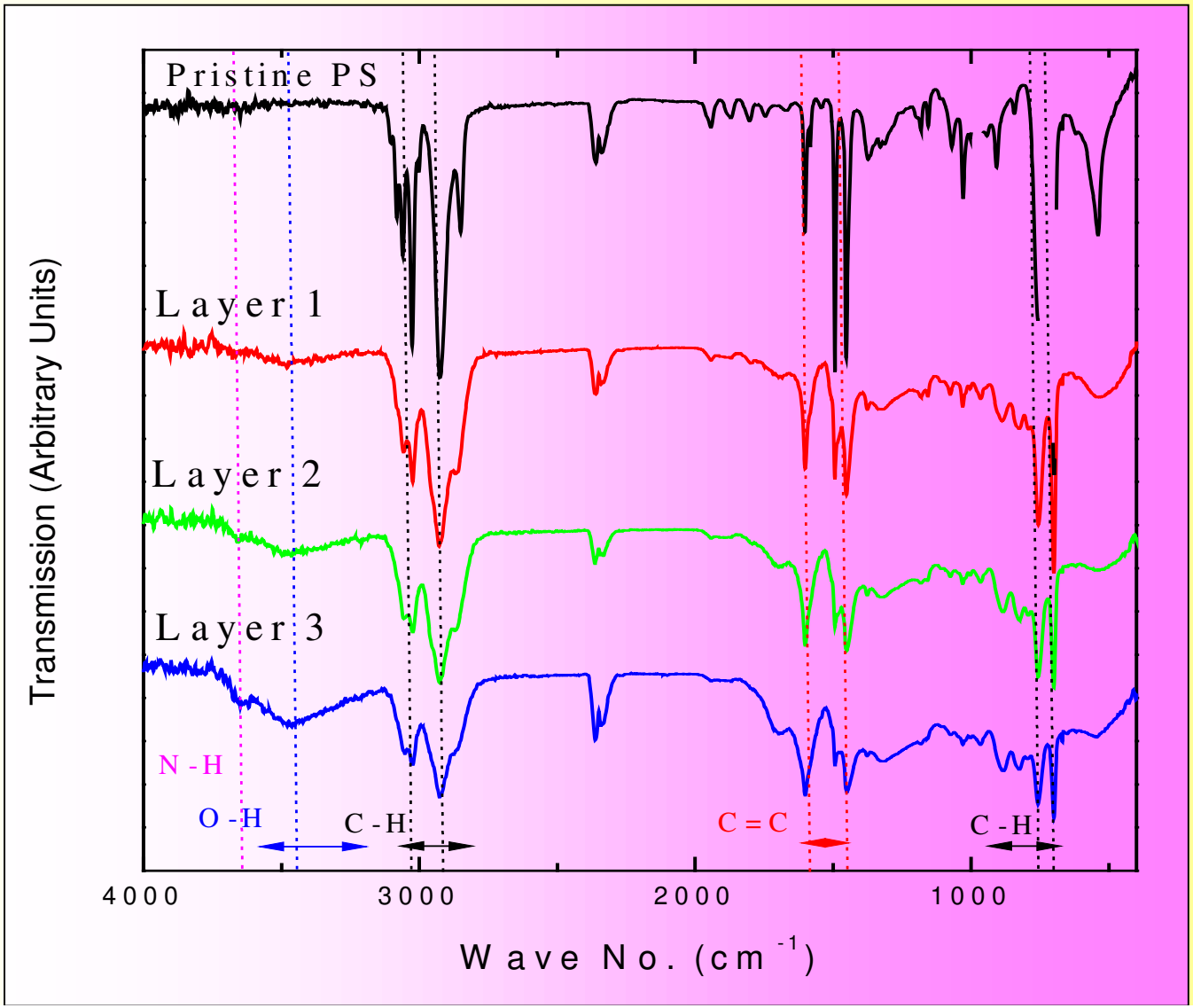


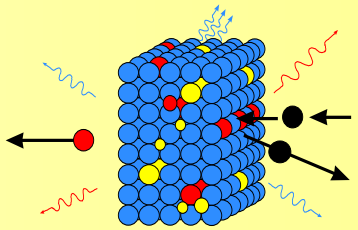


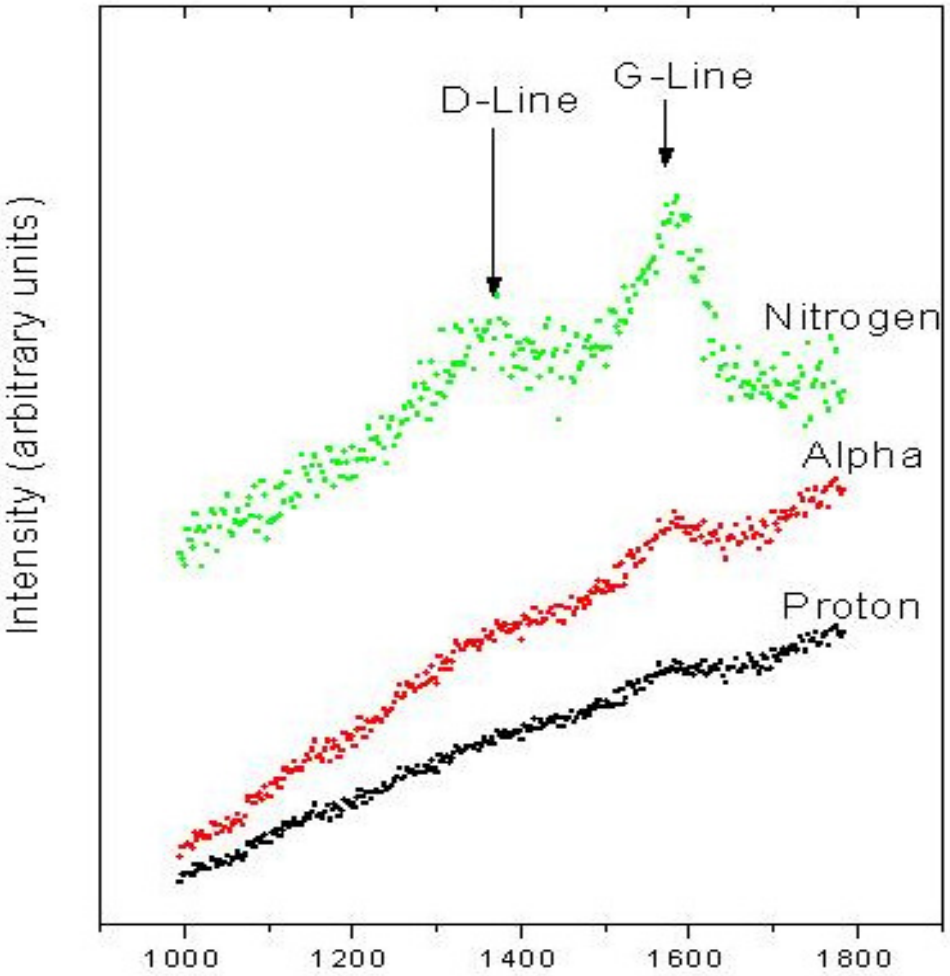
FTIR Spectroscopy

PS: 4 MeV α-irradiated 5 x 10^{15} ions/cm^2

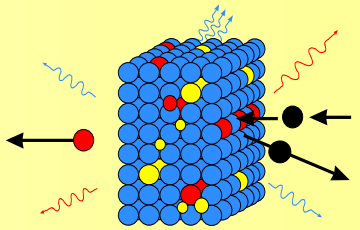


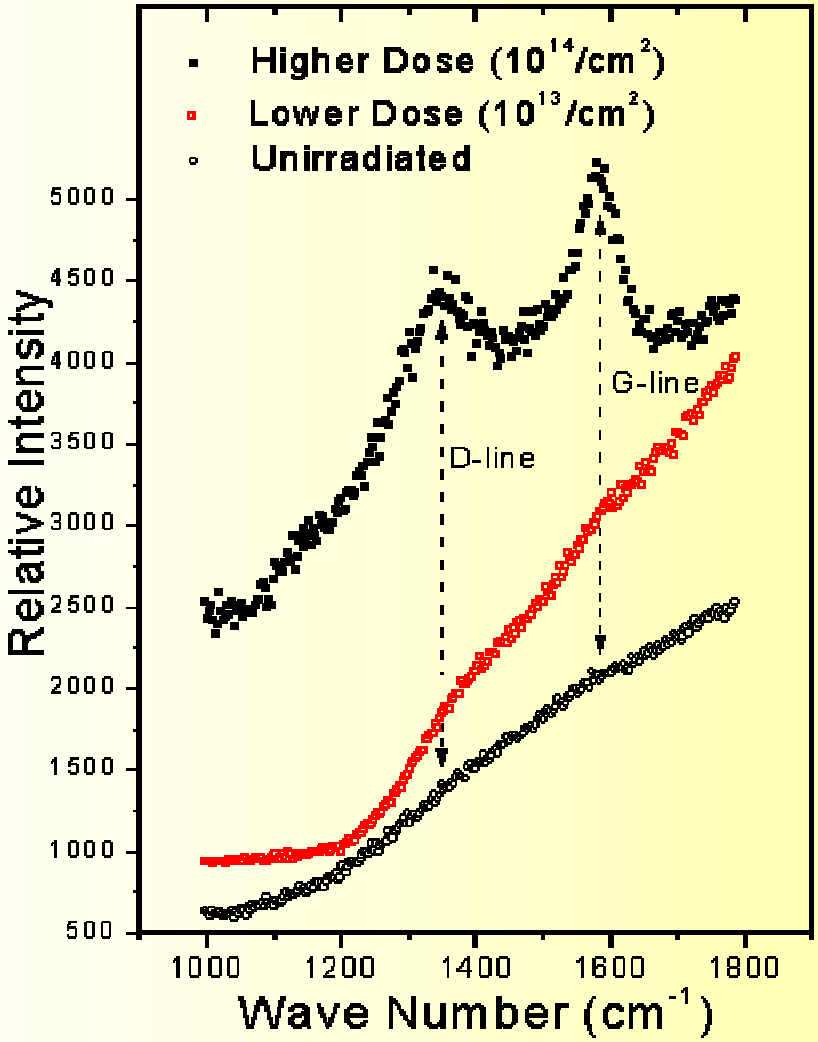




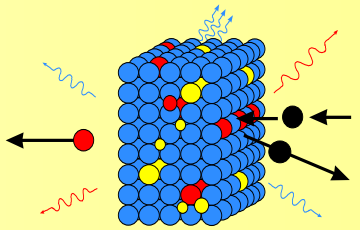

D-Line
G-Line
Nitrogen
Alpha
Proton
Intensity (arbitrary units)
1000
1200
1400
1600
1800
Frequency (cm-1)

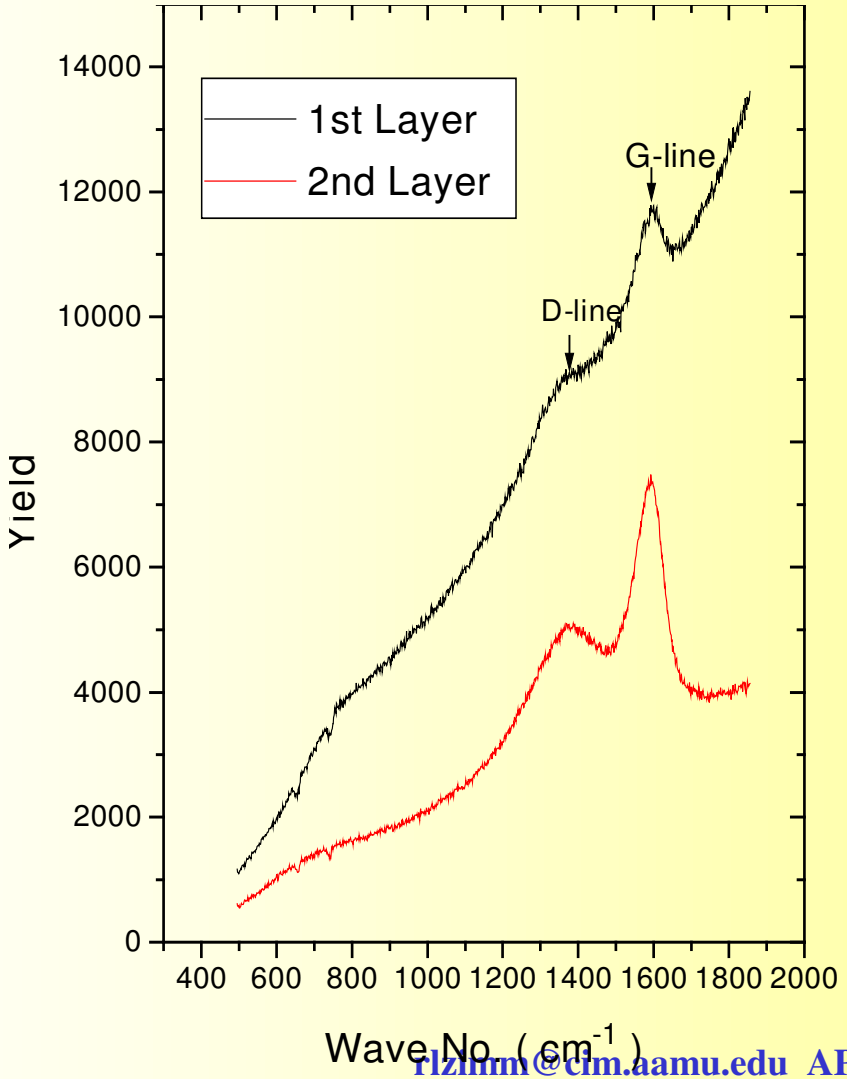
Raman from PF

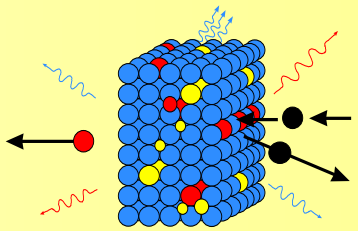




RAMAN SPECTRA FROM 3.5 MeV α-IRRADIATED PE FILMS (5×10^{15} IONS/CM^2)





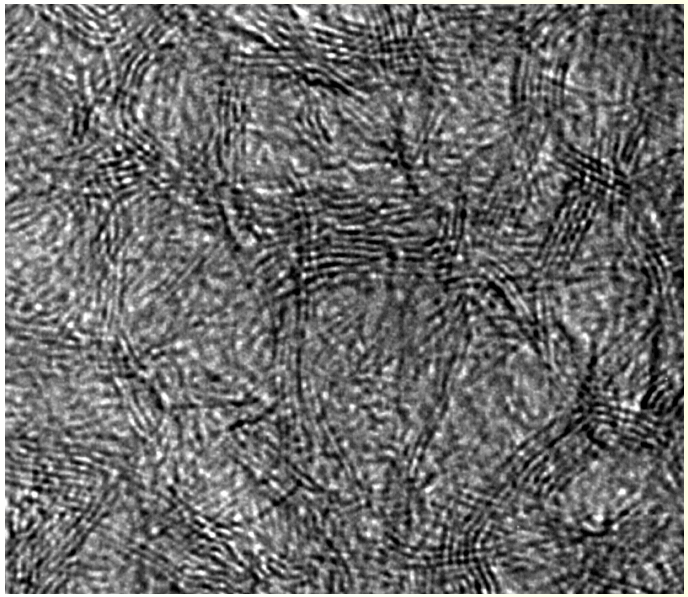


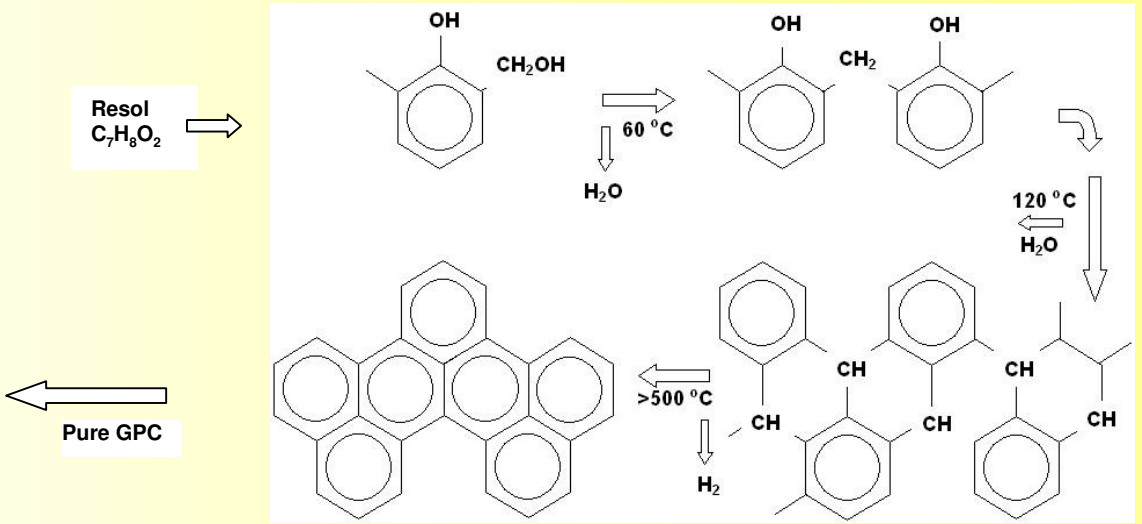
APPLICATIONS

1. Enhancement of GPC heart valve
   By ion implantation

Biplus Cardiac valve of GPC, HP Bioengenharia

São Paulo/SP, Brazil





Low temperature heat treatment produces **Bakelite**

GPC produced by heat treatment to 2800K

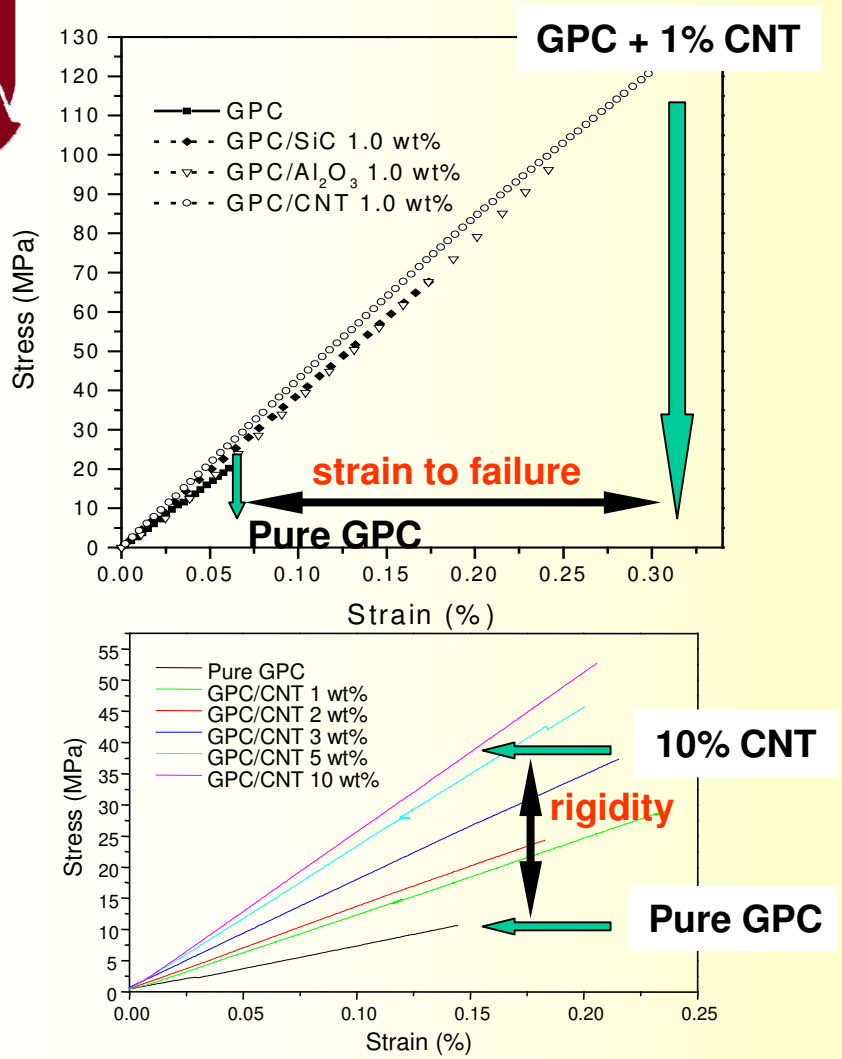
Closed **pores** (30% of the volume)
The material is completely **impermeable**

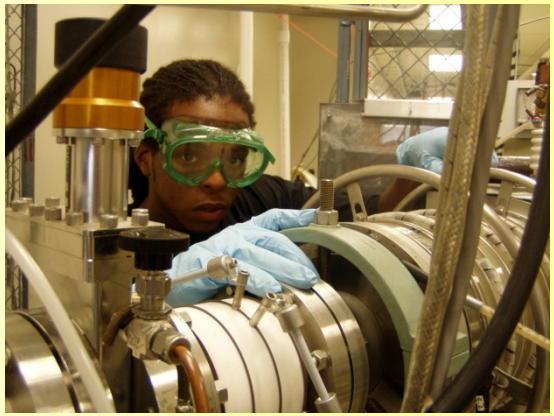
RAMAN spectroscopy reveal amorphous carbon, responsible for eliminating pore connectivity

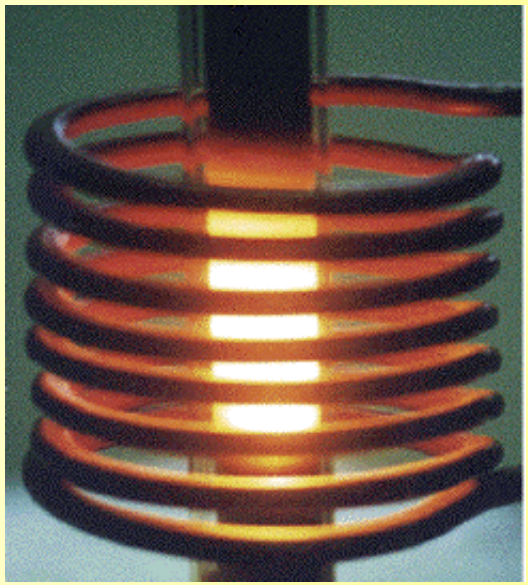
Properties of Polymeric Carbon

Properties	Unit	Typical values
bulk density	Mg/m^3	1.3 - 1.5
tensile strength	MPa	40 - 100
flexural strength	MPa	210 - 260
compressive strength	MPa	480 - 580
young's modulus	GPa	14 - 33
gas permeability	mm^2/s	10^{-4} - 10^{-10}
Vickers hardness	HV_1	230 - 340
coefficient of thermal expansion	1/K	~ 10^{-8}
thermal conductivity	W/(m.K)	0.238 - 1.428
electrical resistivity	ohm.m	10 - 50 X 10^{-6}

CARBON COMPOSITES





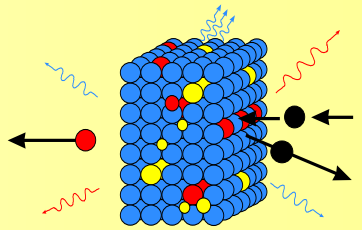


Ultra high (2500C) temperature carbon composites. Carbon nano tubes improve the strain to failure more than factor 5. And the rigidity by factor 3 !

Glassy Polymeric Carbon (GPC)

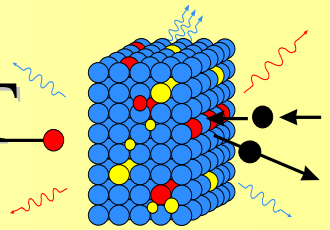
- **Operates above 5000°F**
- **Chemically stable**
- **Biocompatible**
- **Almost as hard as diamond**
- **Good electrical conductor**

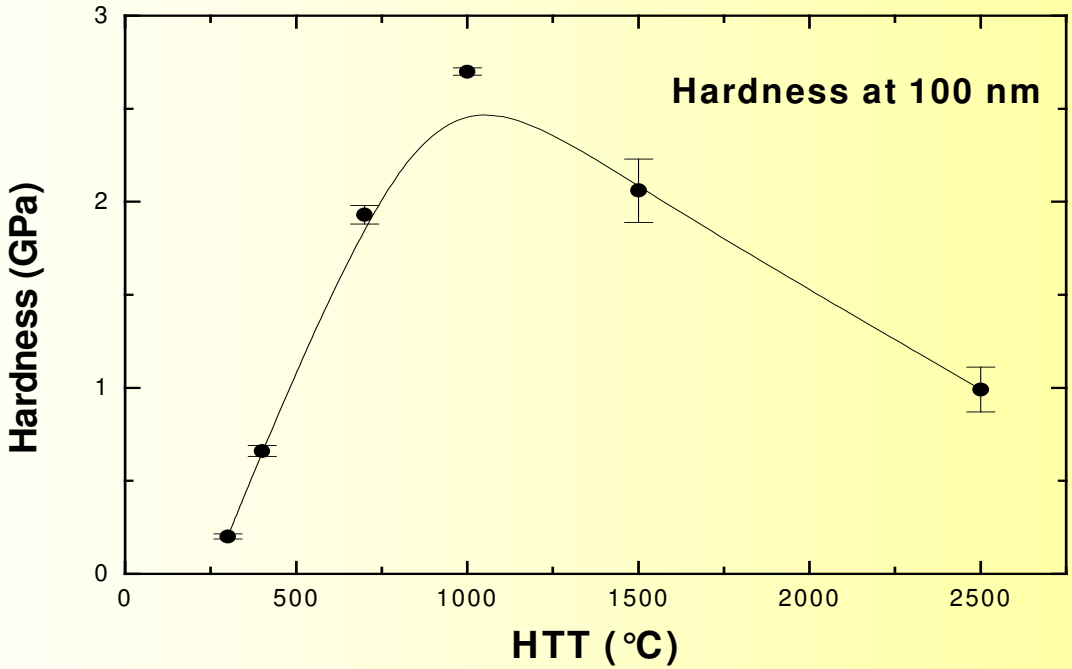
Hardness



- **Increased hardness**
- **Measurement Technique**
- **Results**

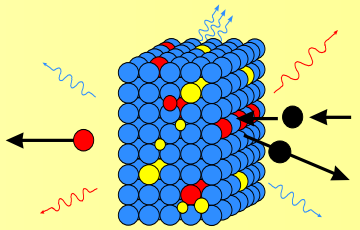
GPC hardness in function on HTT





- GPC samples show an increase of the hardness in function on the HTT due to increase of cross-links, accompanied by dehydrogenation, during the formation of the material. The decrease observed above HTT of 1000°C comes from the rearrangement of the crystallite when inter-ribbon cross-links are broken, leading to a decrease in the intermolecular forces.

Ion Bombardment



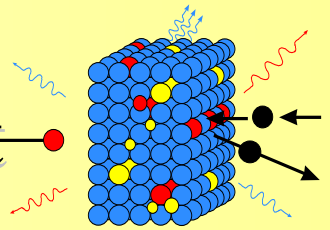
Ions, energies and fluencies used in the bombardment of samples of glassy polymeric carbon, prepared at 700°C, 1000°C and 1500°C.

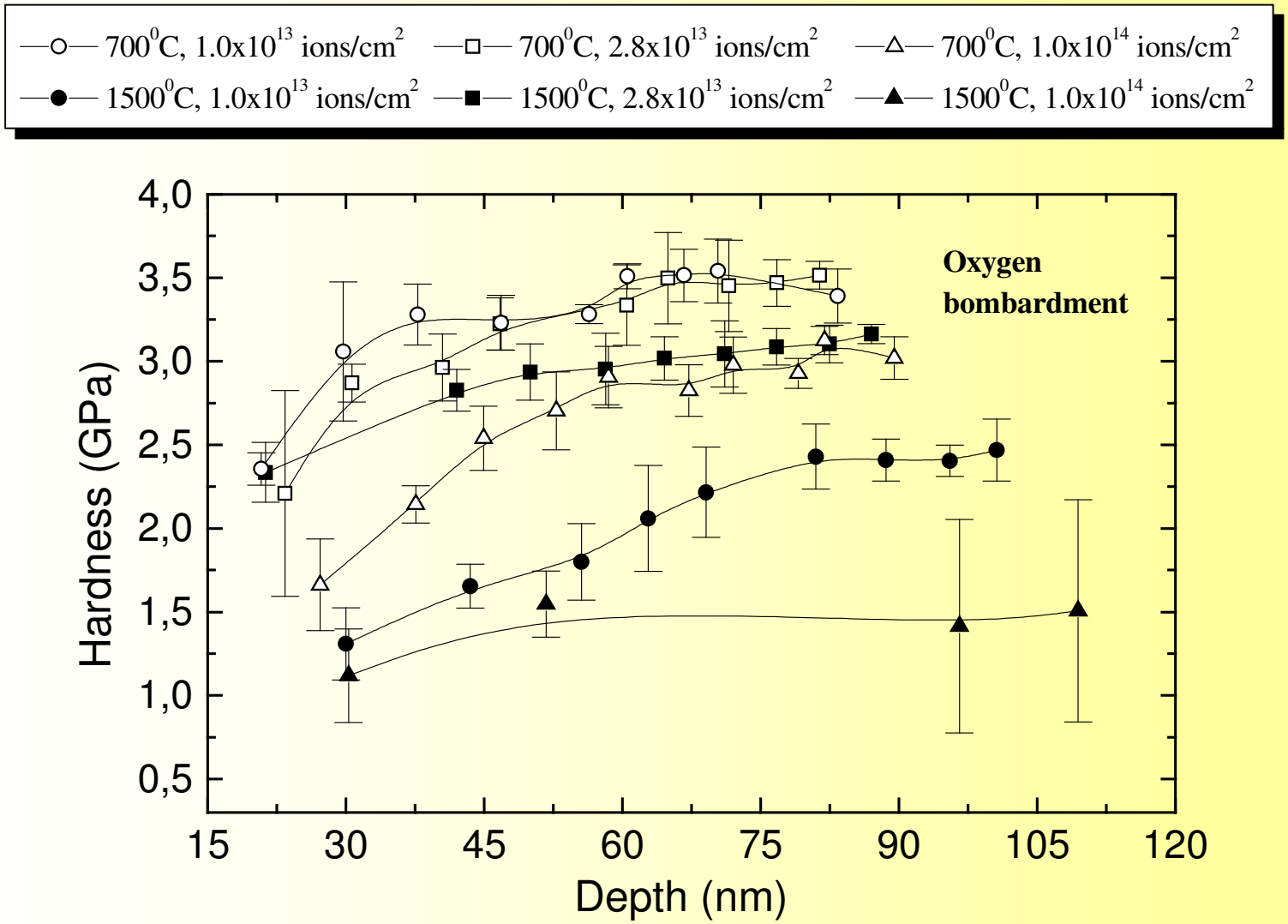
Ion	Energy (MeV)	Fluency (ions/cm^2)		
oxygen*	8	1.0×10^{13}	2.8×10^{13}	10×10^{13}
carbon*	6	3.0×10^{13}	10×10^{13}	30×10^{13}
silicon*	5	0.5×10^{13}	3.4×10^{13}	10×10^{13}
gold**	10	-	1.0×10^{15}	1.46×10^{16}

* samples prepared at 700°C and 1500°C

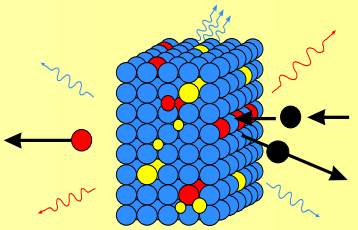
** samples prepared at 700°C and 1000°C

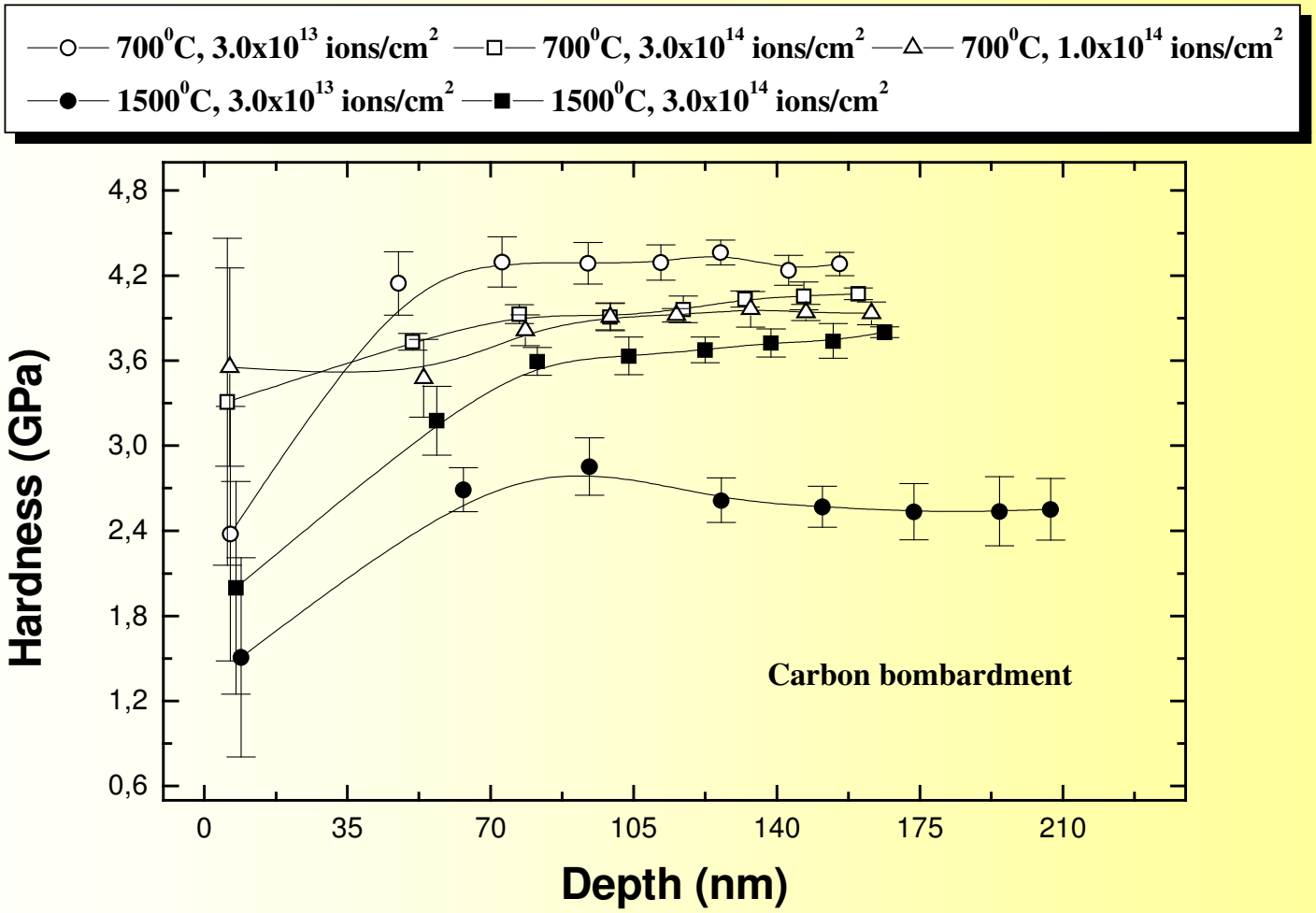
Results for Oxygen bombardment



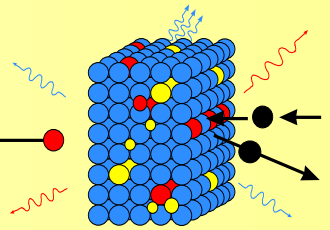


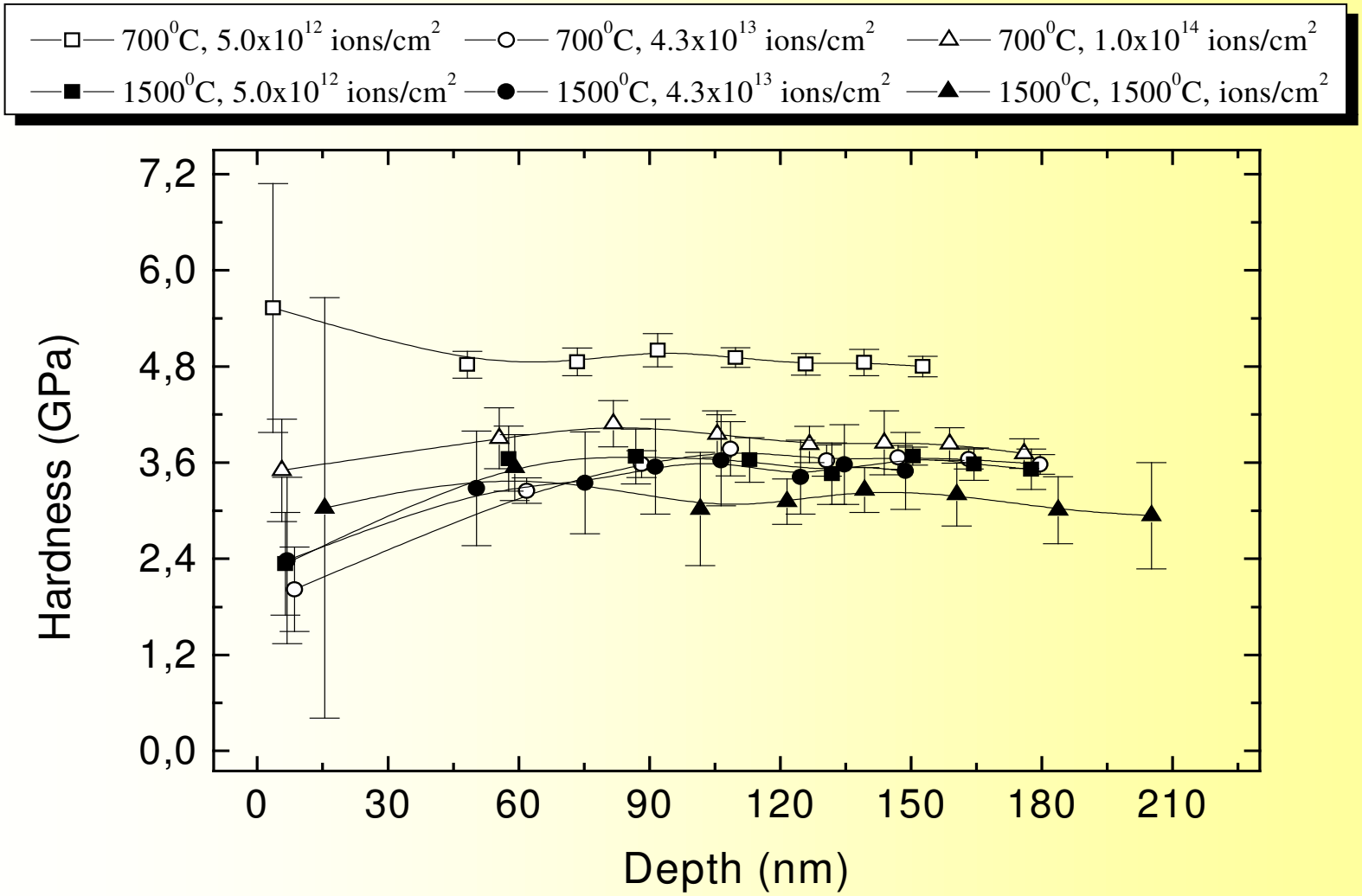
Results for Carbon bombardment



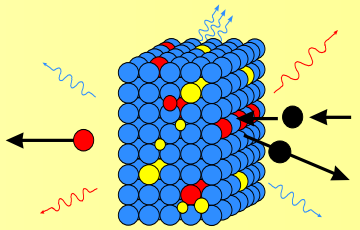


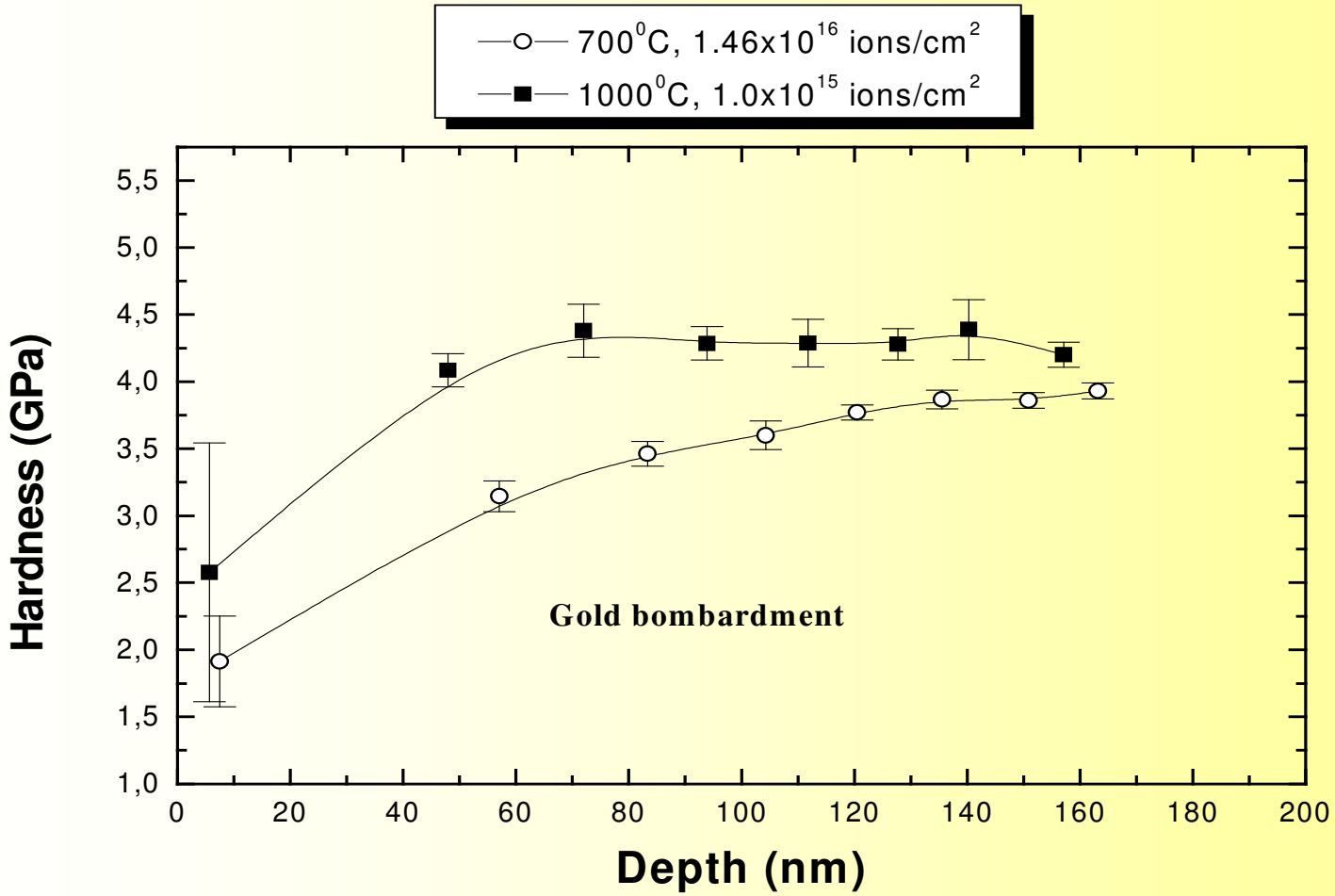
Results for Silicon bombardment

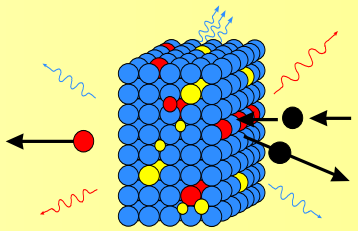




Results for Gold bombardment



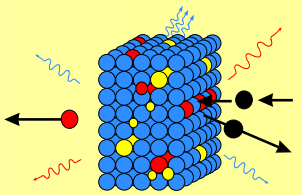




APPLICATIONS

2. Enhancement of UHMWPE hip implants

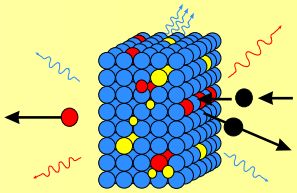
   by Ag ion implantation



- 1. Oks E. M., Yushkov G. Yu., Evans P.J., Oztarhan A., Brown I.G., Dickinson M.R., Liu F., MacGill R.A., Monteiro O.R. and Wang Z., 1997, "Hybrid gas-metal co-implantation with a modified vacuum arc ion source", *Nucl. Instr. and Meth. B, Vols 127-128, pp. 782-786*

- 2. Oztarhan A., Brown I., Bakkaloglu C., Watt G., Evans P., Oks E., Nikolaev A. and Tek Z., 2005, "Metal vapour vacuum arc ion implantation facility in Turkey",
Surface and Coatings Technology, Vol 196, Issues 1-3, pp. 327-332

6. Evelyn AL, Ila D , Zimmerman RL, Bhat K, Poker DB and Hensley, 1998, "Effects of MeV ions on PE and PVDC" , Nucl. Instr. and Meth. B, Vol 141, Issues 1-4 , pp. 164-168

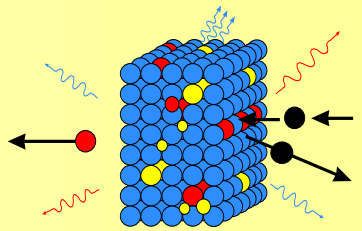


UHMWPE samples were implanted with metal and metal-gas hybrid ions (Ag, Ag+N, C+H, C+H+Ar, Ti+O) by using improved MEVVA Ion implantation technique **[1,2].** with an extraction voltage of 30 kV and fluence of 10^{17} ions/cm2

Table gives the contact angle and roughness results together with the other measured properties. It seems that the wettability increased with ion implantation and that hidroxil bonds and carbonil bonds have dominant effect on wettability

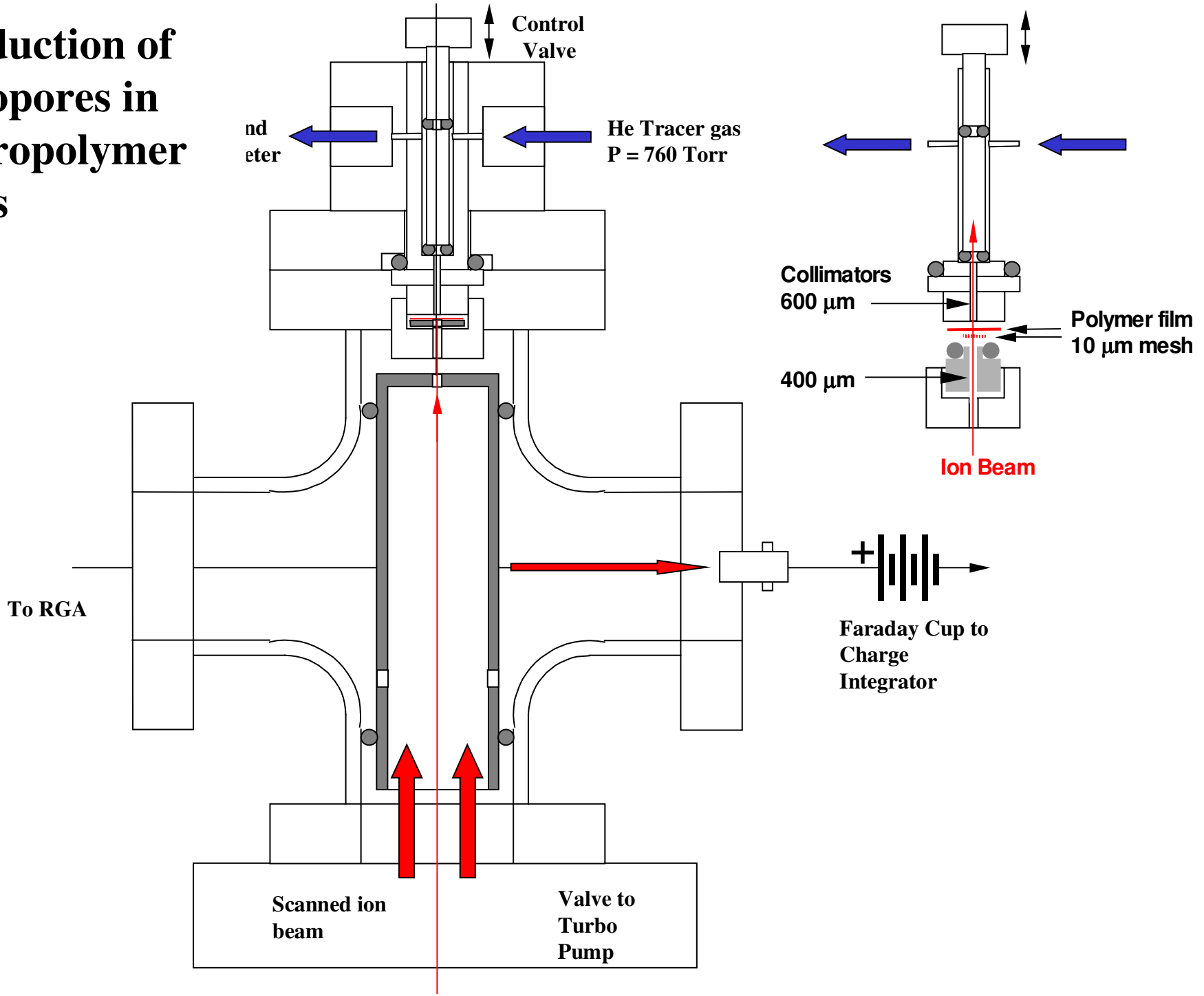
	Roughness (Ra-nm)	**Hardness (Shore-D)**	**Contact Angle(^{o})**	**ΔH_f J/g)**	**Tm (C^0)**	**Crystallinity (DSC - %)**
Untreated	124	58	56	115.07	141	39,5
Ag	30	66.4	45	116.52	137	40
Ag+N	74	63.4	32	119.67	140	41
C+H	69.5	64,2	37.5	115.82	135.2	39,9
C+H+Ar	101	66,1	47.5	117.57	131.8	40,5

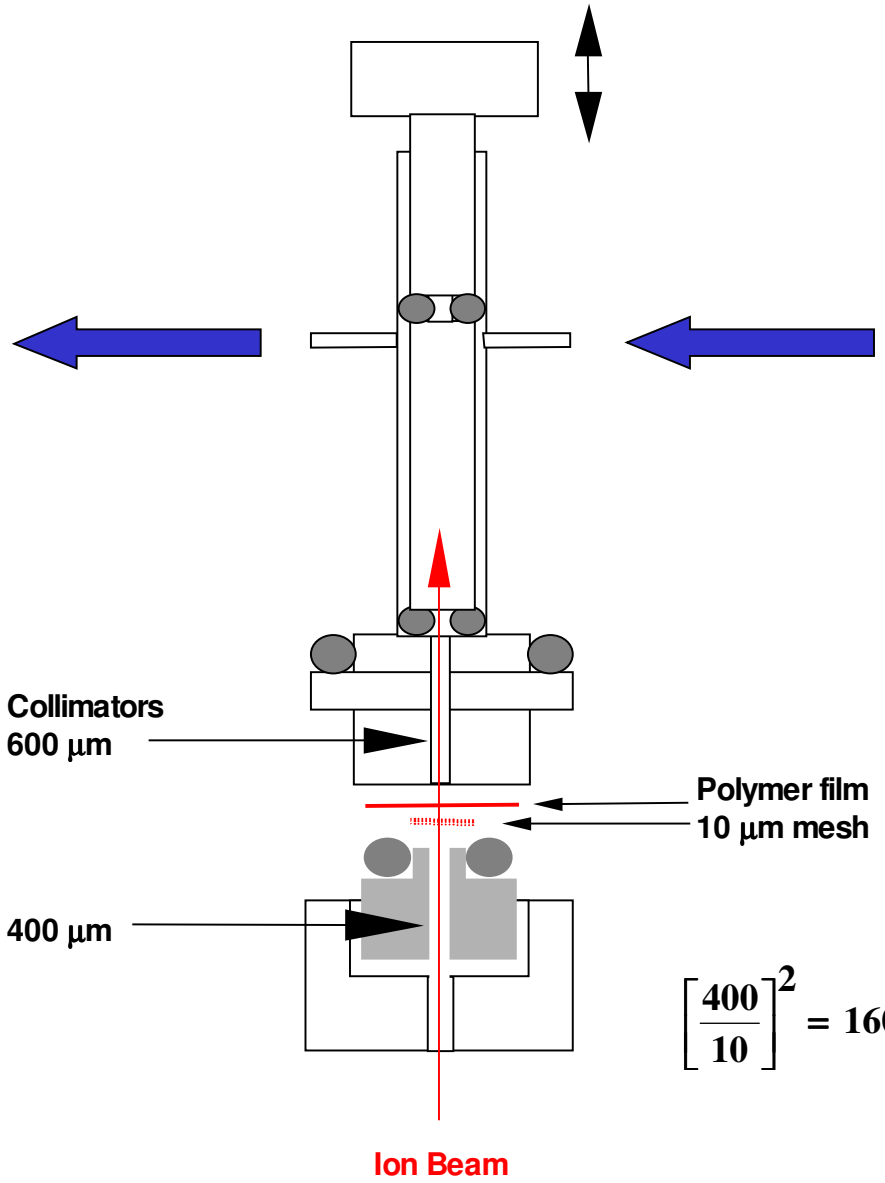
APPLICATIONS



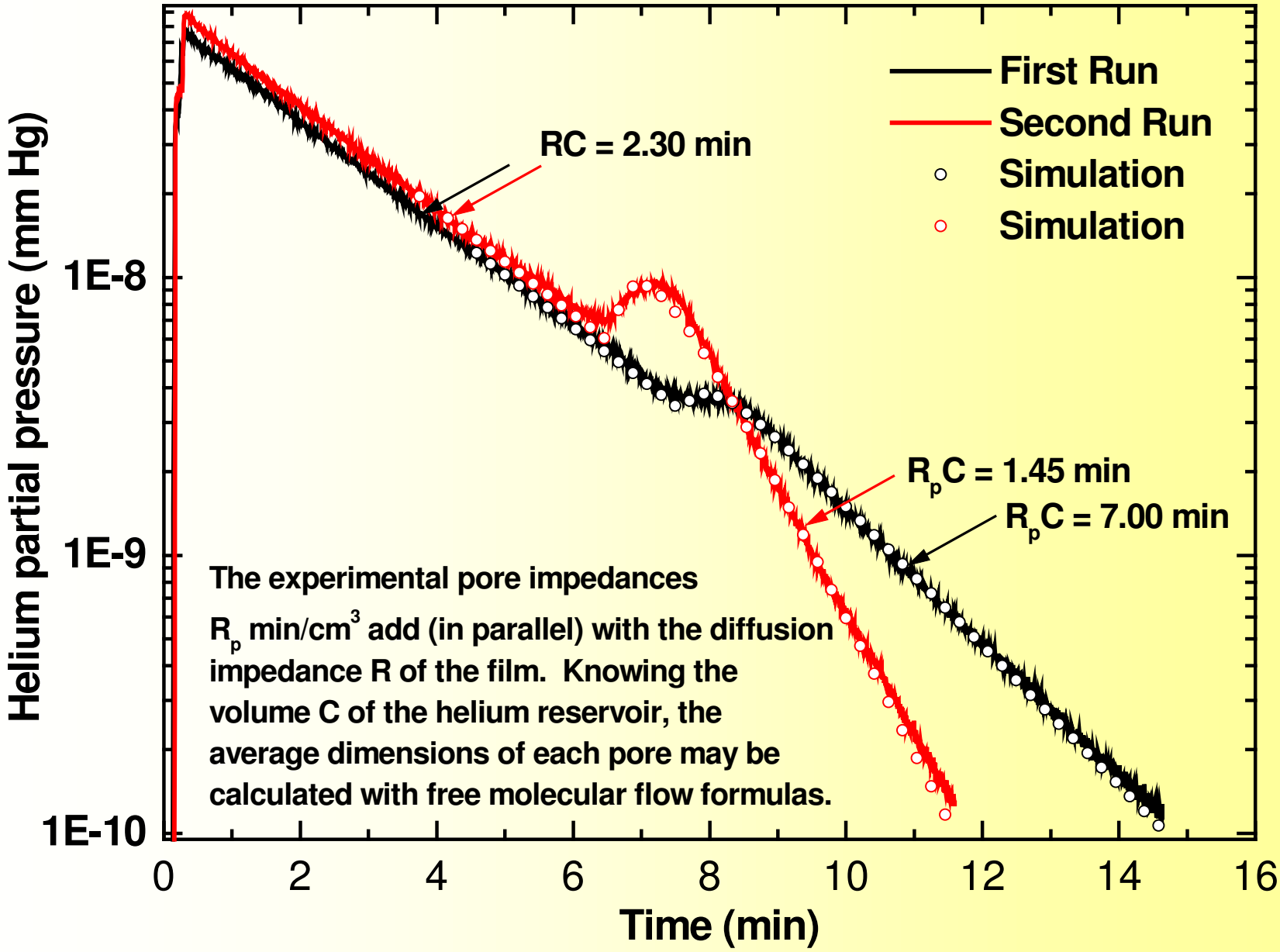
3. Nanopore production in TEFLON by ion bombardment

Production of nanopores in fluoropolymer films



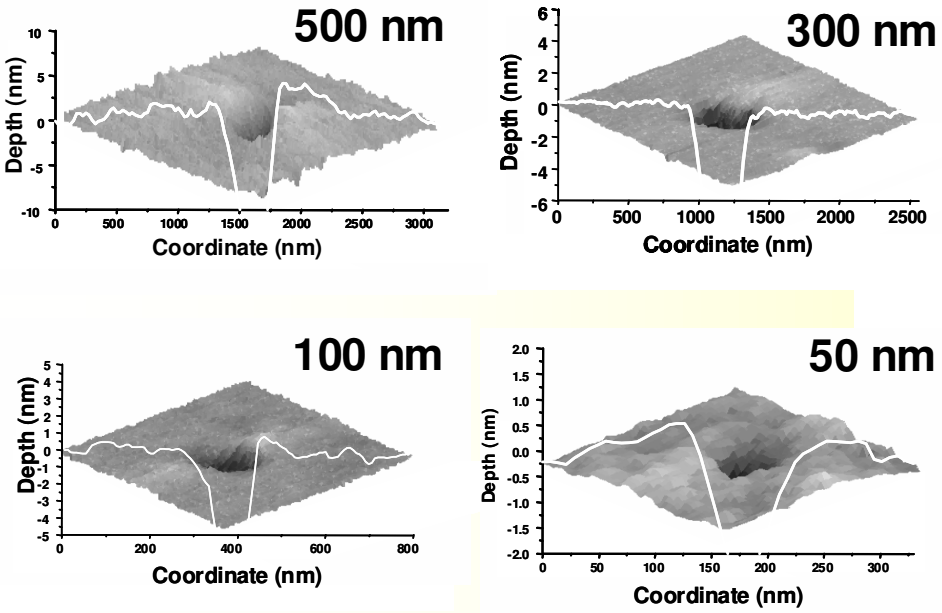


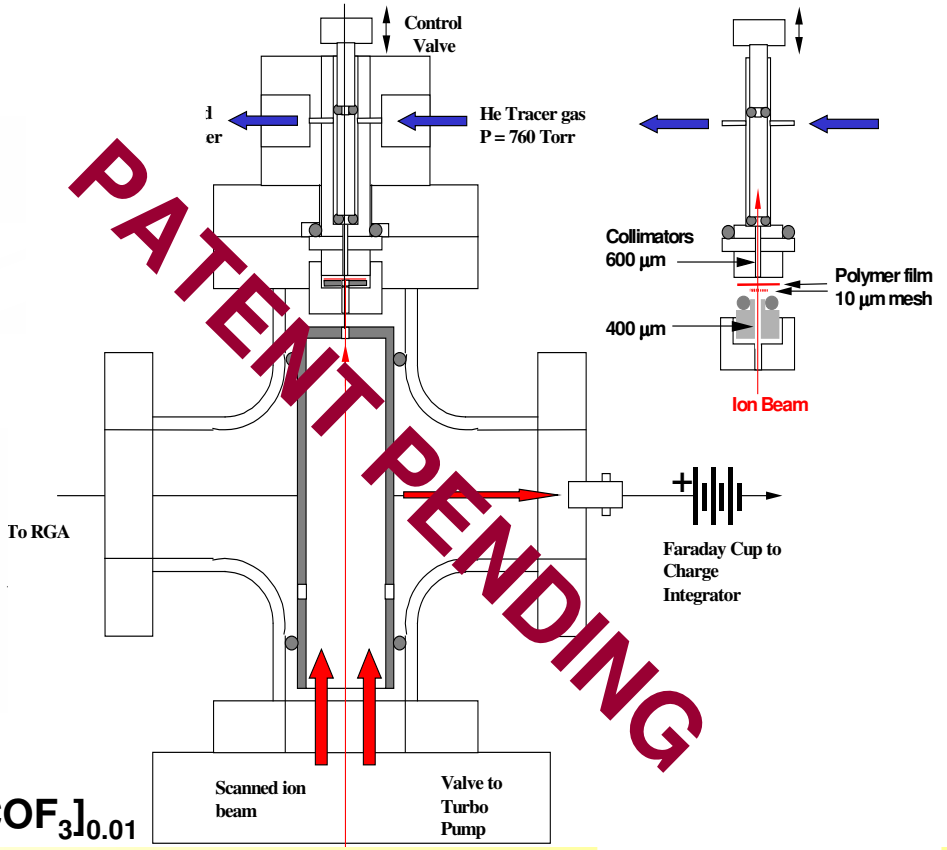
$$\left[\frac{400}{10}\right]^2 = 1600 \text{ nanopores}$$


First Run
Second Run
Simulation
Simulation
RC = 2.30 min
RpC = 1.45 min
RpC = 7.00 min
The experimental pore impedances
Rp min/cm3 add (in parallel) with the diffusion impedance R of the film. Knowing the volume C of the helium reservoir, the average dimensions of each pore may be calculated with free molecular flow formulas.
Helium partial pressure (mm Hg)
1E-8
1E-9
1E-10
0
2
4
6
8
10
12
14
16
Time (min)

ION BEAM MODIFICATION
of materials for medical applications.

Nano pore production for single molecule biochemistry
DNA and Protein characterization





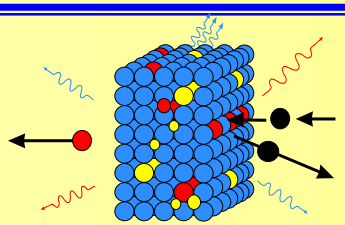
Perfluoroalkoxyethylene (PFA) $[CF_2CF_2]_{0.99}[CF_2COF_3]_{0.01}$

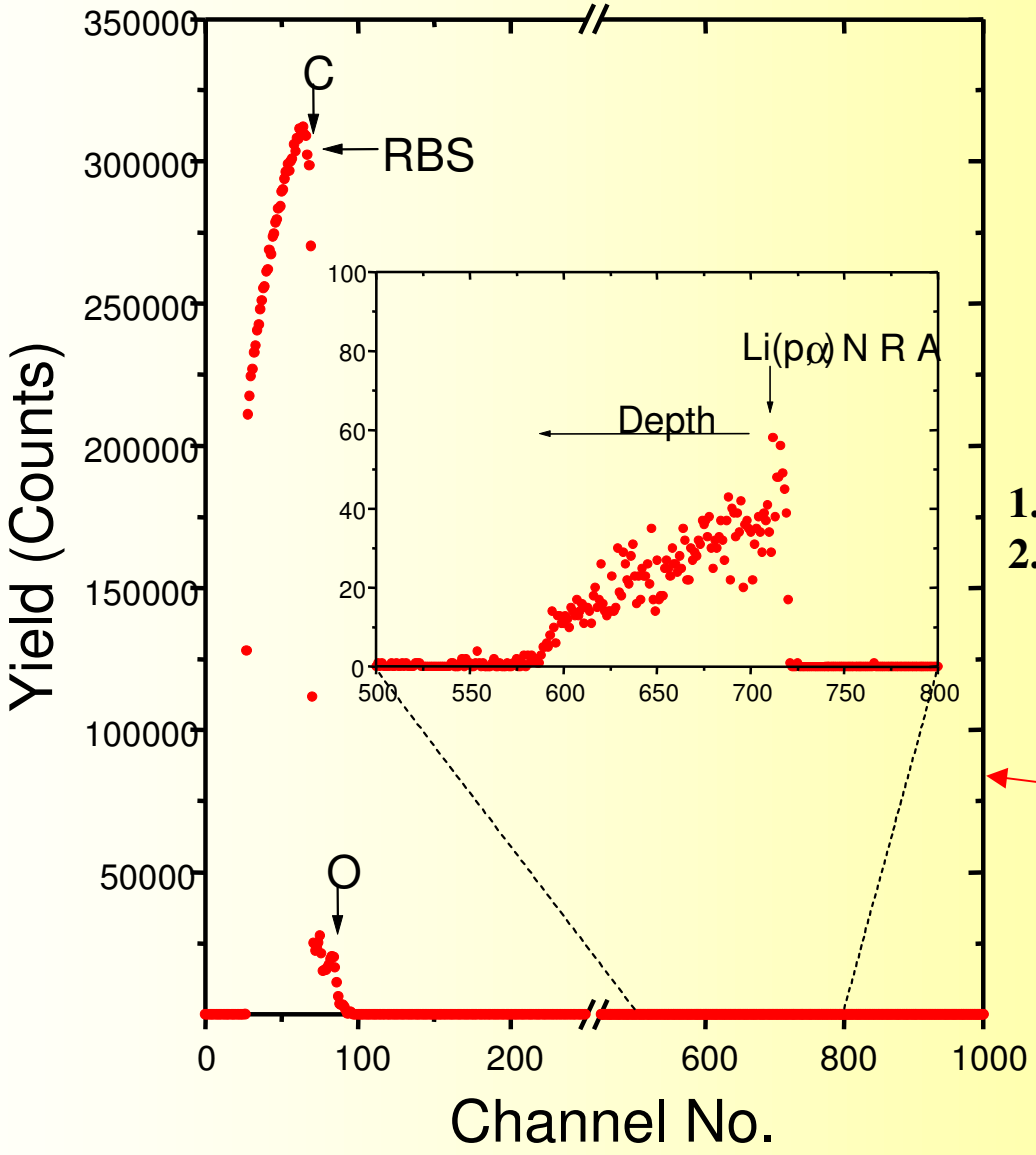
APPLICATIONS

4. **Ion Beam Modifications**
   Increased **available porosity**
   by Ion Bombardment

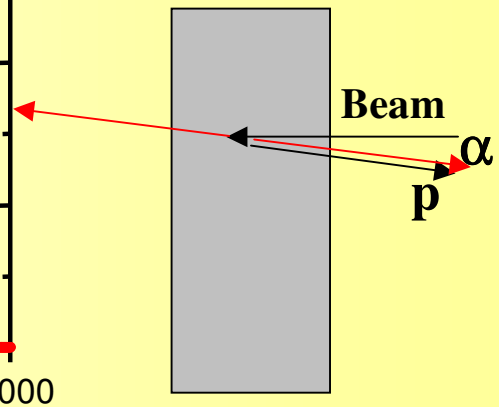
   6 MeV C
   8 MeV O
   5 MeV Si
   10 MeV Au

Determination of Porosity of ion bombarded GPC
RBS and NRA Spectra Produced by 1.03 MeV Protons
from 700°C heat-treated polymeric carbon

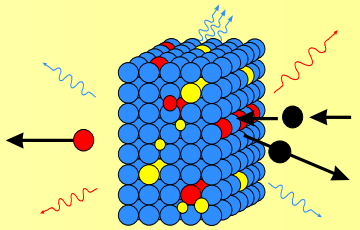


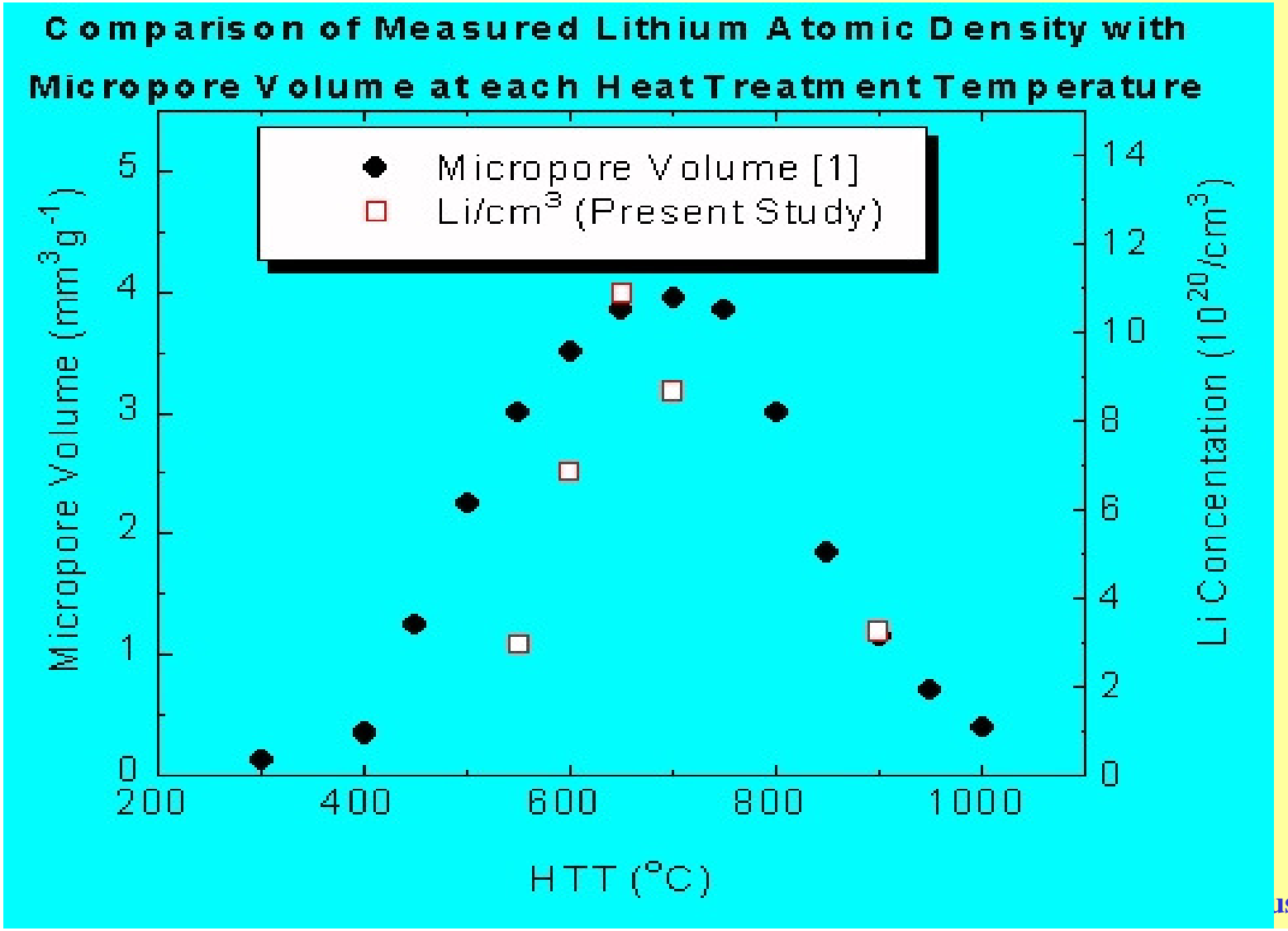


1. Soak in molten $LiCO_3$
2. Depth profile Lithium $Li^7(p,2\alpha)$

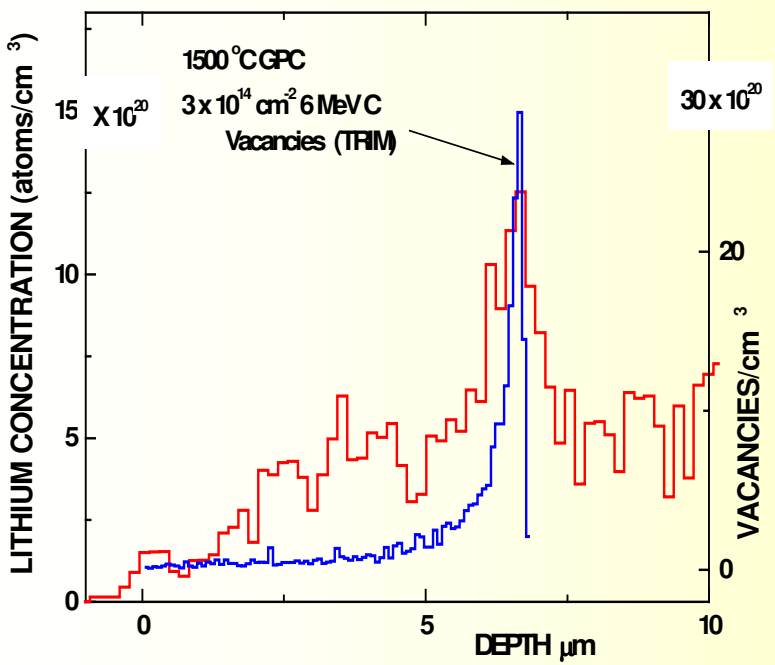


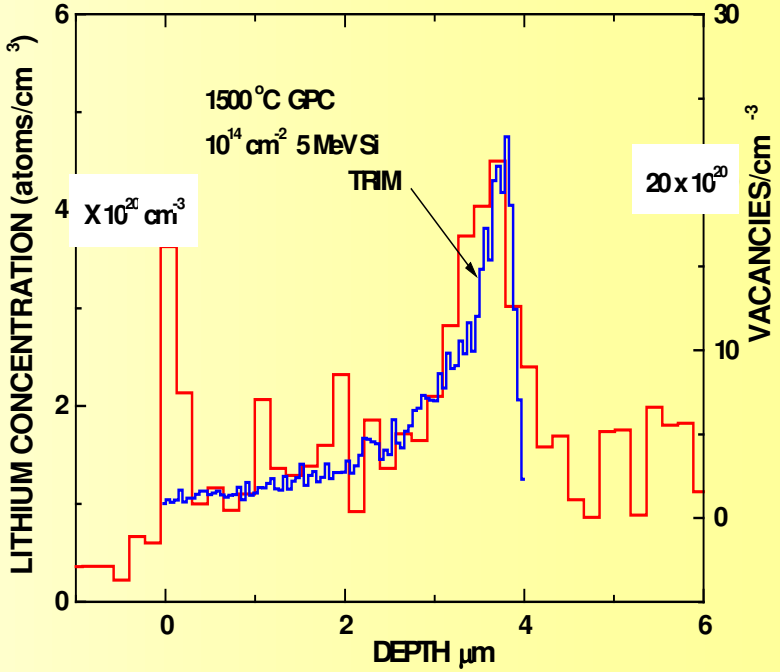
Increased porosity



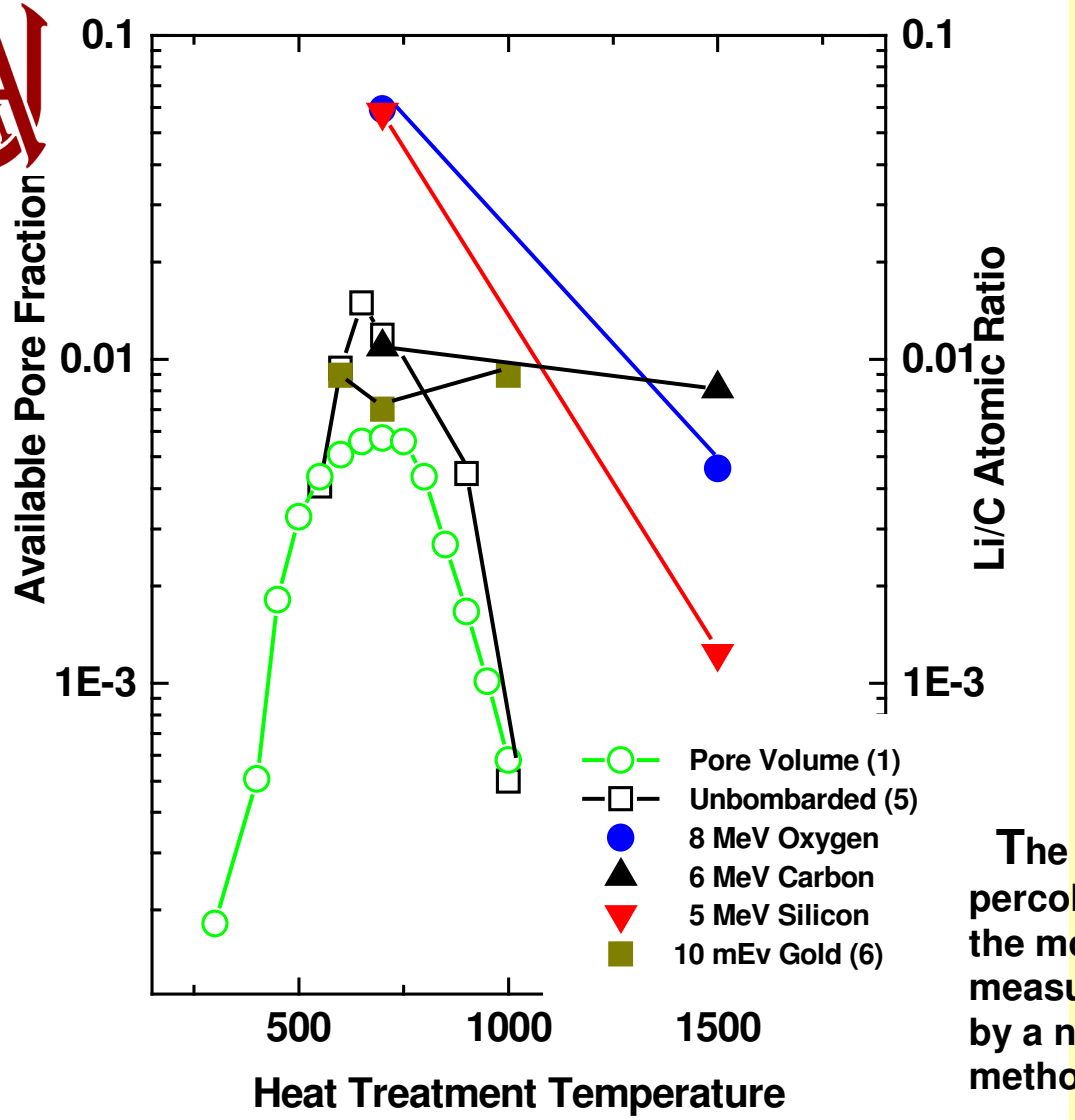


Lithium profile (red) compared with vacancy production (TRIM*)





*J. F. Ziegler, J. P. Biersack and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press Inc., New York, 1985).



The porosity was determined by percolating a molten lithium salt into the modified GPC surface and measuring the lithium concentration by a nuclear resonance analytic method.

$Li^7(p,2\alpha)$

[1] G. M. Jenkins and K. Kawamura, *Polymeric Carbons-Carbons Fiber*, Cambridge University Press 1976.

R.L. Zimmerman, D. Ila, D.B. Poker, S.P. Withrow, *Application of Accelerators in Research and Industry,* Duggan & Morgan (Eds) AIP Press, New York, 1996, 957-959.

APPLICATIONS

5. **Controlled Cell growth on Carbon**

Ion bombardment increases surface **roughness**
Silver Ion implantation changes surface **chemistry**

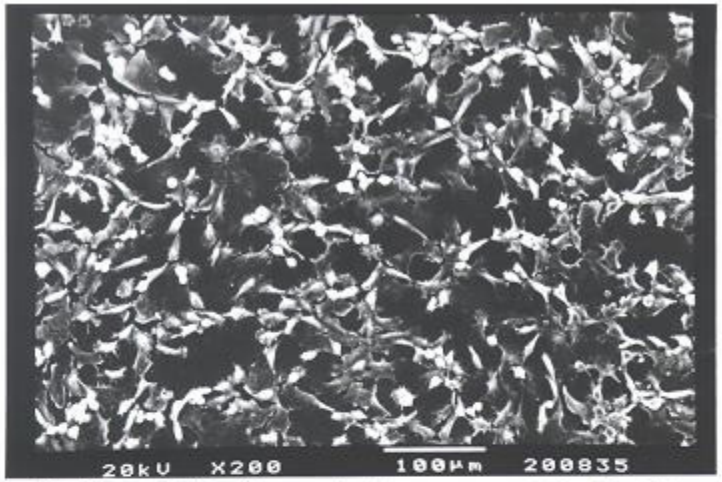
1. **Cell adhesion to GPC was tested with L929 cells mouse fibroblasts (connective tissue cell-line, from the Animal Cell Culture Collection, Ankara, Turkey).**

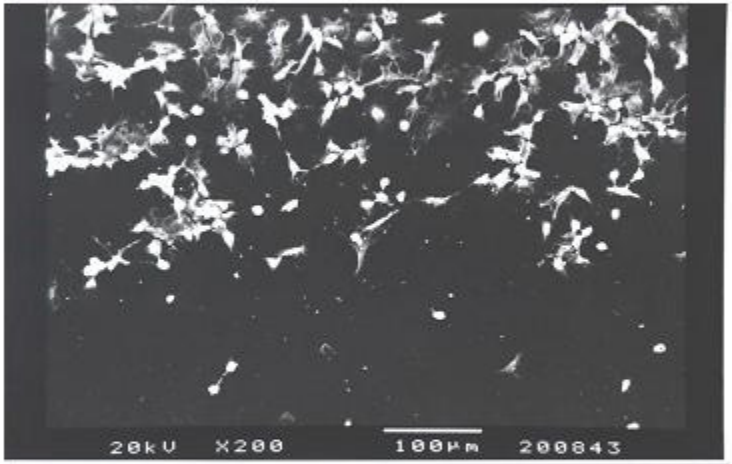
2. **L929 cells were cultured in Dullbecco's modification of Eagle's medium (DMEM) with 10% fetal bovine serum (FBS) in 75 cm^3 tissue culture flasks.**

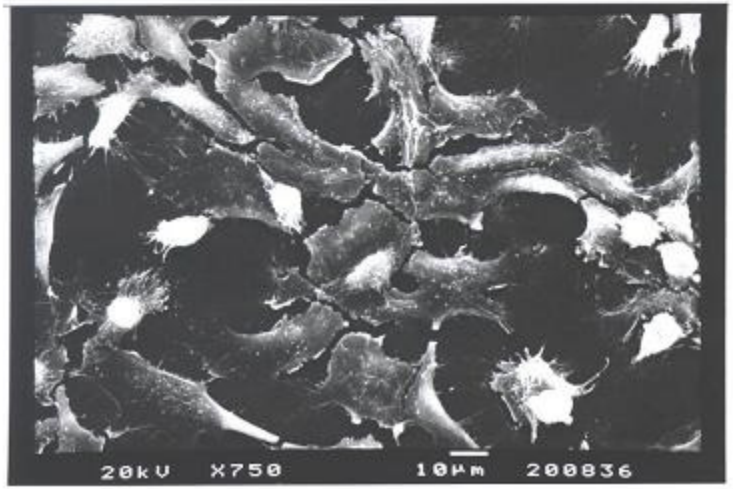
3. **Harvested from monolayers by 0.25% trypsin in 0.53M EDTA solution at 80-90% confluence.**

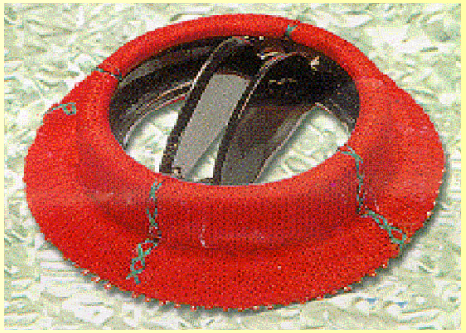
4. **Cells were centrifuged and resuspended in the culture media.**

5. **After staining with the trypan blue (0.4%), the cell density N_S was counted with haemocytometer (Bürker) and adjusted to 3.5 x 10^5 cells/ml.**







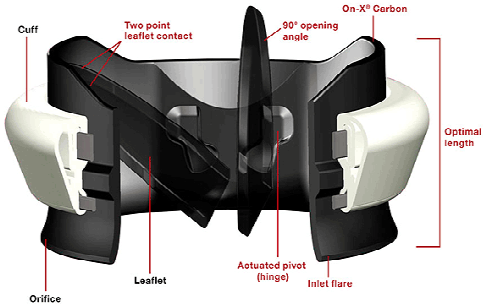


GPC heart valve

GPC Heart Valve

Connective tissue cells

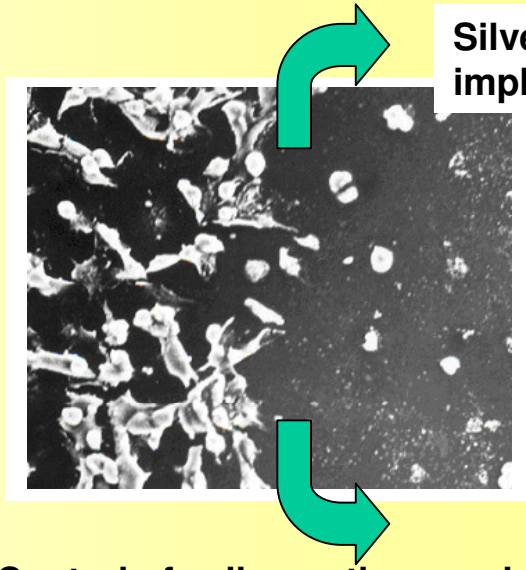
Implanted with silver ions



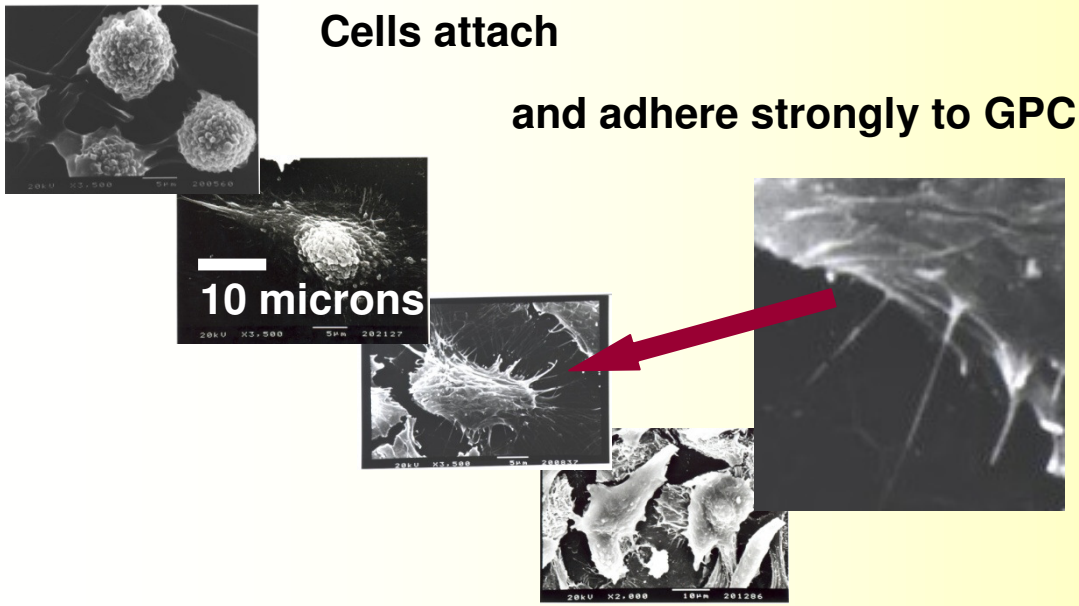
Pyrolytic Carbon valve

Companies manufacturing artificial heart valves: Medtronic, Edwards Lifesciences, and St. Jude.

ION BEAM MODIFICATION of GPC for medical applications.



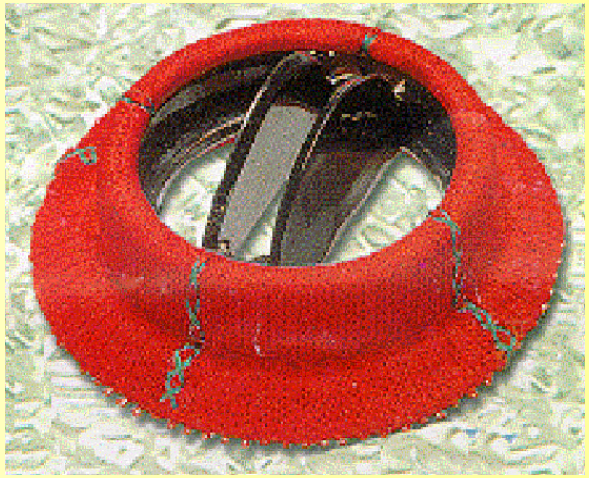
Control of cell growth on carbon for improved medical implants



Cells attach

and adhere strongly to GPC

- Tenuous cell attachment (top)
- Strong adhesion (bottom)



Carbon Heart Valve

Research Partners

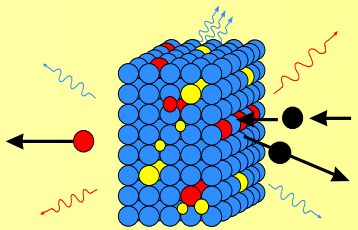
Brazil Turkey

AAMU rlzimm@cim.aamu.edu

Cell adhesion to the surface of GPC implanted with 6 MeV silver ions *

Ag fluence (cm^{-2})	Adhesion %
$3.9x10^{16}$	0
$3.9x10^{15}$	8
$3.9x10^{14}$	28
$3.9x10^{13}$	75
Zero	85

* R. Zimmerman, I. Gürhan, C. Muntele, D. Ila, M. Rodrigues, F. Özdal-Kurt and B. H. Sen,
Surface Modification of Materials by Ion Bombardment 2005, Izmir, Turkey.



END

Thank you