The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR/1758-11

"Workshop on Ion Beam Studies of Nanomaterials:
Synthesis, Modification and Characterization"

26 June - 1 July 2006

Creation of nano structuring by ion beams

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ICTP, Trieste, 26th June- 1st July, 2006


Inter University Accelerator Centre
(Formerly known as Nuclear Science Centre

Introduction

Nano structuring by low energy ions

(i) Atom beam co sputtering

(ii) low energy ions (0.5 to a few keV) co-sputtering

(iii) Ripple formation at surface by keV ions

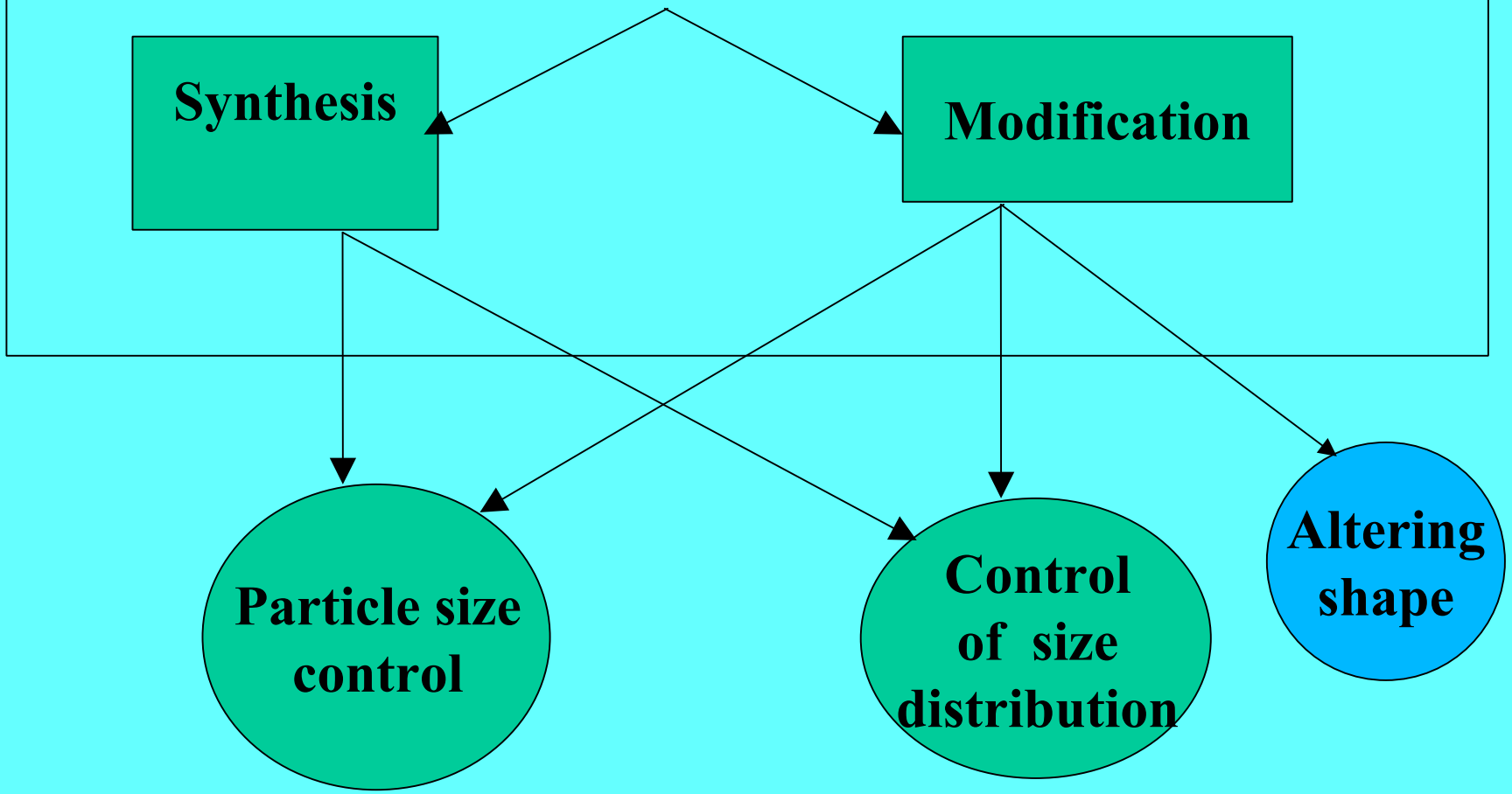
(iv) Ion implantation

Nano structuring by swift heavy ions

Influence of SHI on nano particles

Summary

Role of energetic ion beams in nano materials



Energetic ion beams (keV to a few MeV):

Up to a few keV ions are used

*To sputter the target material and the sputtered atoms re-assembles at suitable surface to form nano particles

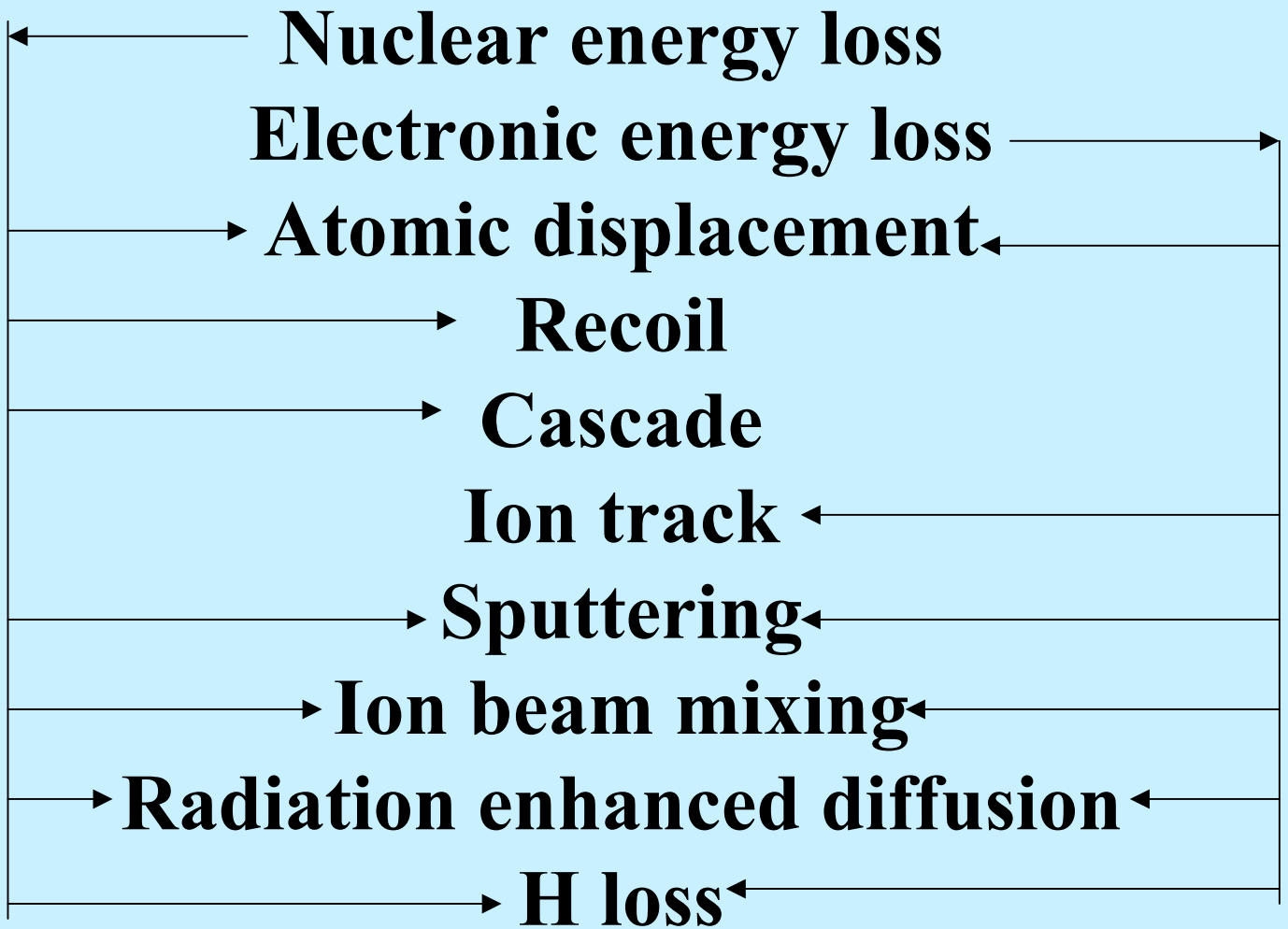
* To generate nanostructures at surface which acts as template to grow nanostructure

Up to a few MeV are used for:

* Creating nanostructures by ion implantation and subsequent annealing

* Creating nanostructures by irradiation

Basic ion beam interaction and phenomena



Specific features of ion beams

increasing energy

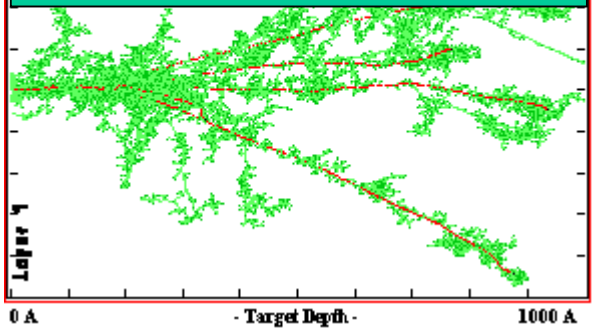
time

10^{-15}s

10^{-13}s

10^{-11}s

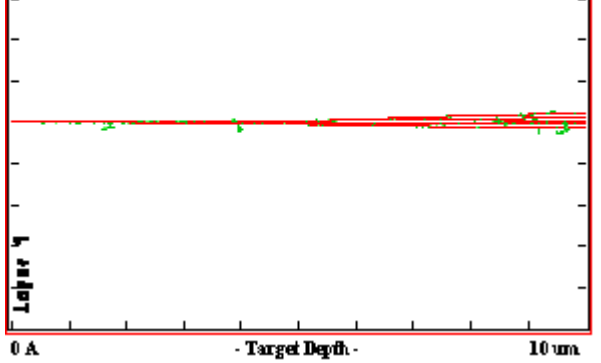
Kr in Si 1keV/u



collision cascade

defects

Kr in Si 1 MeV/u



electronic excitations

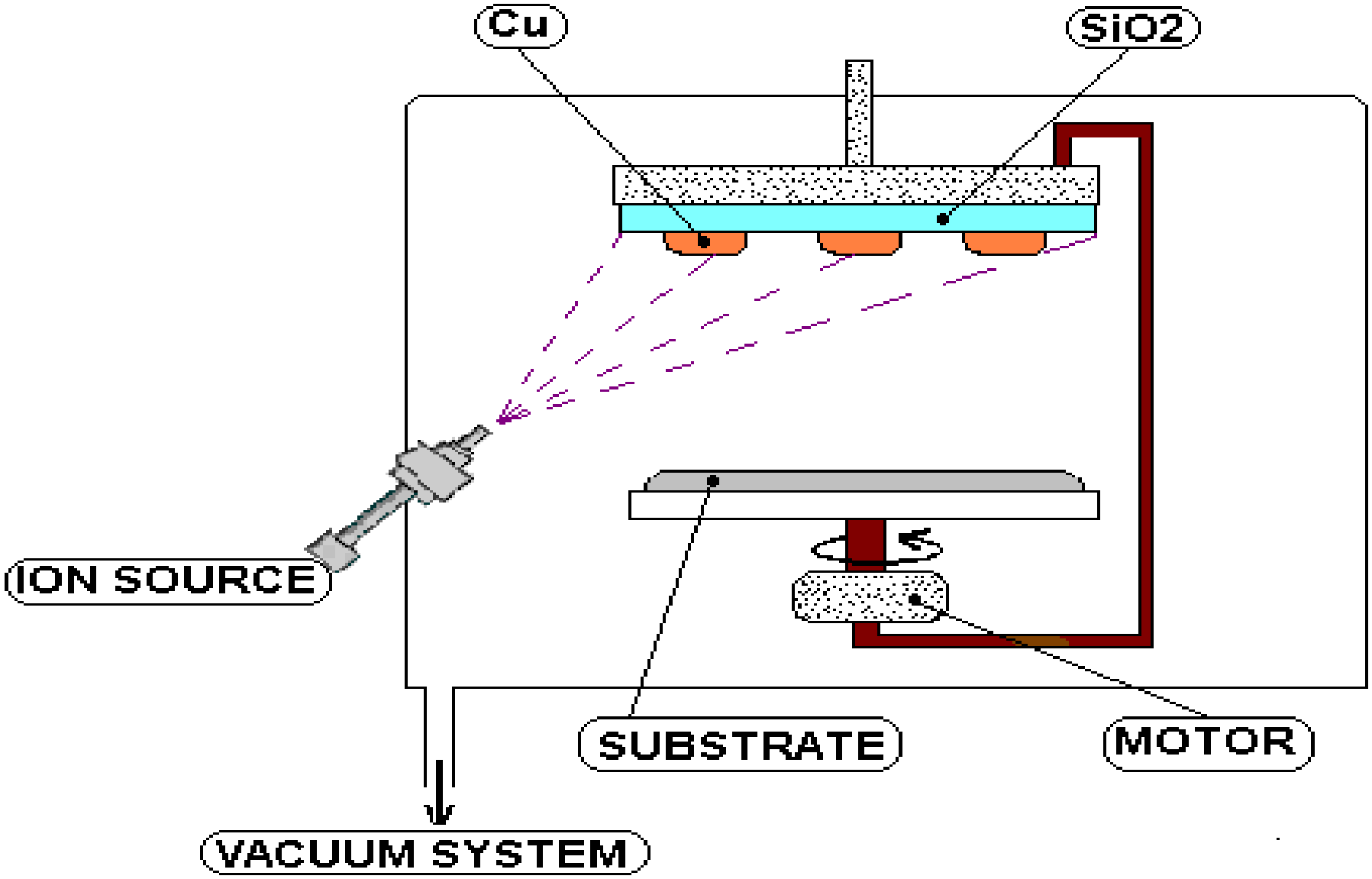
coupling to lattice

transient disorder

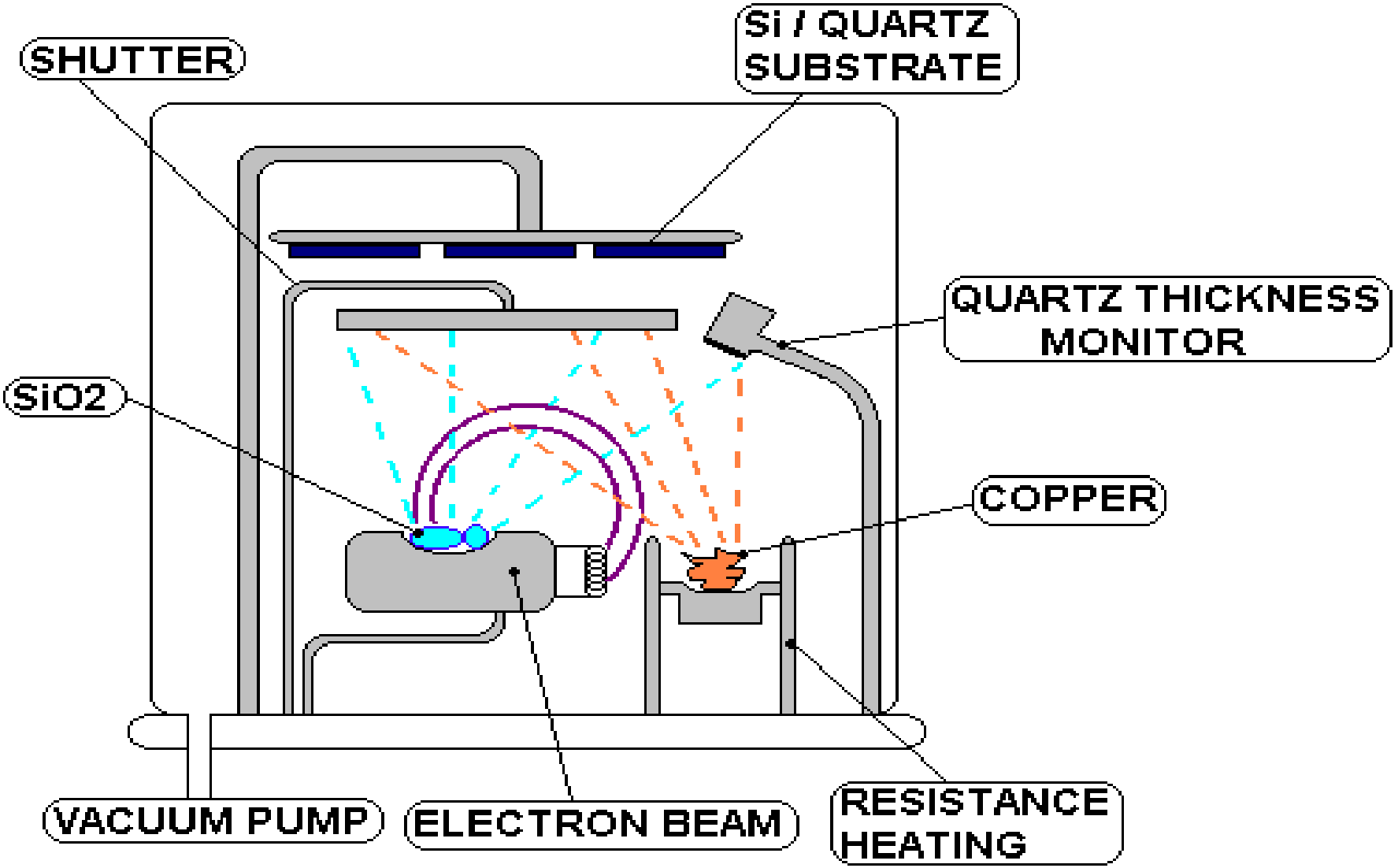
keywords: tracks, cylinder of 20 nm, collision cascade

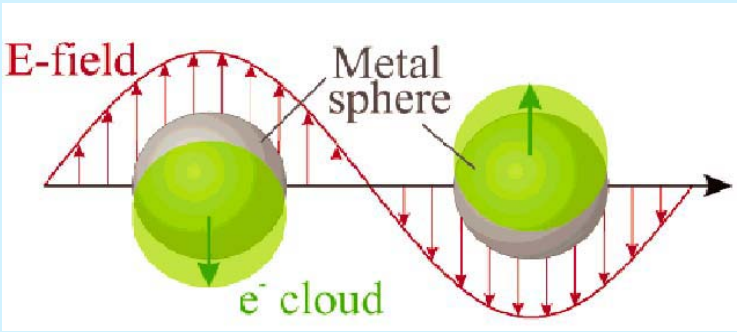
Nano structuring by low energy ions

Growth of nano particles by ion beam co-sputtering



Growth of nano-particles in silica by co deposition





$\omega_{plasmon}$ **tuned by:**

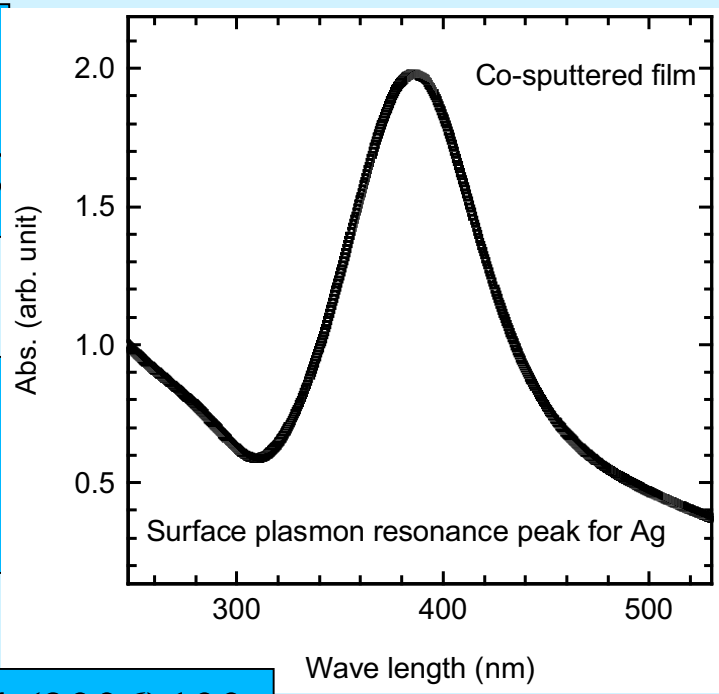
- **nature of metal**
- **cluster size, shape, separation**
- **dielectric matrix**

Atom beam co-sputtering

Thermal co-deposition

SPR peak observed without annealing

Uniform concentration of Ag in silica seen by RBS

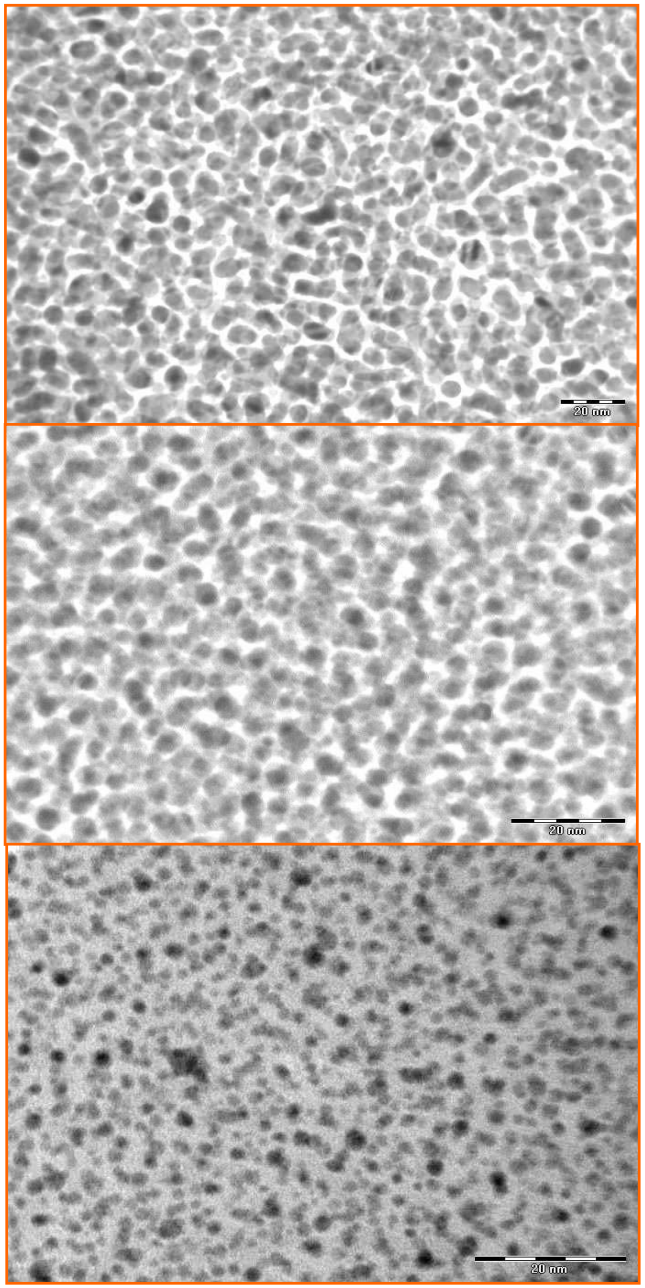


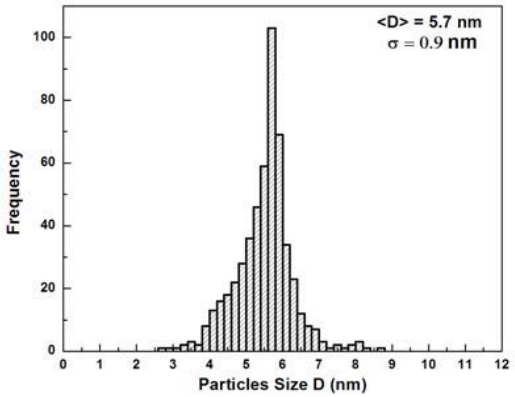
SPR peak observed with annealing

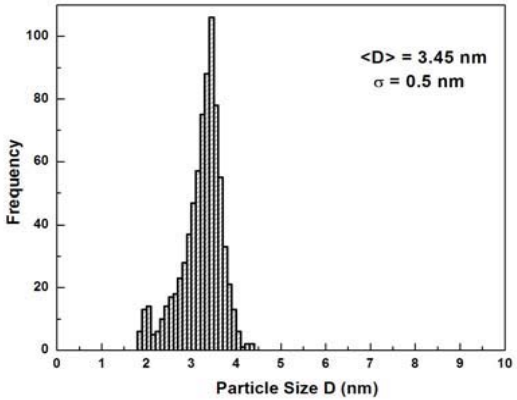
Uniform concentration of Ag in silica seen by RBS

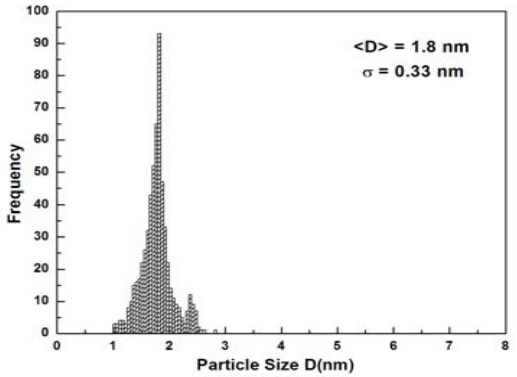
Kabiraj et al, NIM B244 (2006)100

Au nanoparticles by co-sputtering

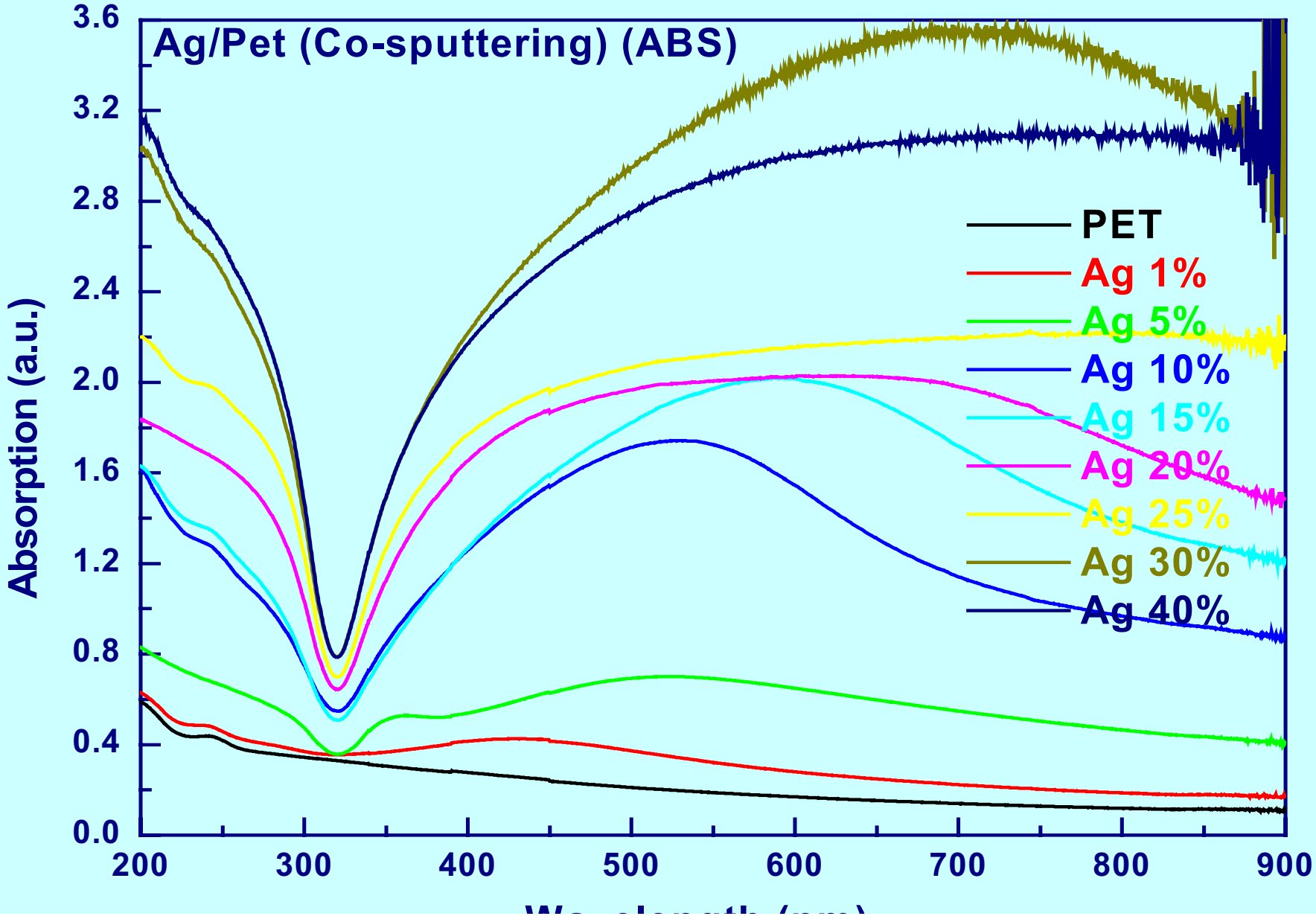




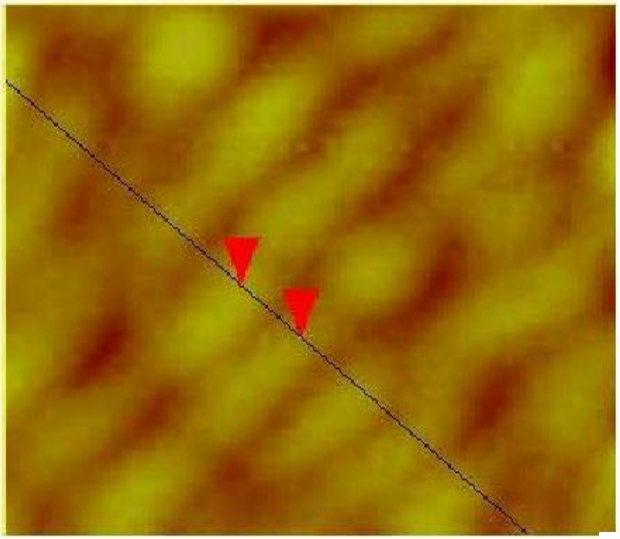




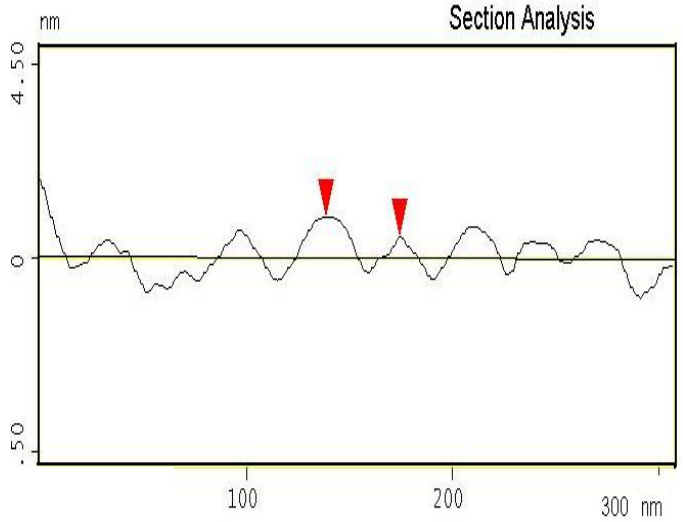
Application of metal polymer nanocomposite as band pass filter



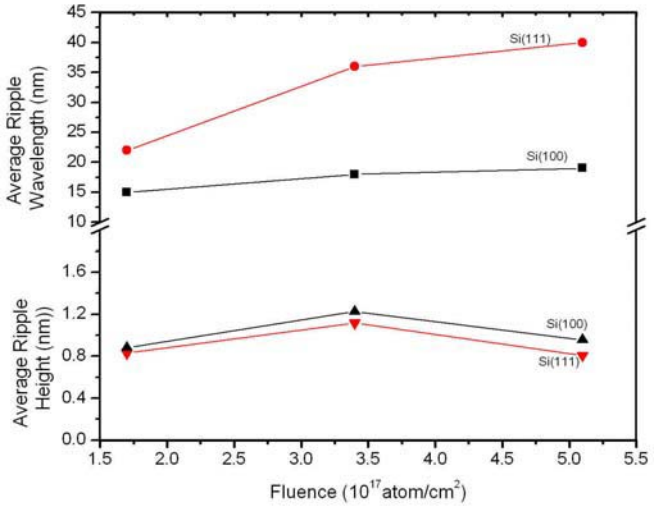
Ripple formation in Si by 1.5 keV Ar atom beam



Kulriya et al,NIM B 244(2006)95.
IUAC Delhi

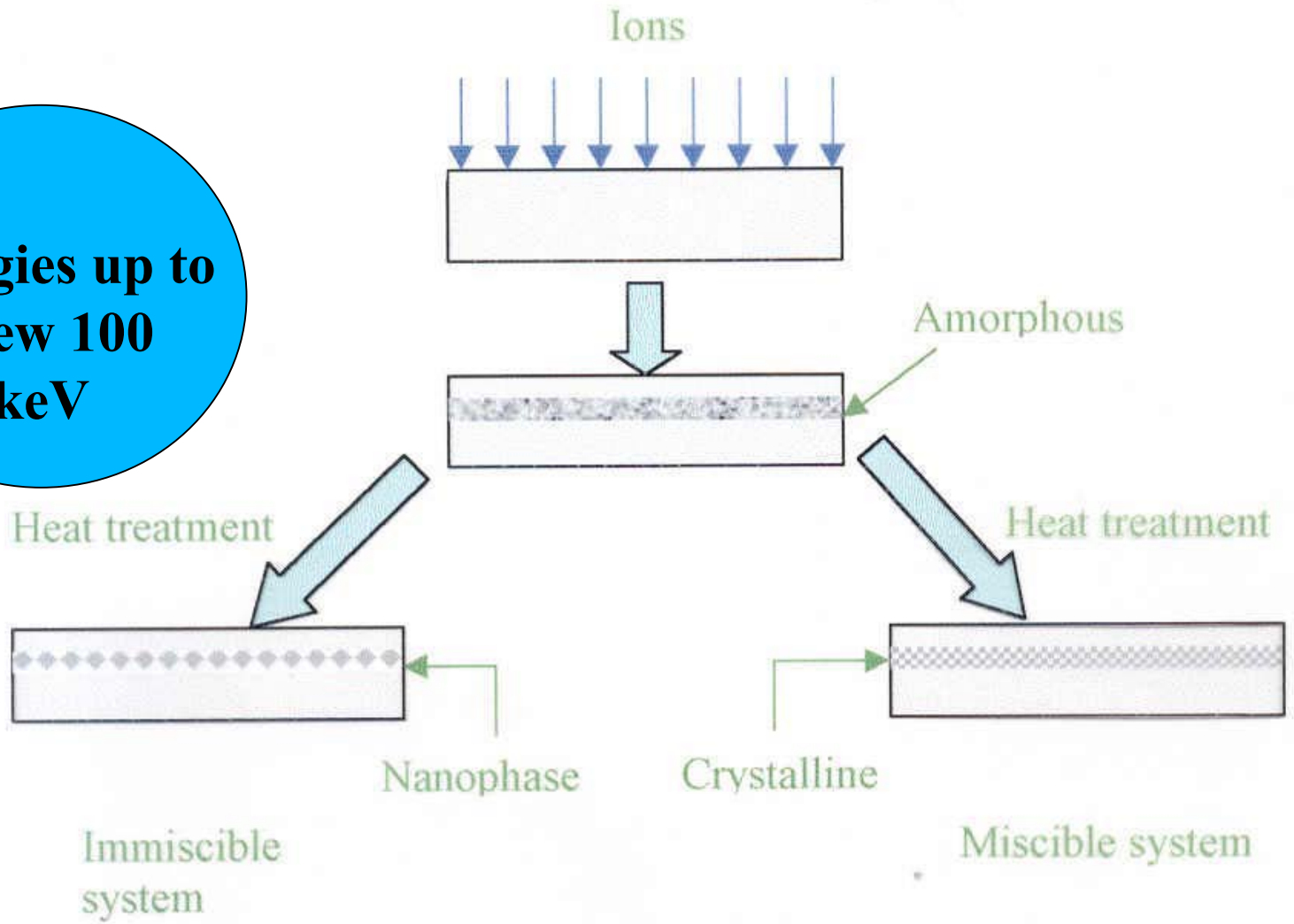


Erosion and surface diffusion resulting in surface ripples

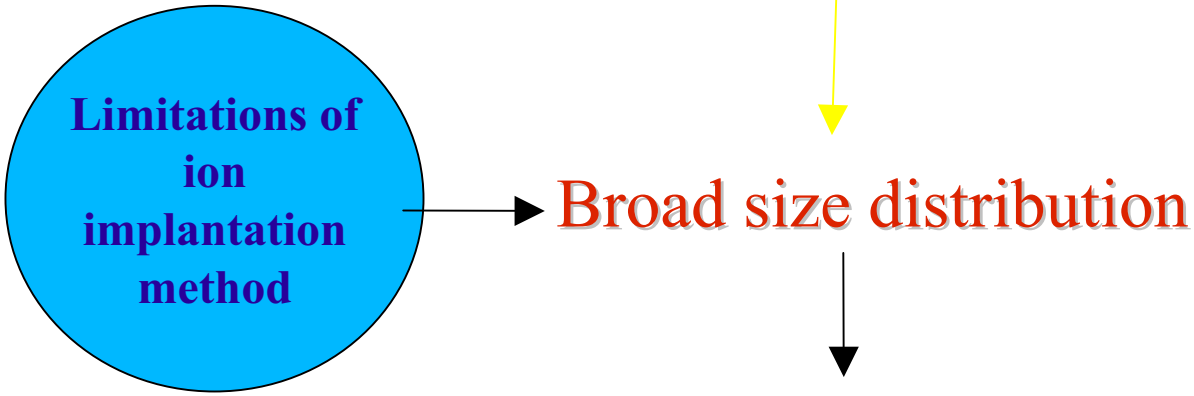


Synthesis by ion implantation

Energies up to a few 100 keV

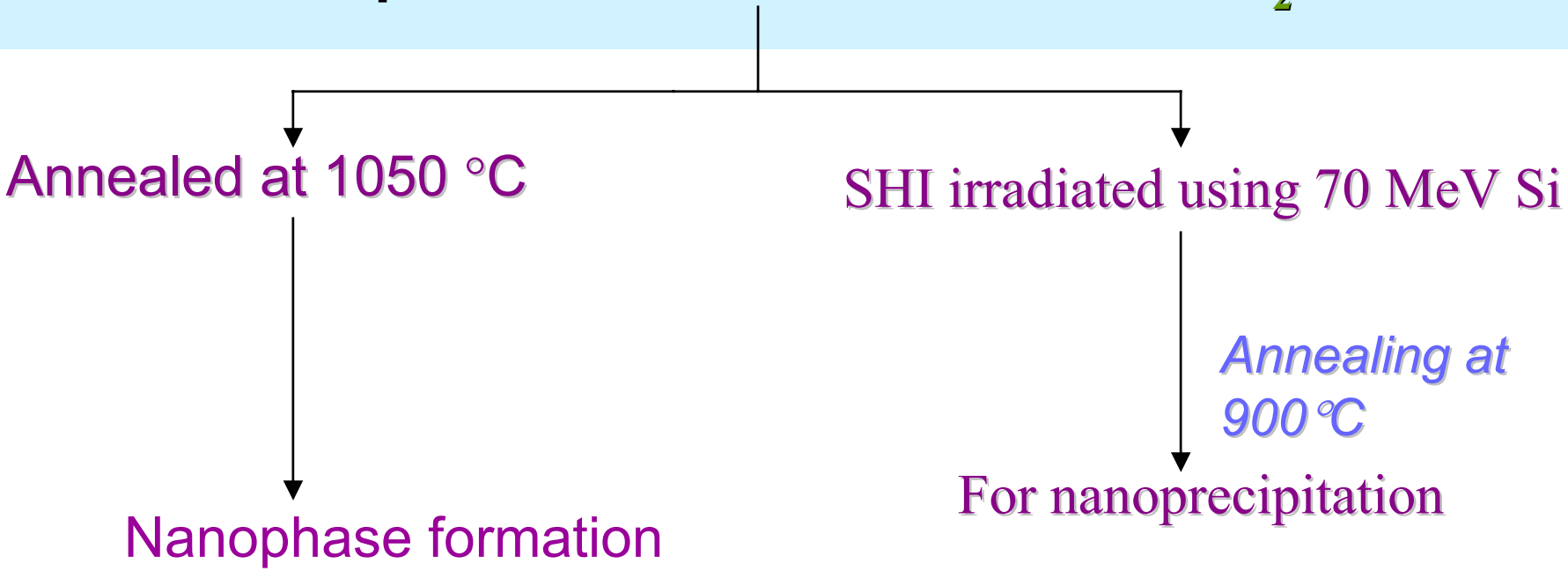


Ion implantation followed by high temperature thermal annealing which leads to Ostwald ripening



This problem may be over come using Swift Heavy Ion (SHI) Irradiation

Implantation of 200 keV Si on SiO_2



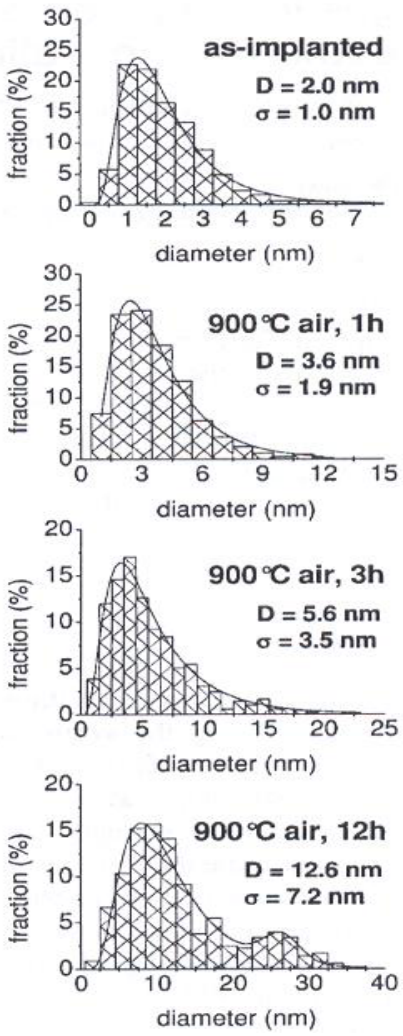
Characterization

- Photoluminescence
- UV-Visible Absorption

T.Mohanty et al,
Nanotechnology 15 (2004) 1620

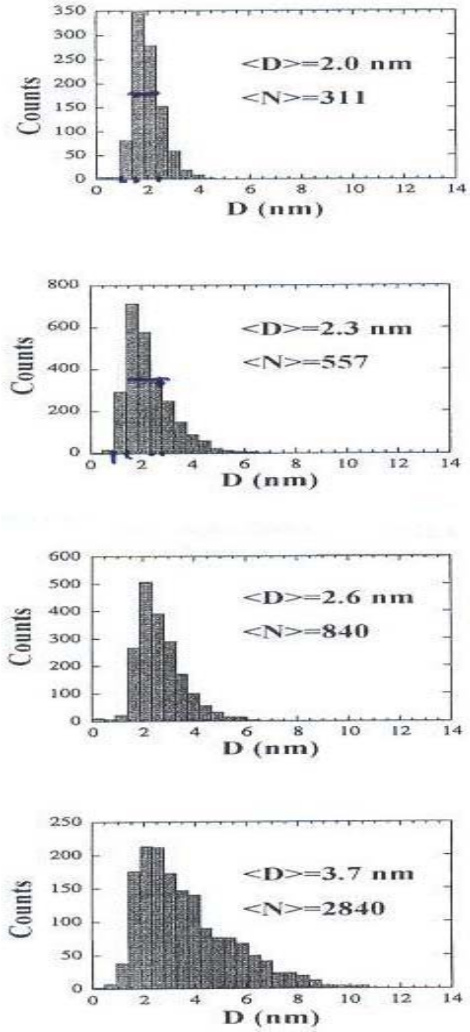
Size distributions of Au nanoparticles achieved from different techniques

Ion Implantation



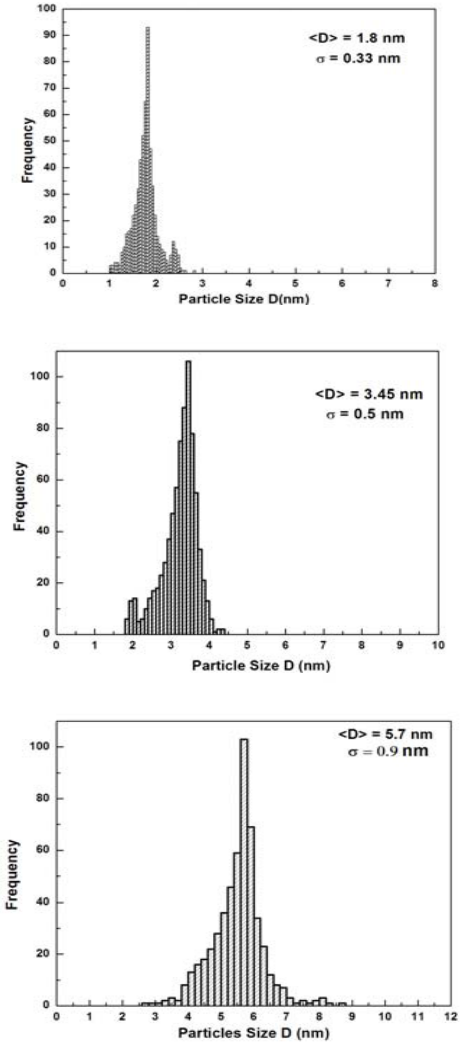
*G. D. Marchi, JAP, **92**, 4249 (2002)*

Pulse Laser Deposition



*B. Palpant, PRB, **57**, 1963 (1998)*

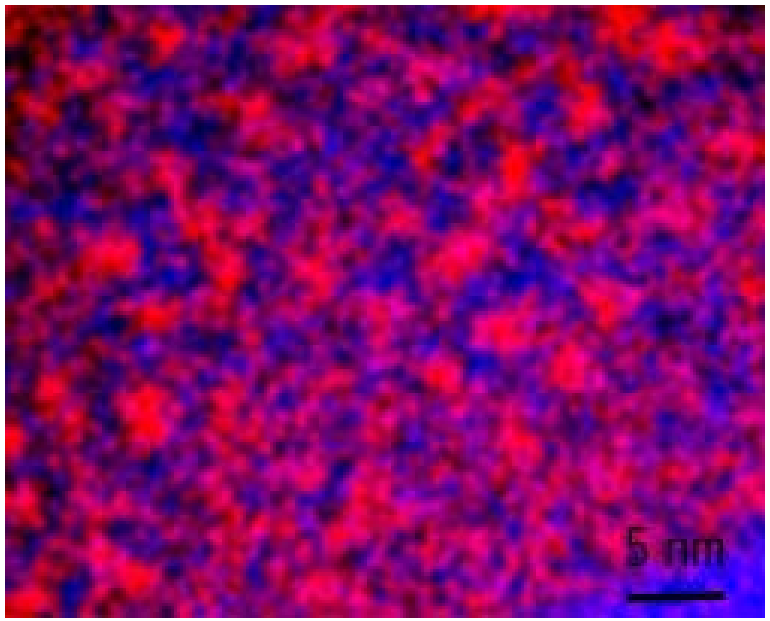
Atom Beam Sputtering



Nano phase by low energy ions

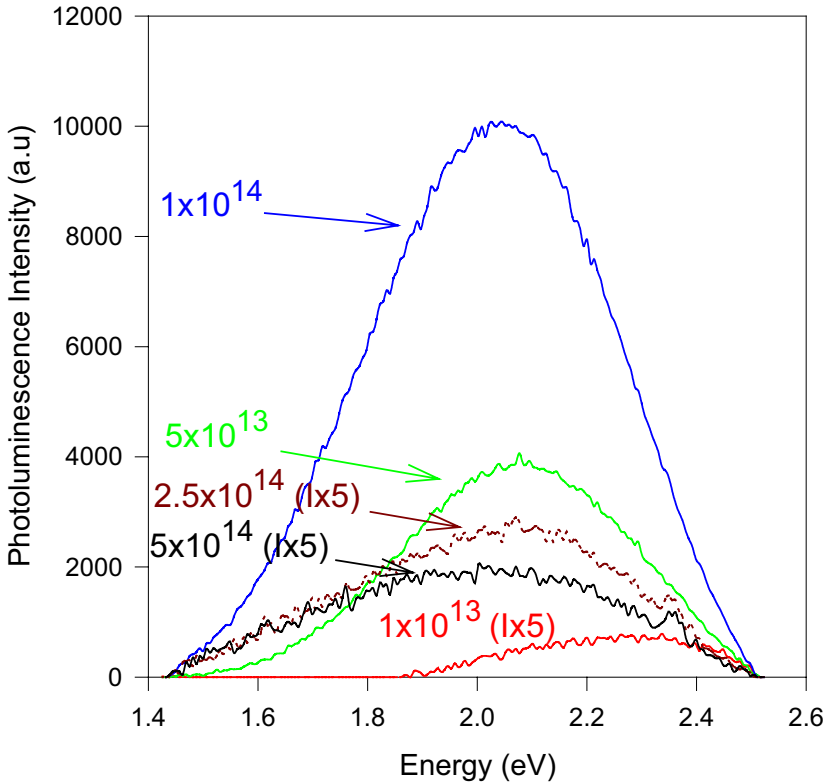
The C precipitation is characterized by TEM and a strong red luminescence

TEM image with energy filtering: electronscattered by C in red, by Si in blue
example: MTES+10^{14} Au 3 MeV

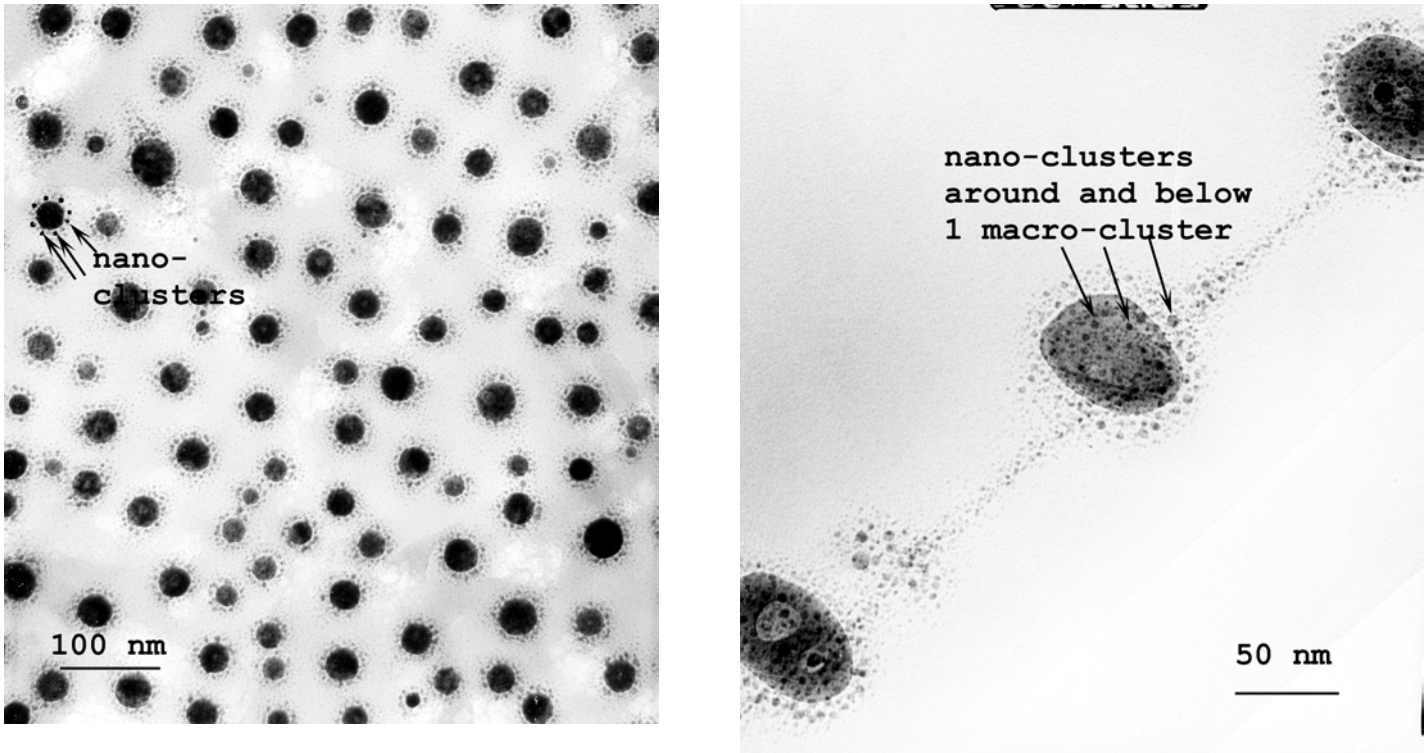


CSNSM Orsay/NSC Delhi
Indo French Project
NIMB 236 (2005) 73.

Clusters grow and become graphitic (like in thermally treated films) with increasing fluence ϕ
example : MTES + 3 MeV Au



Particles formed by mixing-reprecipitation



2 sets of Ag particles formed by (a) spheroidization and (b) mixing + reprecipitation from a 8 nm layer under 4 MeV Au irradiation (10^{16}/cm^2)

- **Pivin et al (2002) *European Physical Journal D* 20 , 251**

Nano structuring by swift heavy ions

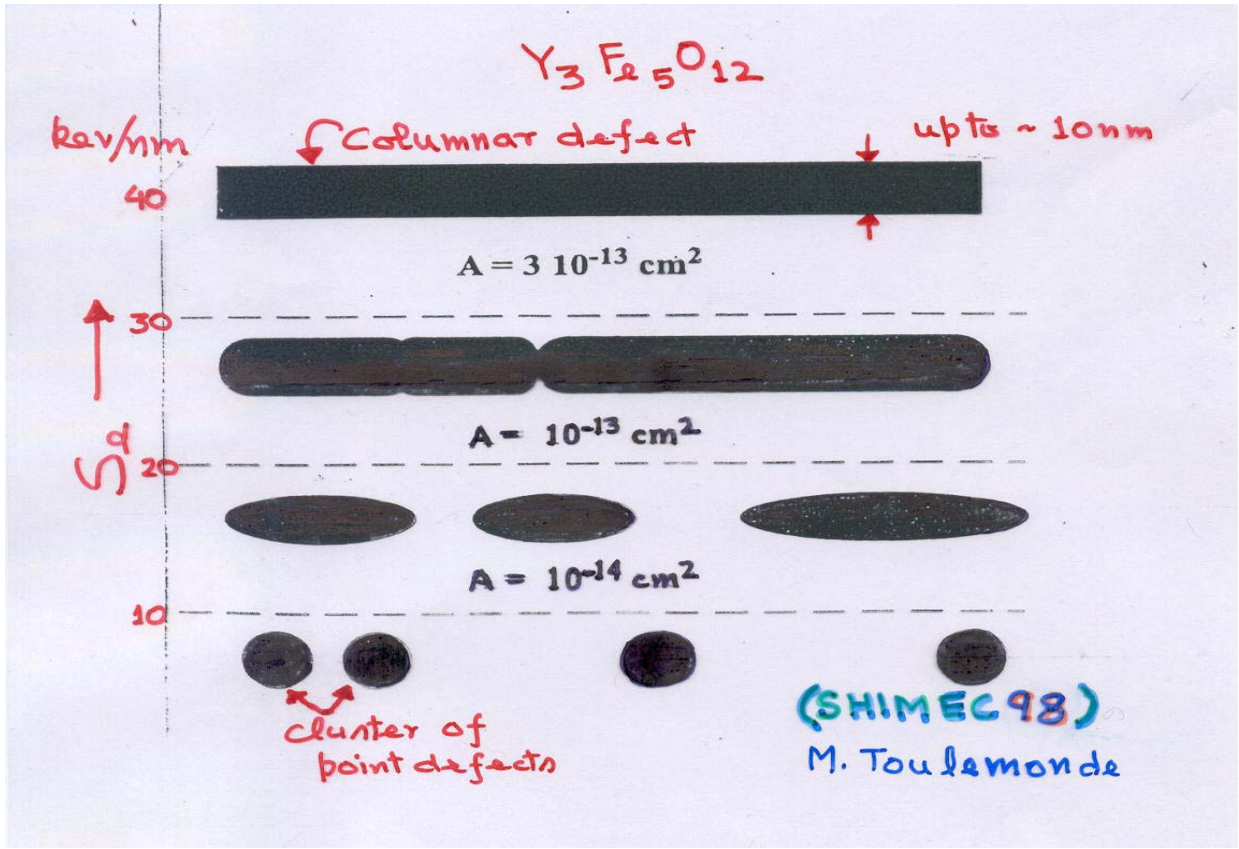
- **Engineering of defects by ion beams**

  Ion mass and Energy : S_e

  Type of defects

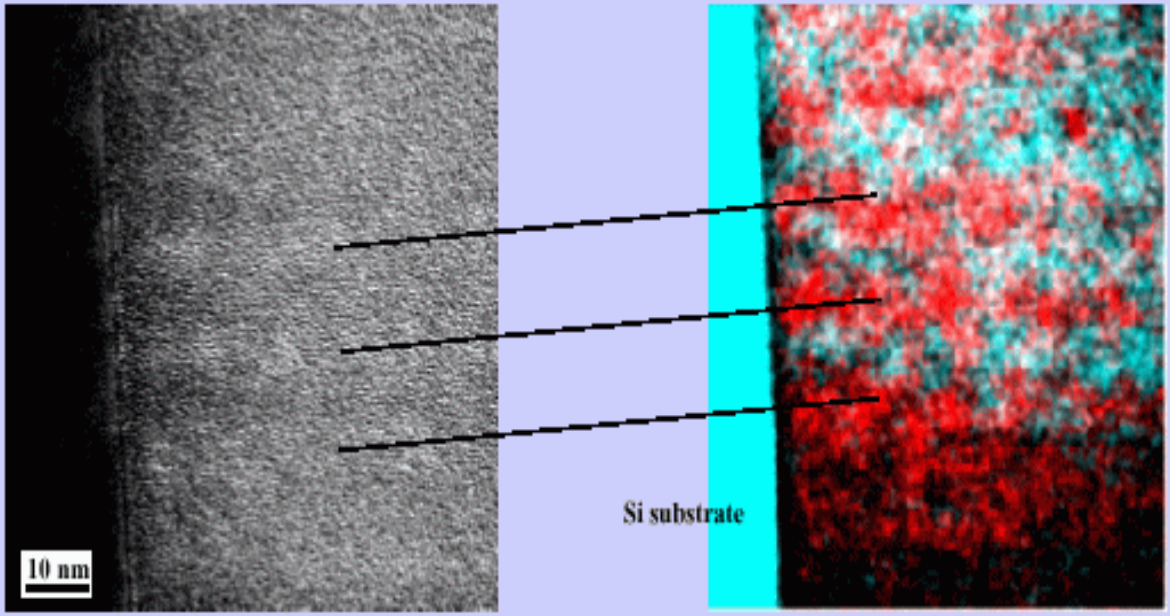
  Fluence (ions / cm^2)

  No. of defects



Nano phase generation by swift heavy ion beam

HPCS films, irradiated with $2*10^{12}$ Au ions at 100MeV



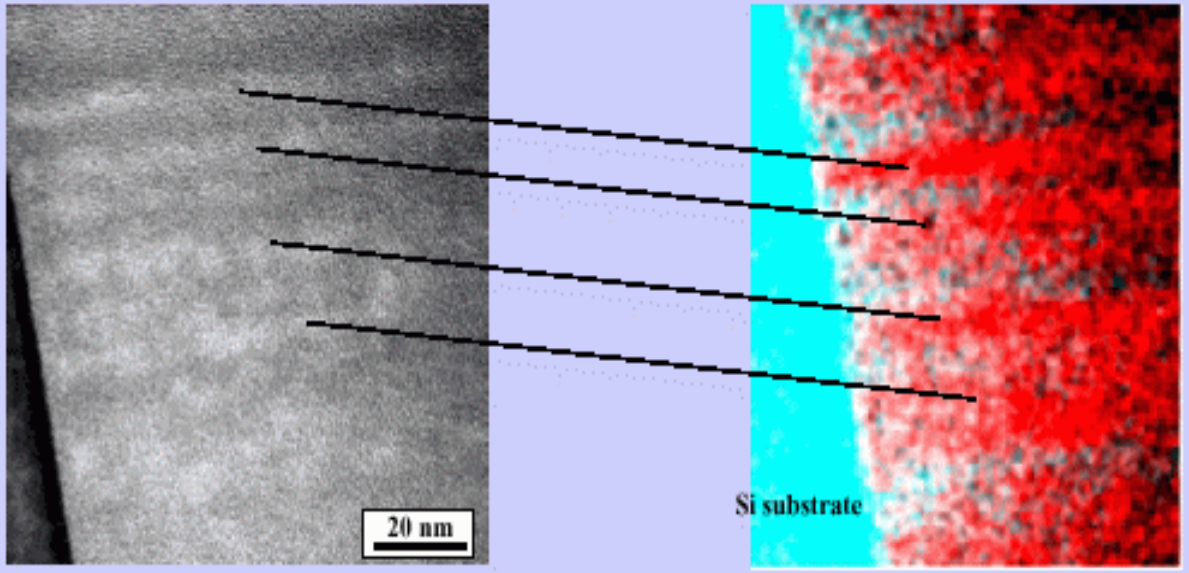
TEM image

EFTEM image
(red: carbon, turquoise: silicon)

IUAC
Delhi
CSNSM
Orsay

Nano phase generation by SHI

HPCS films, irradiated with $5*10^{12}$ Au ions at 100MeV



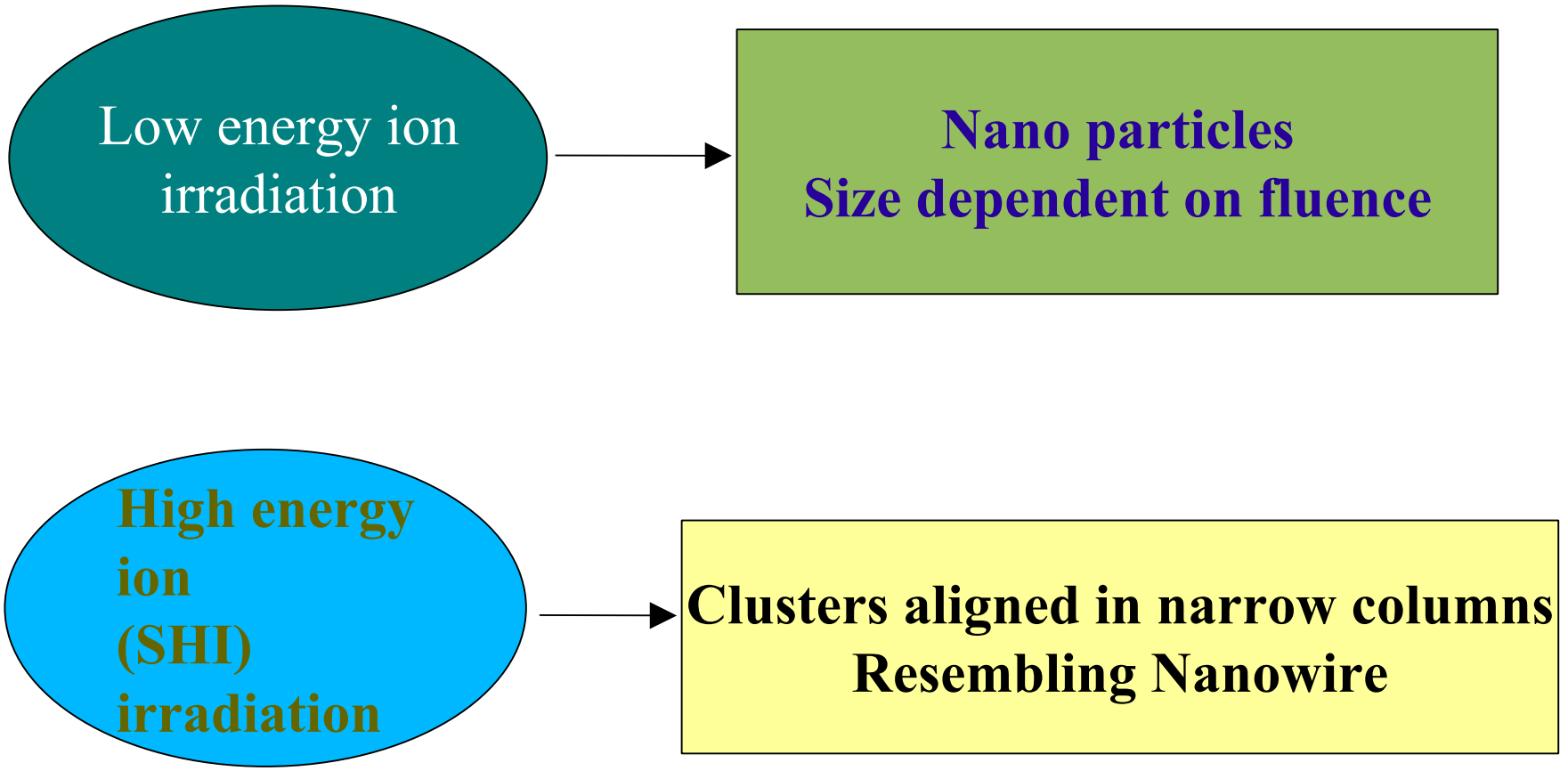
TEM image

EFTEM image
(red: carbon, turquoise: silicon)

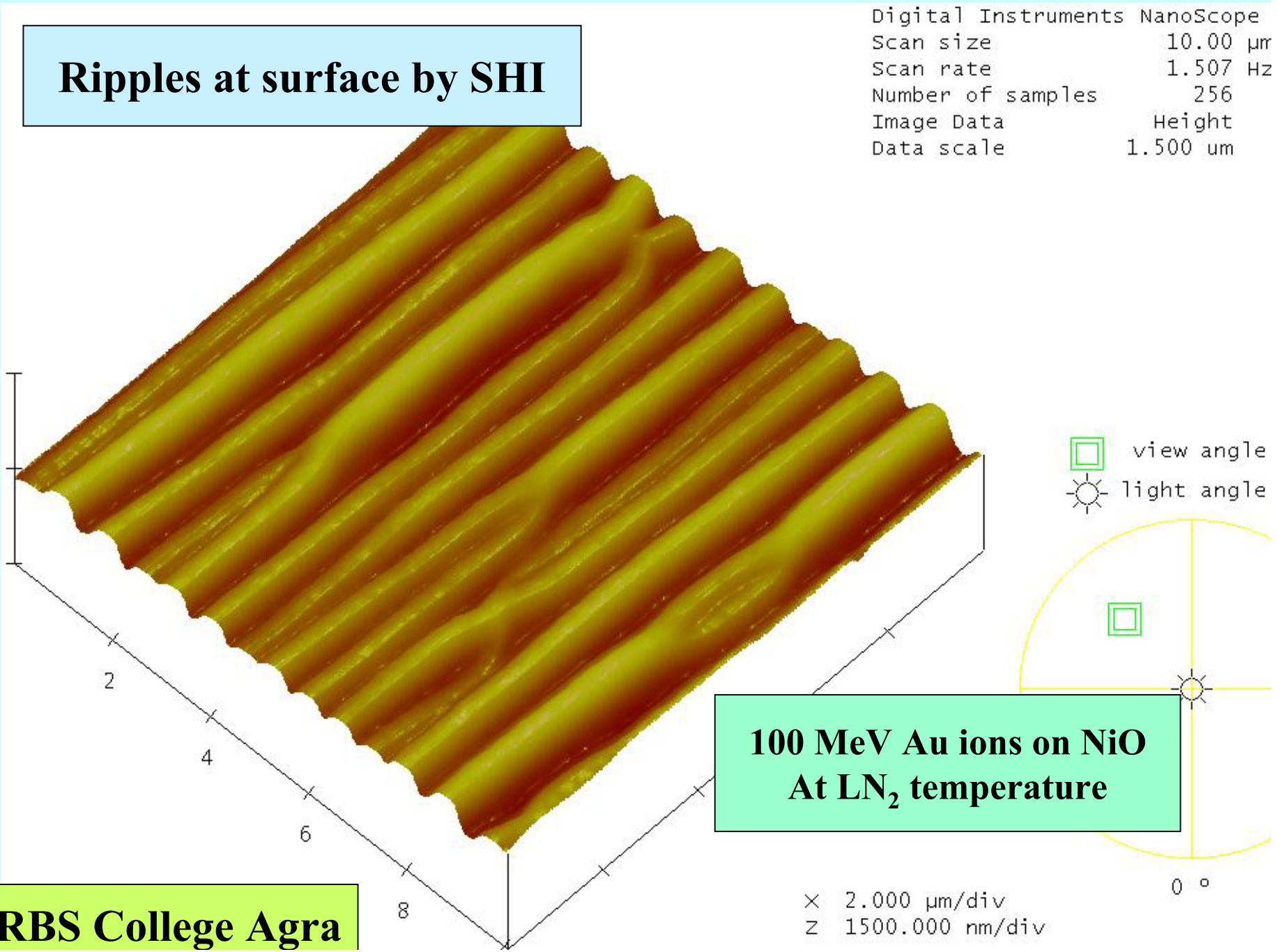
IUAC
Delhi
MPI Halle
CSNSM
Orsay

S.K. Srivastava et al, Nanotechnology (in press)

Low energy & SHI irradiation of Si based polymers

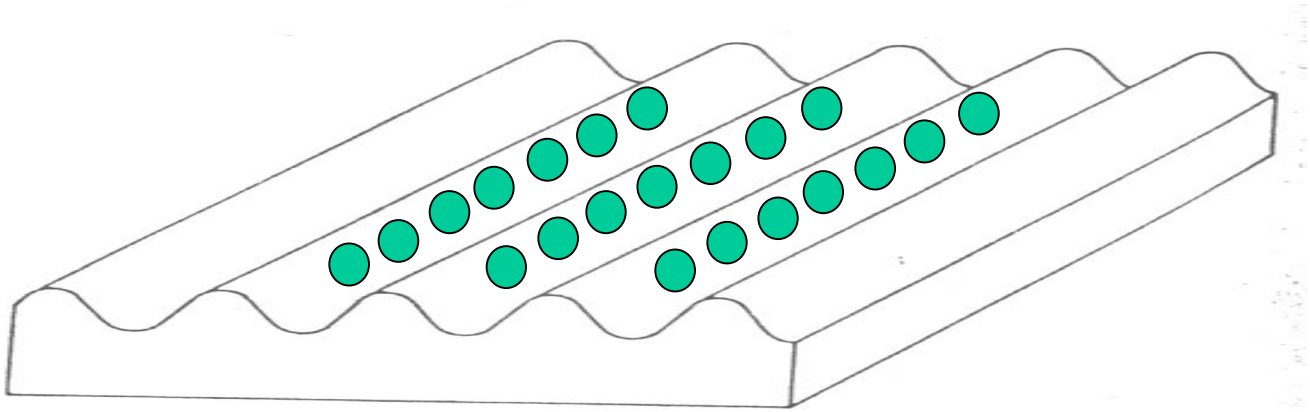


Ripples at surface by SHI



100 MeV Au ions on NiO
At LN_2 temperature

RBS College Agra



Potential applications

- **Strain-free patterned substrates for heteroepitaxial growth of quantum dots or wires in nanotechnology**
- **Templates**

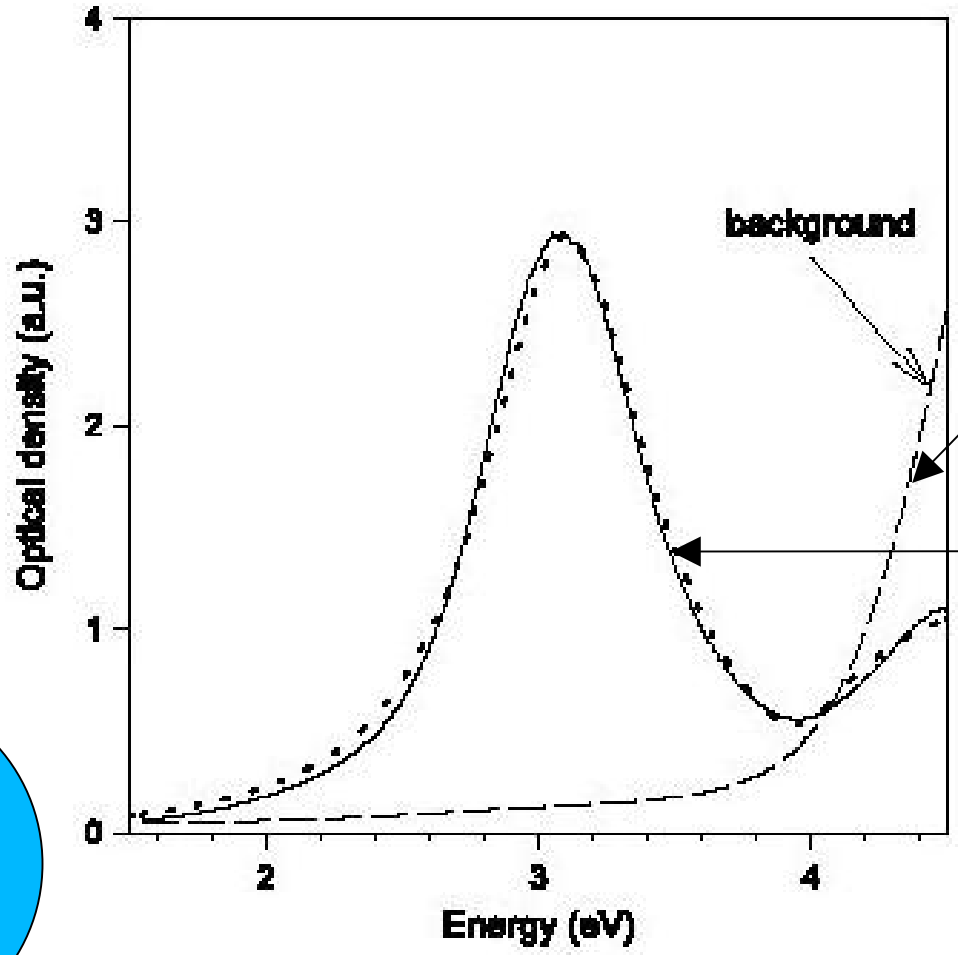


Fig. 1. Optical density of Ag clusters in a glass exchanged for 2 days in a bath containing 0.04 mol% $AgNO_3$ and irradiated with 10^{16} He/cm^2. The cluster size used in the fit (dotted line) is of 1.075 nm and the matrix refractive index that of pure silica. The matrix contribution (dashed line) has been subtracted for obtaining the resonance peak shown with the continuous line.

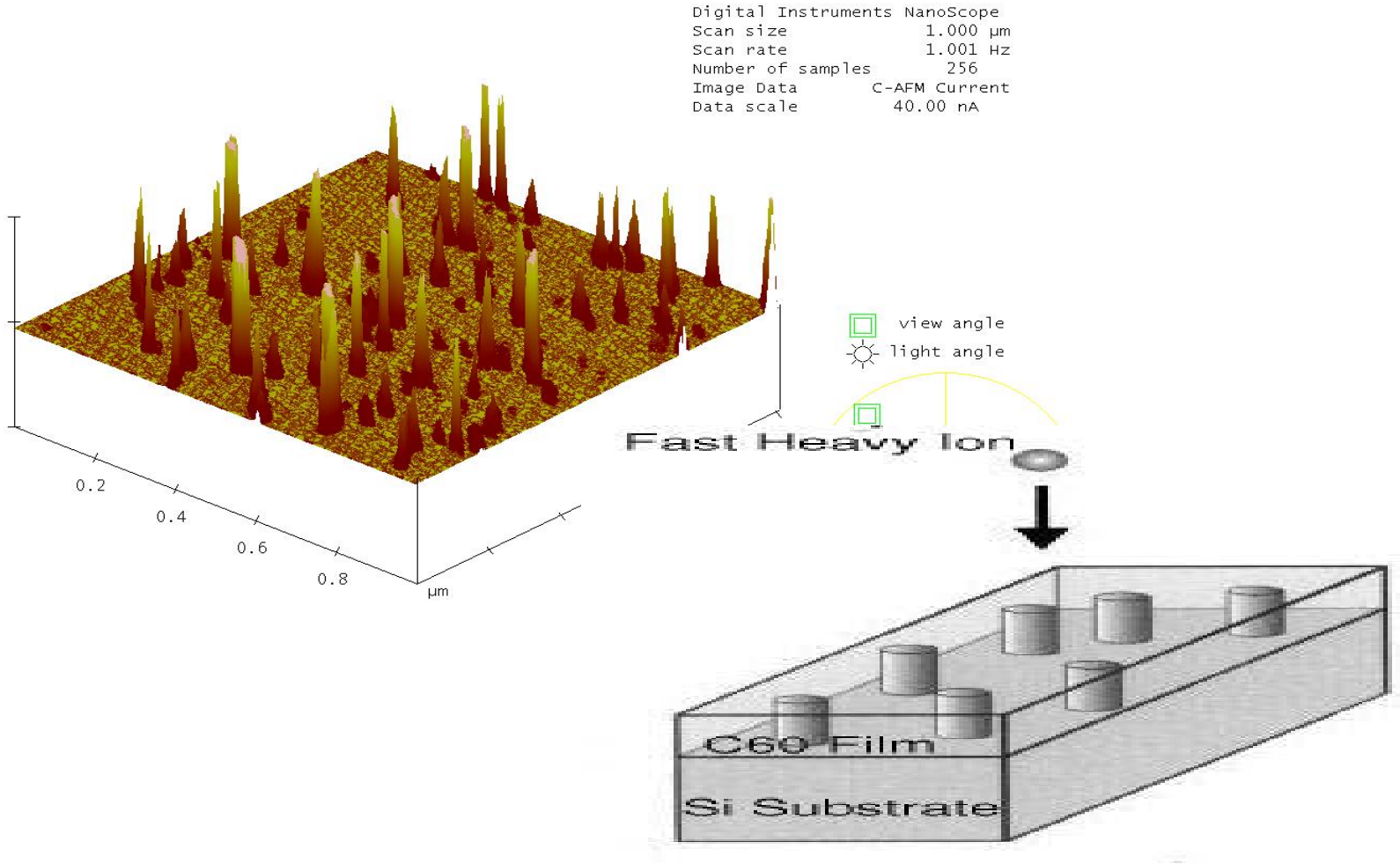
Ag dissolved in glass

Ag dissolved in glass + He irradiation at 10^{16} ions/cm^2

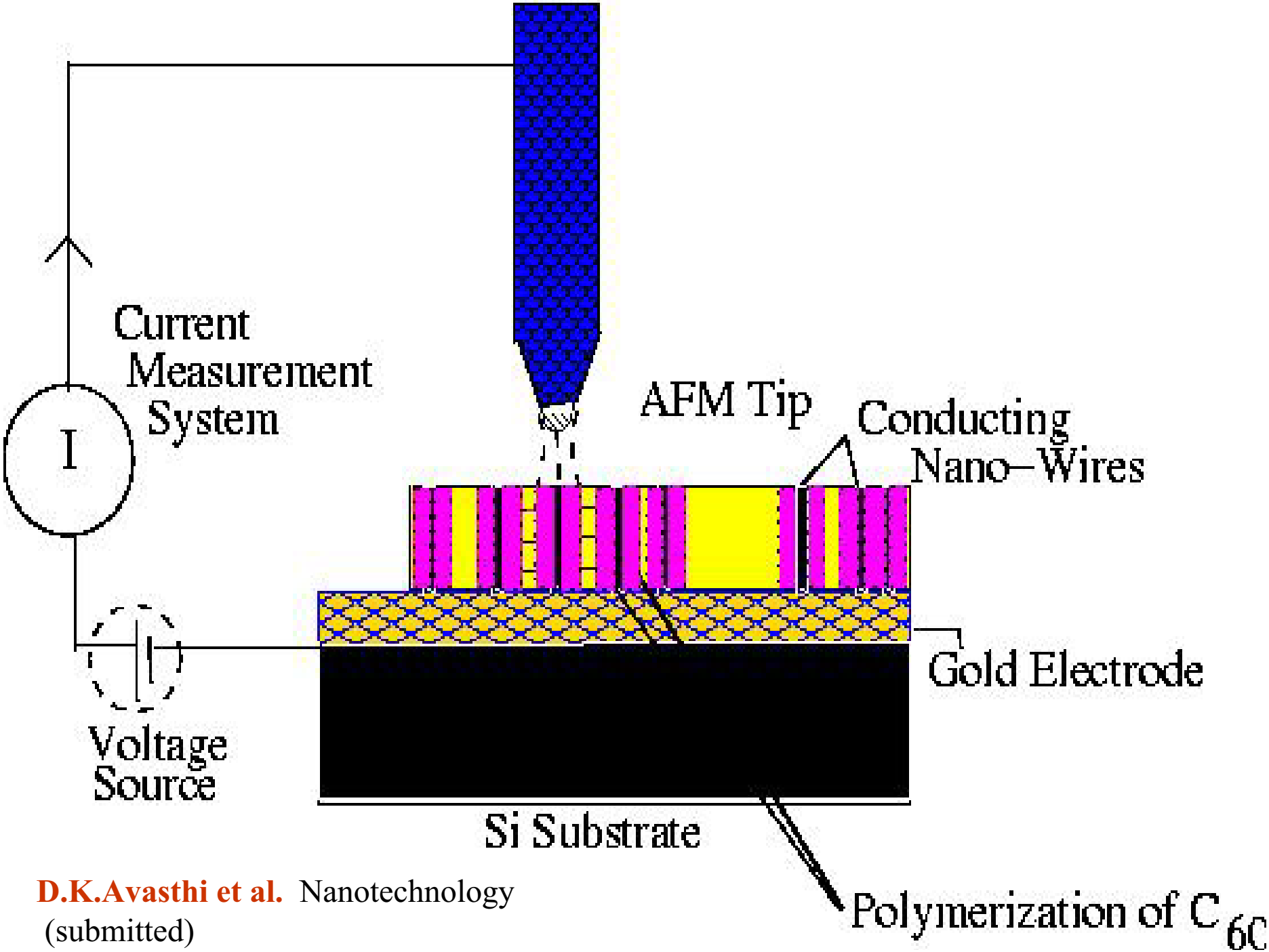
Pivin et al NIM B 215 (2004) 373

CSNSM Orsay NSC Delhi

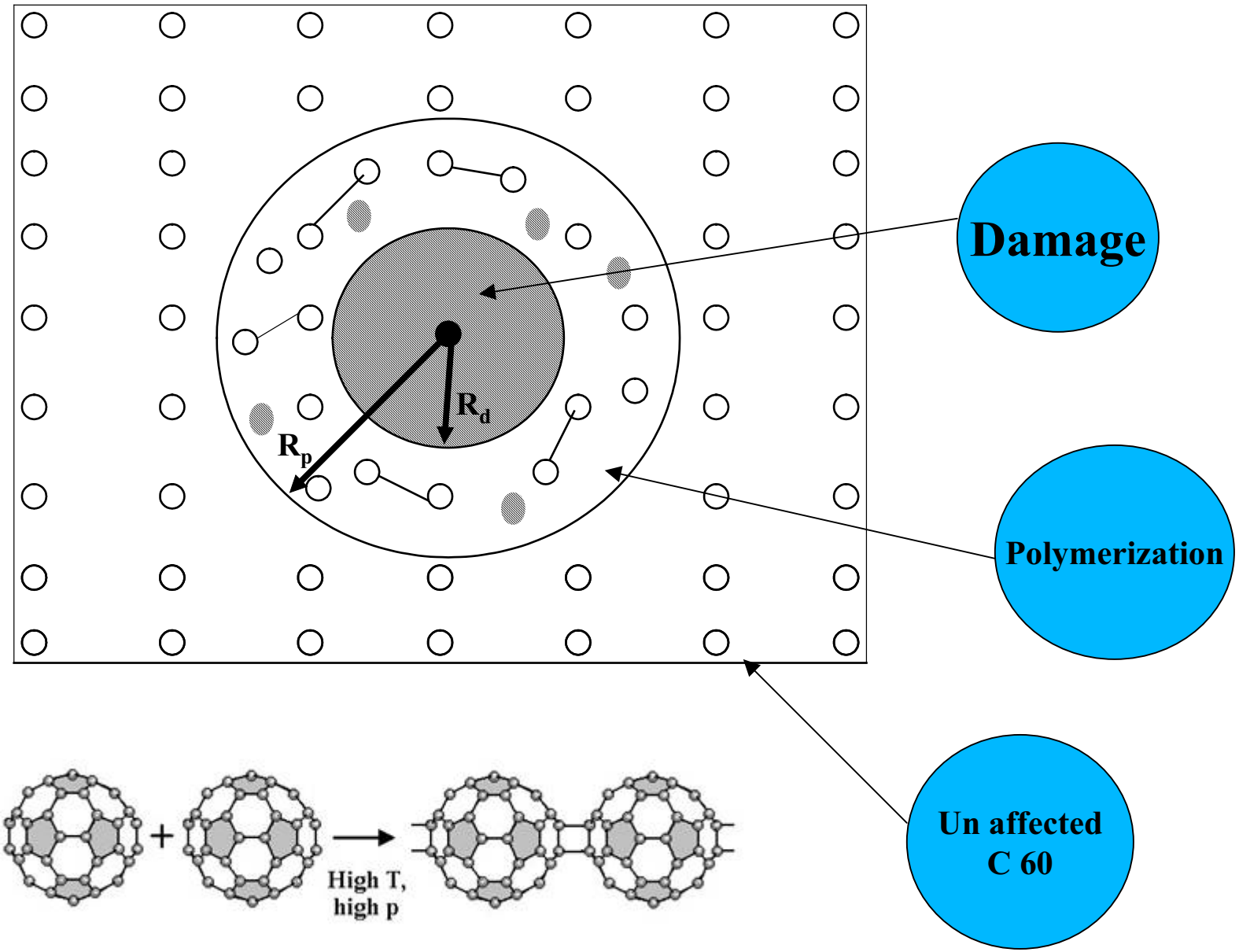
Creation of conducting carbon channels in fullerene film by irradiation of 120 MeV Au ions: Evident by conducting atomic force microscopy

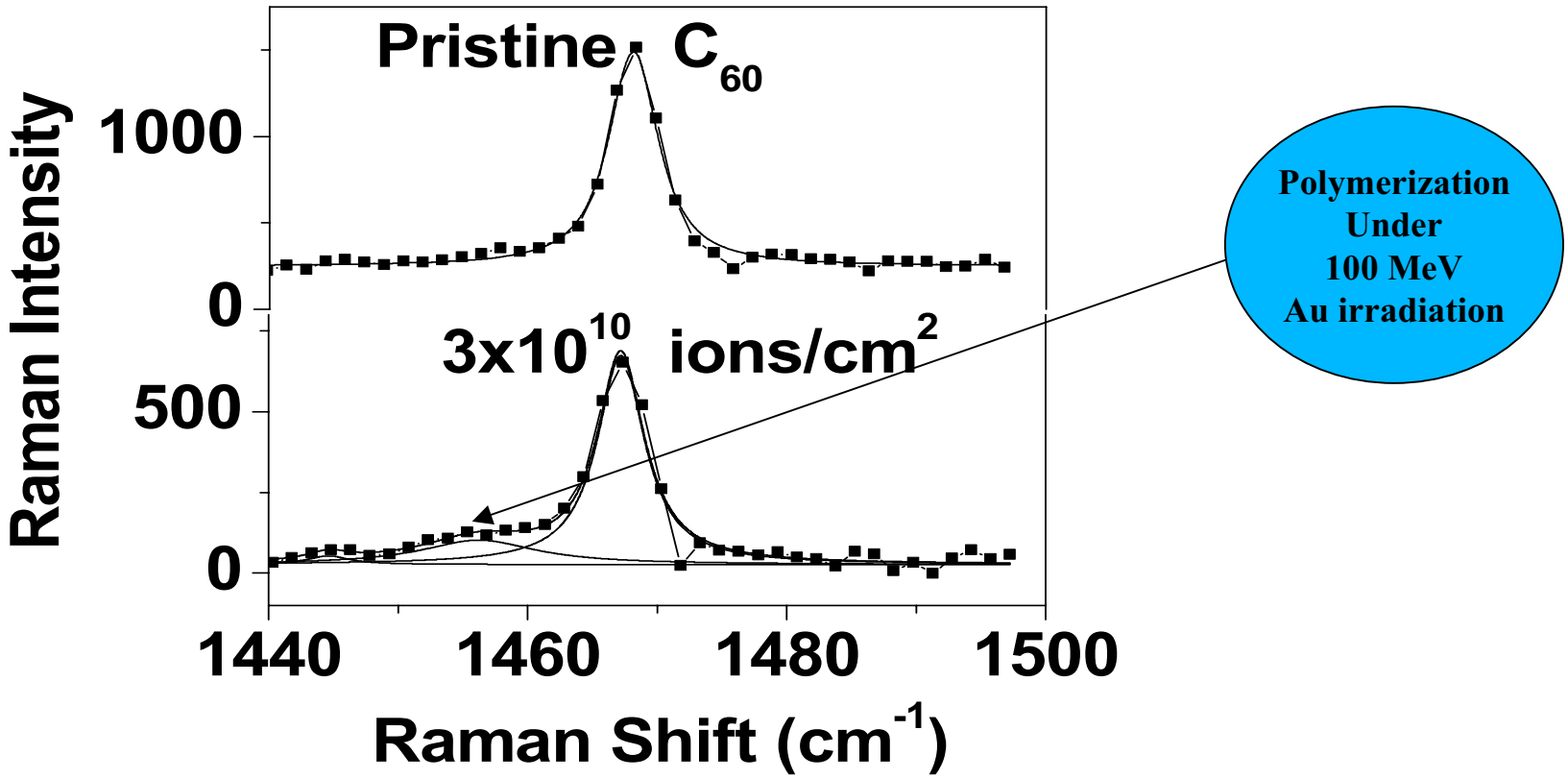


A.Tripathi et al. NIMB 244(2006) 15

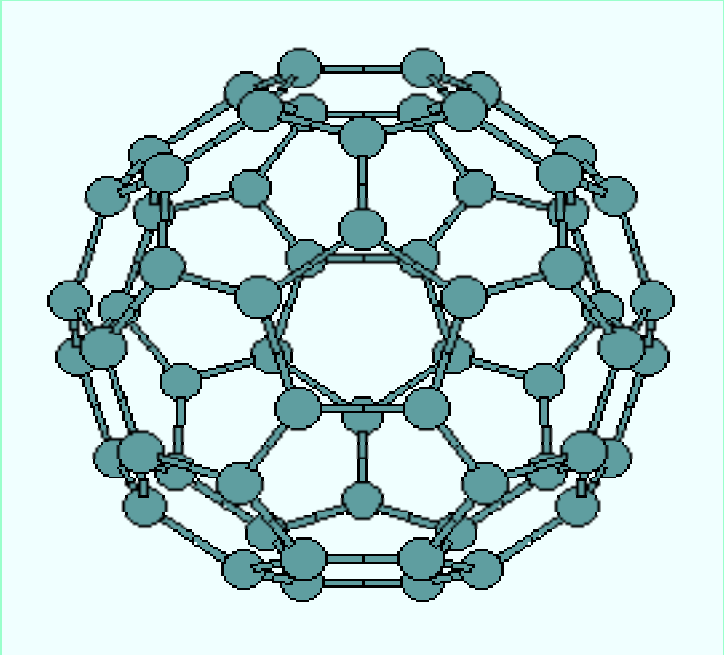


D.K.Avasthi et al. Nanotechnology (submitted)


Damage
Polymerization
Un affected
C 60
R_d
R_p
High T,
high p


Pristine C60
1000
0
3x10^10 ions/cm^2
500
0
Raman Intensity
1440
1460
1480
1500
Raman Shift (cm^-1)
Polymerization
Under
100 MeV
Au irradiation

Fullerene pentagon pinch mode vibrations

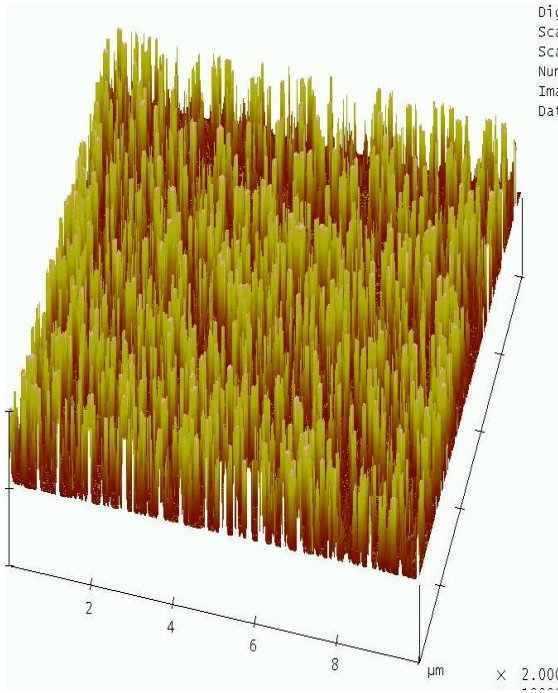


C atoms forming 12 pentagons & 20 hexagons
Density - 1.65 (g cm^{-3})
Diameter of Molecule -10 Å
Length of C-C - 1.46 Å

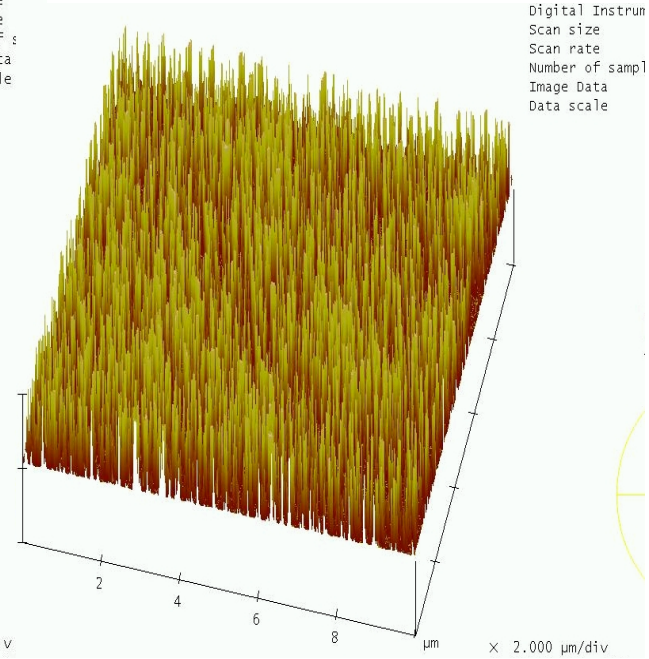
Role of Electronic Energy Deposition on conducting channels

200 nm C60/Au/Si films were irradiated (Fluence: $6x10^{10}$ ions/cm^2) with different energy region ions

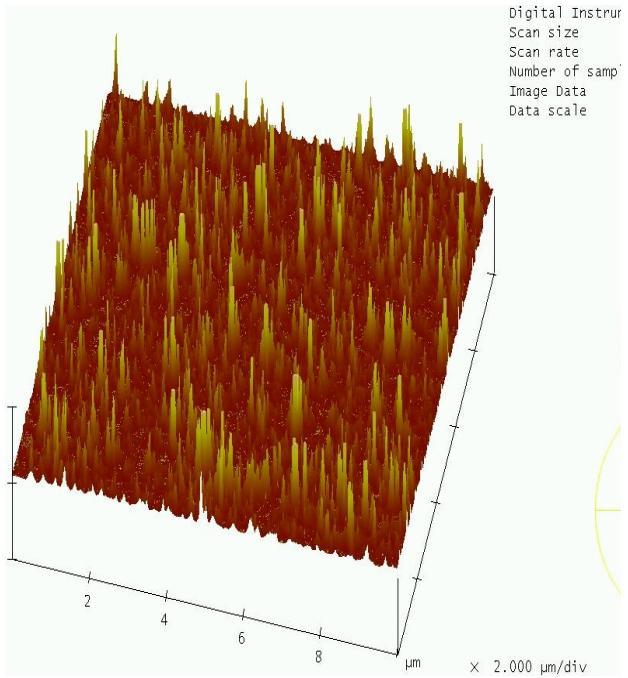
120 MeV Au ion
Applied Bias: 0.5 V
Se: 1300 eV/A
Sn: 15.3eV/A



180 MeV Ag ion
Applied Bias: 2 V
Se:1100 eV/A
Sn: 2.7eV/A

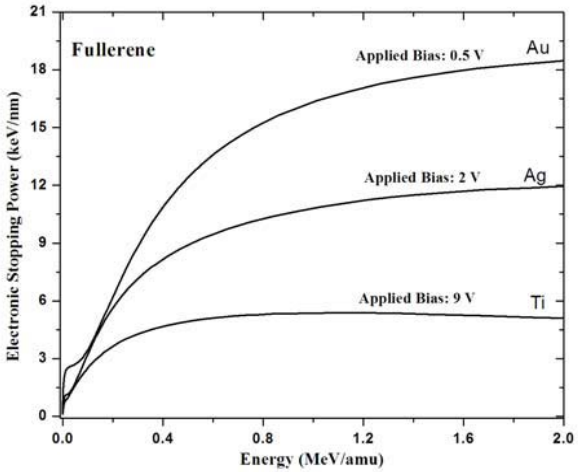


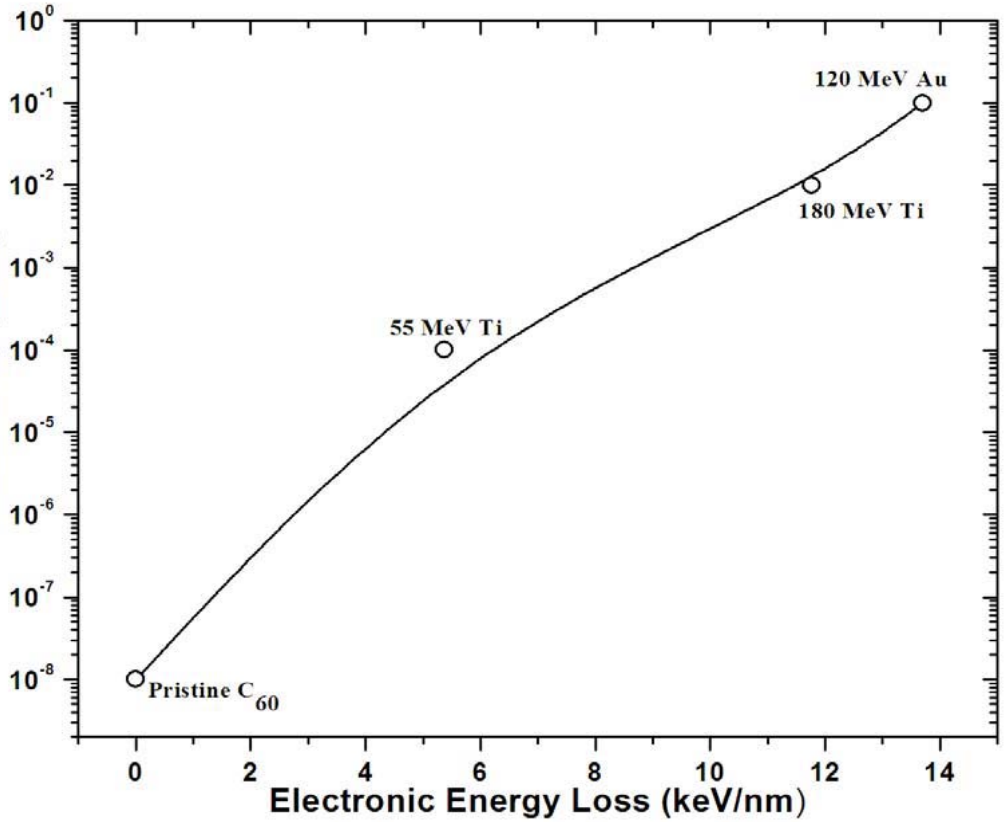
55 MeV Ti ion
Applied Bias: 9 V
Se: 505.5 eV/A
Sn: 0.8 eV/A



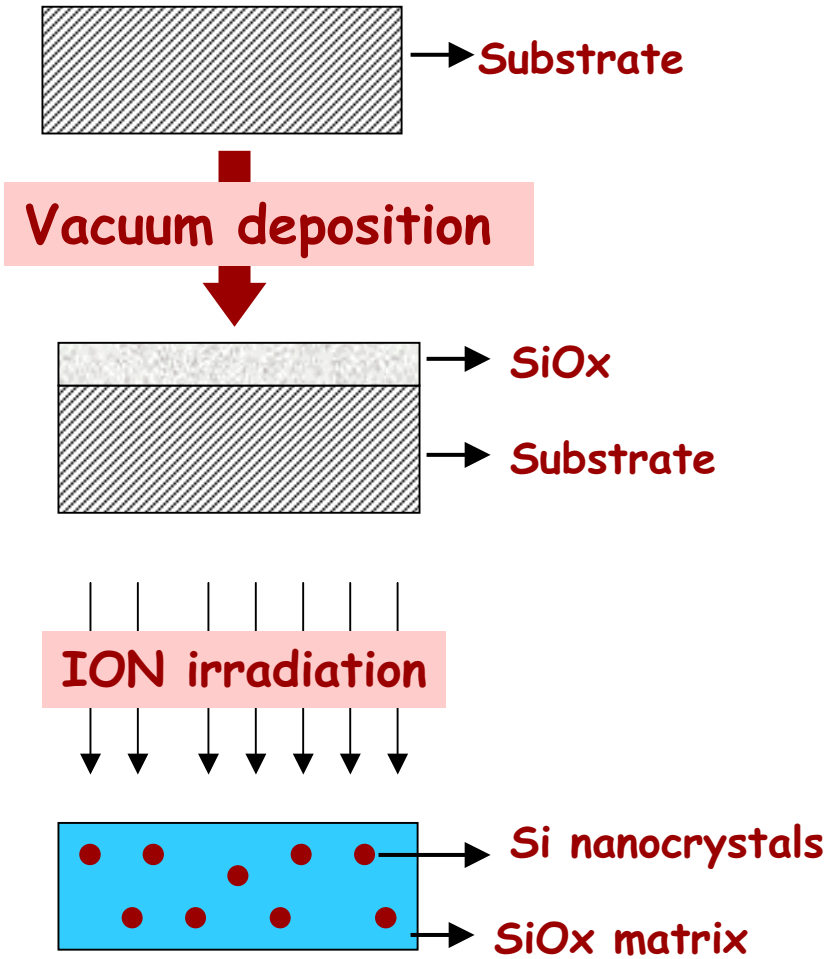
Electrical conductivity variation with electronic energy deposition

Electronic Energy loss in fullerene Matrix

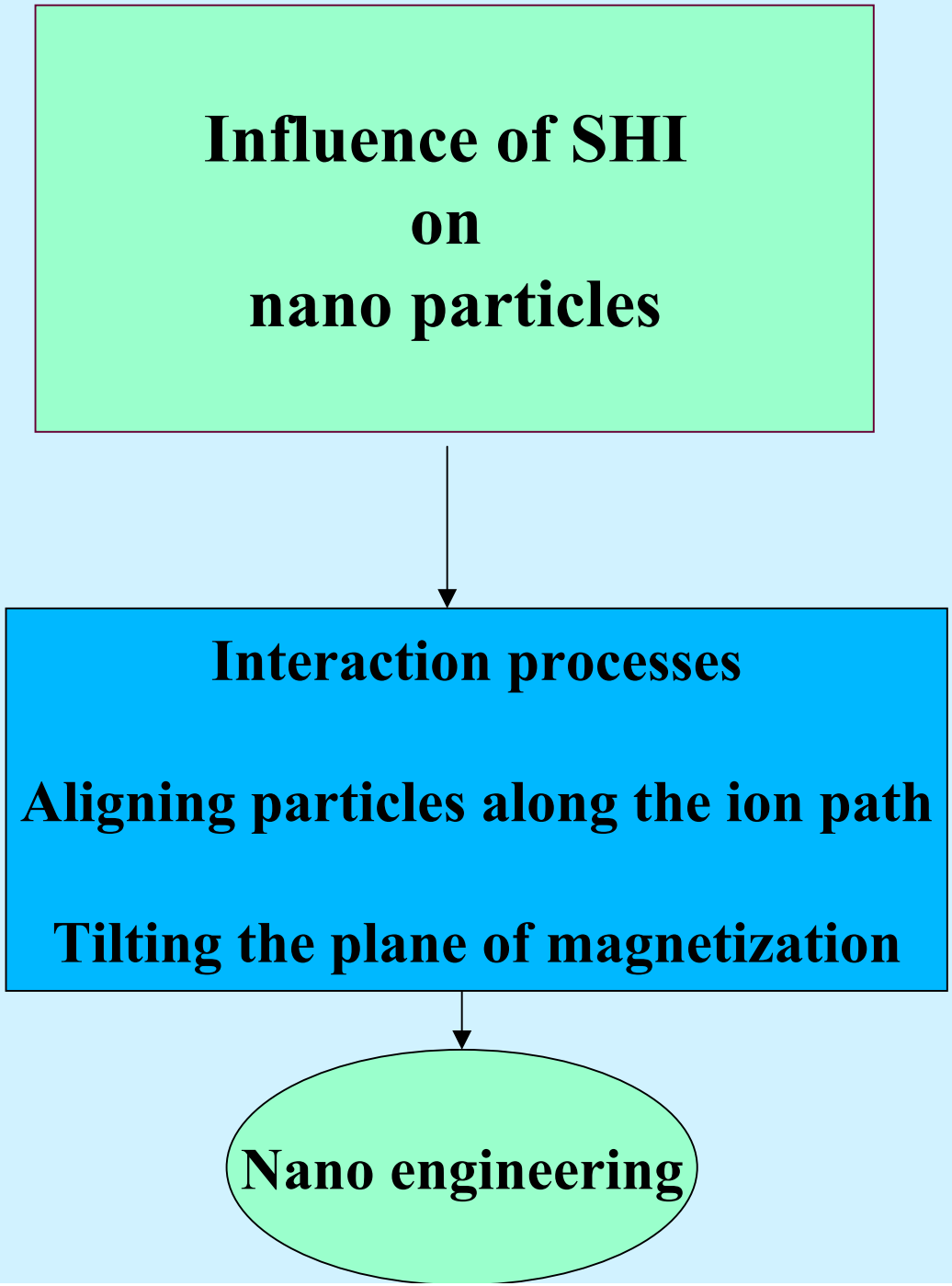




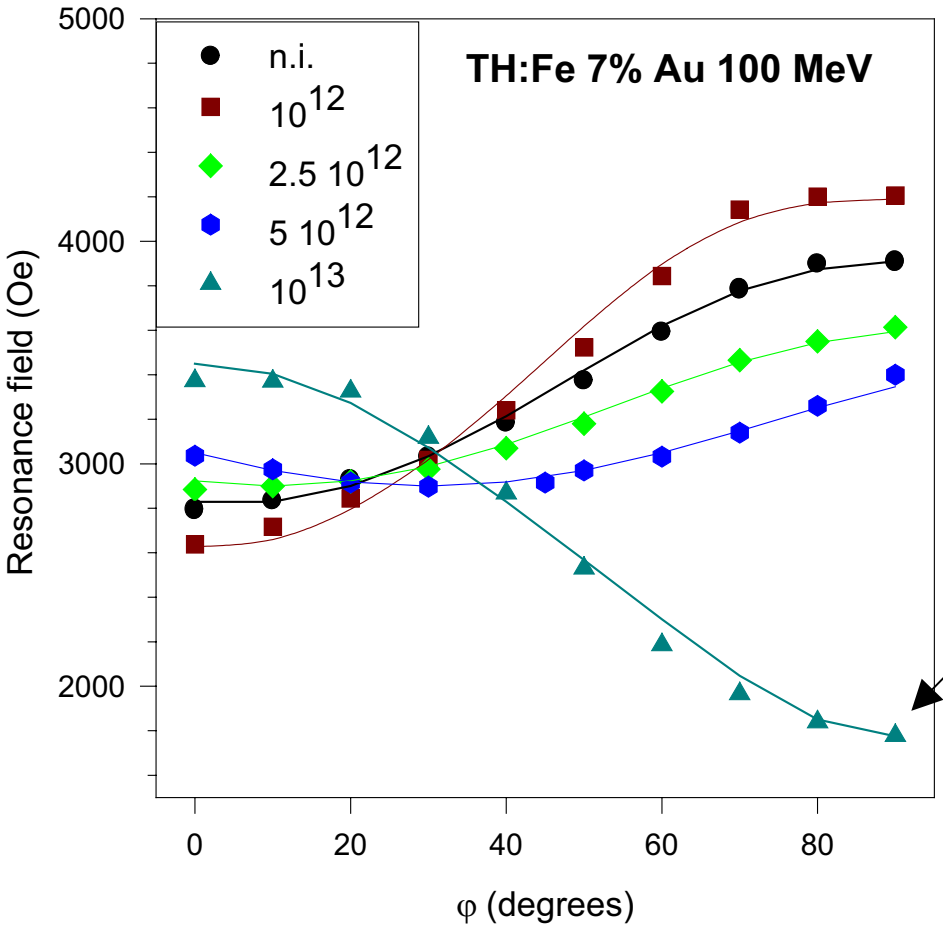
Synthesis by SHI irradiation

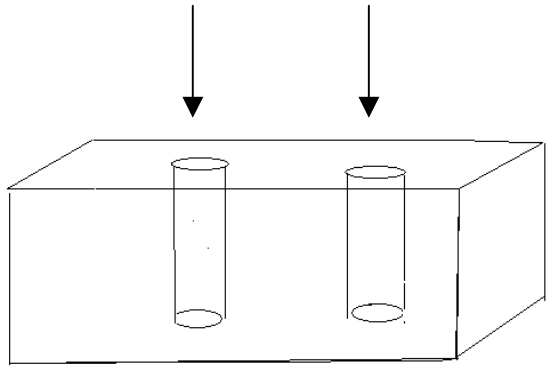


S.V. Bhoraskar
Pune University
JAP 93(2004)3486


Influence of SHI
on
nano particles
Interaction processes
Aligning particles along the ion path
Tilting the plane of magnetization
Nano engineering

Tilt of the magnetization easy axis of Fe nanoparticles by SHI



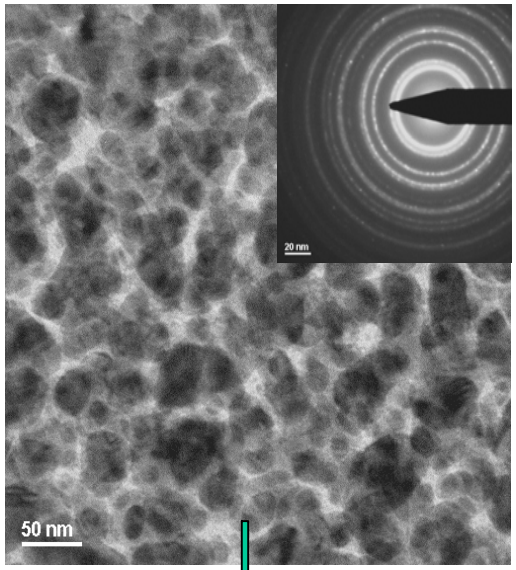


Minimum resonance field ⇔ easy magnetization

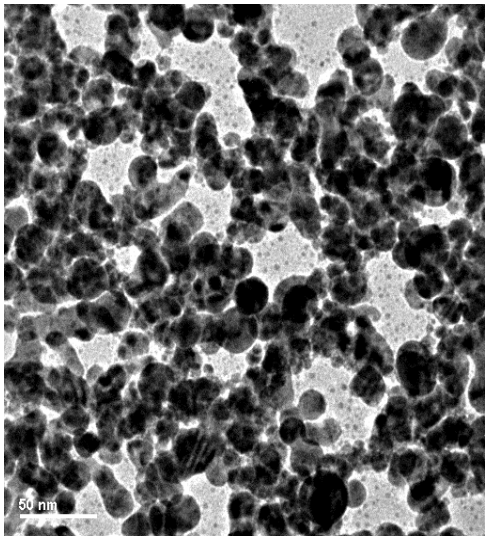
JAP 98 (2005)023908

Application: perpendicular magnetic recording

Tandem deposited Teflon AF/Au nanocomposite irradiated by 120 MeV Au beam at different ion fluences (Kiel Univ./NSC)

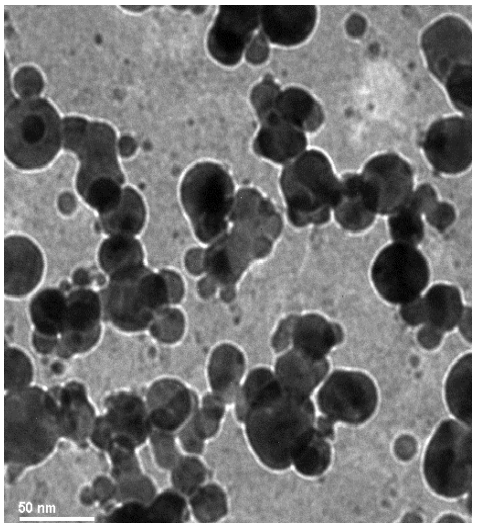


Unirradiated film

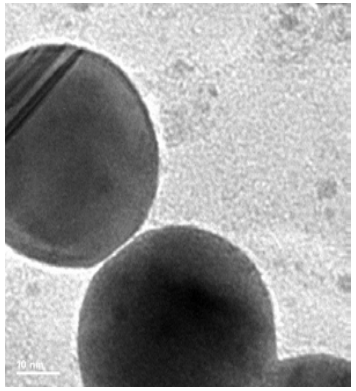


10^{11} ions/cm^2

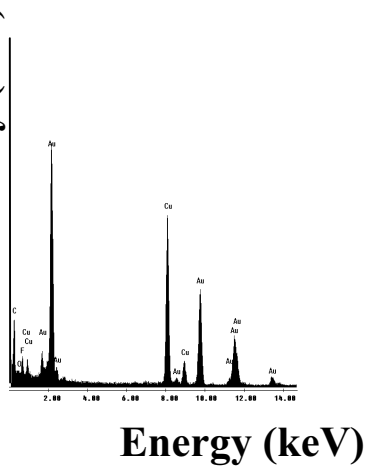
Kiel Univ.
IUAC
Delhi



3×10^{12} ions/cm^2



Close view of irradiated clusters



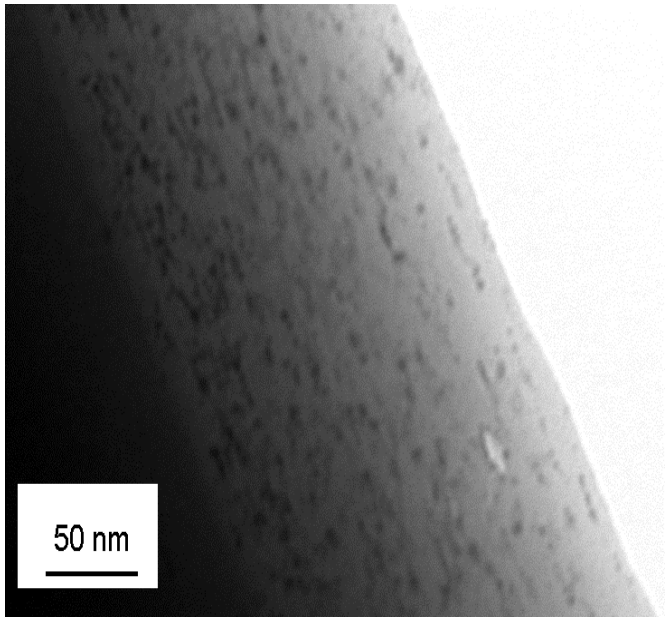
EDAX of pristine film

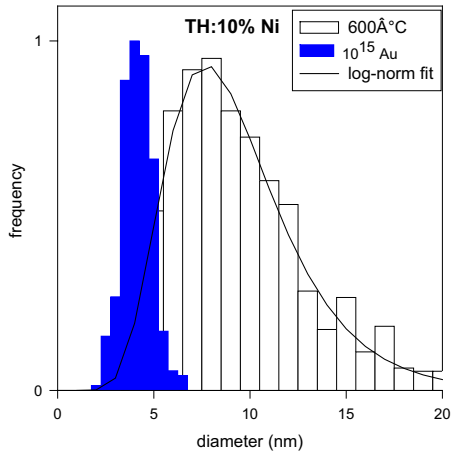
NIM B 217 (2004) 39

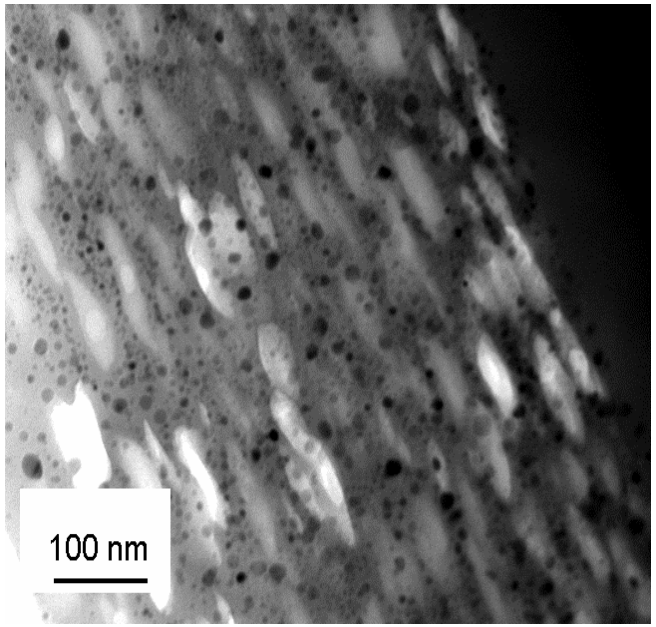
Achieving narrow particle size distribution in 3d magnetic metals in triethoxysilane by ion irradiation

TH-3%Ni irradiated 10^{15} Au:
gaussian, mean D=4.0 nm

TH-3%Ni annealed 1h at 1000°C in vacuum:
log-normal, mean D=5.5 nm, and porosities

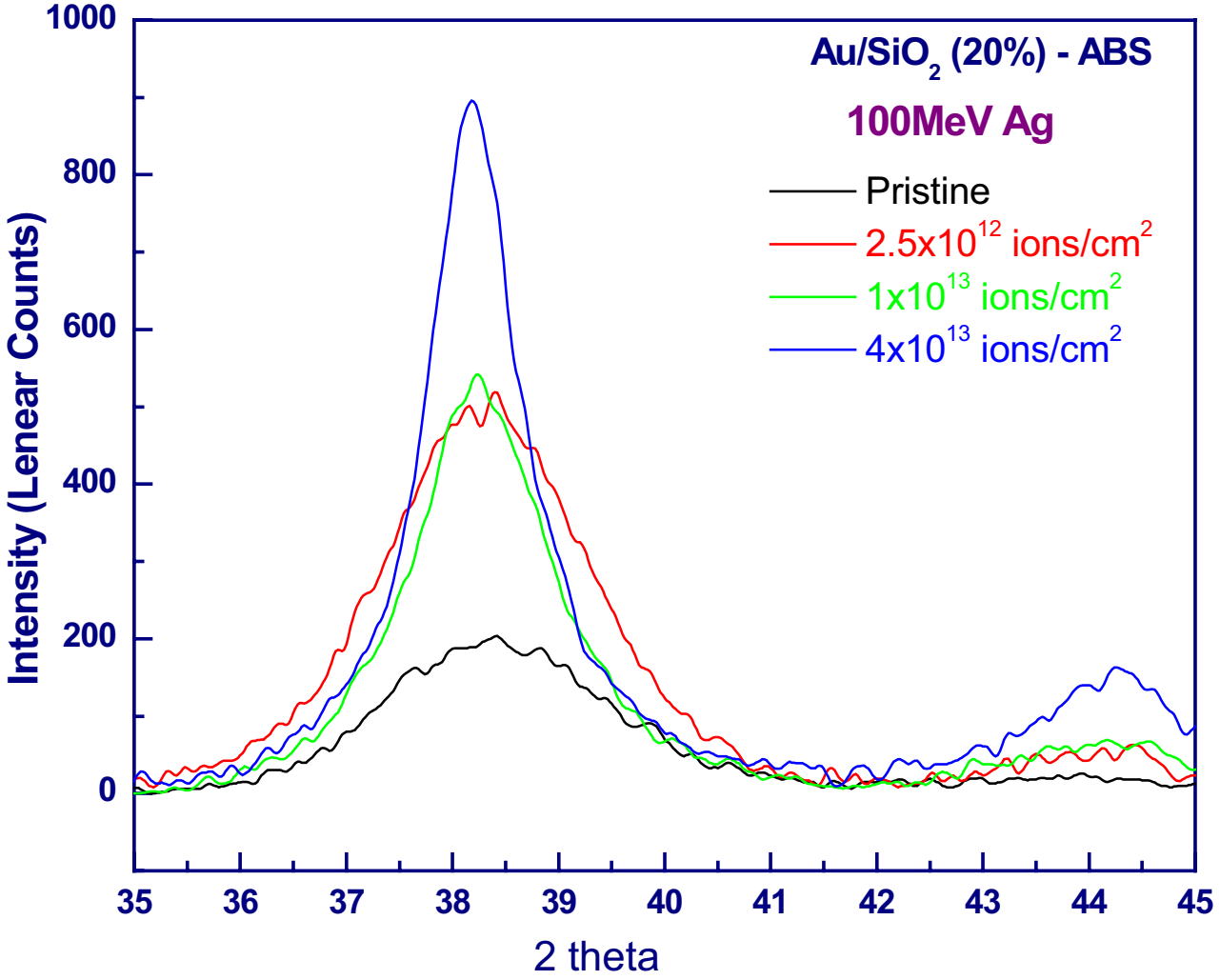






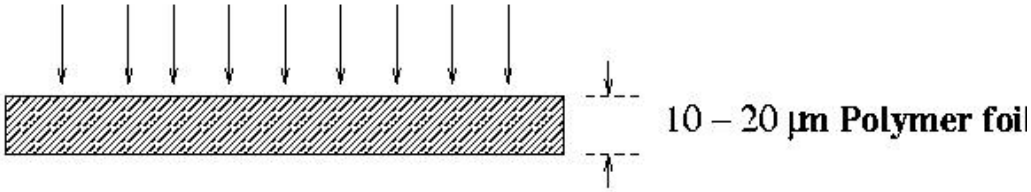
Pivin et al, Eur. Phys. J. B37 (2004) 329

Growth of Au particle size in silica matrix by SHI

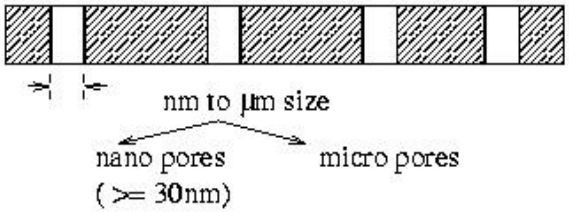


SHI for creating submicron pores in polymer

1. SHI



2. Chemical Etching



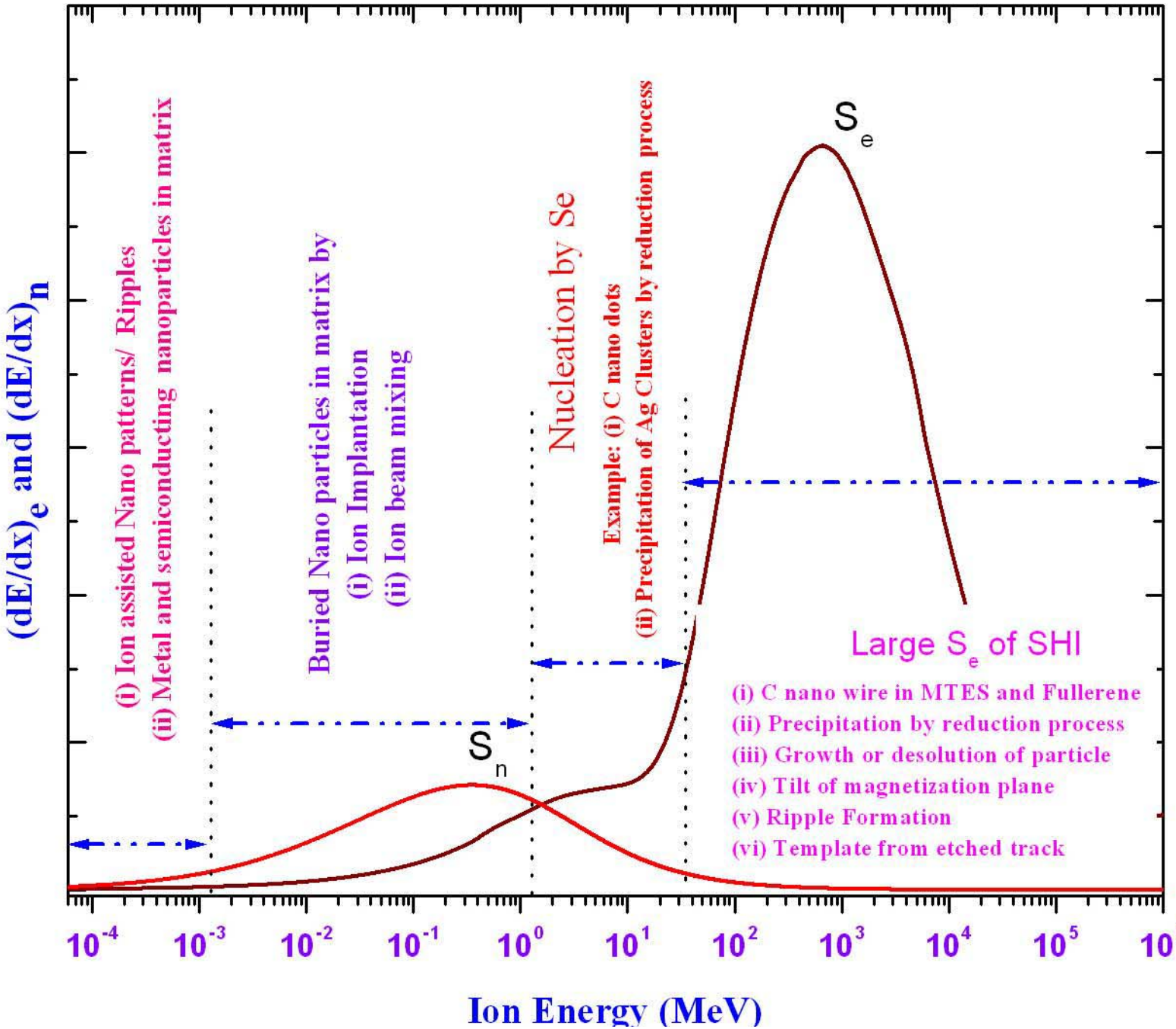
3. Application of μpores & nano pores

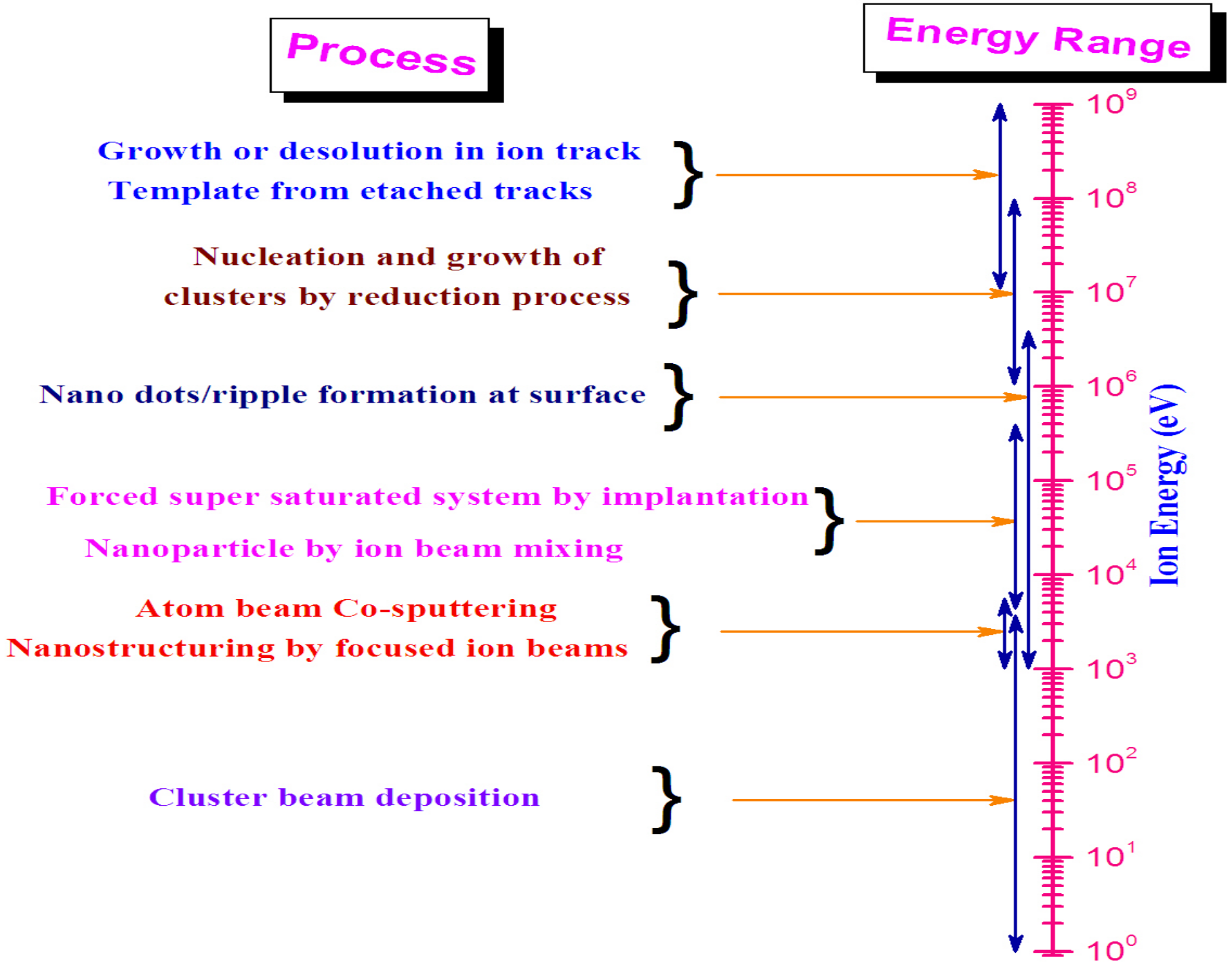
(a) Diode array

(b) μ – channel plate

(c) Variable size pore → μ filter

Micropores used for controlled drug delivery Mangalore/ IUAC


(dE/dx)e and (dE/dx)n
(i) Ion assisted Nano patterns/ Ripples
(ii) Metal and semiconducting nanoparticles in matrix
Buried Nano particles in matrix by
(i) Ion Implantation
(ii) Ion beam mixing
Nucleation by Se
Example: (i) C nano dots
(ii) Precipitation of Ag Clusters by reduction process
Se
Sn
Large Se of SHI
(i) C nano wire in MTES and Fullerene
(ii) Precipitation by reduction process
(iii) Growth or desolution of particle
(iv) Tilt of magnetization plane
(v) Ripple Formation
(vi) Template from etched track
10-4 10-3 10-2 10-1 100 101 102 103 104 105 106
Ion Energy (MeV)


Process
Energy Range
Growth or desolution in ion track
Template from etached tracks
Nucleation and growth of
clusters by reduction process
Nano dots/ripple formation at surface
Forced super saturated system by implantation
Nanoparticle by ion beam mixing
Atom beam Co-sputtering
Nanostructuring by focused ion beams
Cluster beam deposition
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Ion Energy (eV)

Possible Applications

Antibacterial effects
Localized heating by SPR
Bio sensor
Gas sensor
Magnetic recording
Flat panel display
Field emission
High frequency applications

The influence of Au and Ag particles embedded in PTFE with Si as substrate on growth of bacteria

Kiel Univ Inst. Of Virology

Jaypee Univ. Noida

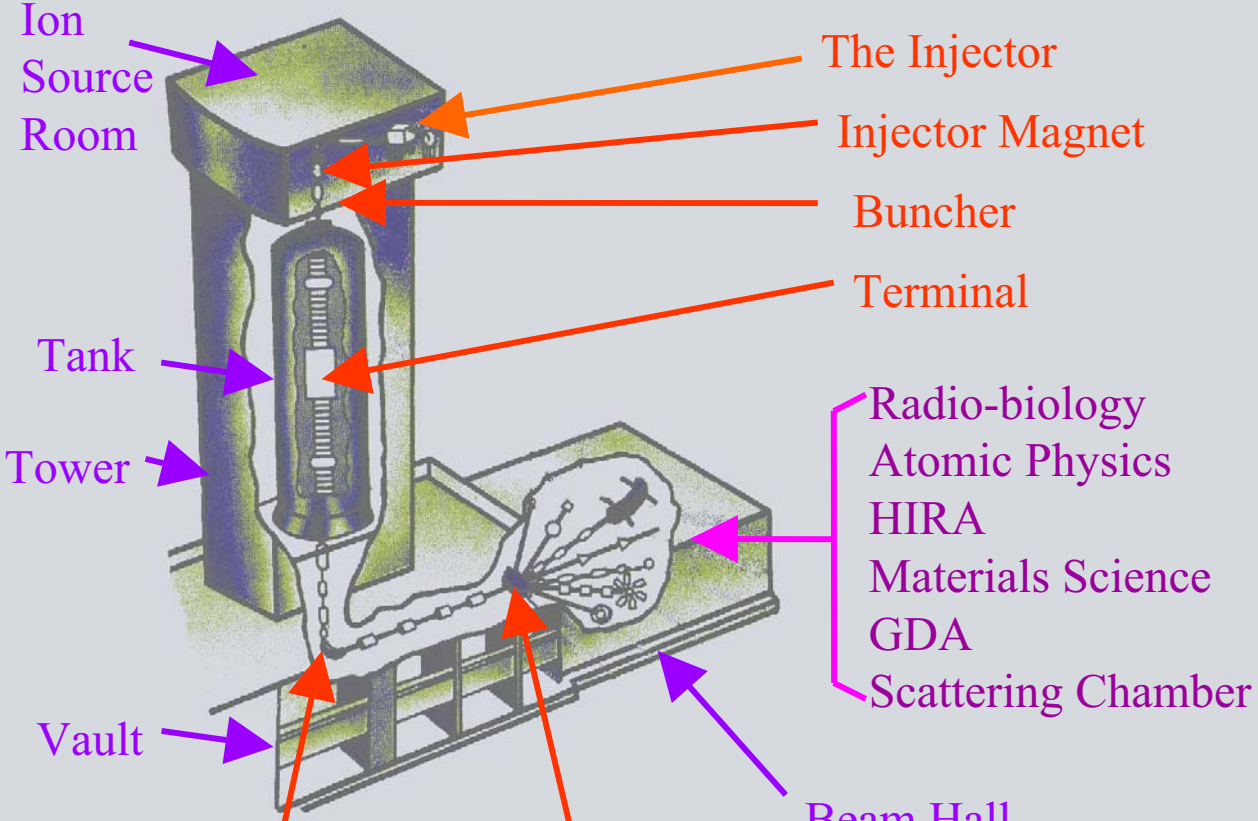
The Pelletron Accelerator

Tank ht: 26.5 m
Diameter: 5.5 m
Pressure: 86 PSI
of SF_6 gas

Ions accelerated:
H to Au beams

Ion Currents:
Typically
5 - 50 pnA

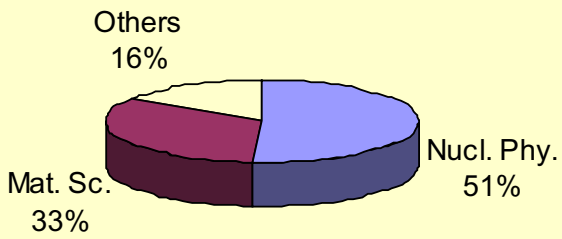
Energy : 30 -
250 MeV



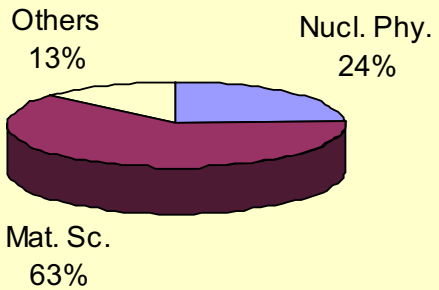
USER COMMUNITY OF NSC

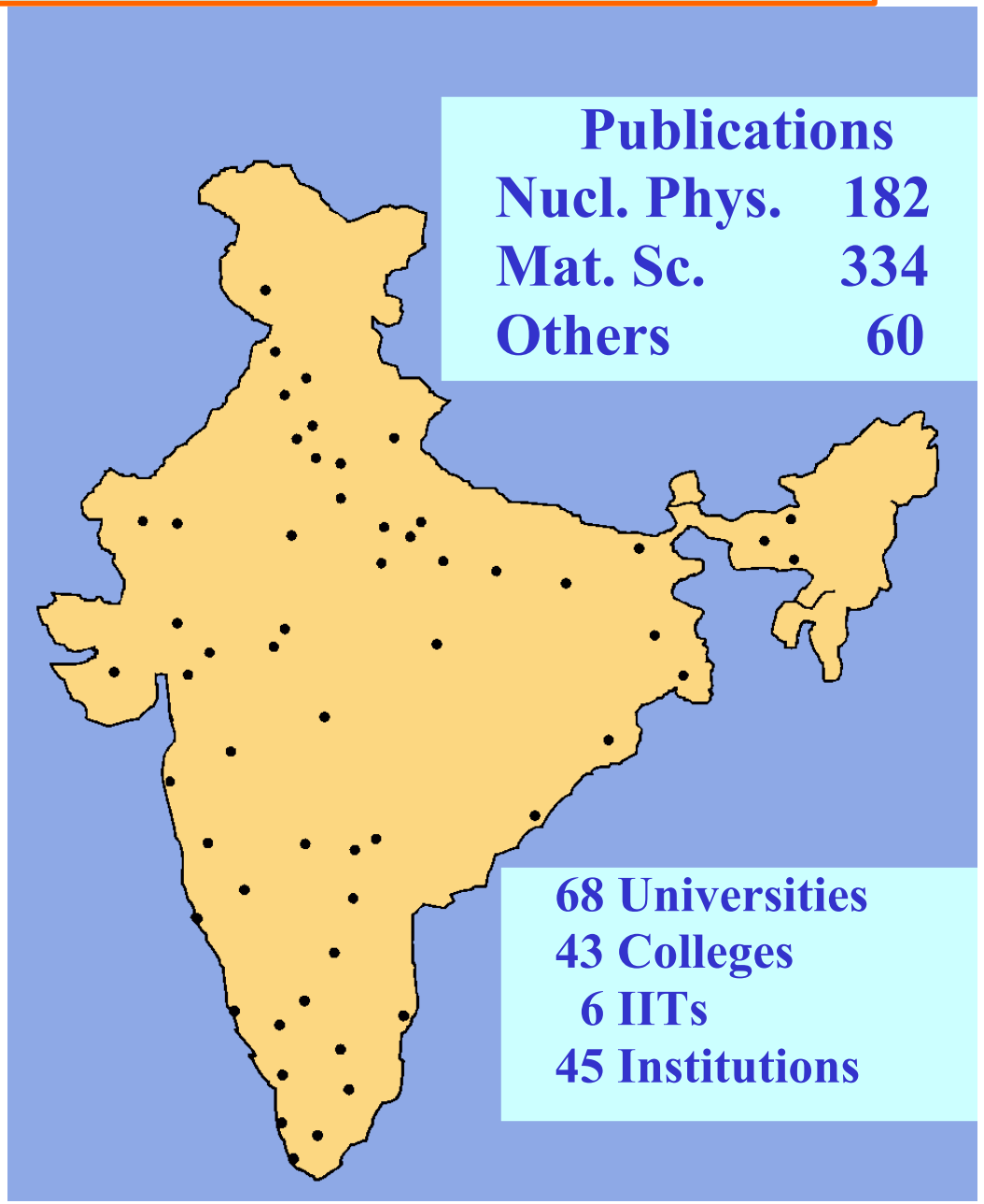
250 Users

FIELDWISE BREAKUP OF UTILIZED BEAMTIME (JULY-OCTOBER, 2003)



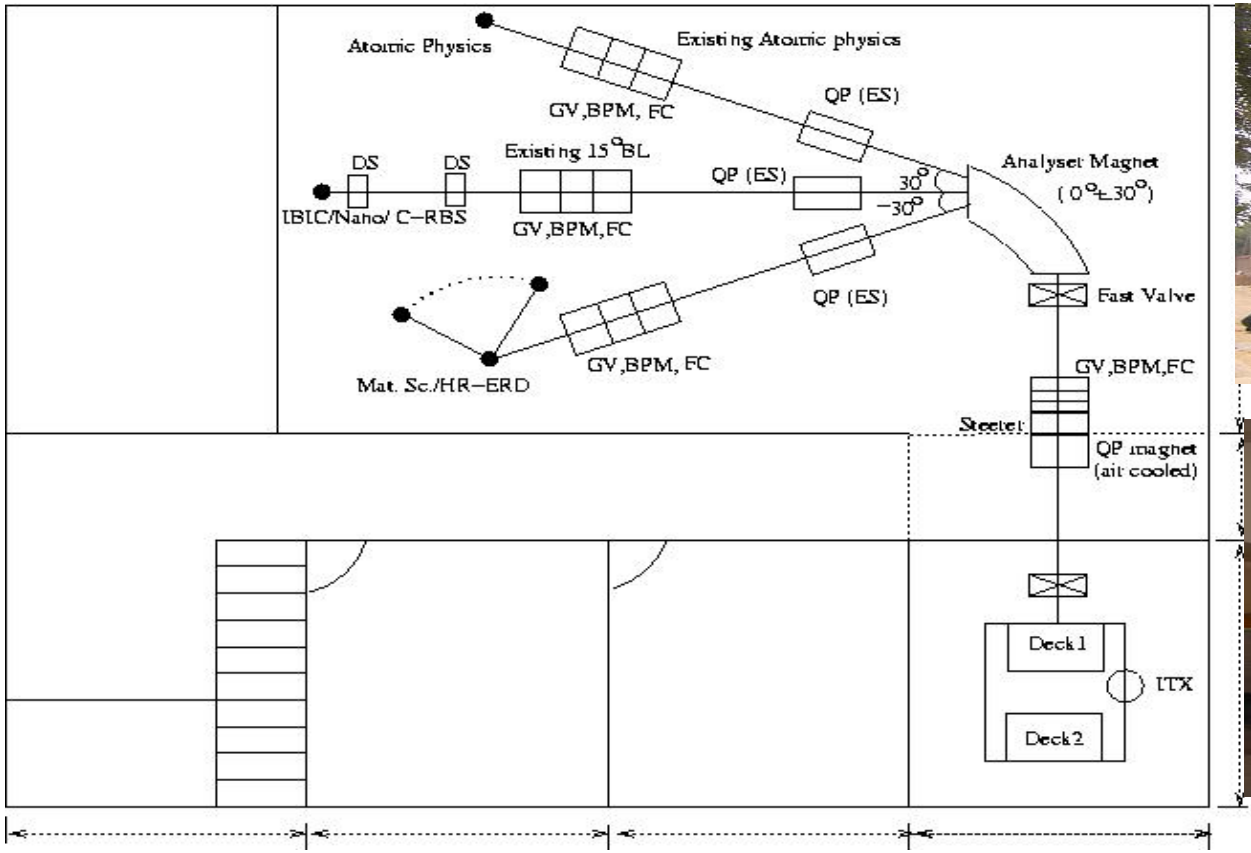
USERWISE BREAKUP OF UTILIZED BEAMTIME (JULY-OCTOBER, 2003)

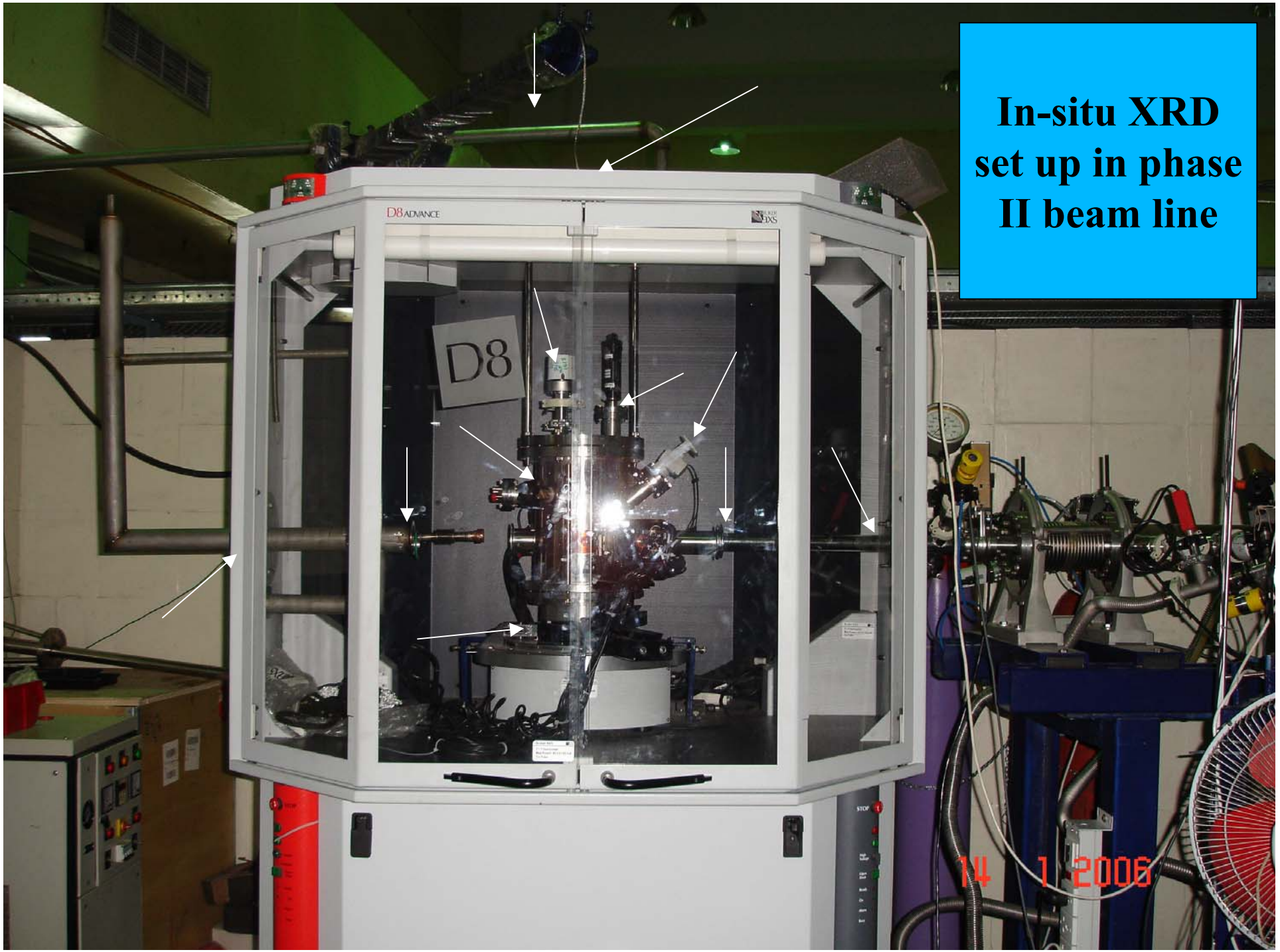




LEIBF with HR Spectrometer

New Materials Science building: Low energy ion beams from 200 kV deck potential with ECR source. High resolution ERD/RBS, implantation based work.




In-situ XRD
set up in phase
II beam line
D8 ADVANCE
D8
14 1 2006

Conclusion

Nano structure synthesis

Atom beam co-sputtering: Ag particles in silica

Low energy ion irradiation: Ripple formation

Si particles in silica

Swift heavy ion irradiation:

- Conducting C tracks in fullerene
- C clusters along ion path in Si based polymers
- Ripple formation at surface in Ni oxide films

Influence of SHI on nano particles

- Metal particles in insulating matrix
- Tilt of plane of magnetization

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THANK YOU