The Abdus Salam
International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

International Atomic Energy Agency

SMR/1758-20

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

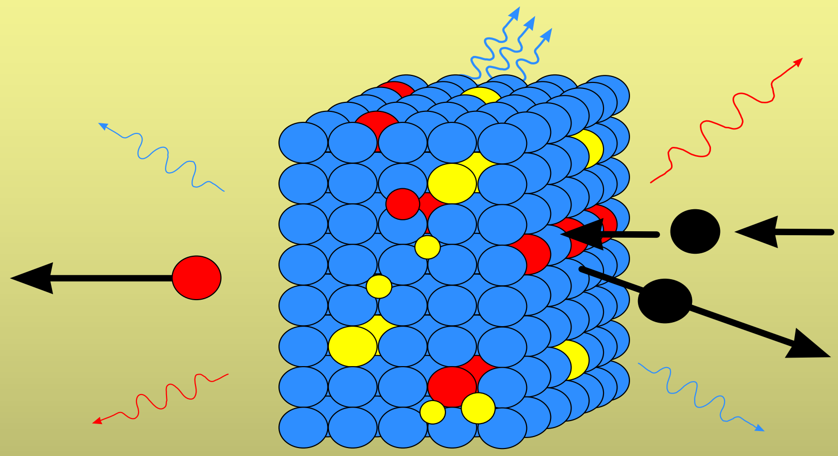
26 June - 1 July 2006

Center for Irradiation of Materials

Daryush ILA
Center for Irradiation of Materials
Alabama A&M University
Normal, Alabama
USA

Strada Costiera 11, 34014 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.ictp.it

Center for Irradiation of Materials



Daryush ILA, Prof. of Physics

Center for Irradiation of Materials

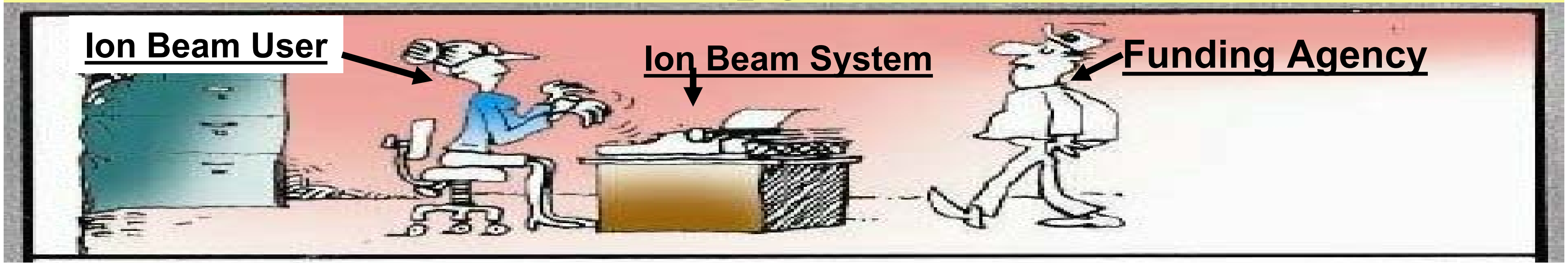
Alabama A&M University

P.O. Box 1447

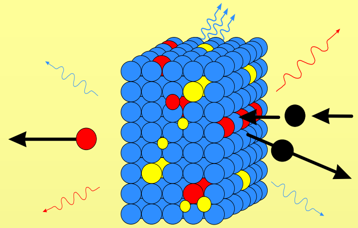
Normal, Alabama, 35762-1447

http://cim.aamu.edu/ Voice: (256)372-5866

Upgrade the Ion Beam System, Adopt to the Nano-Era, or Upgrade the user! ☺



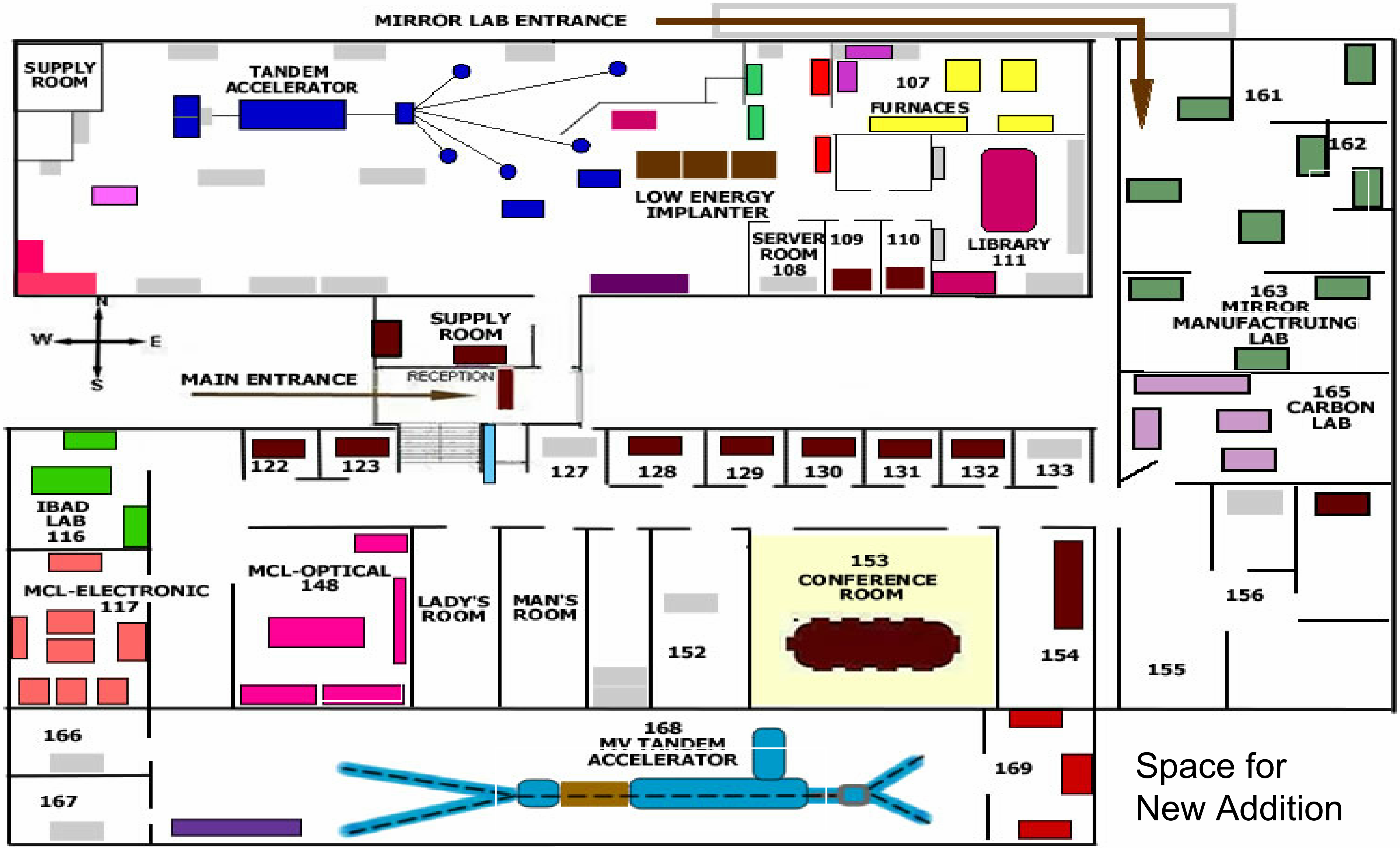
Where are we?



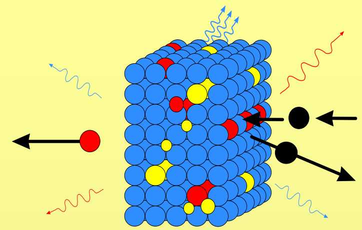
Center for Irradiation of Materials, Alabama A&M University Huntsville(Normal), AL

(http://cim.aamu.edu/)

Http://CIM.AAMU.EDU

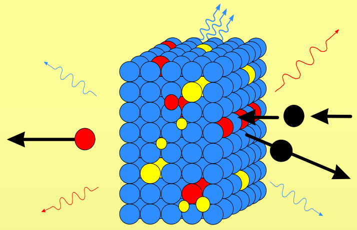


Introduction to CIM



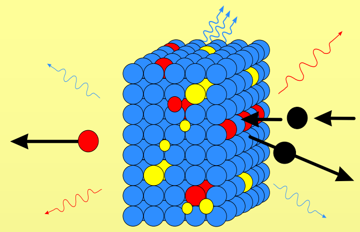
- **Ion Beam Modification of Materials (IBMM)**
- **Materials Characterization**
- **Materials Processing/Synthesis**
- **Nanoscale Materials processing**
- **Device Fabrication/Prototyping**
- **Environmental Remediation (R&D)**

IBMM



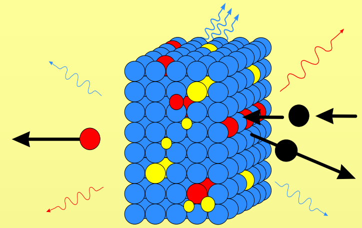
- **Polymers**
  GPC, PPS, PMMA, PE, PTFE, PES, PS, PVDC, PVC, ETF, …..
- **Semiconductors**
- *AlGaAs, GaAs, Si, SiC,…….*
- **Photorefractive Materials**
  $LiNbO_3$, MgO, Al_2O_3, Quartz,Vitreous Silica, SiC, LiF, ….
- **Various Metals**

Materials Characterization



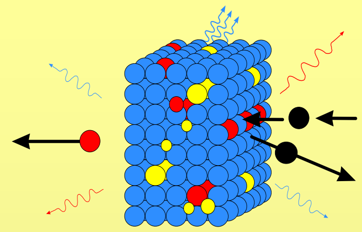
- **Elemental Analysis/Characterization**
  RBS, NRA, PIGE, PIXE, SEM, EDX,UPS, RHEED, SAM, XPS/ESCA, ISS, AES, PES (UV), PE-EM, …
- **Chemical Structure**
  FTIR, Micro-Ramman, RGA,TGA, Cyclic Voltametry, ……
- **Electrical/Thermal Measurements, Surface Profile**
  I-V, C-V, Hall Effect, Seebeck Coif., Thermal Conductivity, AFM, & ….
- **Optical Measurements**
  Index of refraction, NLO properties, waveguides, ….

Materials Processing



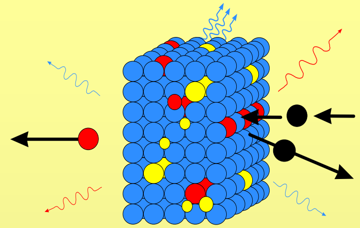
- High Temp Materials (3000°C)
  carbon based Composites
- Biocompatible Materials
- Thin films
- Compound/Alloy Semiconductors
- Nanomaterials
- Crystal Growth
  (http://www.physics.aamu.edu/Research/)

Nanoscale Materials processing



- *Nano-Crystals and Quantum Dots (Powder, ..) (R&D)*
- *Nano-layers of Nanocrystals*
- *CNT +Composites (R&D)*
- *Nanopowders + Composites (R&D)*
- *Regimented Nanostructures (layers, lines, and dots) (B.Sc.)*

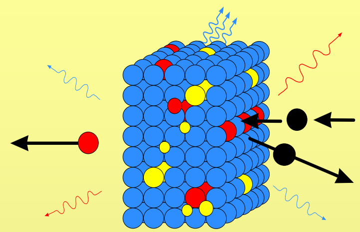
Devices



- Holloware Devices
  Crucibles, Heat exchangers, ...

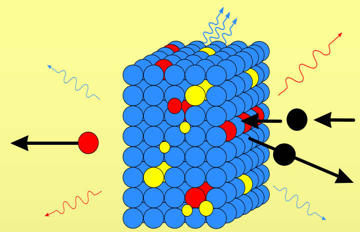
- Biocompatible Devices
  e.g. implants
- Optical Devices (mirrors, waveguides, ..)
- Hydrogen Detectors (0.1 ppm) and Sensors
- Thermoelectric Generators

Environmental Remediation



- Site Assessment
- Trace Element (Forensic/specificity) (CIM, Chemistry & Env. Sc.)
- Sorbent Selection and Production *(Env. Cleanup)*

CALL FOR PAPERS



MRS Symposium II-S06:

“Materials in Extreme Environments”

CAARI06: A session & a roundtable Discussion “Projection Ion Beam/NanoFab”

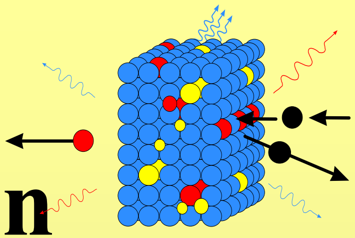
MRS Symposium GG-S07:

“Ion Beam Based Nanofabrication”

http://www.mrs.org/s_mrs/sec.asp?CID=6765&DID=175838

MRS S07: Symposium GG

Ion Beam Based Nanofabrication



It is increasingly apparent that ion-beam-based processing offers unique capabilities for fabrication and complex patterning of 3-D, 2-D, and 1-D structures at the few-nanometer scale, (e.g., nanowires and quantum dots), and for custom tailoring of nanocomposites, nanoporous materials, catalyst surfaces, optical materials, and nanoparticle assemblies. This symposium addresses recent achievements, applications, and insights in such areas. It also seeks to identify potential dimensional limitations to the future practical implementation of this approach.

Examples of appropriate topics include:

Projection ion-beam lithography and direct-pattern delivery, Focused ion-beam processing, Nanoscale surface topography smoothing, ripples, orientation, etc, Surface activation for selective bio-adhesion and molecular manipulation, Defect engineering, Optimization of ion-beam processing, Resolution limits for pattern registration, Robust techniques for industrial applications

Tutorial: A half-day tutorial complementing this symposium is tentatively planned. Further information will be included in the program that will be available in January

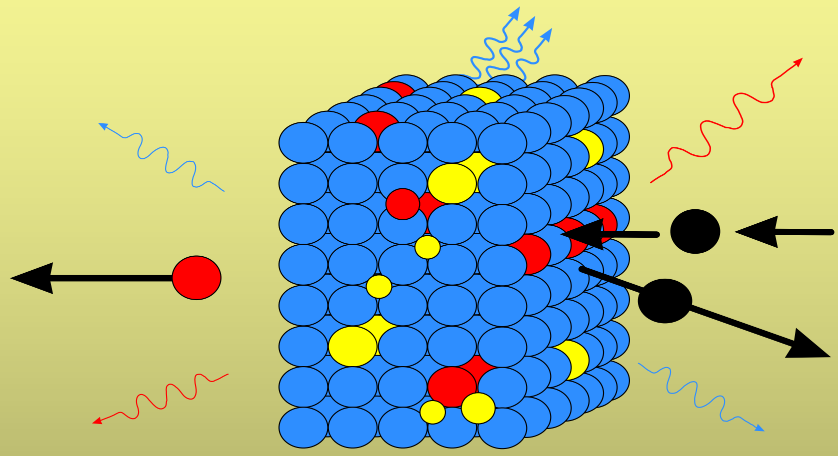
Invited Speakers Include: **Michael Aziz** (Harvard Univ.): *Nanoscale Morphology Control and Surface Ripples*; **Lee Chow** (Univ. of Central Florida): *FIB Fabrication of Carbon Nanotube Devices*; **Robert Elliman** (Australian National Univ., Australia): *Defect Engineering in Silicon*; **Gene Golovchenko** (Harvard Univ.): *Ion-Beam Sculpting Nanopores for DNA Molecule Manipulation and Registration*; **Ka-Ngo Leung** (Lawrence Berkeley National Lab): *Ion-Beam Projection Techniques for Nanometer-Scale Patterning*; **Seiichi Tagawa** (Osaka Univ., Japan): *Nanospace Reactions Induced by Ion and Electron Beams*; **Frank Watt** (National Univ. of Singapore): *Nanoscale Fabrication in 2-D and 3-D Using MeV Proton Microbeam Writing*; **Isao Yamada** (Univ. of Hyogo, Japan): *Nanoscale Surface Modification Using Gas Cluster Ion Beams*; and **Robert Zimmerman** (Alabama A&M Univ.): *Patterned Adhesion of Cells*. Topics indicated are subject to change.

Symposium Organizers

Daryush ILA, John Baglin, Naoki Kishimoto, Paul K. Chu

http://www.mrs.org/s_mrs/doc.asp?CID=6765&DID=176177

Ion Beam Assisted Formation of Nanolayers of Nanomaterials



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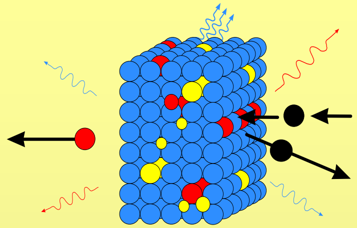
TEAM I



AAMU:

Faculty and staff:

D. ILA, R. L. Zimmerman, G. M. Jenkins, A. L. Evelyn, L. R. Holland, C. I. Muntele, D. Nisen (R), I. C. Muntele, M. Schilloff, S. Sarkisov, Z. Xiao, B. Zheng, H. Bowman, S. Budak, M. Saafi, A. Batra, A. Sharma, R. Taylor, M. Alim, T. Montgomery, T. Kukhtareva, J. Wang, J. Campbell, H. J. Caulfield, J. Fisher (Ind), G. Terry (Ind), S. Celaschi (Ind), J. Williams (Ind),

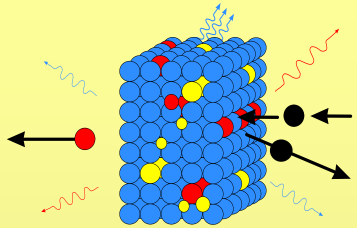
Students:

B. Chhay, R. Ichou, G. Deceprit, T. Meng, M. Kambal, R. Minamisawa, S. Wu, B. Zheng, J. Wang (S), C. Smith, (Eight more)

Others:

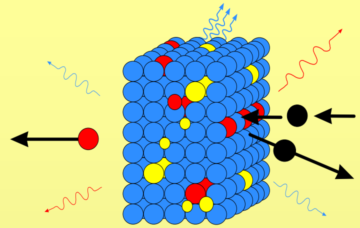
R. Mu (Fisk), I. Ozen (Sabanci Univ. Turkey), A. Elsamadicy (+ UAH Students), I. Gurhan and A. Ozterhan (Ege U, Turkey + students), P. Thevenard (+ UCB Students), A. de Almeida (+ USP Students),

TEAM II



1. **NRL, ARL, AMRDEC, DOE Labs, AFOSR, AFRL.**
2. ***UAH, UAB, UA, AU, TU, GTRI, UCB, TSU, USP, FU, EU, SU, NU, UA, DELF, UC-Davis, and few more***
3. ***Boeing, SAIC, Jacobs Eng., BAE, MRC, Raytheon, NG, LM, Hightek, Brontek, VLOC, II-VI, TBE, SRS, (20 more SB)***

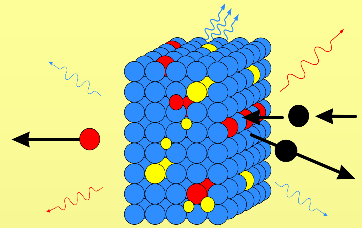
ACKNOWLEDGEMENTS



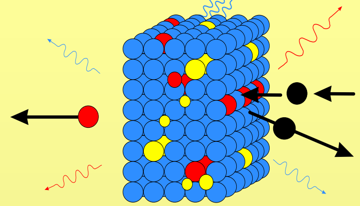
Supporting Agencies

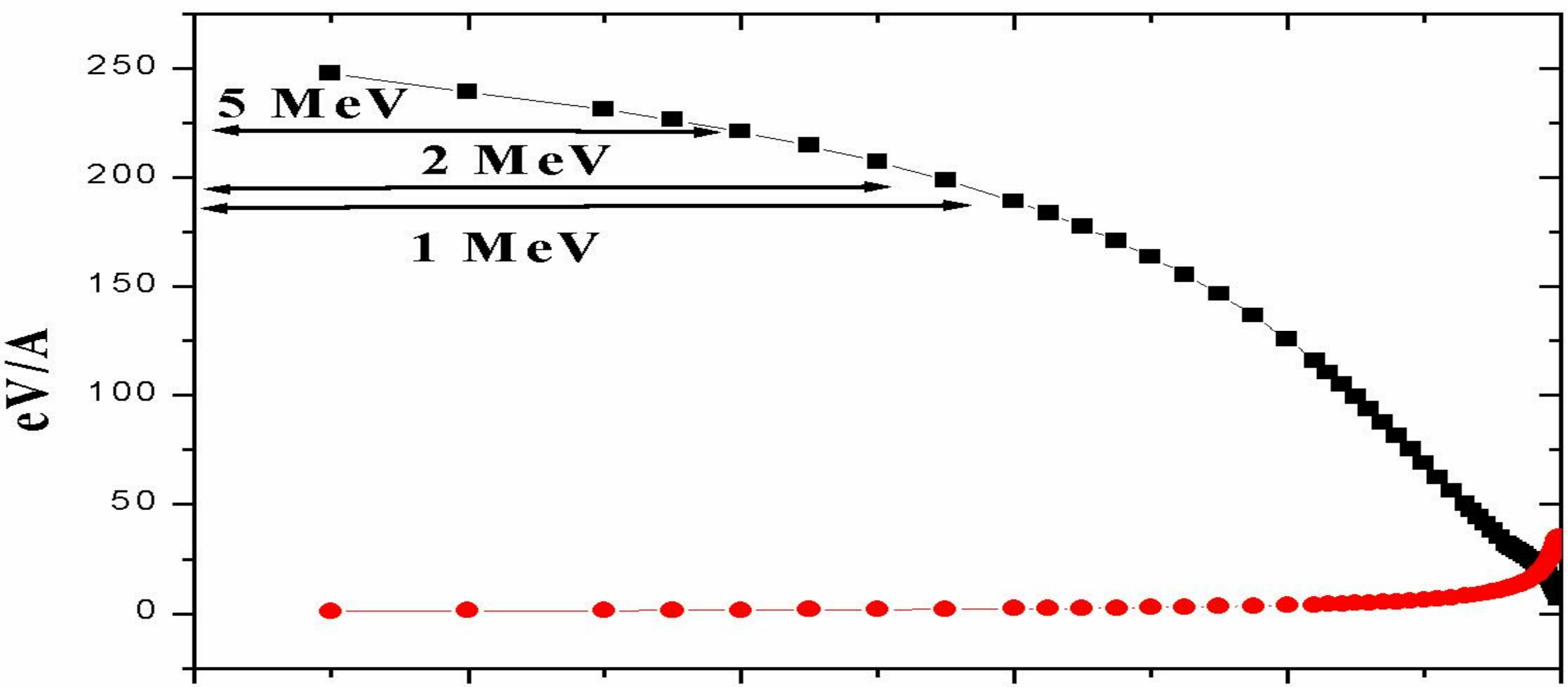
- **AAMU (AAMURI and CIM) (***)**
- **NSF(***)**
- **DoD (**)**
- **NASA (****) (HQ, MSFC, Glenn, JPL)**
- **INDUSTRIES (**)**

Past & Present R&D

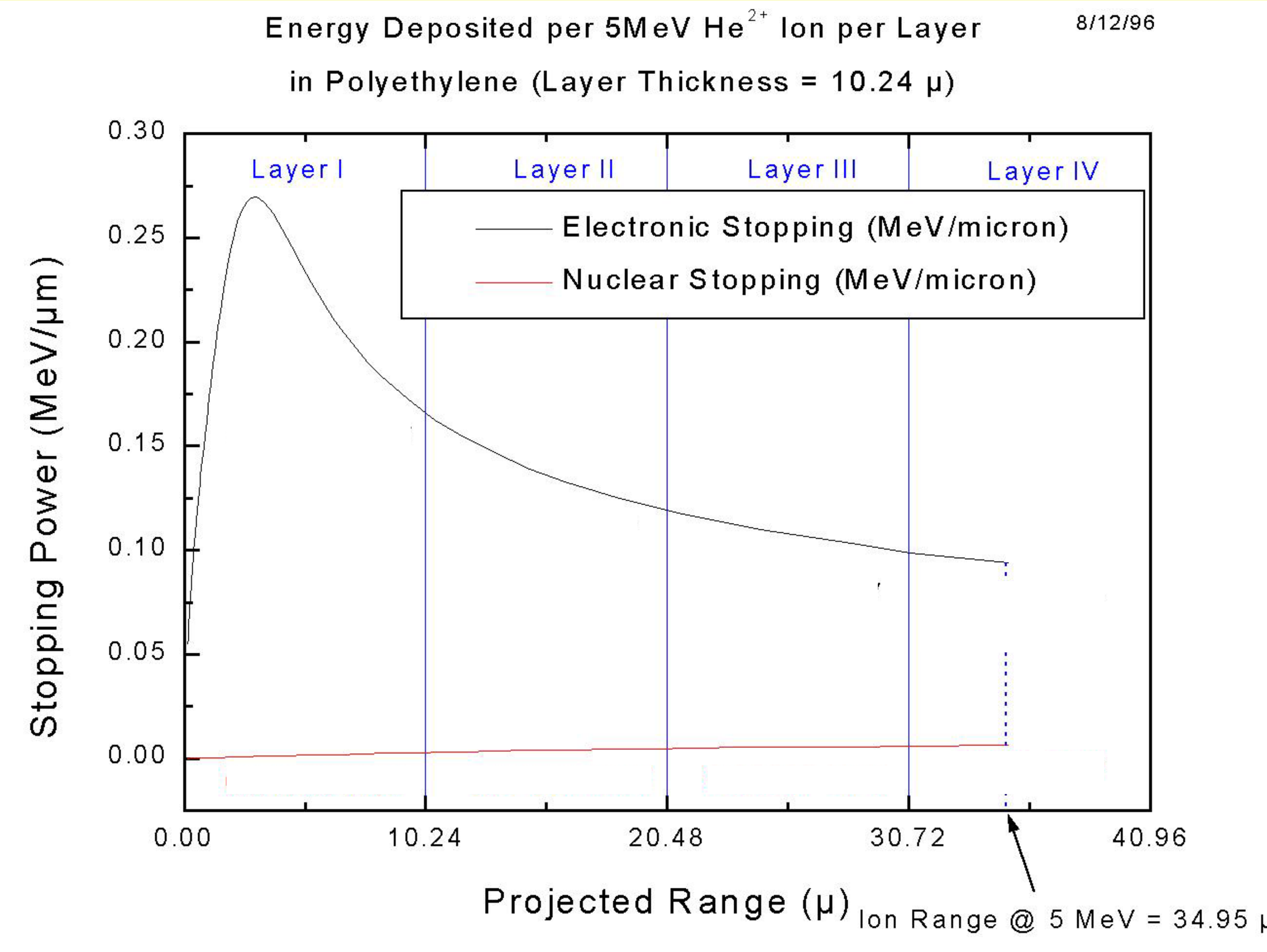


- Separating stopping power effects on thin polymers (early 90s MRS and REI-Japan)
- Formation of Nano-Crystal by Implantation followed by Annealing (early 90s, MRS)
- Formation of Nano-Crystals by Implantation followed by Irradiation (mid 90s US-IBMM and MRS)
- Formation of Nano-Crystals by Co-Deposition, sometime followed by Annealing and/or by MeV Ion Beam Irradiation (Late 90s, MRS, SMMIB & REI 01)

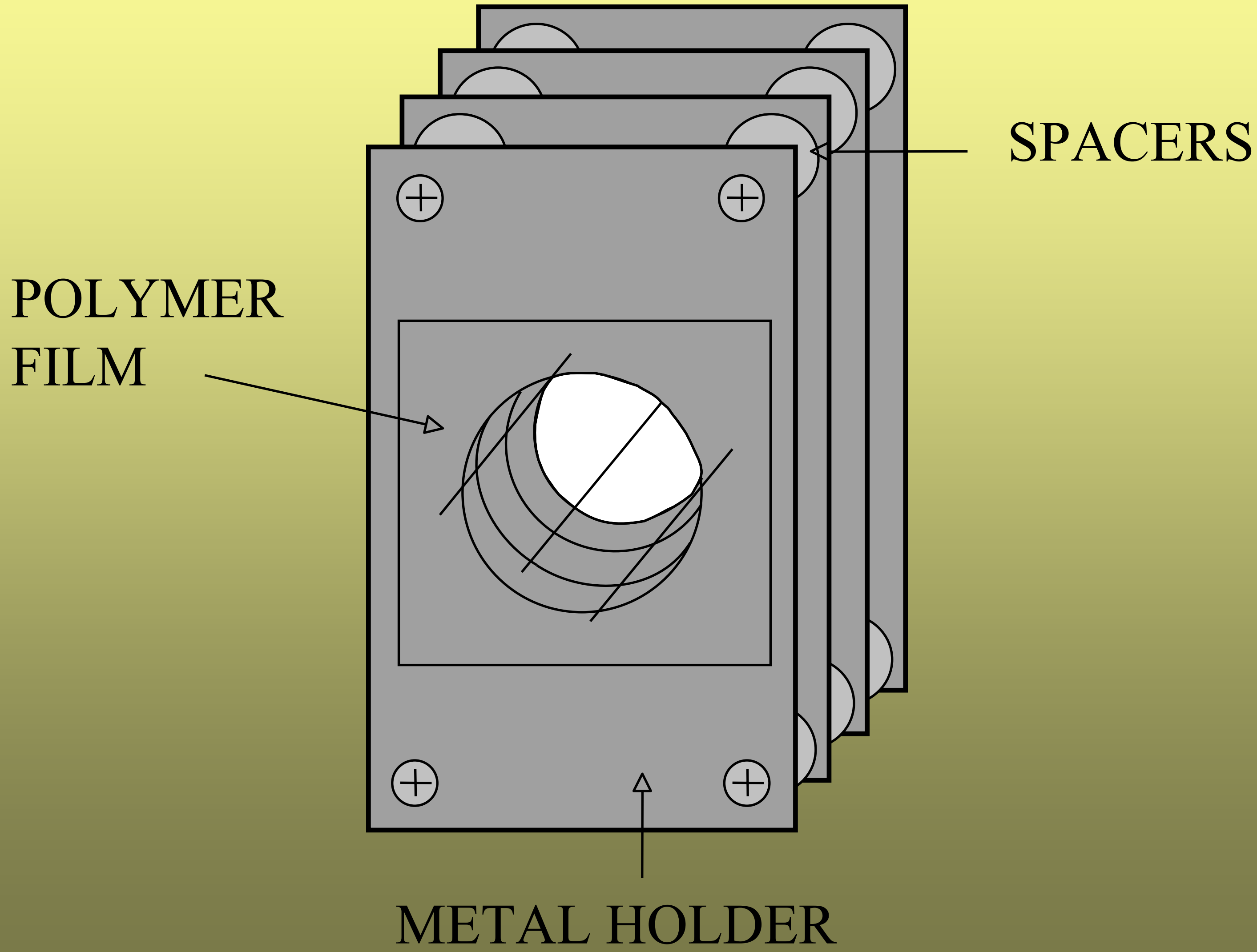



250
200
150
100
50
0
eV/A
5 MeV
2 MeV
1 MeV

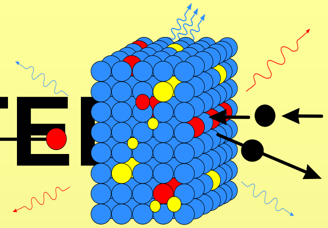
The Stopping Power Profile

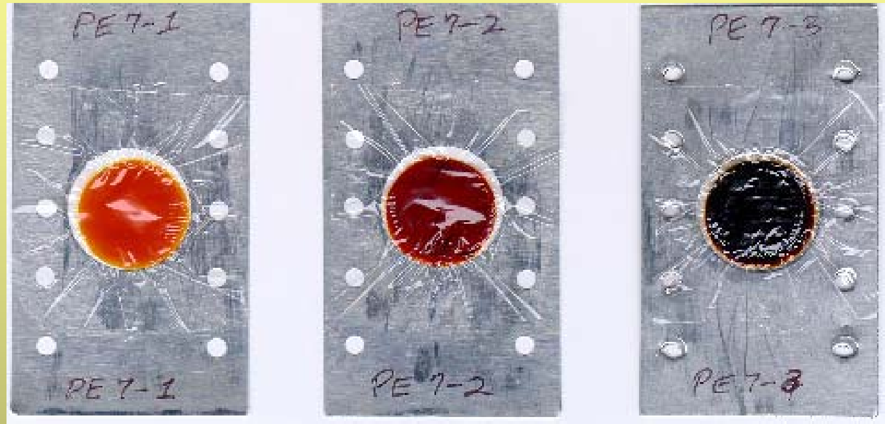


Polymer films are stacked



COLOR CHANGES IN IRRADIATED POLYMER FILMS

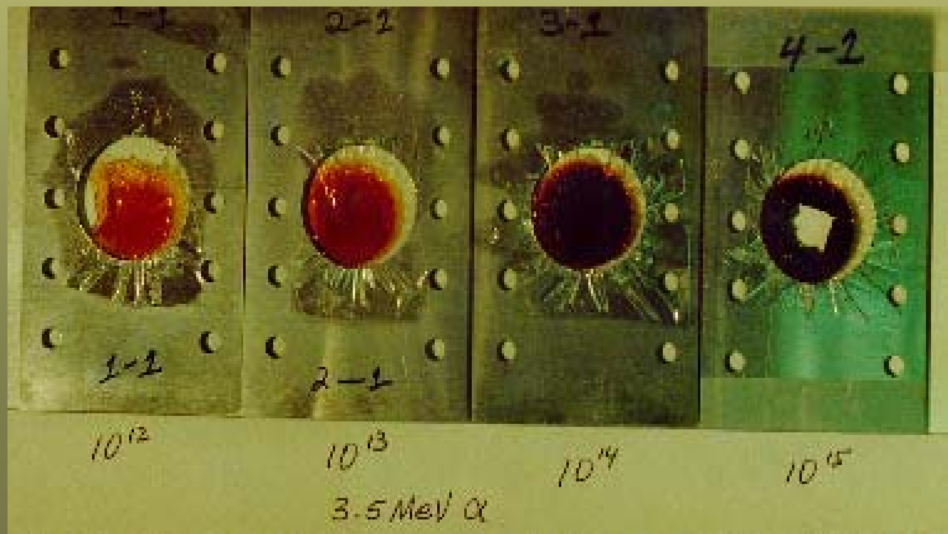




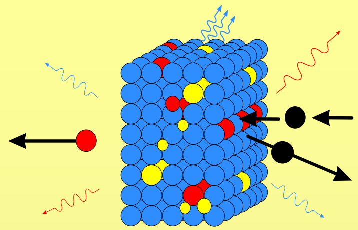
Layer 1
Front

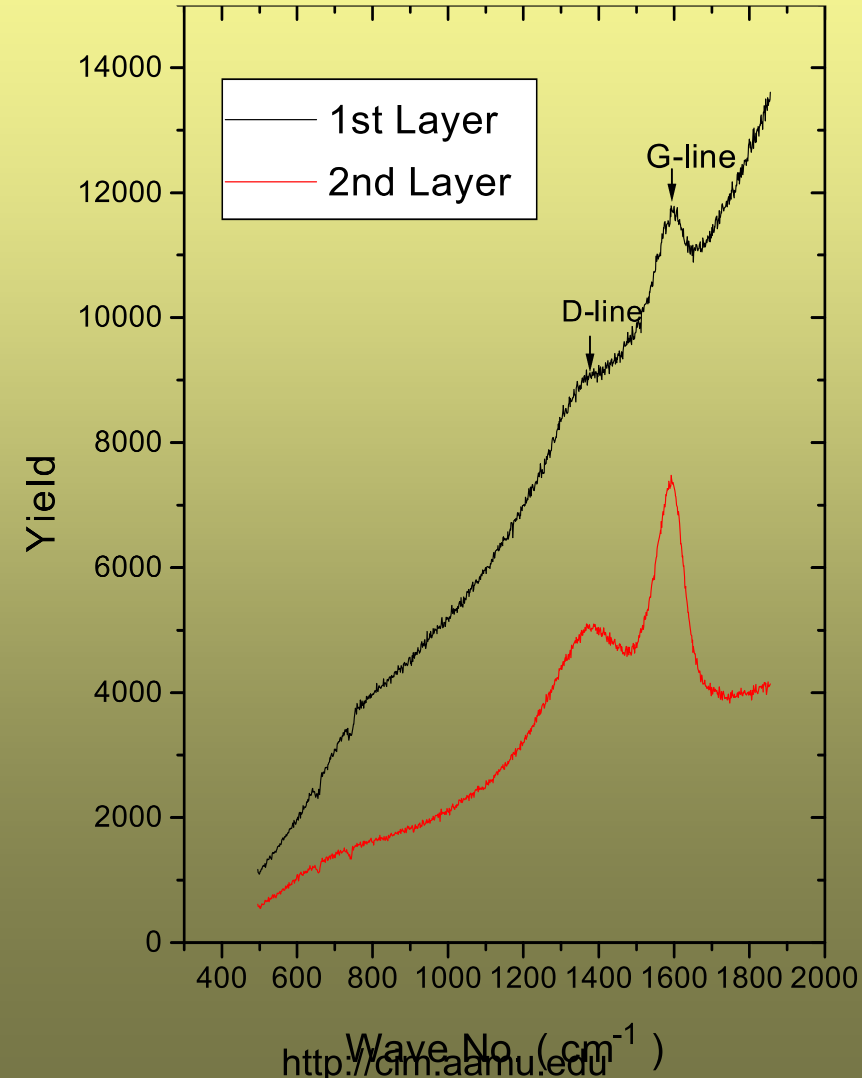
Layer 2
Middle

Layer 3
Back

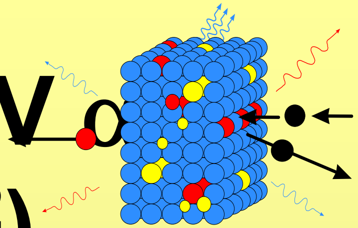


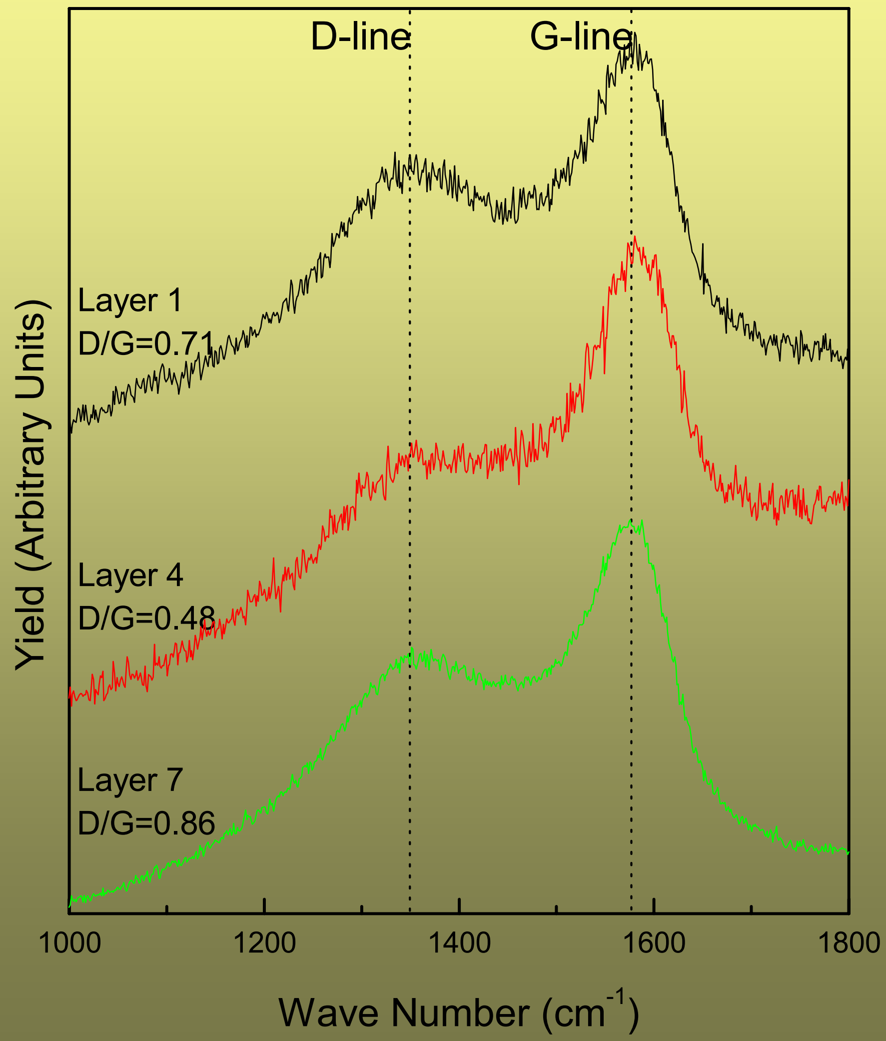
RAMAN SPECTRA FROM 3.5 MeV α-IRRADIATED PE FILMS (5 x 10^{15} IONS/CM^2)



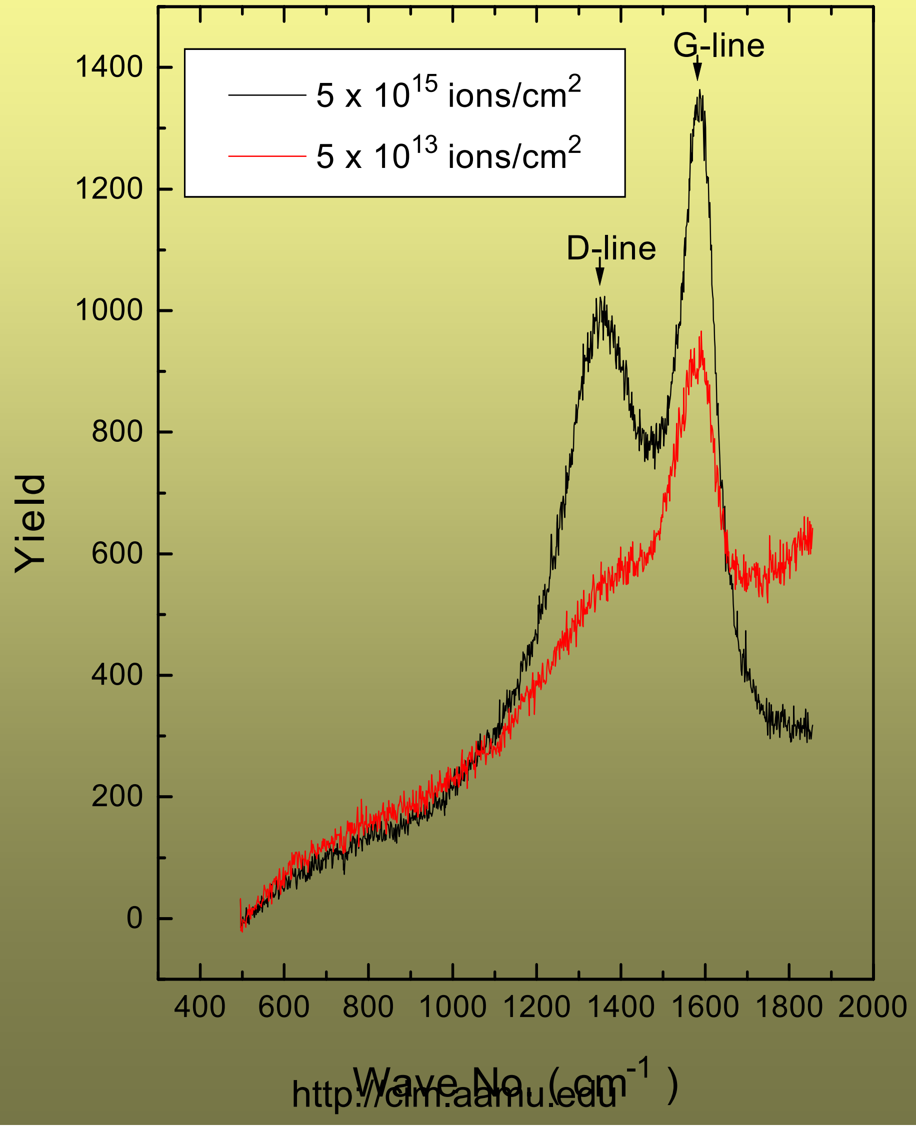


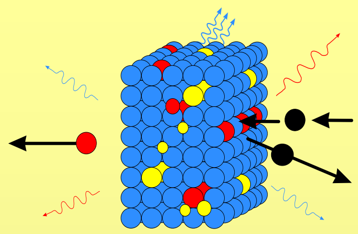
Raman Spectra From 5.0 MeV O Irradiated PES (1E16 cm^{-2})



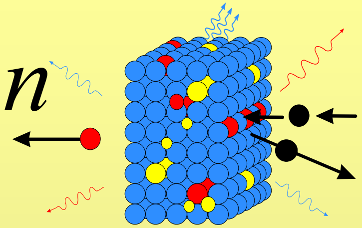


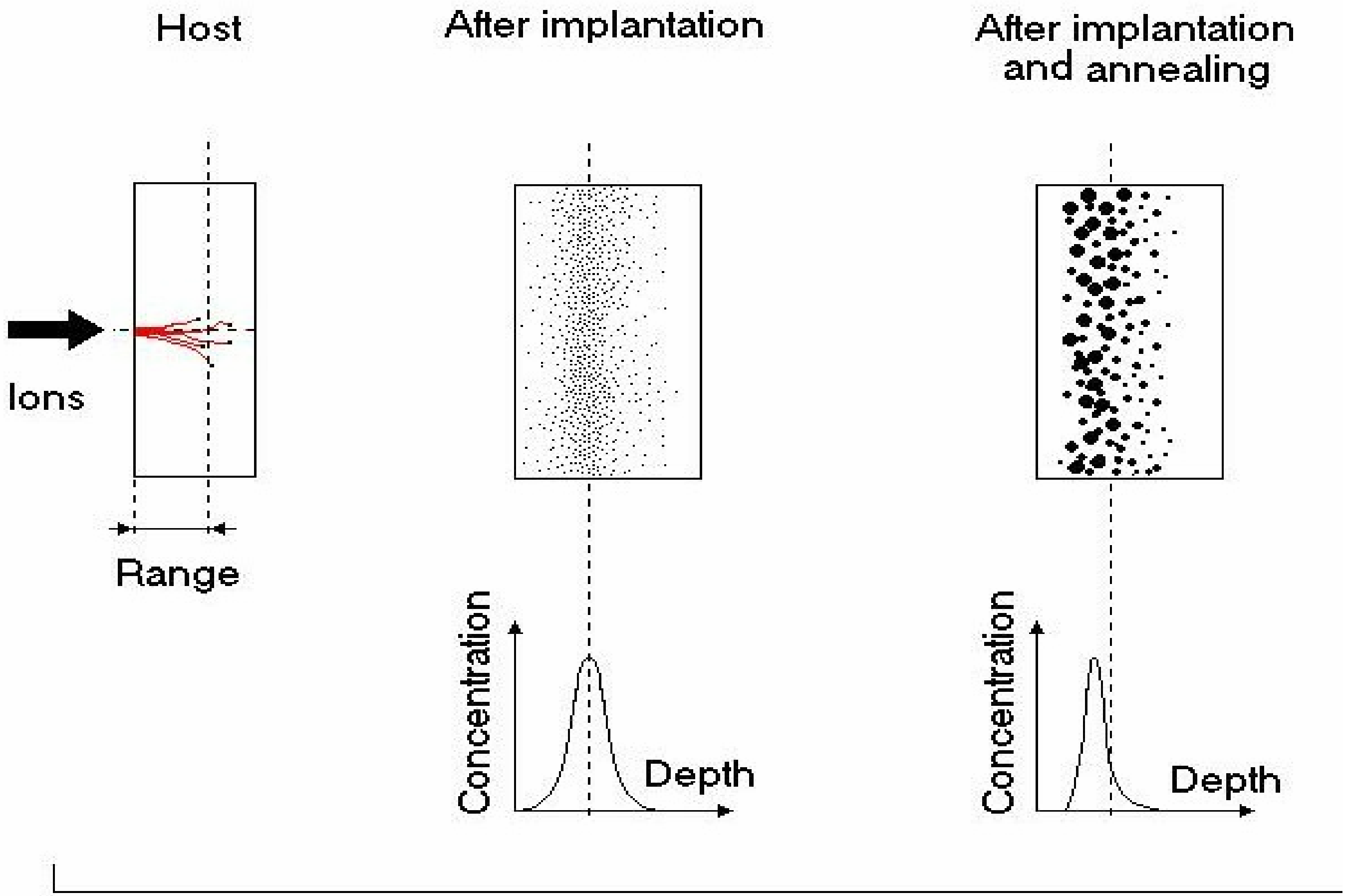
RAMAN SPECTRA FROM 3.5 MeV α-IRRADIATED PVDC FILMS





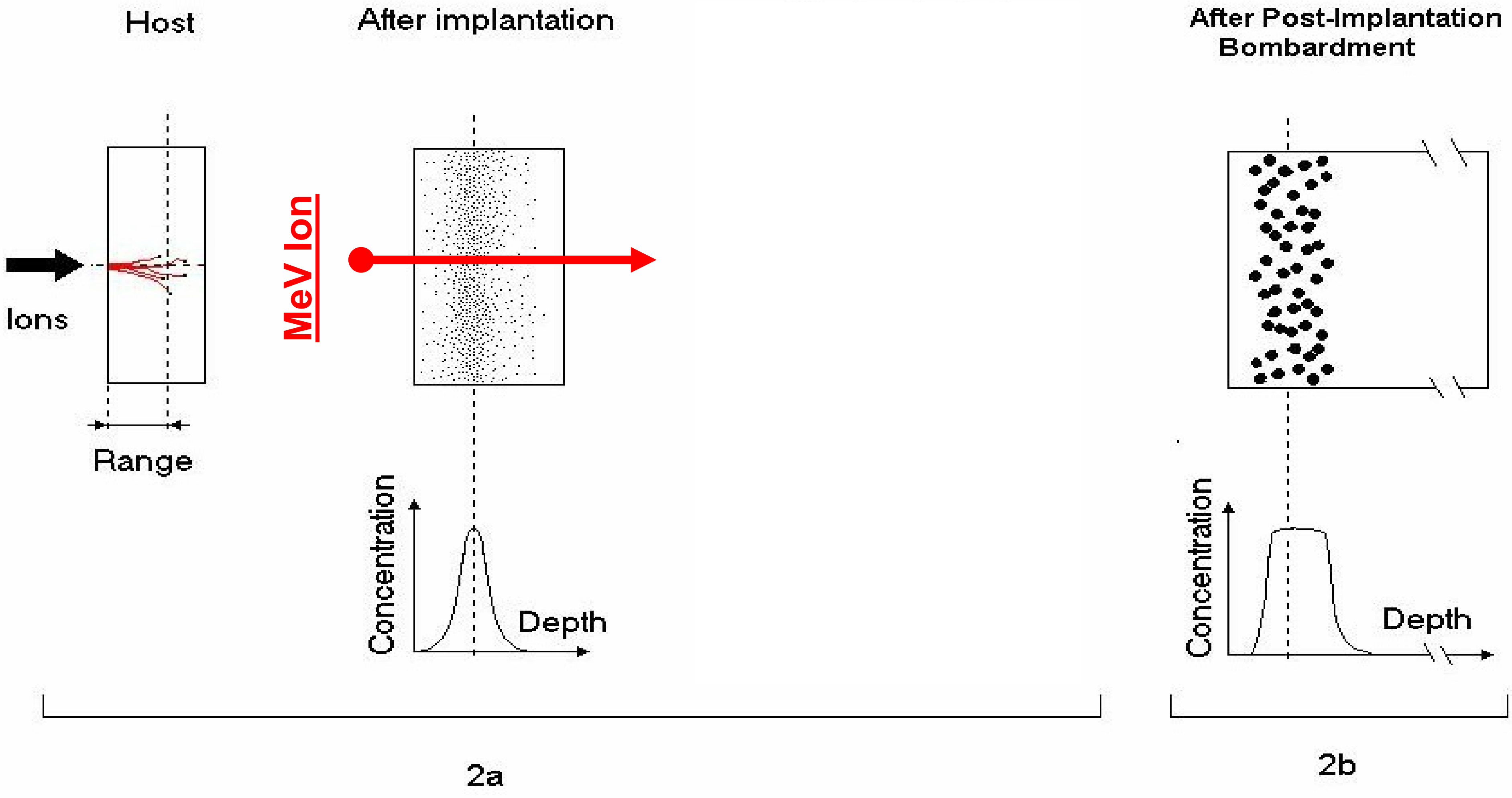
Implantation Followed by Annealing or Post Irradiation (95-2000)



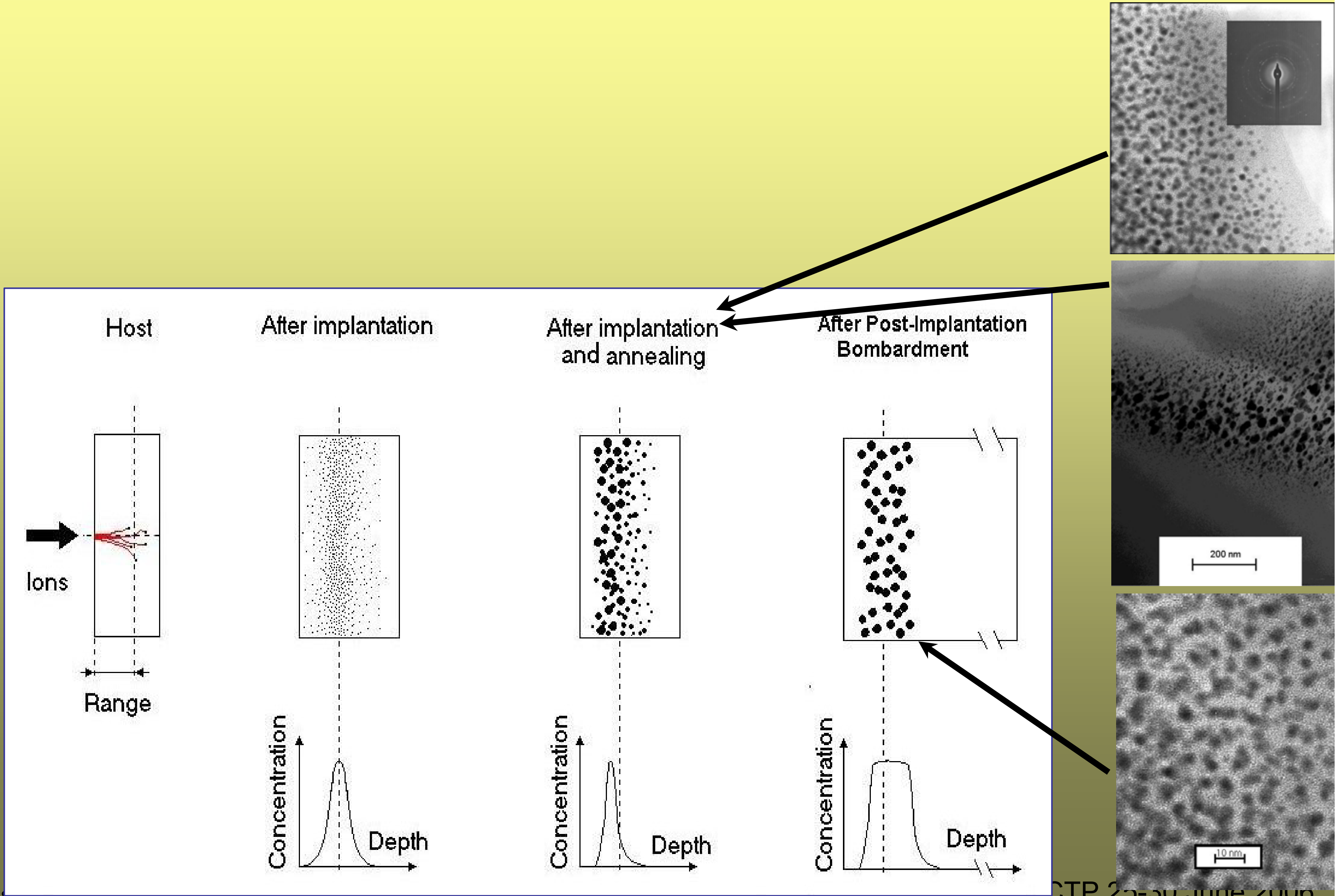


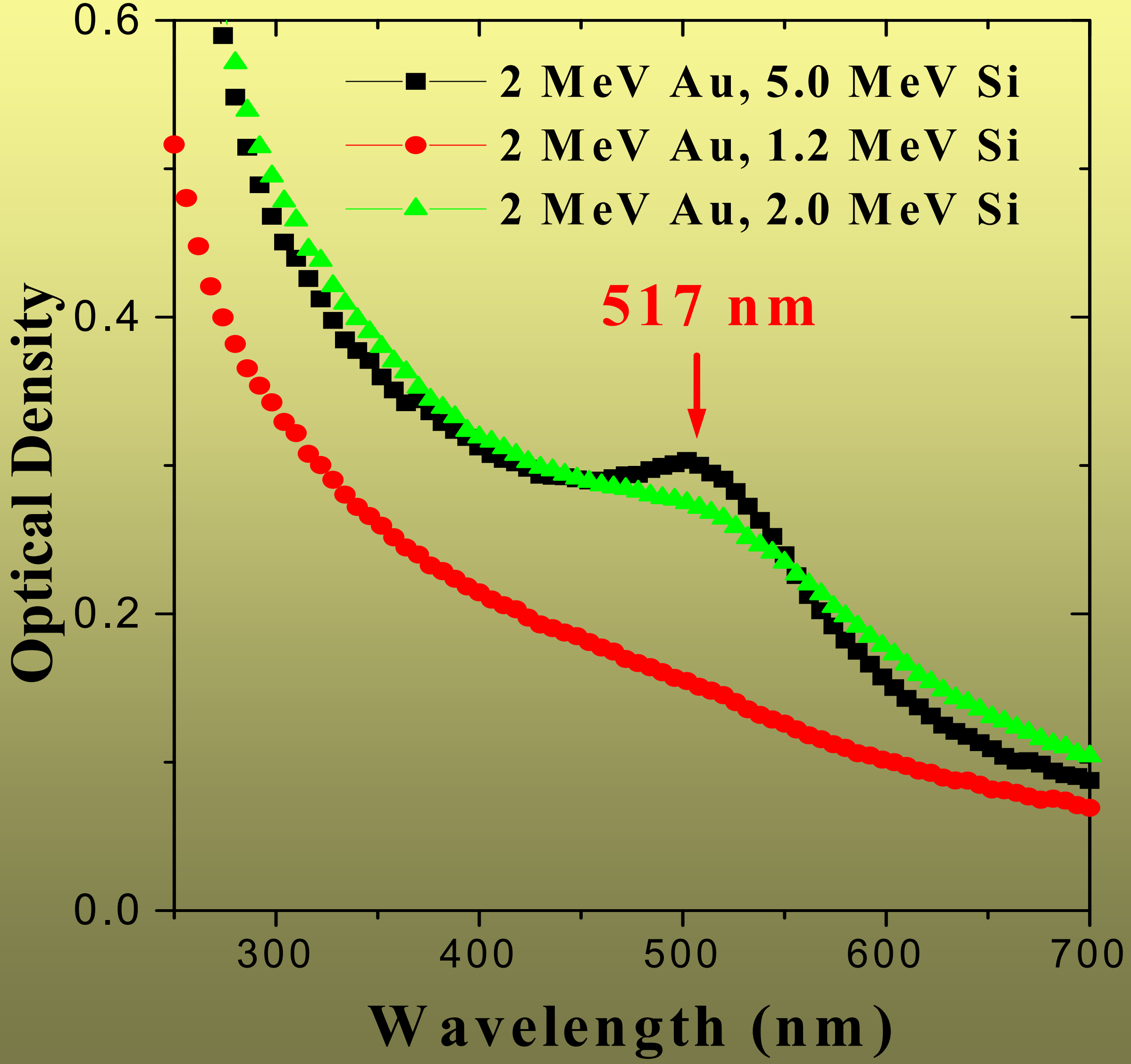
2a

Implantation Followed by Annealing or Post Irradiation (95-2000)



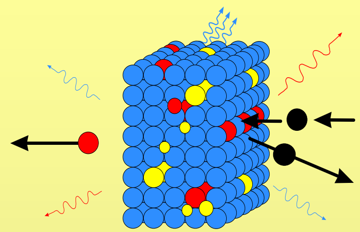
Innovative clustering methods: post-implantation ion bombardment




0.6
0.4
0.2
0.0
Optical Density
2 MeV Au, 5.0 MeV Si
2 MeV Au, 1.2 MeV Si
2 MeV Au, 2.0 MeV Si
517 nm
300
400
500
600
700
Wavelength (nm)

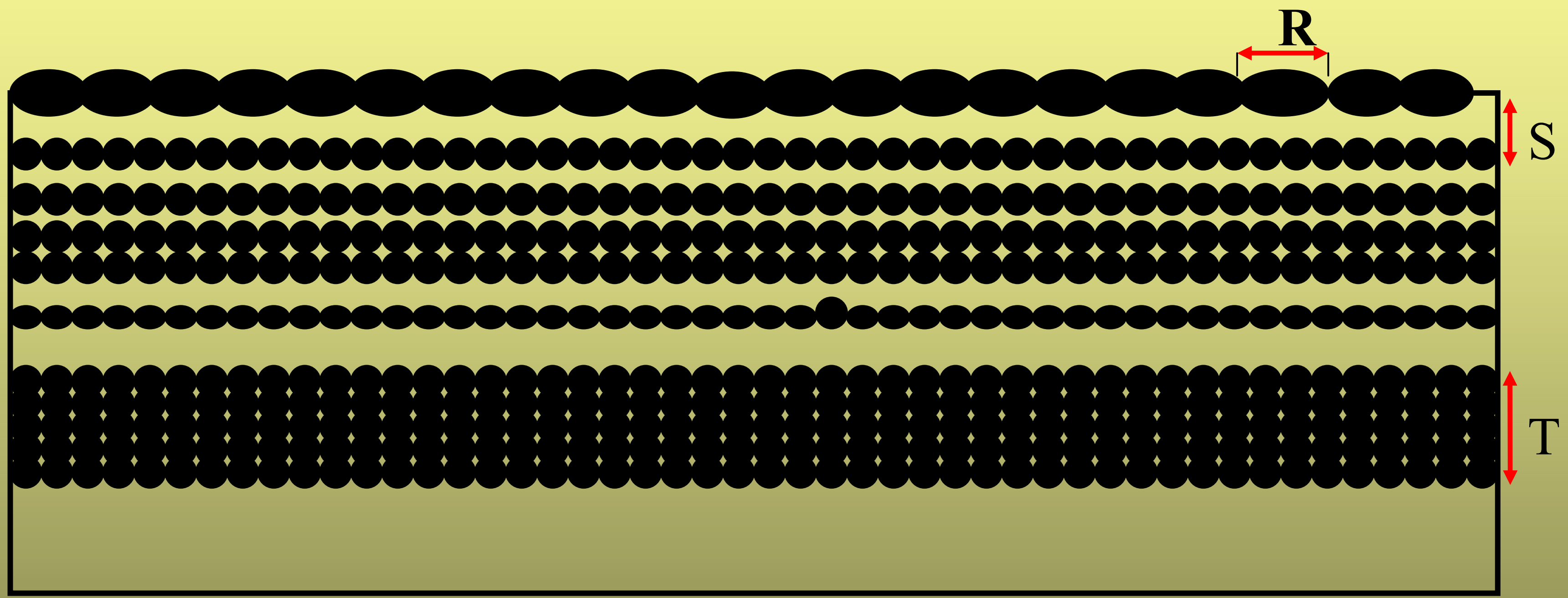
Si (MeV)	ΔE (keV) due to ε_ε	ΔE (keV) due to ε_ν	$\alpha . \lambda$ (nm)
1.2	107	7	4
2	176	5	9
5	373	3	27

Advantage



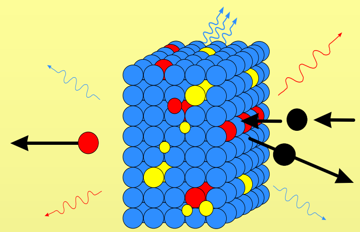
- Producing NC @ lower initial implantation fluence or lower concentration in co-deposition
- Uniform NC size
- NC location Control
- Volume Fraction Control

Layered Nano-Structures
Cross section view



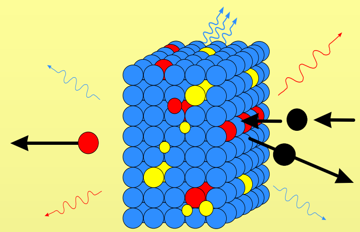
R: QD Radius
S: Layer Spacing
T: Layer Thickness

Control Requirements



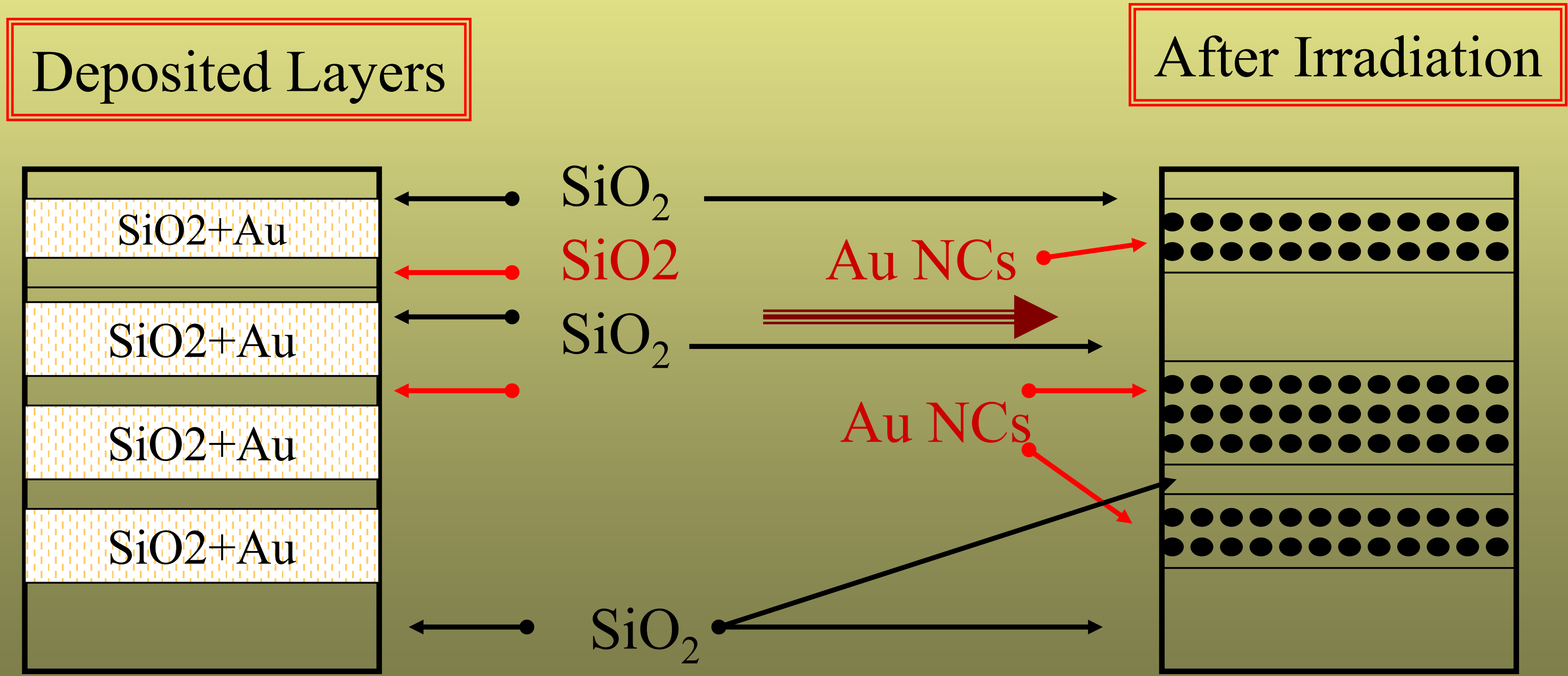
- Size
- Location (X,Y,Z)
- Layer Thickness
- Volume Fraction

Synthesis Requirements

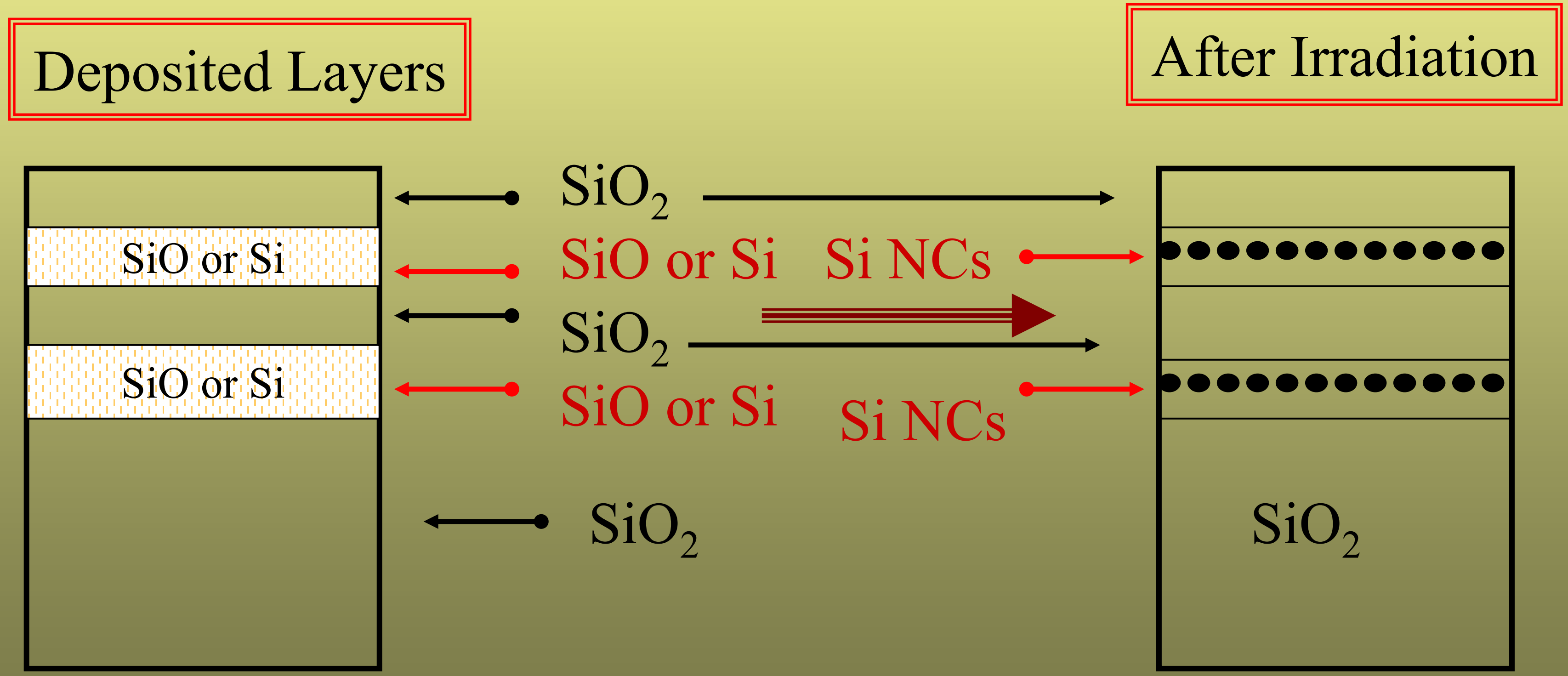


- Mass Production
- Embedded
- Surface Processing
- Multi-Layered systems
- Co-processing of host and NCs

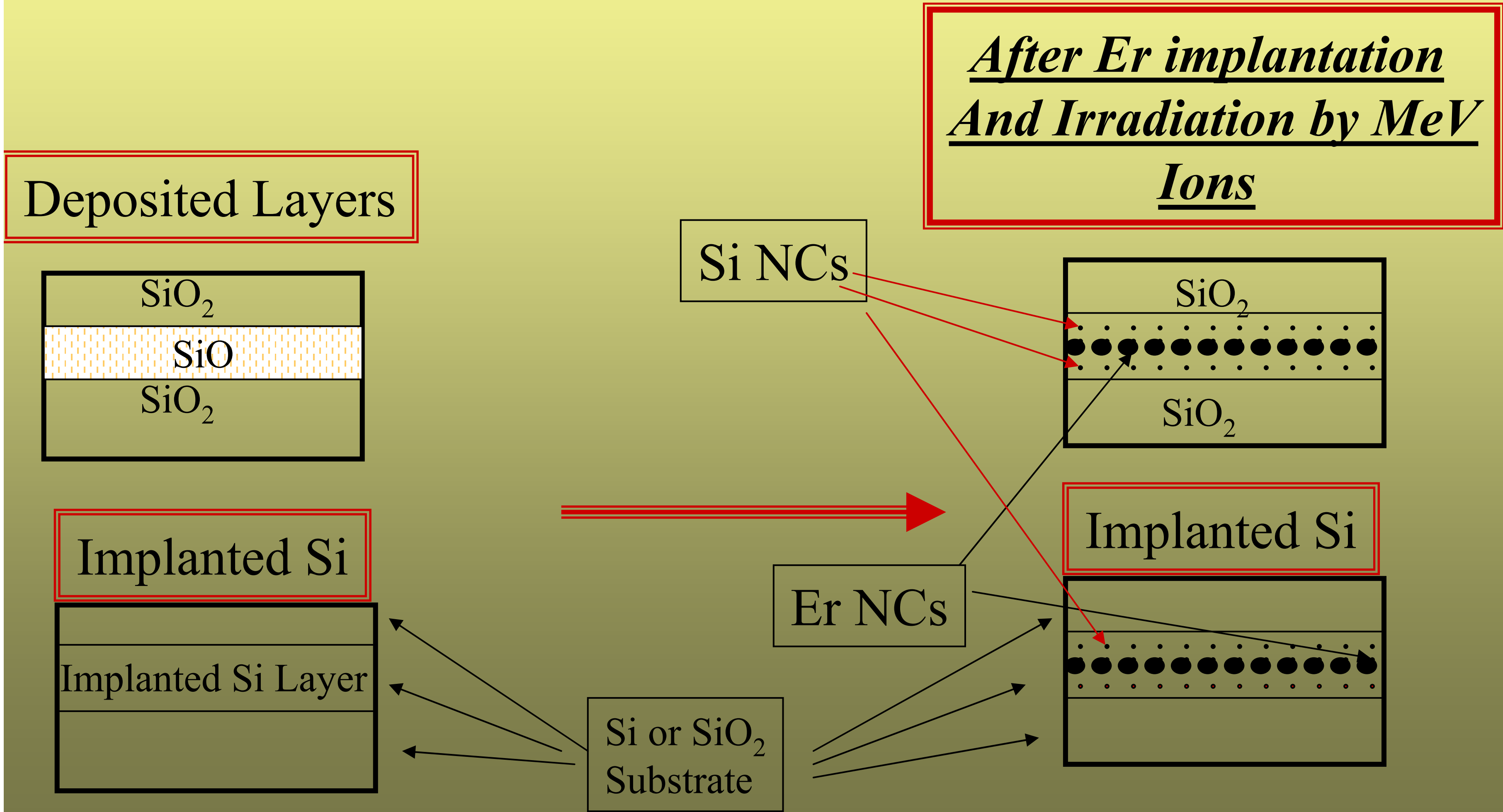
Layered Au NCs Formation by Deposition and Post Irradiation



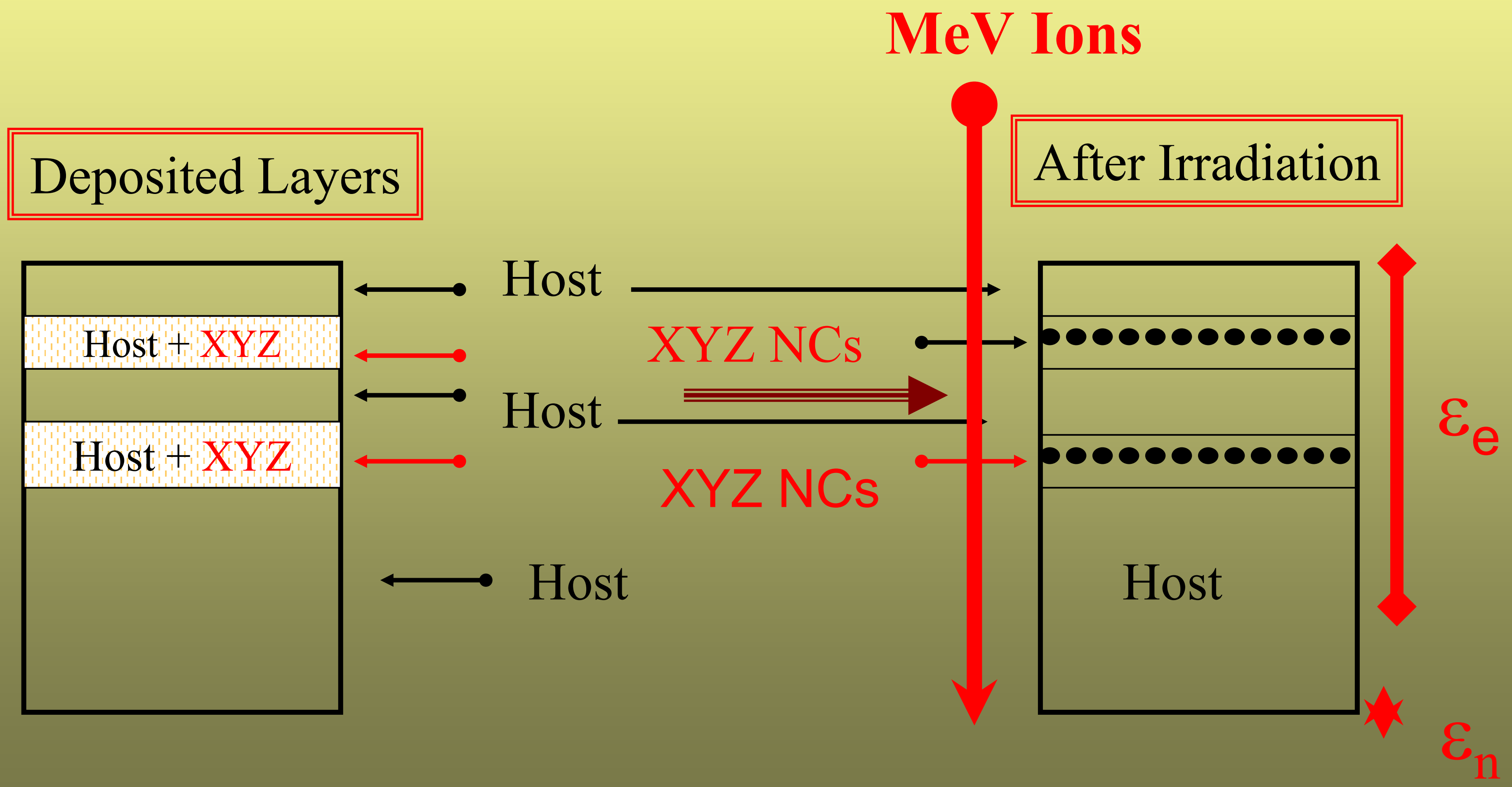
Layered Si NCs Formation by Deposition and Post Irradiation



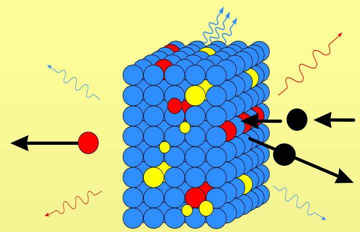
Layered Si NCs Formation by Deposition and Post Irradiation



Layered XYZV- NCs Formation by Deposition and Post Irradiation



Example 1



Optical Properties

Mie Theory a<r<λ

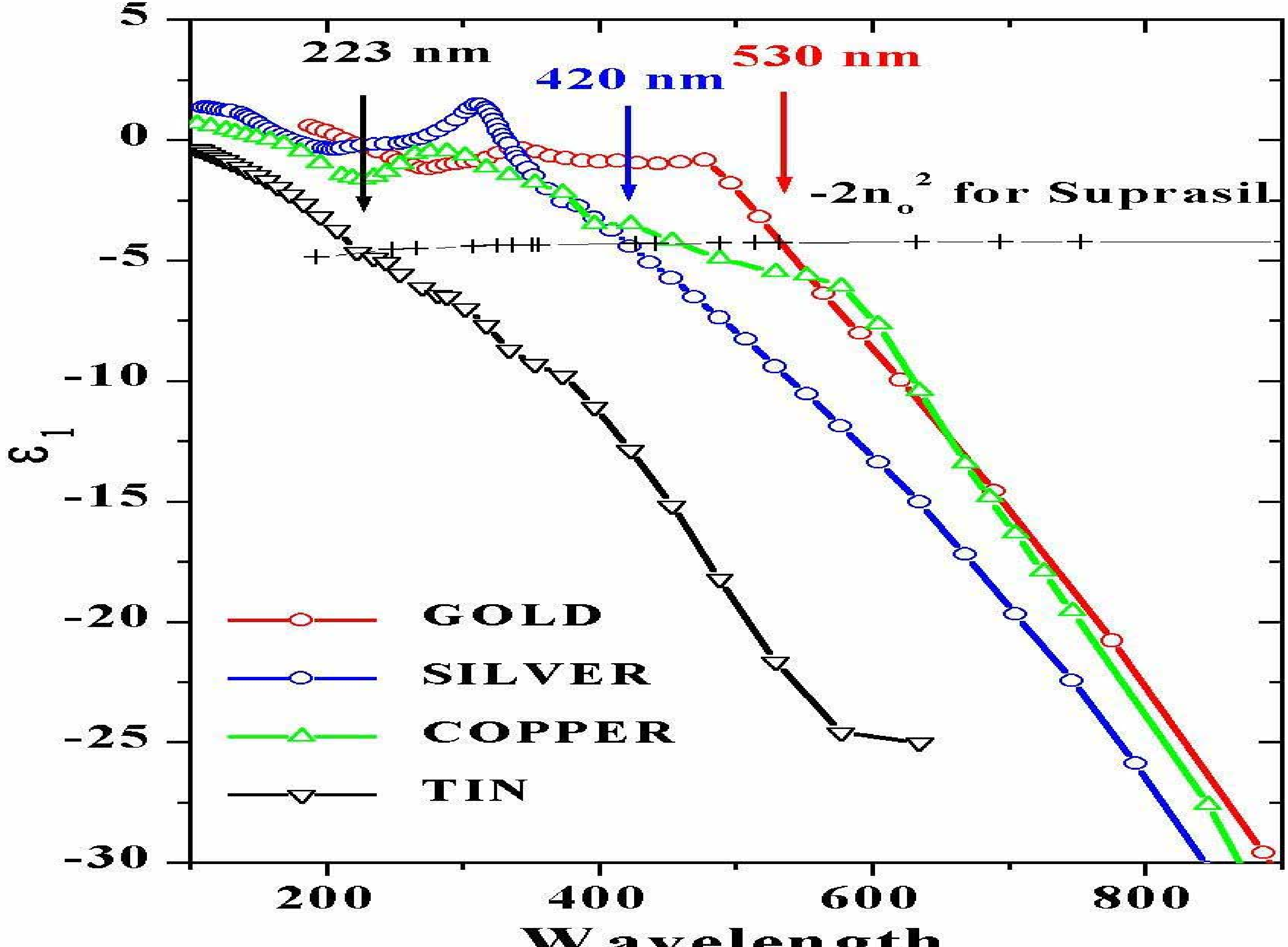
$$\alpha = \frac{18\pi Q n_o^3 \varepsilon_2}{\lambda\left[(\varepsilon_1 + 2n_o^2)^2 + \varepsilon_2^2\right]}$$

n^{-1}

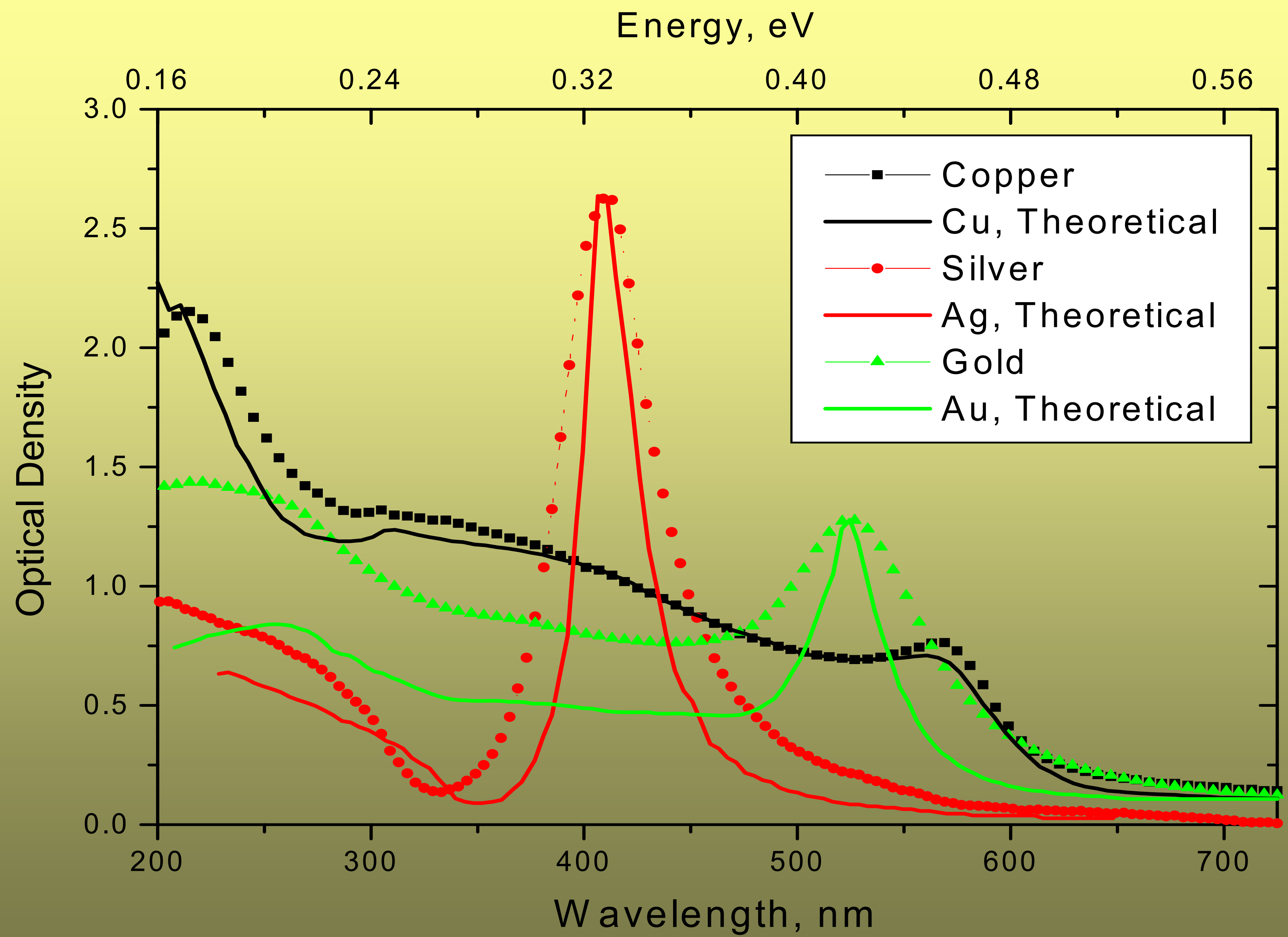
Maximum when $\varepsilon_1 + 2n_o^2 = 0$

α	**Linear coefficient of absorption**
Q	**Volume fraction of metal in insulator host**
N_0	**Index of refraction of insulator host**
$\varepsilon_1 + j\varepsilon_2$	**Complex dielectric constant of bulk metal**
r	**Radius of metal nanocrystal**
λ	**Vacuum wavelength of incident light**
a	**Electron mean free path in bulk metal**

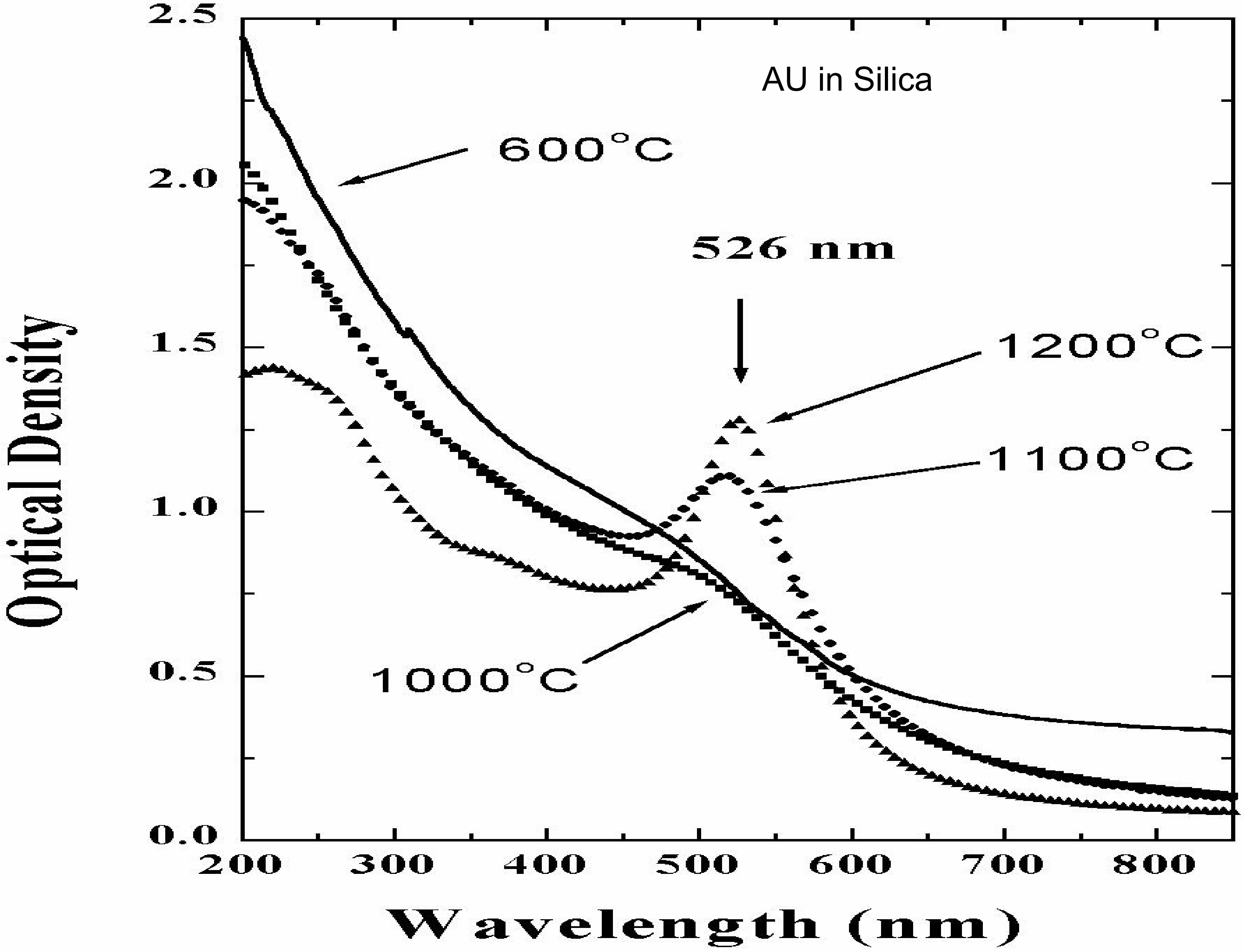
<u>**Gustav Mie, *Ann. Physik*, 25, 377 (1908)**</u>



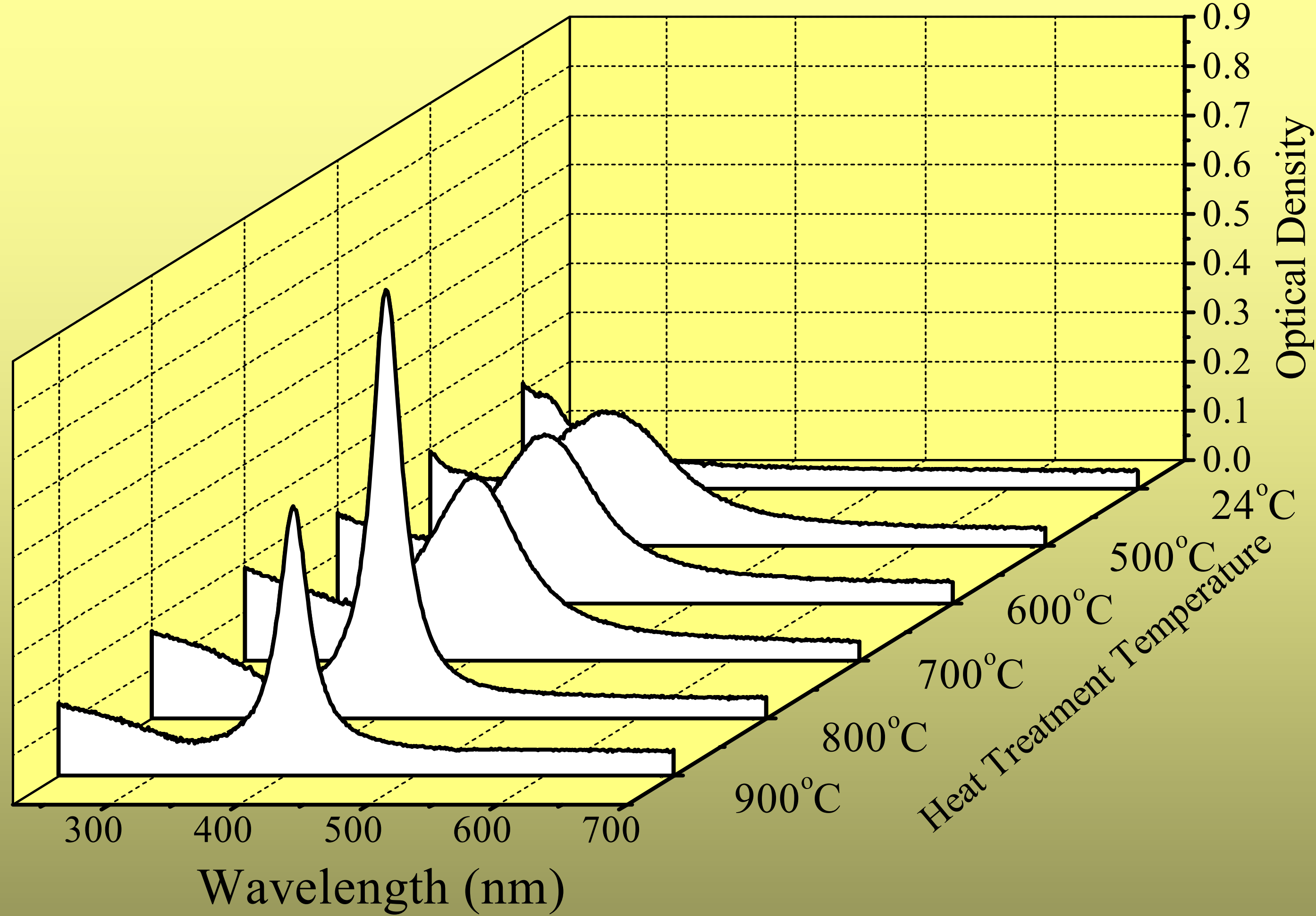
5
0
-5
-10
-15
-20
-25
-30
200
400
600
800
Wavelength
ε1
223 nm
420 nm
530 nm
-2no2 for Suprasil
GOLD
SILVER
COPPER
TIN



Energy, eV
0.16
0.24
0.32
0.40
0.48
0.56
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Optical Density
200
300
400
500
600
700
Wavelength, nm
Copper
Cu, Theoretical
Silver
Ag, Theoretical
Gold
Au, Theoretical

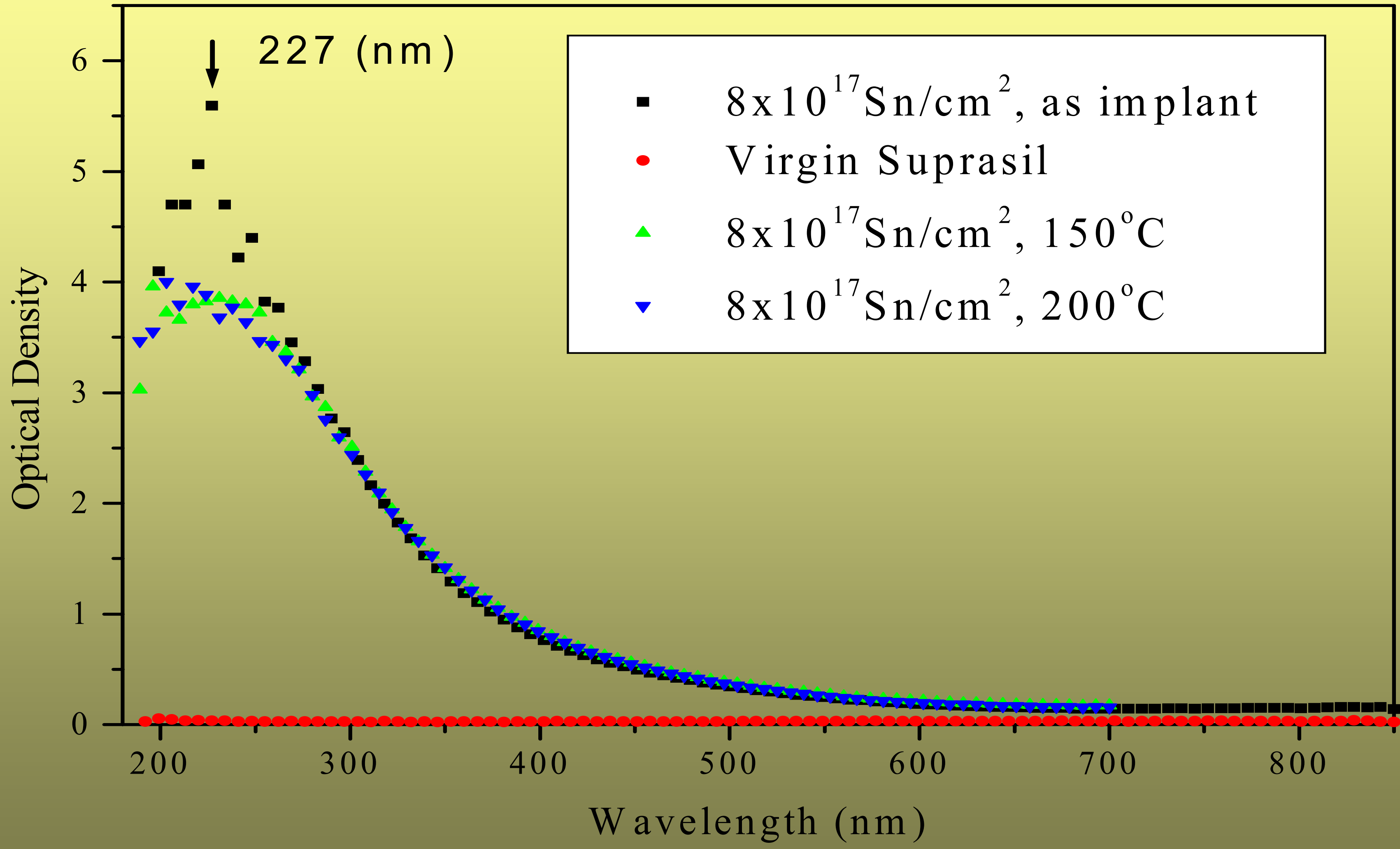


AU in Silica
600°C
526 nm
1200°C
1100°C
1000°C
Optical Density
Wavelength (nm)
2.5
2.0
1.5
1.0
0.5
0.0
200
300
400
500
600
700
800



Optical Density vs. Wavelength after 1 hr heat treatments
for 1.5 MeV Ag into Suprasil 1 to a fluence of 2 x $10^{16}/cm^2$

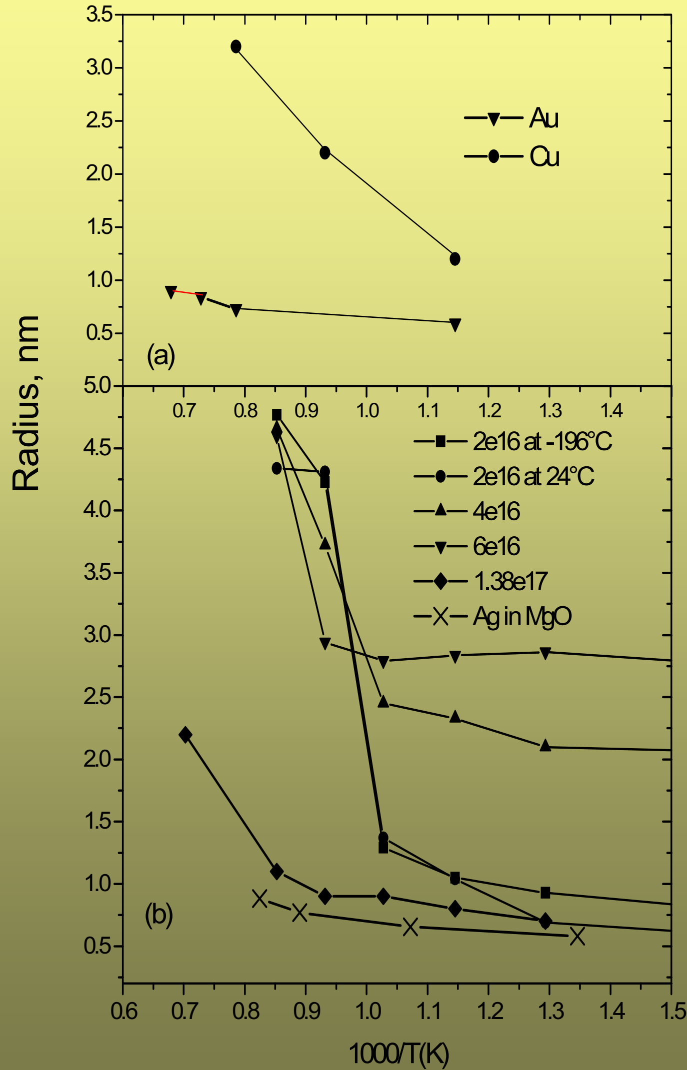
350 keV Tin implanted into Suprasil-1 at room temp.

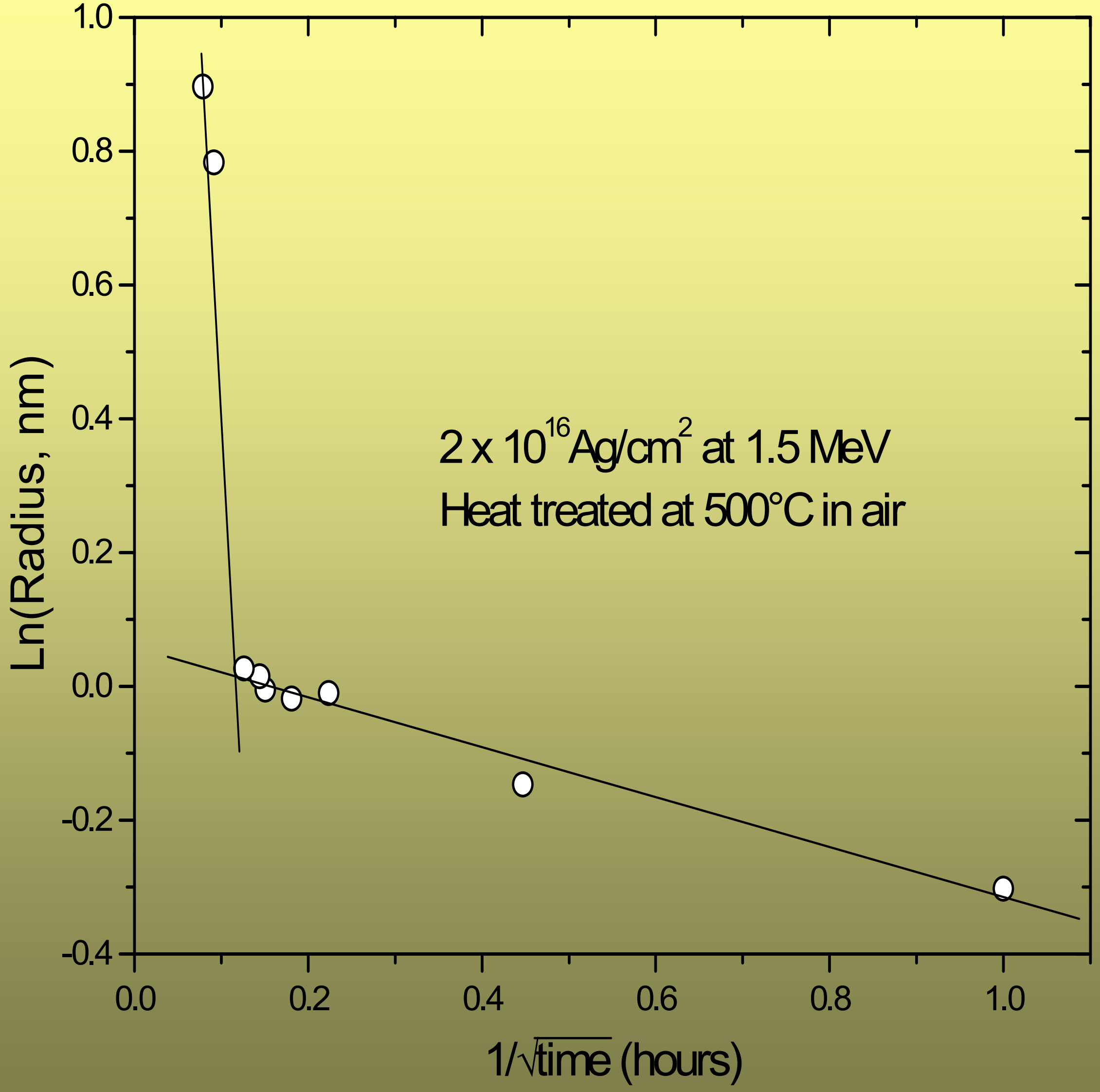


 http://cim.aamu.edu ICTP 25-30 June 2006

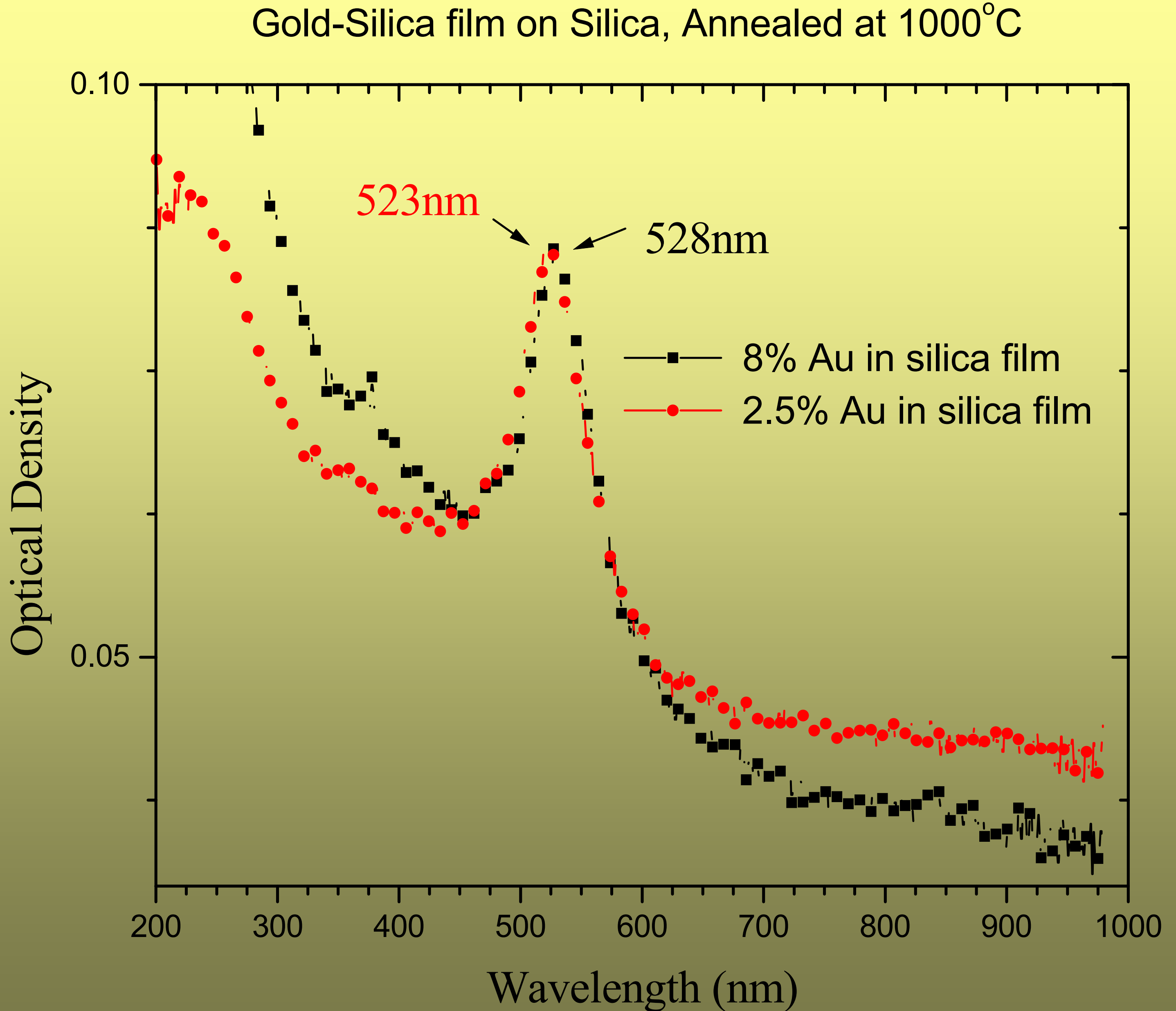
Data from 1997-1999

Figure 3. Radius vs. 1000/T(°K) for 1.2 x 10^{17} Au/cm^2 at 3.6 MeV and 5 x 10^{17} Cu/mc^2 at 2.0 MeV into Suprasil(Fig. 3a, top). Fig 3b is 1.5 MeV Ag into Suprasil at fluences indicated. Also shown is 1.2 x 10^{17} Ag/cm^2 at 1.5 MeV into MgO.

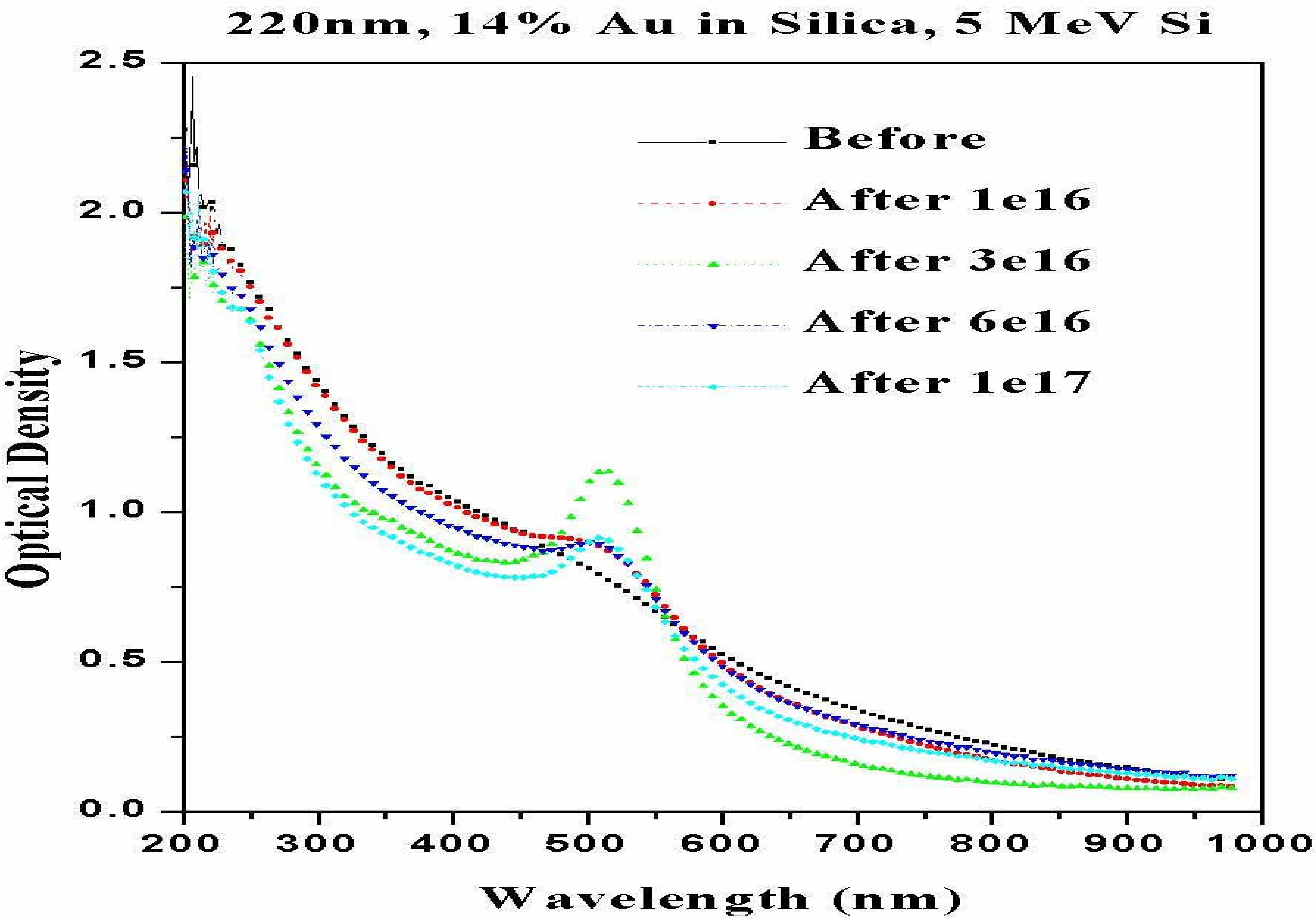




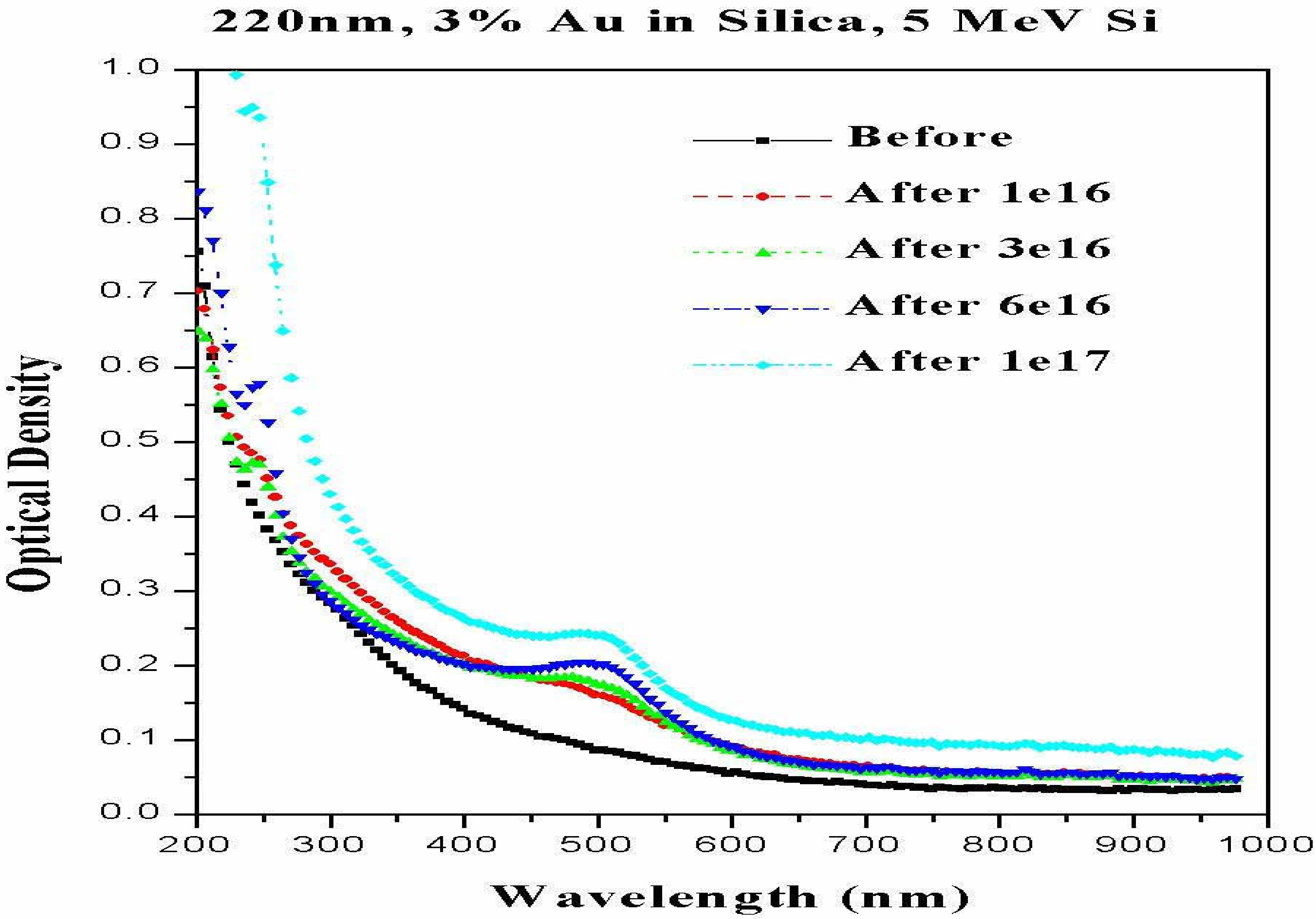
(Co-Deposition of Au and Silica)



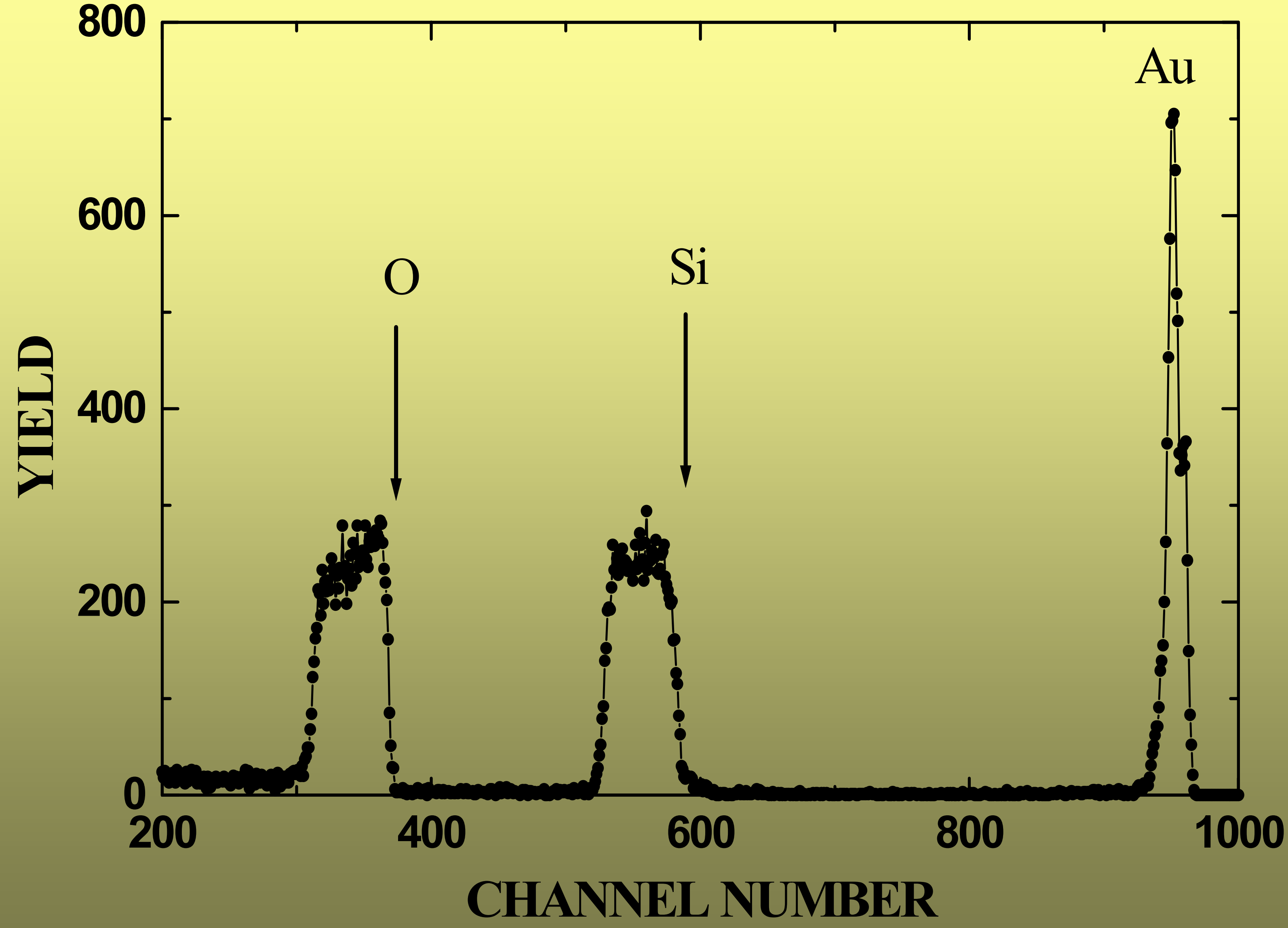
(Co-Deposition of Au and Silica)



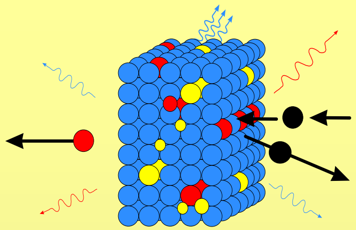
(Co-Deposition of Au and Silica)



3.0 MeV RBS from Gold-Silica Film on Carbon

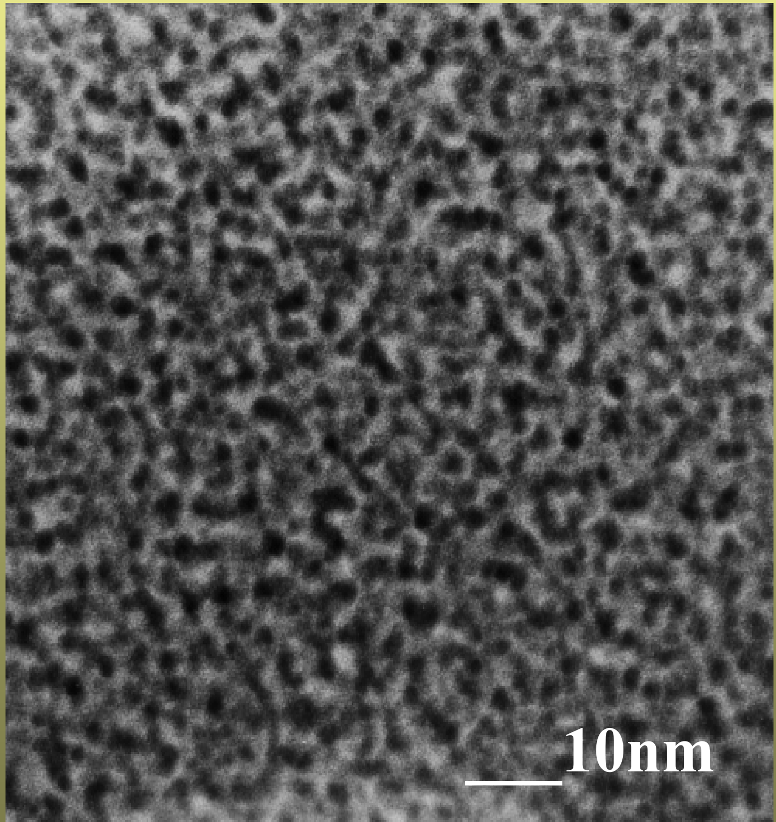


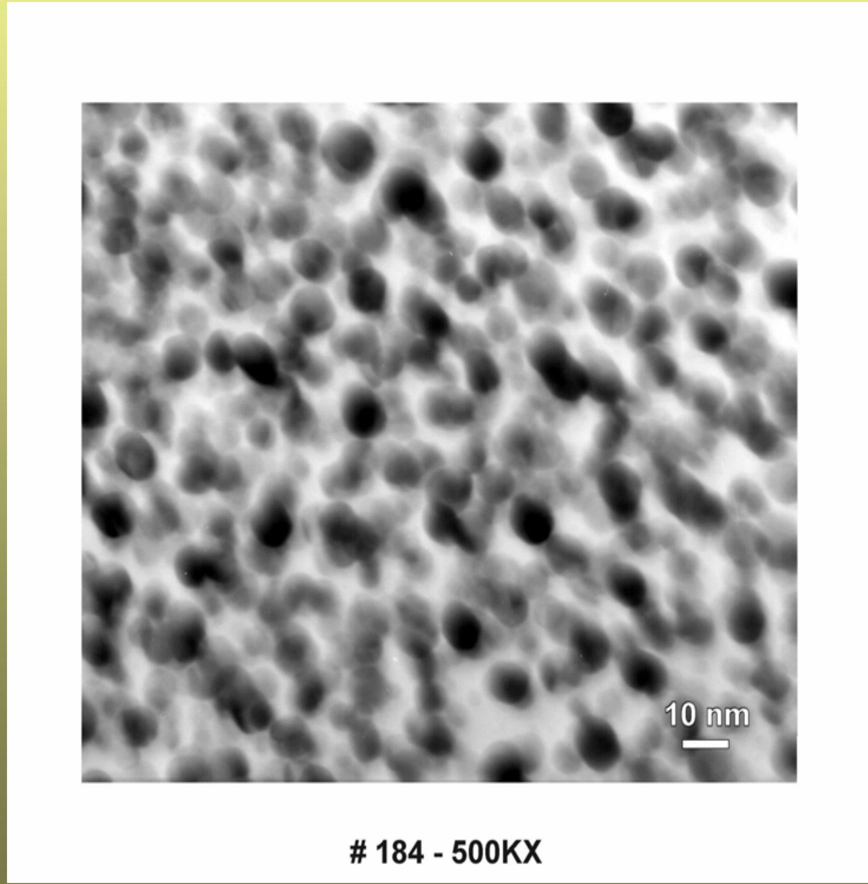
Au nanoclusters in Silica
Au-Silica Co-deposited



Low Au Concentration

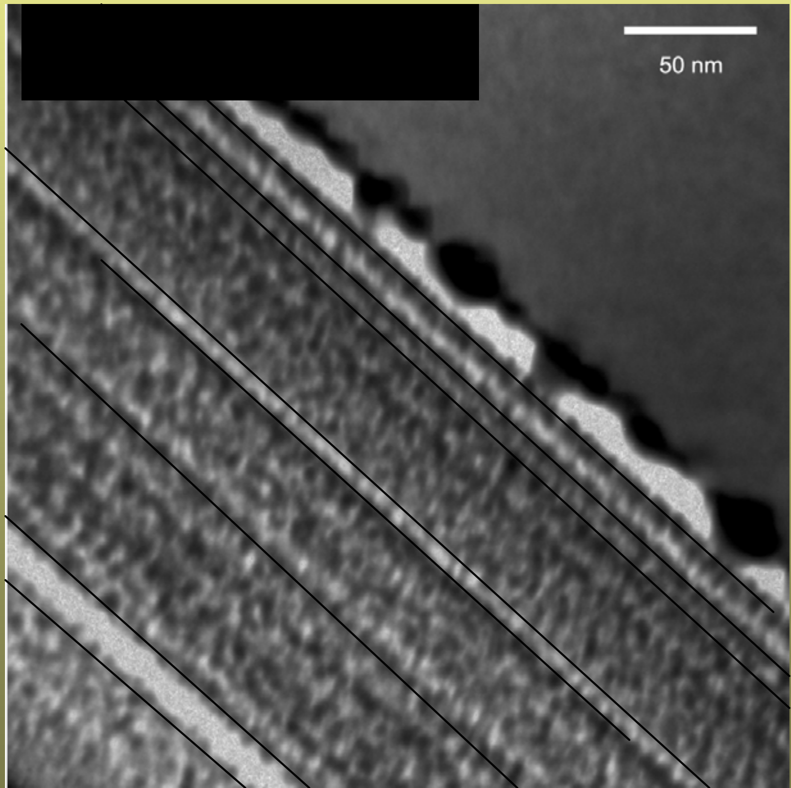
High Au Concentration



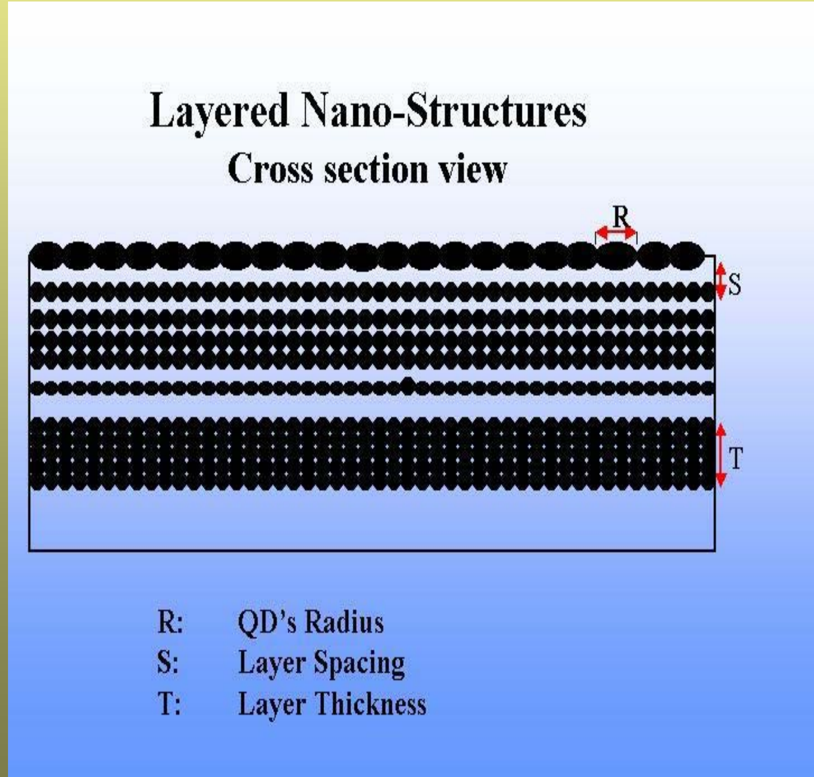


Metallic Nanoclusters in a Host Material Cross Section View

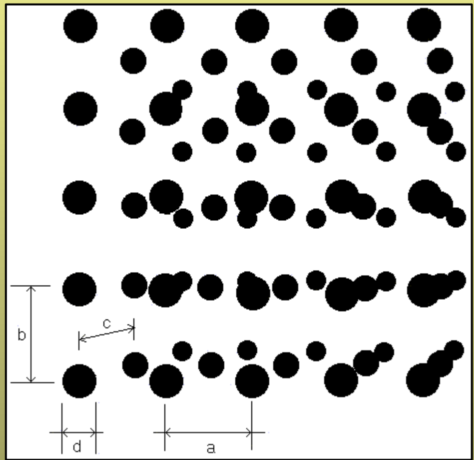
Prep Parameters XXX

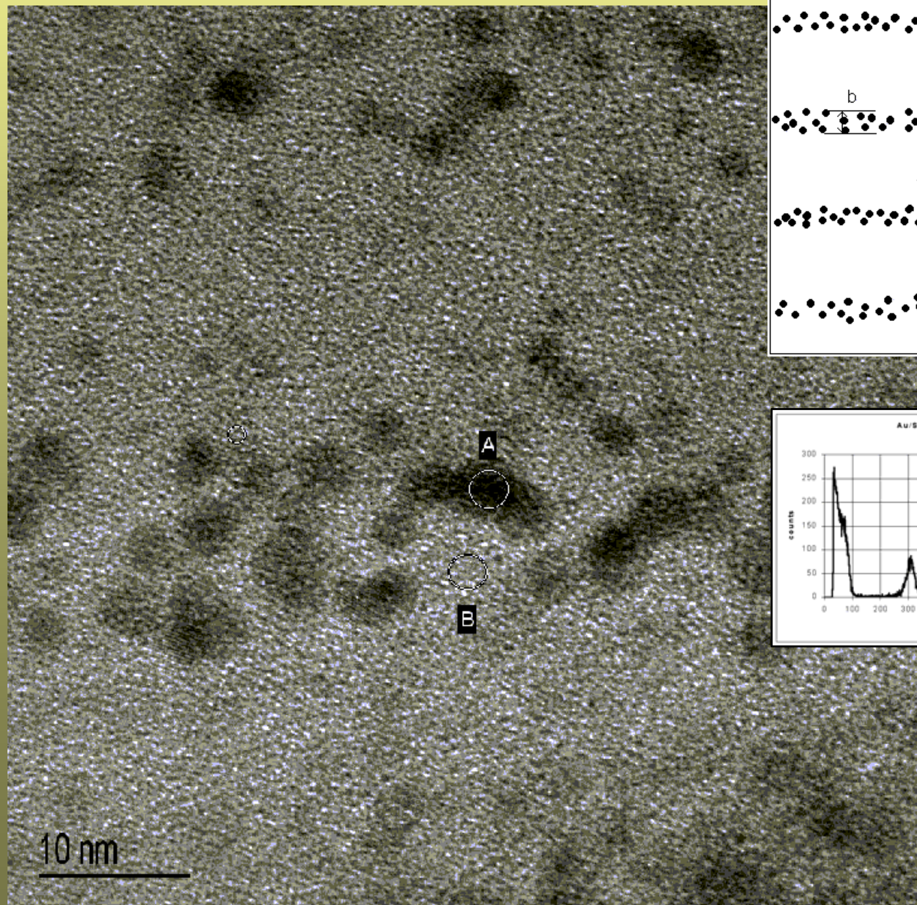


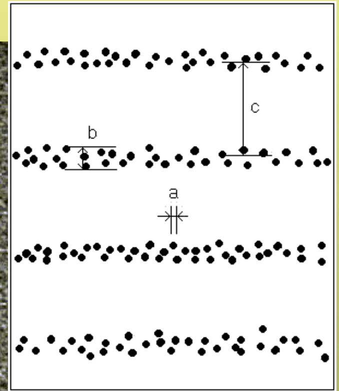
Prep Parameters XXX

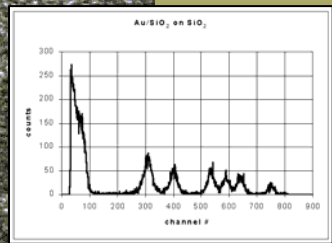


Hyper-crystal-like materials using self-assembled/self-organized nanostructures



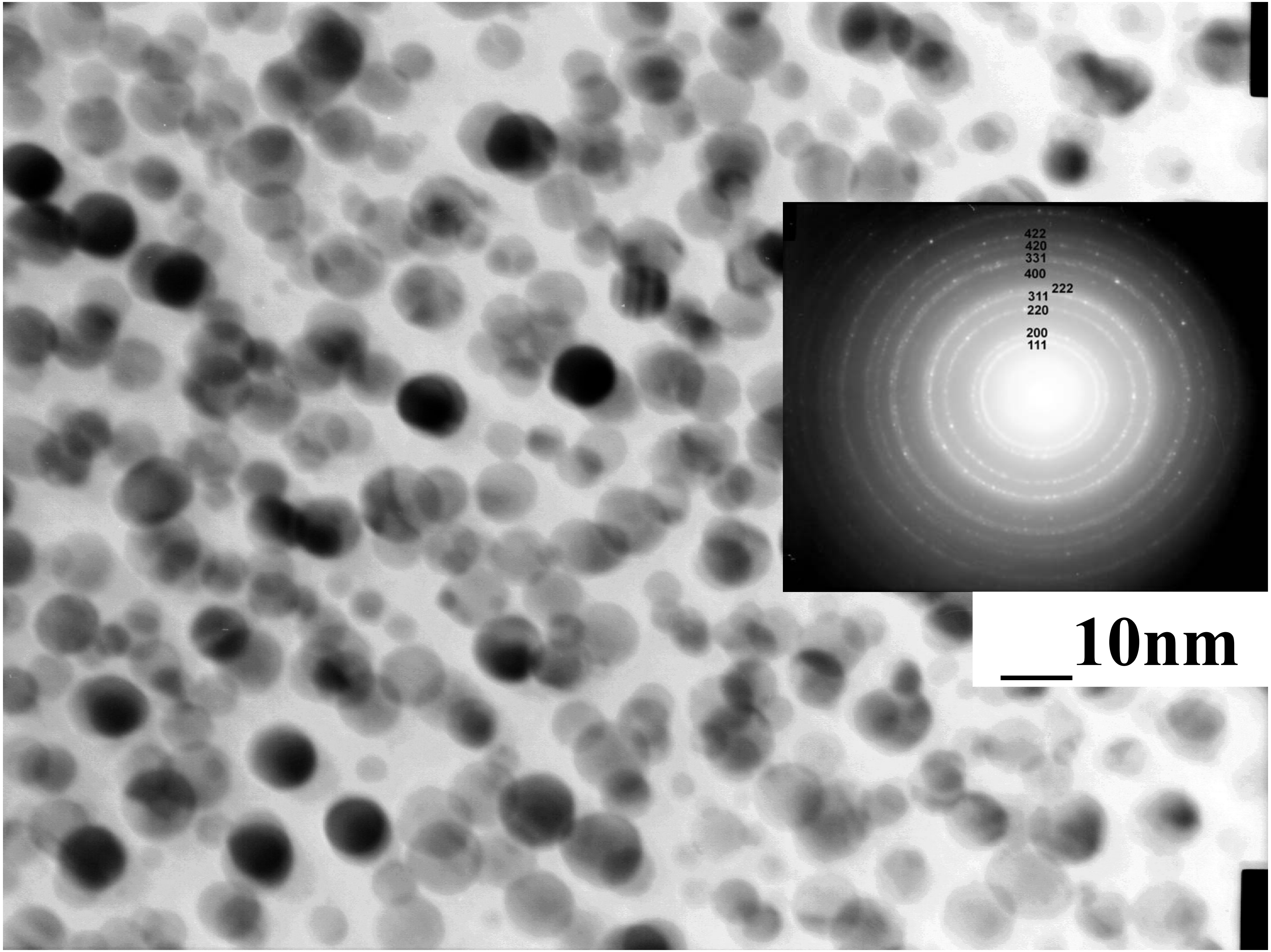


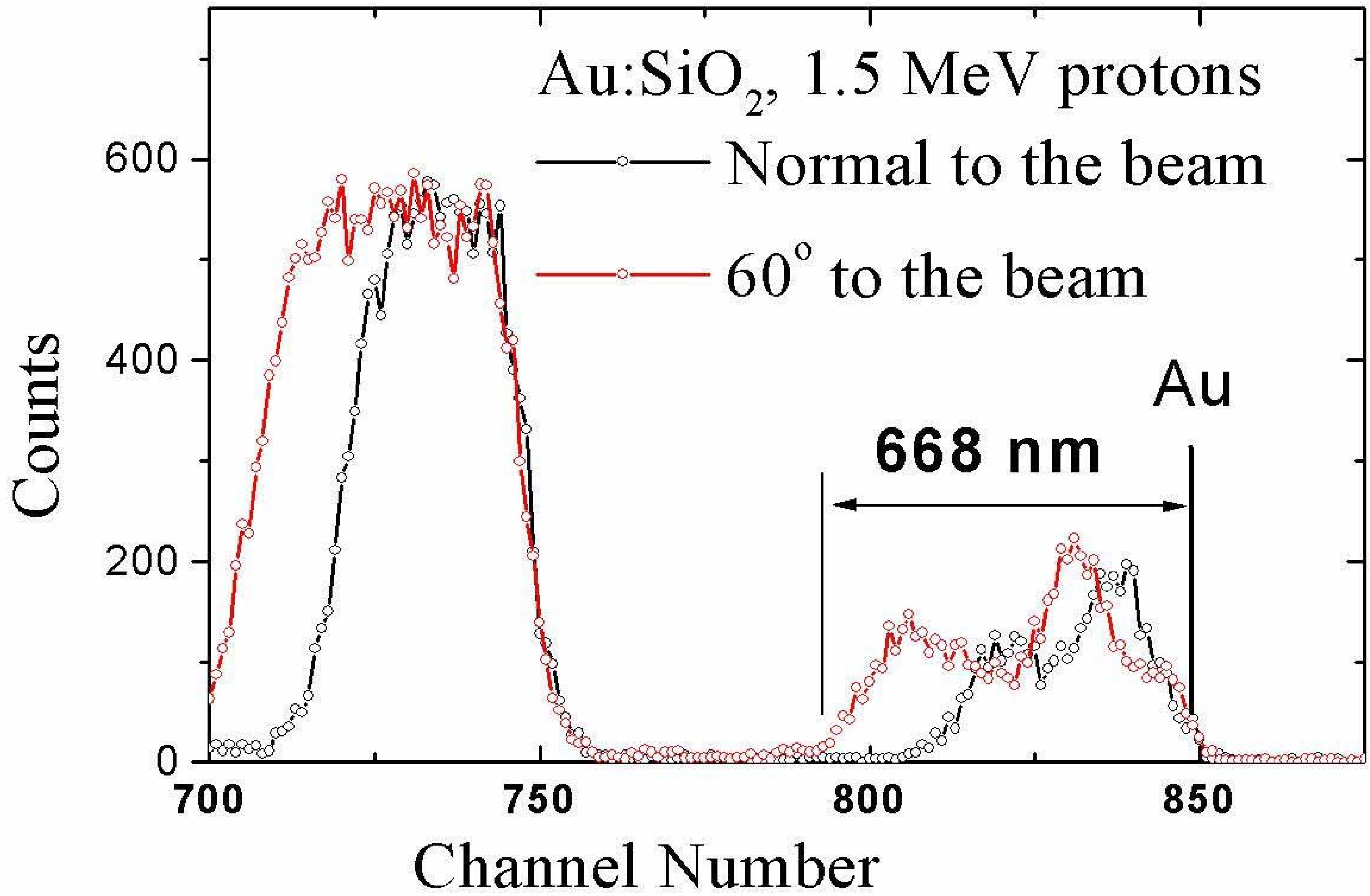




Applications

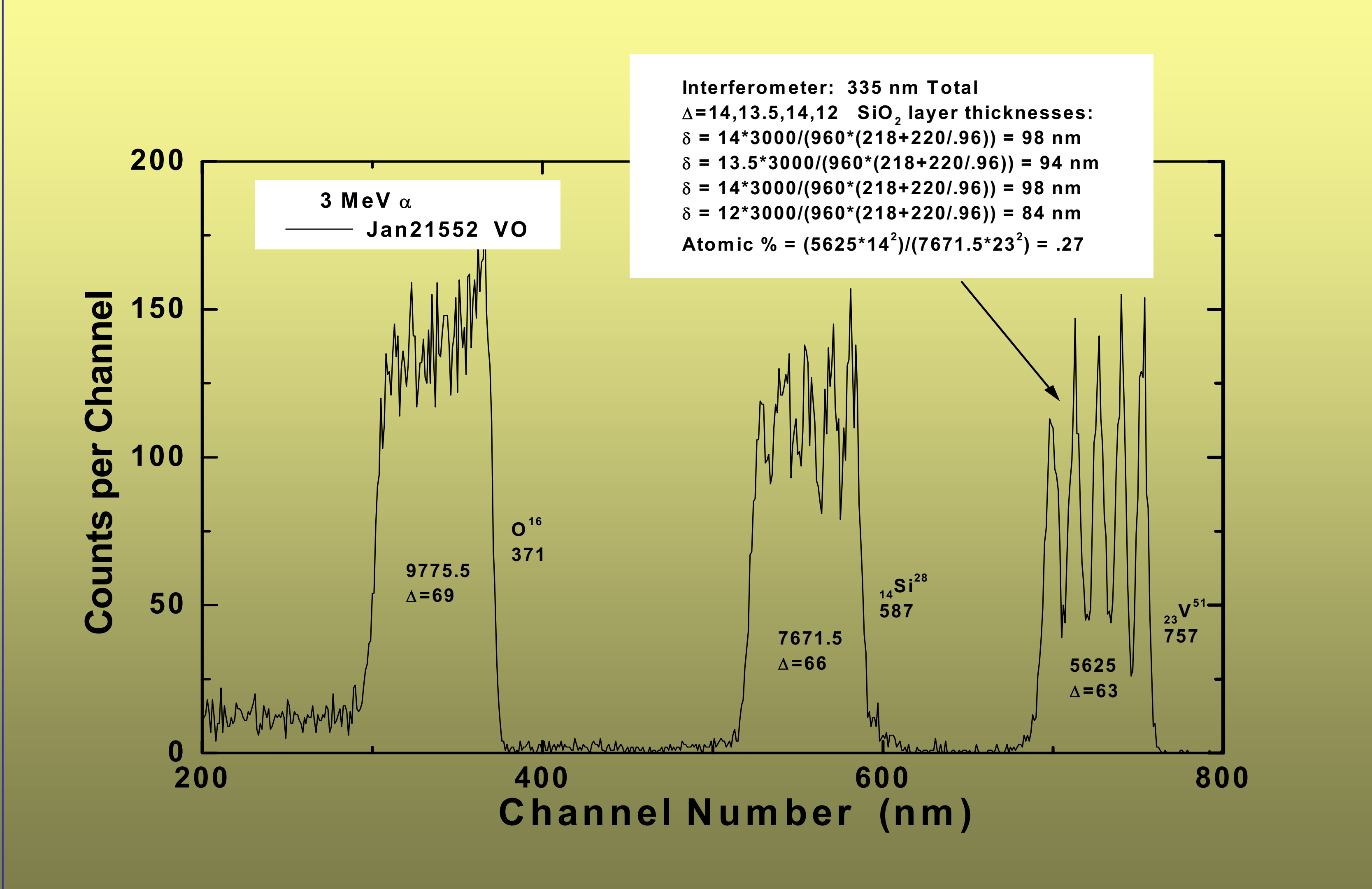
- Thermoelectric energy conversion
- Tunable photonic bandgap
- Tunable optical filtering (UV-Vis-IR)
- Electron emission for electric propulsion or display systems


422
420
331
400
222
311
220
200
111
10nm



Au:SiO2, 1.5 MeV protons
Normal to the beam
60° to the beam
Au
668 nm
Counts
600
400
200
0
700
750
800
850
Channel Number

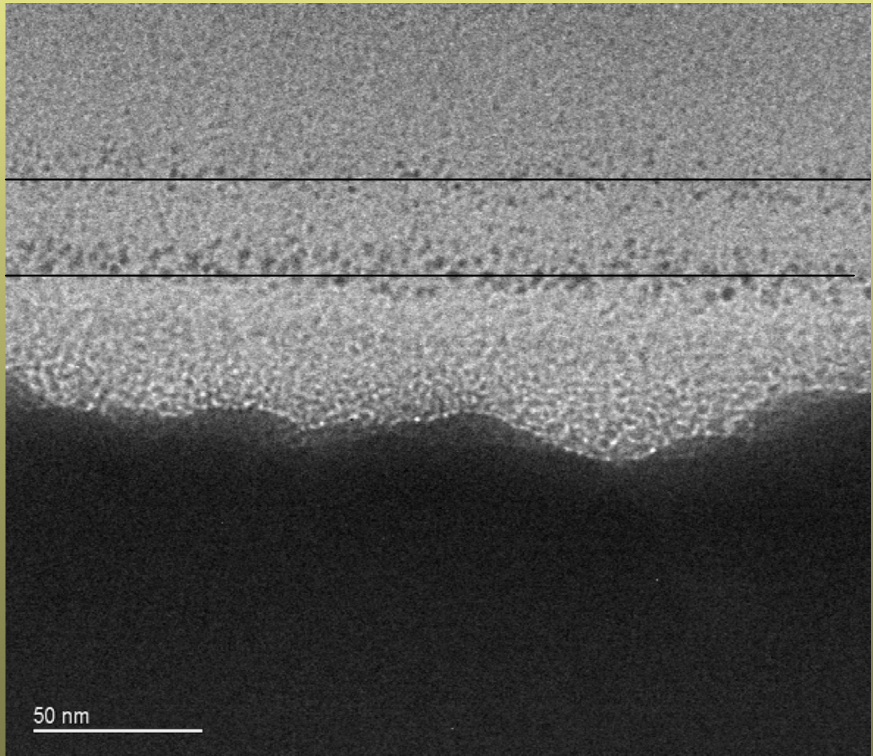
Layered Structures



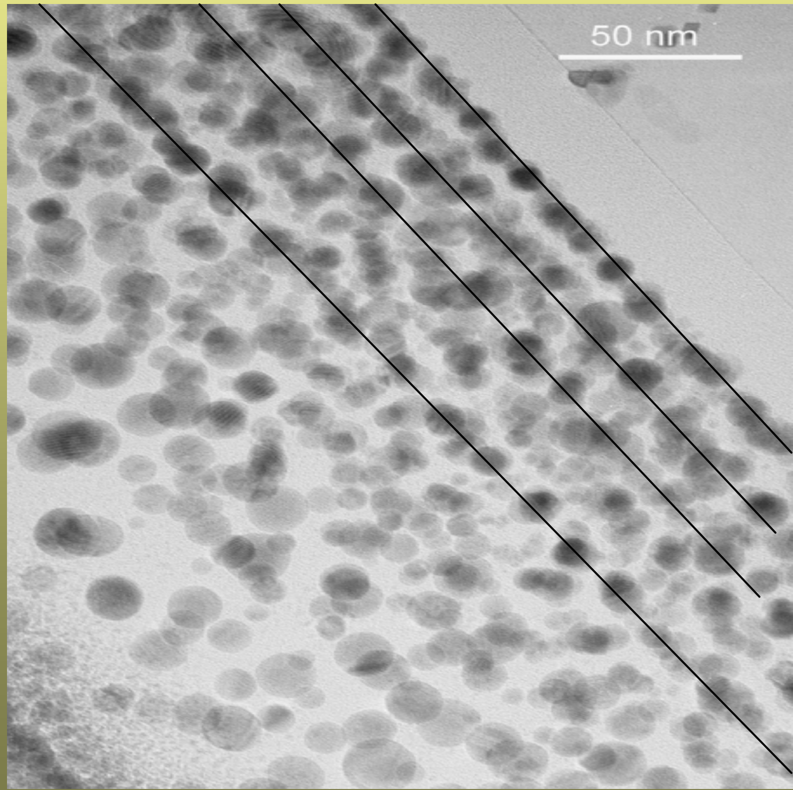
RBS spectrum of five Vanadium oxide layers in SiO_2 host

Au and SiO_2 Layer after Irradiation

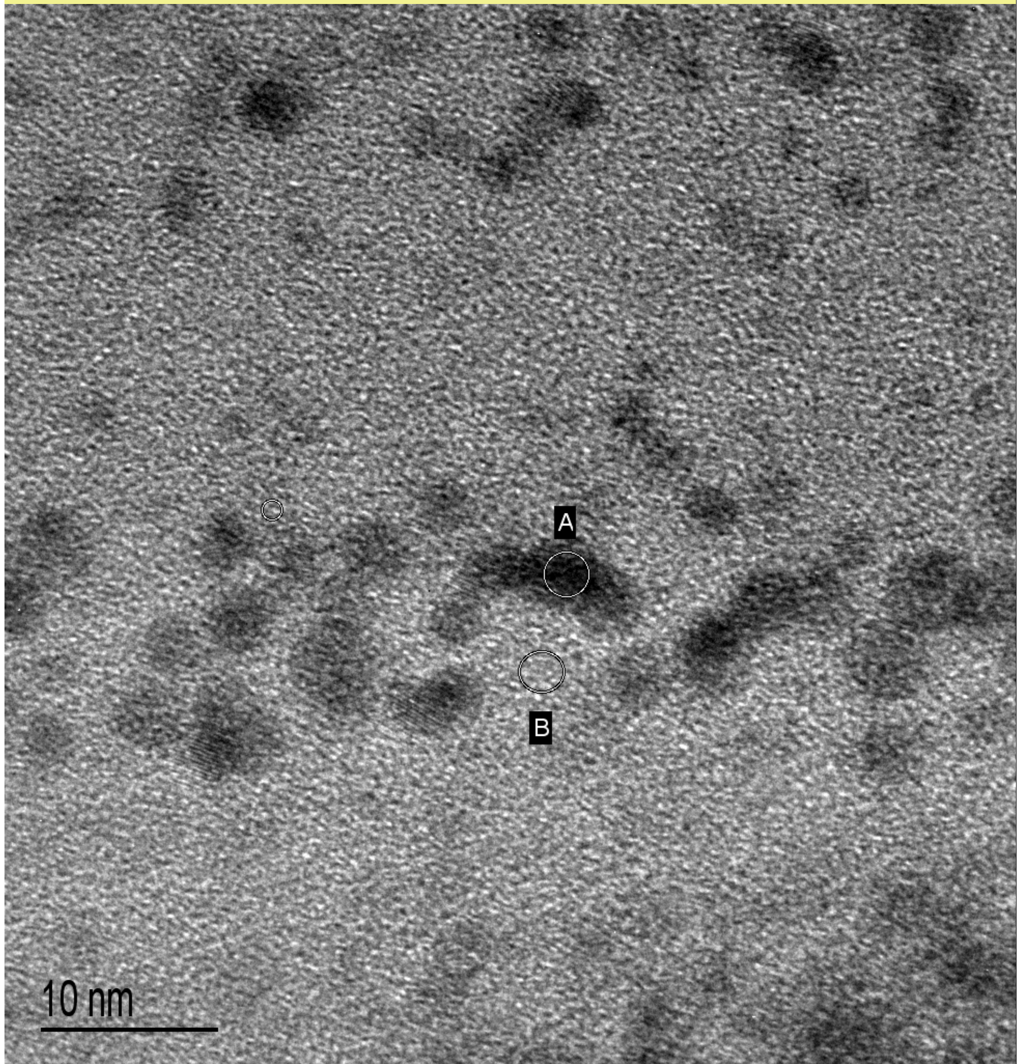
Two layers of SiO_2/Au

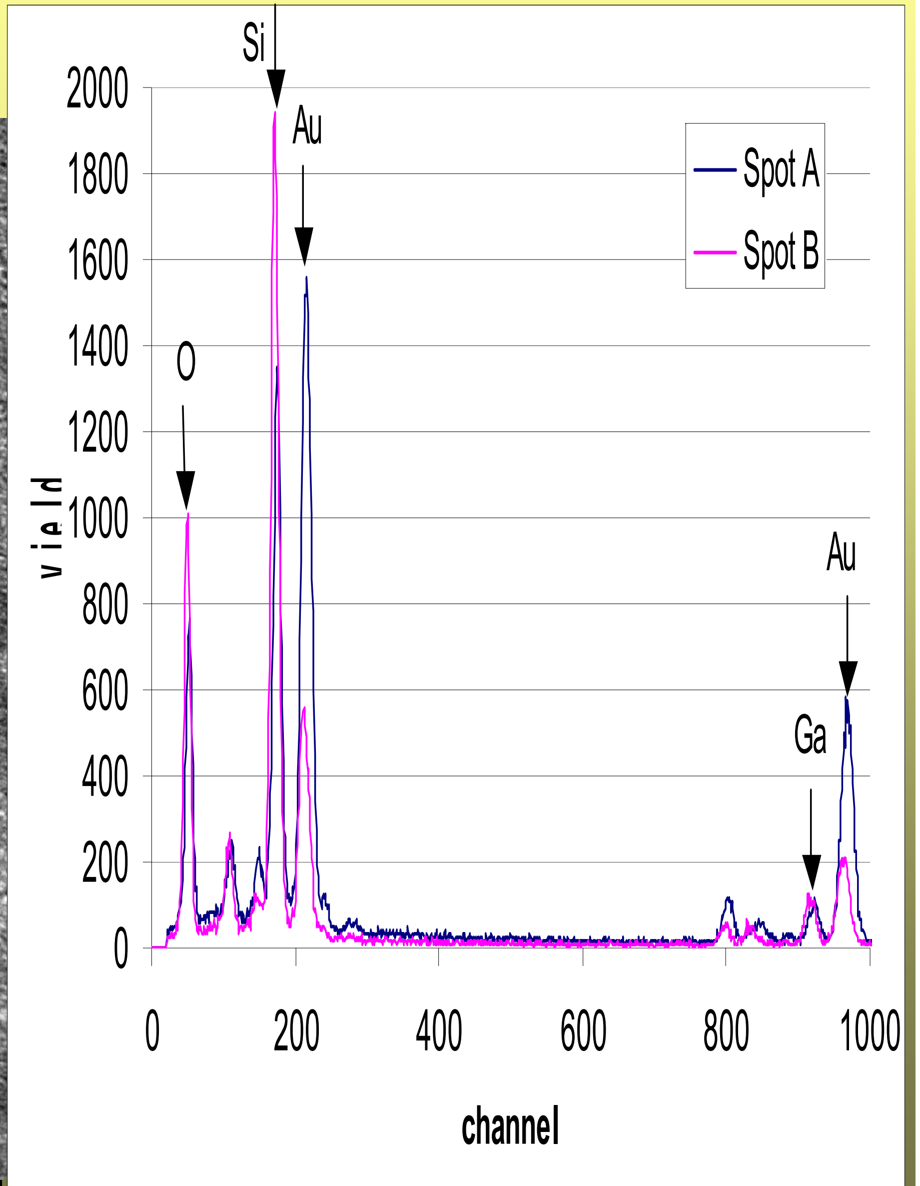


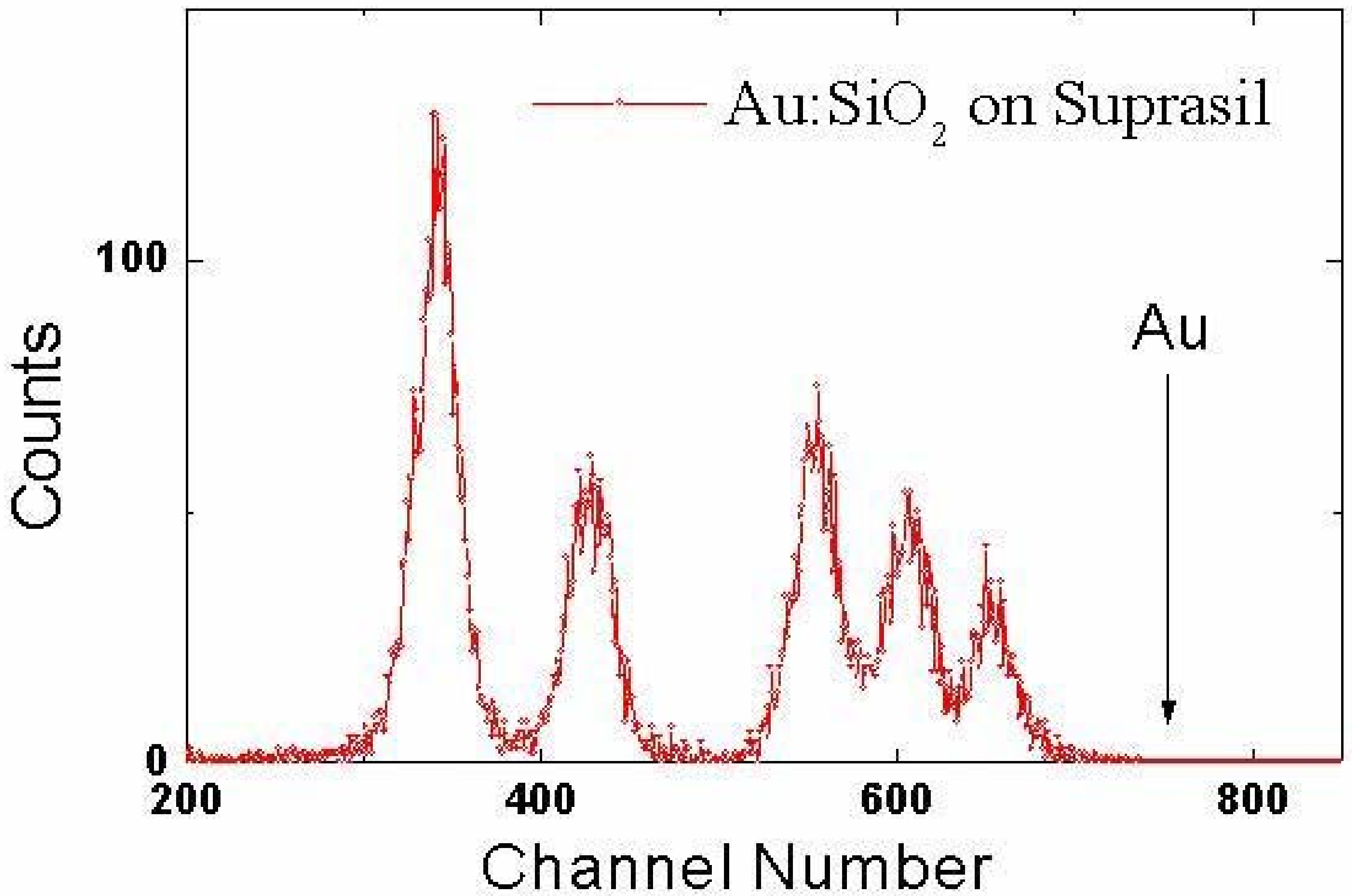
One layer of SiO_2/Au



X-ray spectrum on a Au nanocluster (A) and between clusters (B)

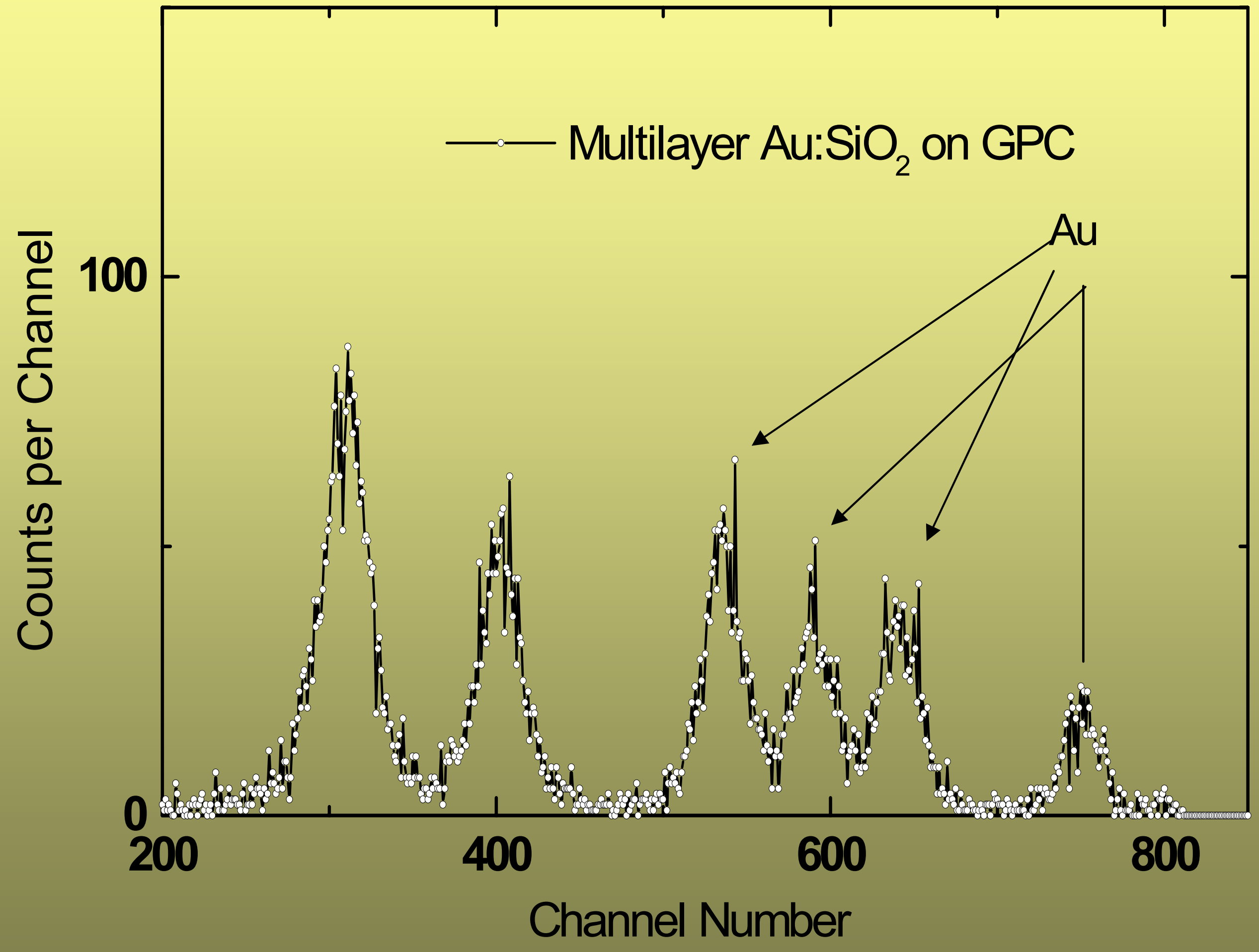






Au:SiO_2 on Suprasil
100
0
Counts
Au
200
400
600
800
Channel Number

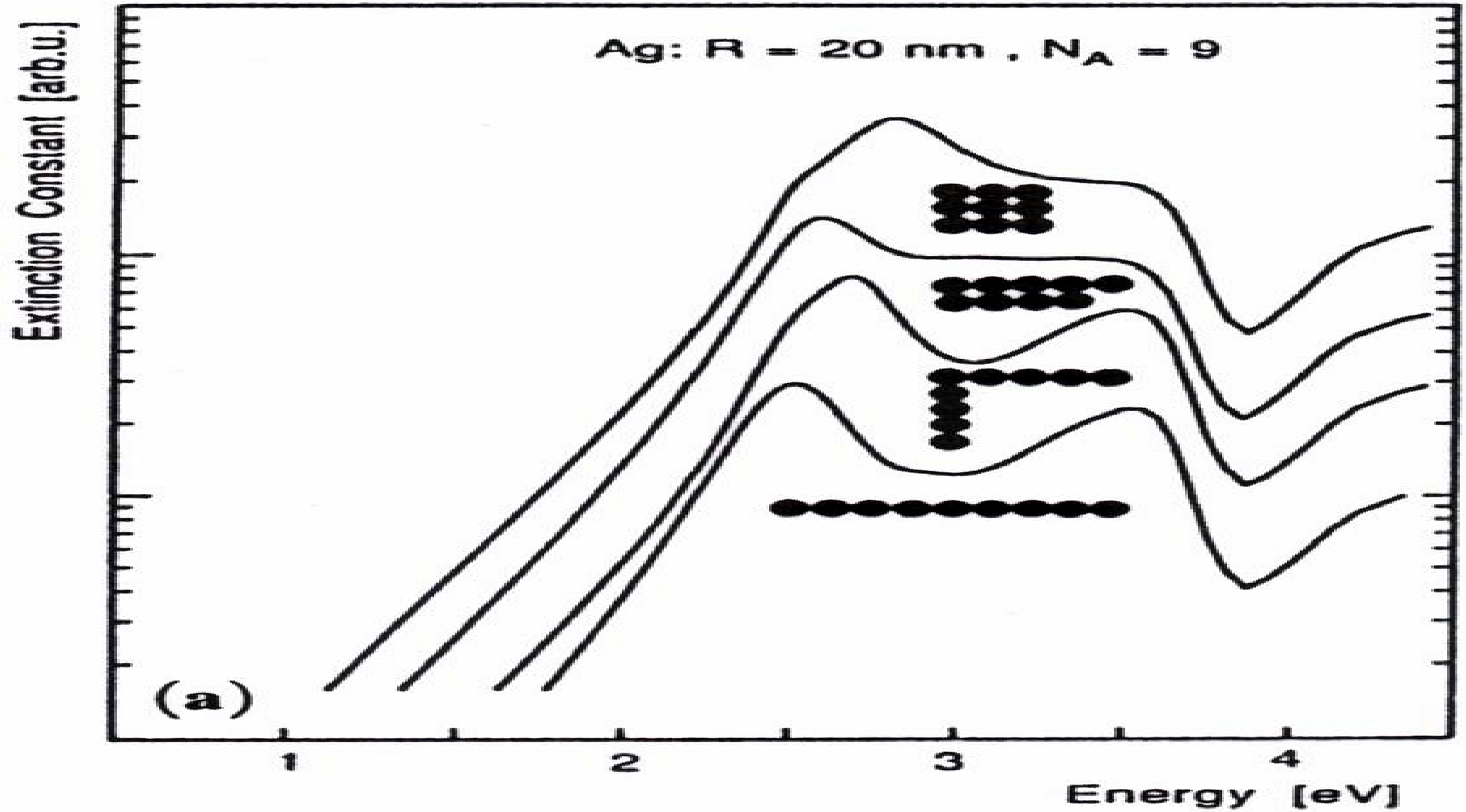
(B)

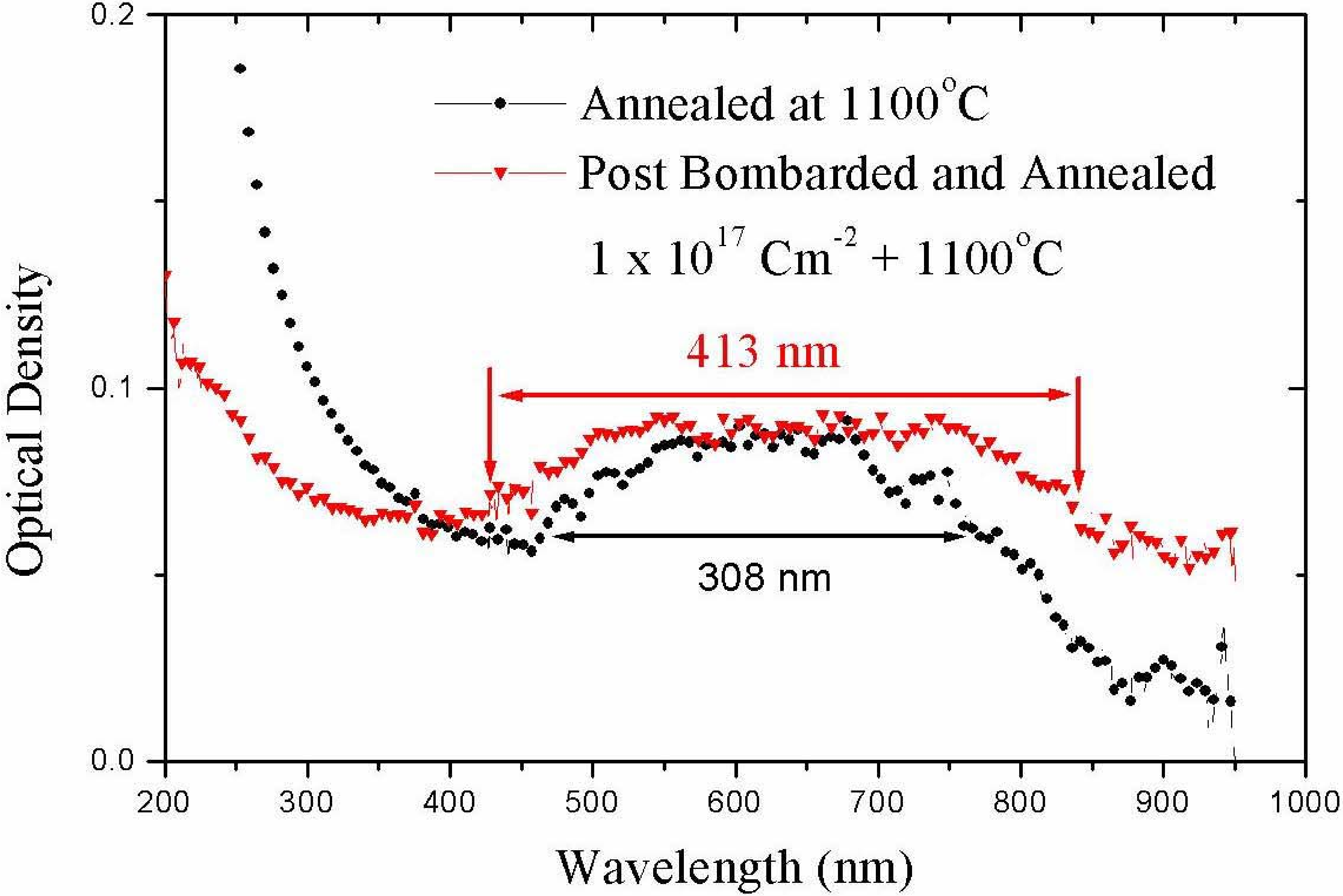


Multilayer Au:SiO_2 on GPC
Au
100
0
200
400
600
800
Counts per Channel
Channel Number

Shape of α as NCs interact through thinner layers of SiO_2 Buffers

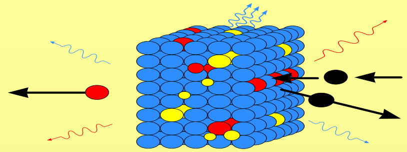
Kreibig, U. and Vollmer, M., Optical Properties of Metal Clusters, (Springer-Verlag, Berlin Heidleberg, 1995), p. 167.





Annealed at 1100°C
Post Bombarded and Annealed
1 x 10^17 Cm^-2 + 1100°C
413 nm
308 nm
Optical Density
Wavelength (nm)
0.0
0.1
0.2
200
300
400
500
600
700
800
900
1000

Conclusion

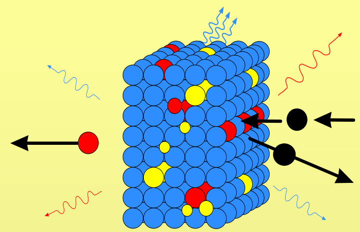


- **Combined Co-deposition and MeV irradiation is a viable tool for formation of regimented layered quantum dot systems (layered structures)**
- **Nanocrystals interacting through nanolayers**

Recommendation

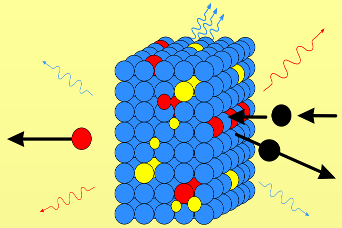
Use the wave-guiding properties of the nanolayers of nanocrystals to measure layer integrity (leaky layers).

Example 2



Thermoelectric Materials

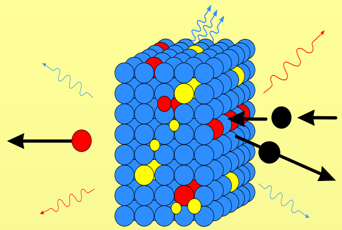
Introduction



Thermoelectric devices performance quantified by the dimensionless figure of merit **ZT**

$$ZT=(S^2\sigma T)/\kappa$$

- S is the Seebeck coefficient
- σ is electrical conductivity
- T is temperature
- κ is thermal conductivity



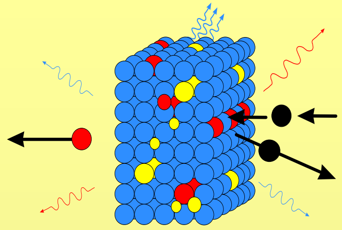
Introduction

Three ways to increase Figure of Merit

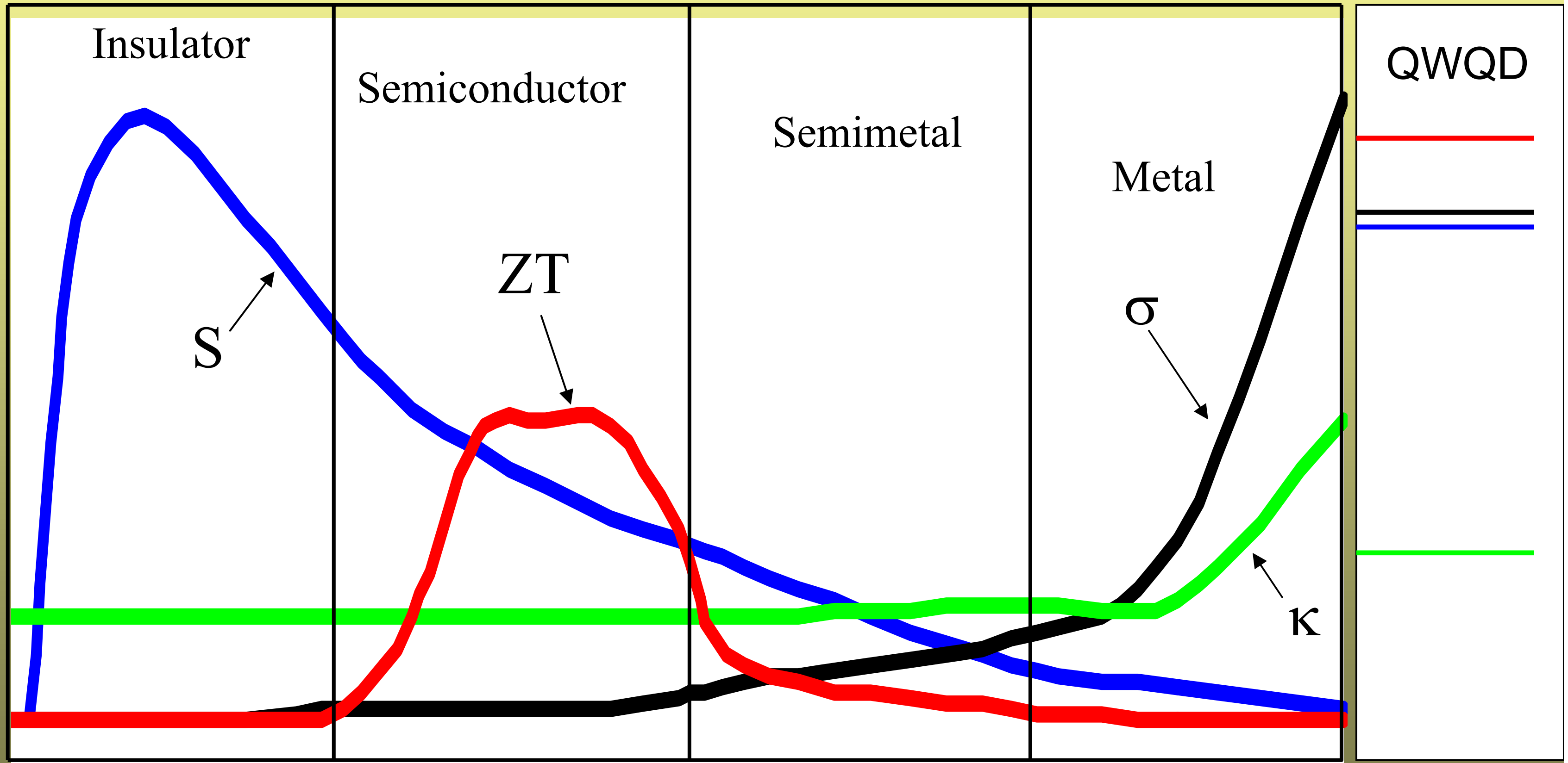
- Increase the Seebeck coefficient S
- Increase the electrical conductivity σ
- Decrease the thermal conductivity κ

Hard to have all three cases (high S value, high σ value, low κ value) simultaneously.

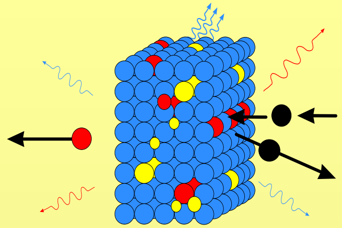
Introduction

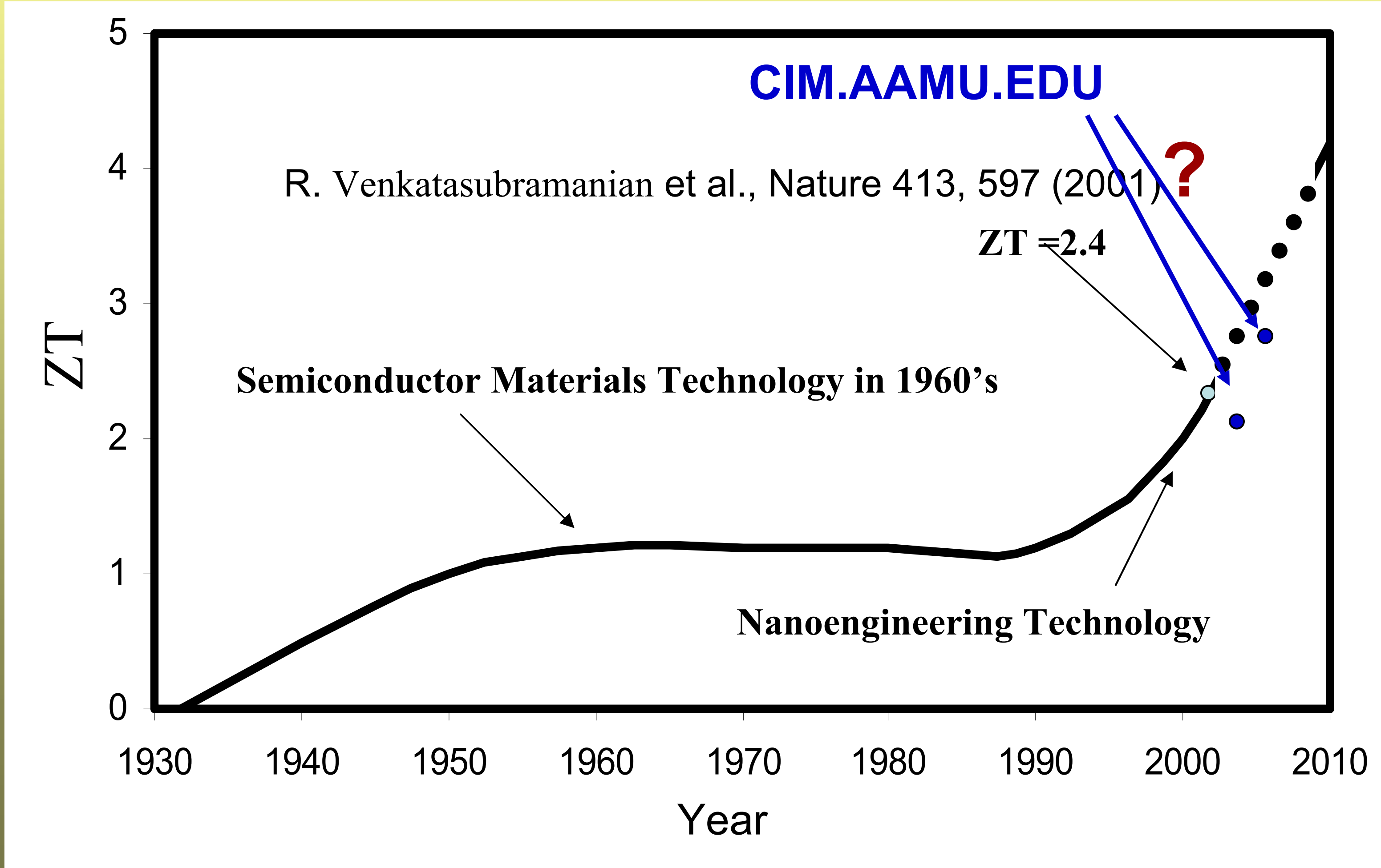


$ZT=(S^2\sigma T)/\kappa$

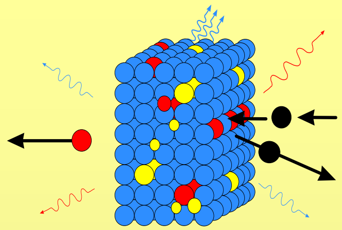


Introduction





Introduction



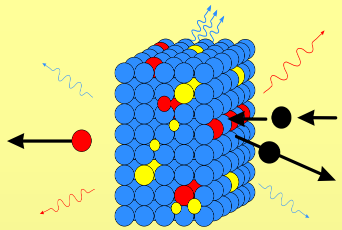
Why Nanolayered?

Nanolayered superlattice heterostructures does increase ZT (L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B. 47, 12727 (1993)).

Reasons:

Quantum confinement results in higher impedance to phonon transport

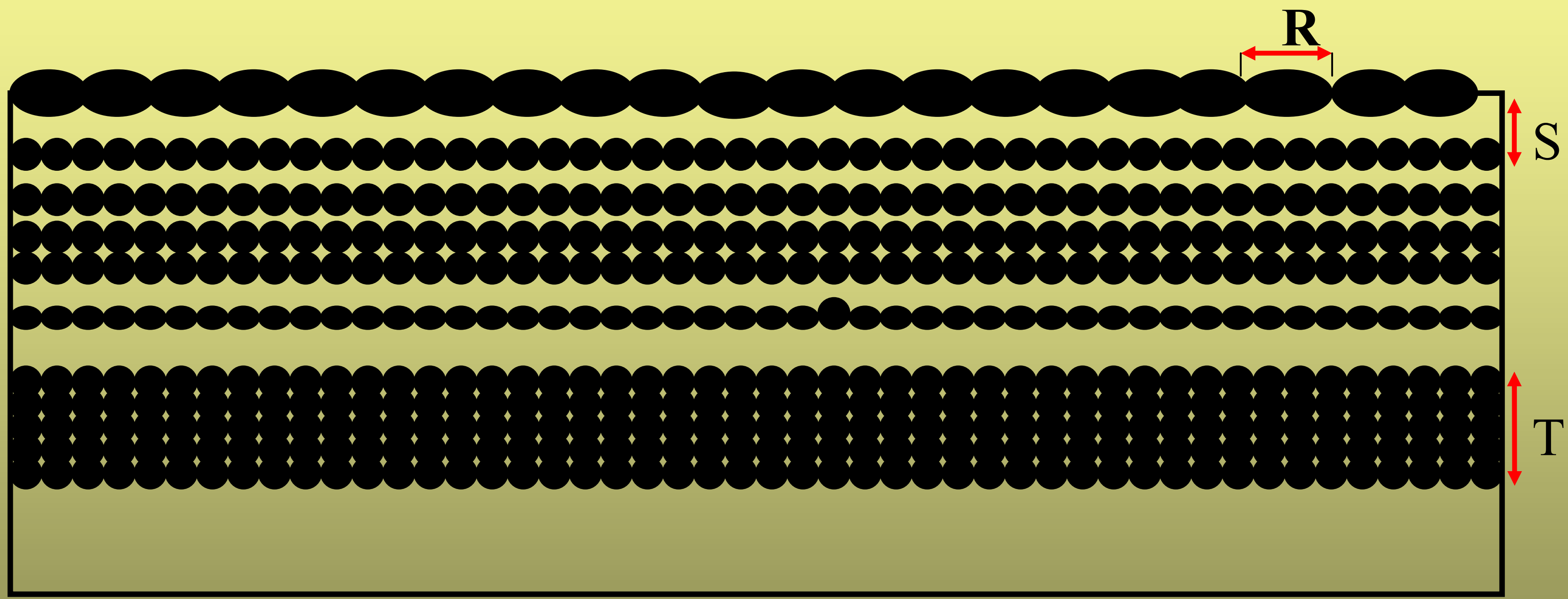
Objective



1- Produce multilayer of nanoscale materials such as Bi_xTe_3/Sb_2Te_3, SiO2/SiO2+Au and many others

2- Produce layers of nanocrystals.

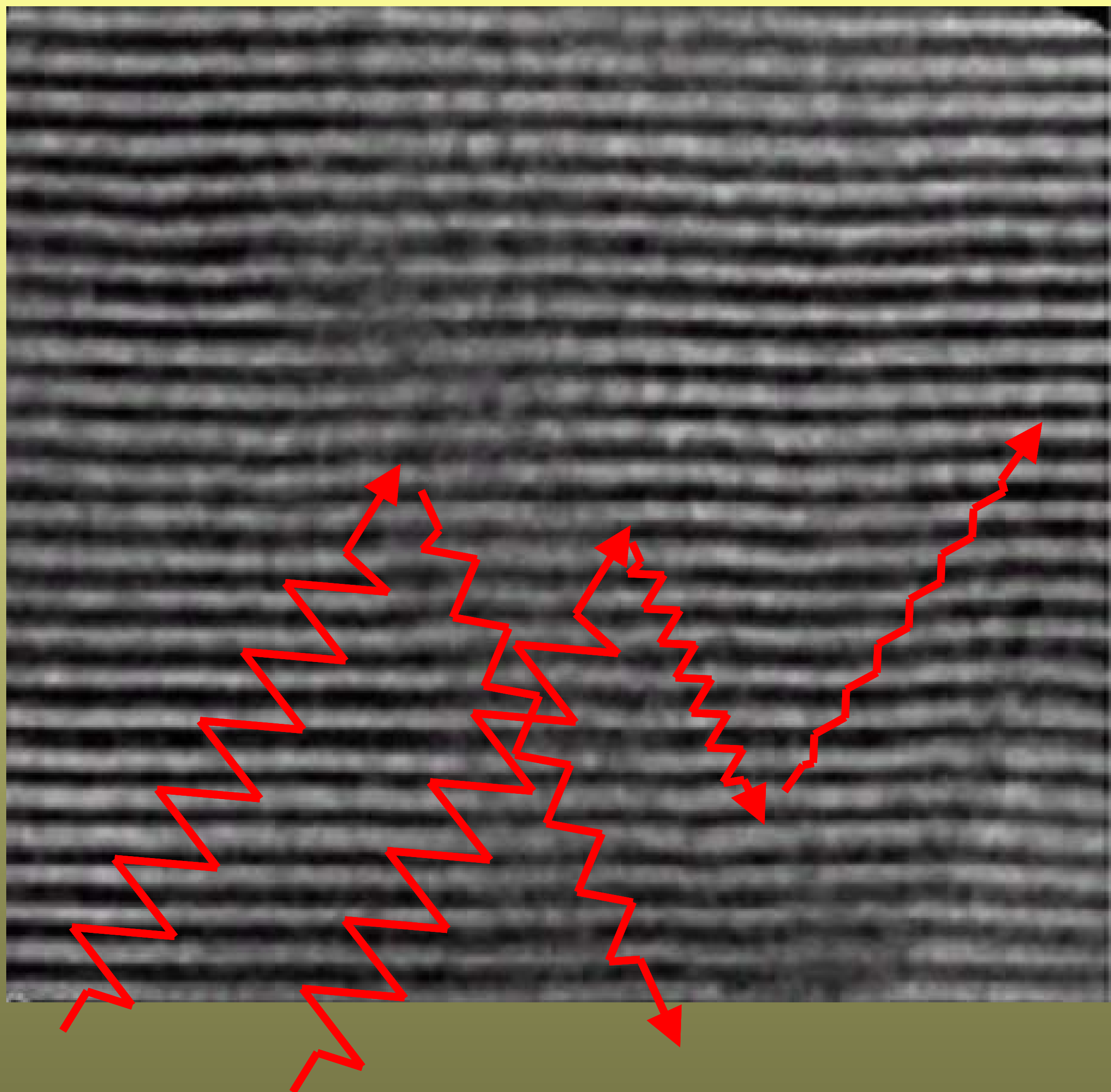
Layered Nano-Structures
Cross section view



R: QD's Radius
S: Layer Spacing
T: Layer Thickness

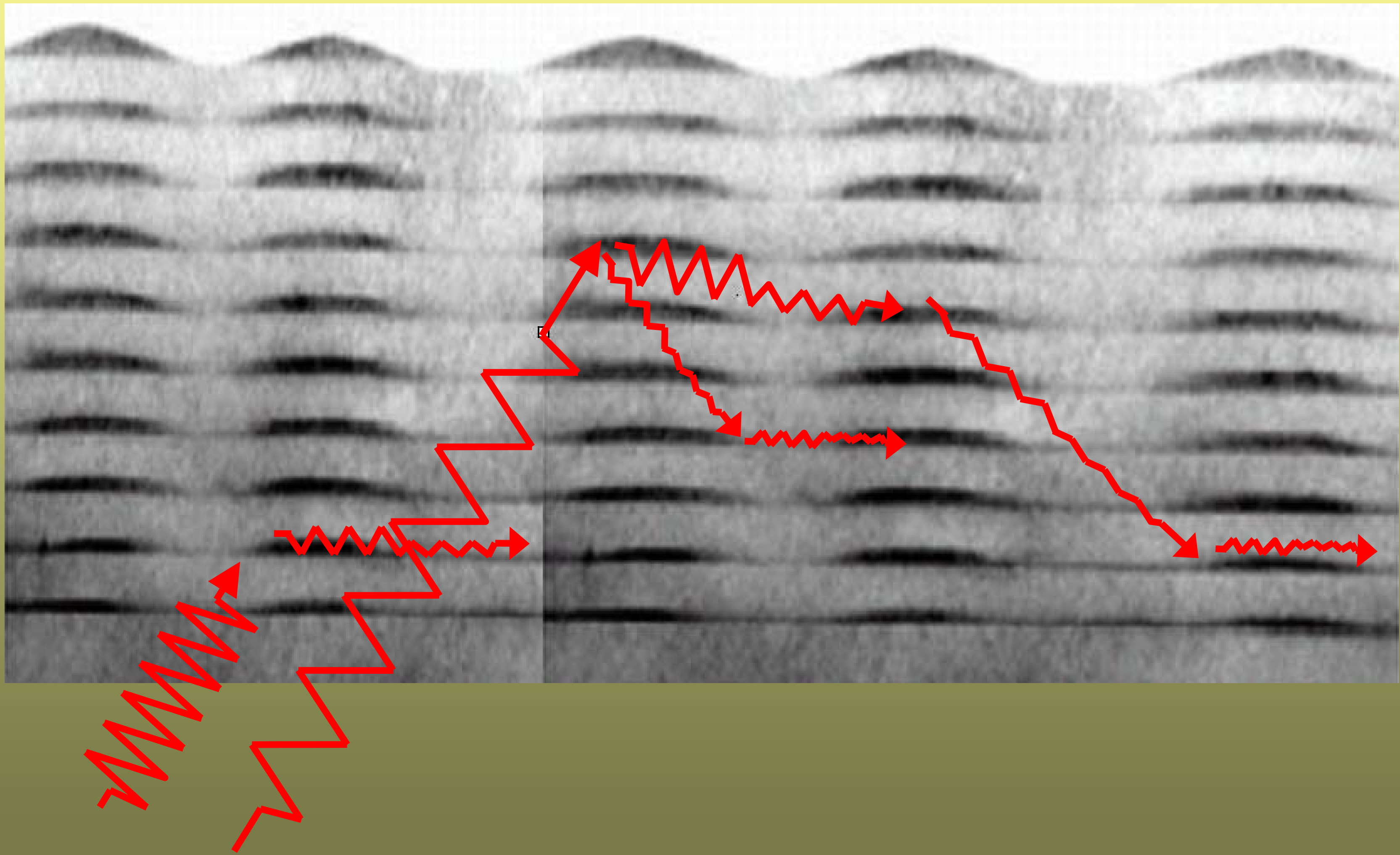
Phonon in quantum well

click mouse to see the detail

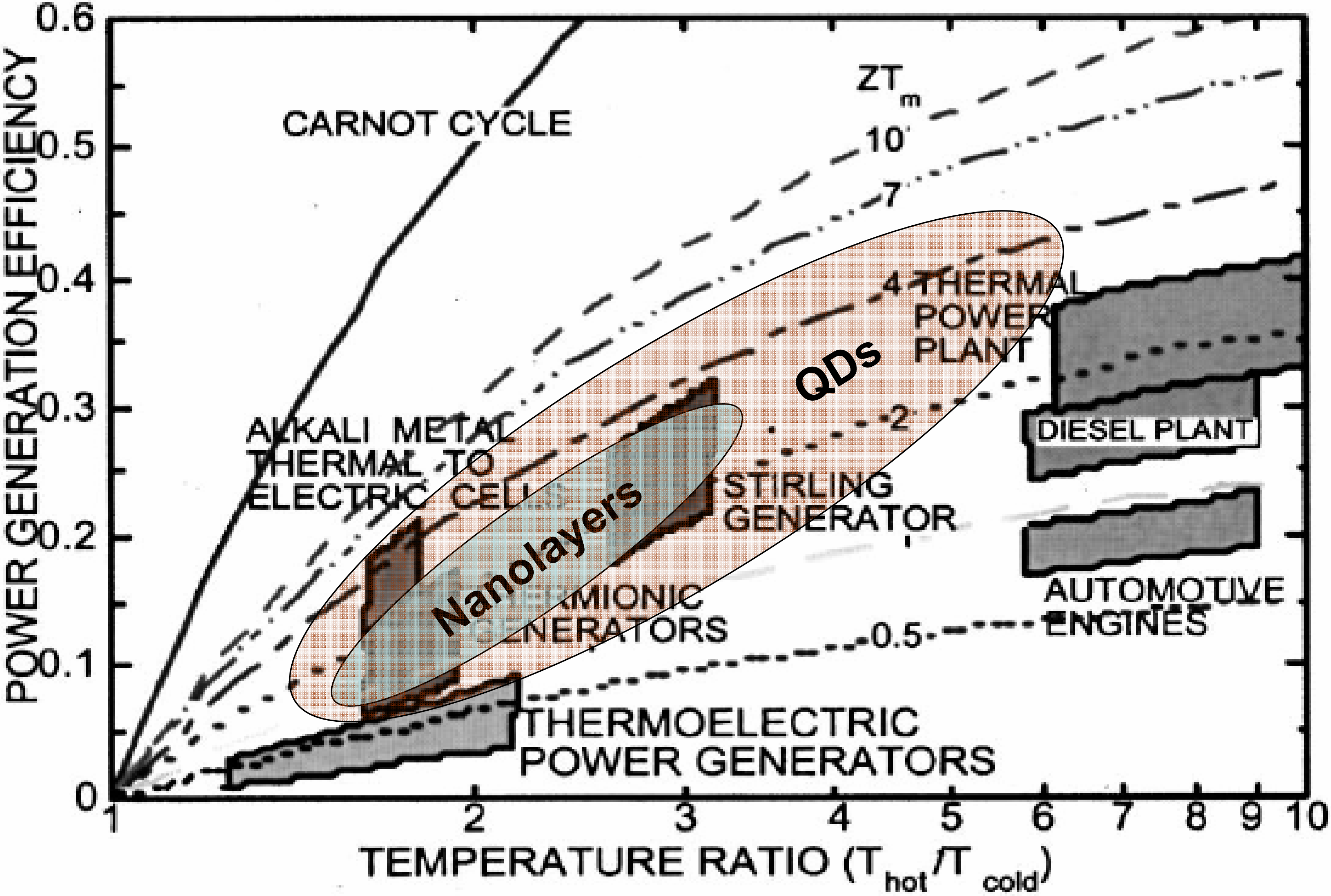


Phonon propagation in QDQW

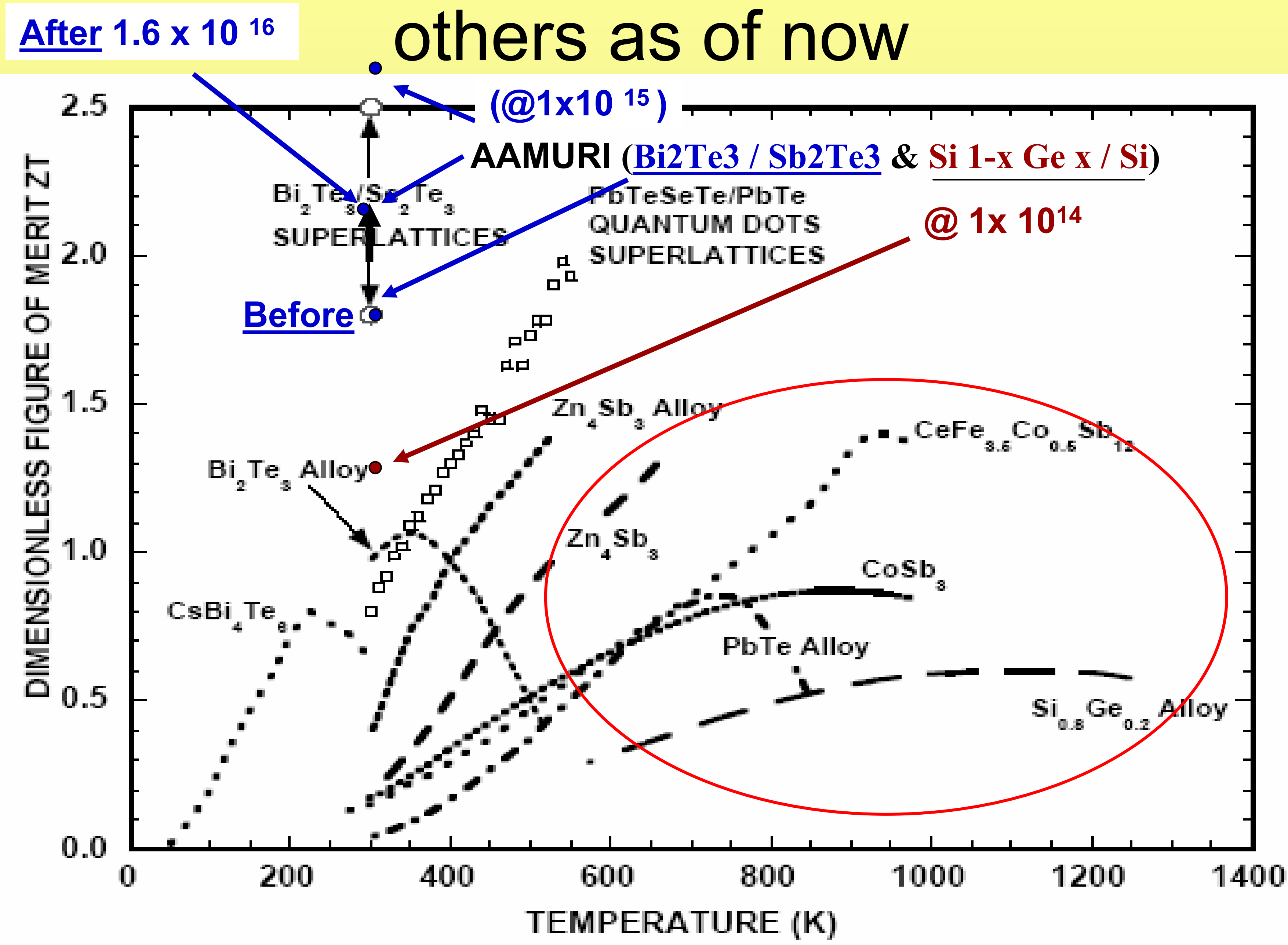
click mouse to see the detail



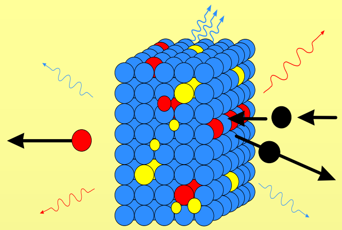
Power Generation Efficiency



Results obtained by AAMU and others as of now



Summary



- 50 to 1000 nanolayers were produced in house.

- Post Irradiation reduced thermal conductivity, increased electrical conductivity as well as increase Seebeck Coef.
- Thus Figure of Merit increased.

Studies underway:

1. Operational temperature limits (RT and at 1000C)
2. Detail Study of the Electrical Conductivity
3. Detail TEM Studies
4. Varying QD and host materials (i.e. metal QDs in Polymer host, Semiconducting or metal QDs in SiC host)