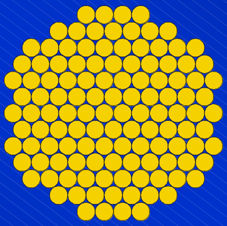
NANOCRYSTALLINE THIN FILMS:

A bridge between Nanoscience & Nanotechnology



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Tata Institute of Fundamental Research
Mumbai, INDIA (http://www.tifr.res.in/~dcmpms)

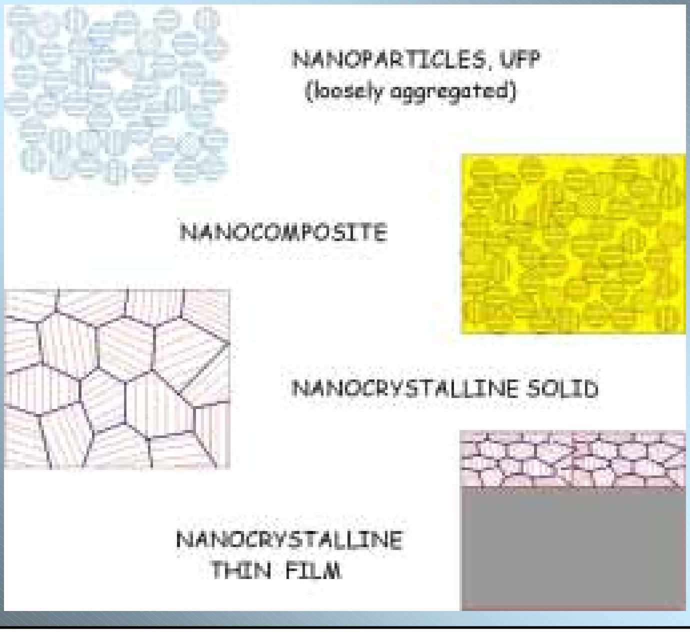
OUTLINE

NANOCRYSTALLINE THIN FILMS:
- Motivation for study

SYNTHESIS:
- Laser ablation
- Sputtering

APPLICATION:
- Semiconductors (CdS/ZnO)
- Superconductors (Nb)
- Metals (Ag, Cu)

NANOMATERIALS



NANOMATERIALS: APPLICATIONS (1)

- **INFORMATION STORAGE**
  - audio/video tapes, high density recording
- **OPTICAL COMPUTERS**
  - quantum dots, NLO devices
- **SOLAR CELLS**
  - photovoltaic (electricity), water-splitting (H_2)
- **ENVIRONMENT**
  - air purification (chemisorption of toxic gases)
  - water purification (metal NP bind chlorocarbons)
- **CATALYSIS (high surface area)**

NANOMATERIALS: APPLICATIONS (2)

☐ **HIGH PERFORMANCE CERAMICS**

low temp. densification,
superplasticity (formability)

☐ **MAGNETIC FLUIDS**

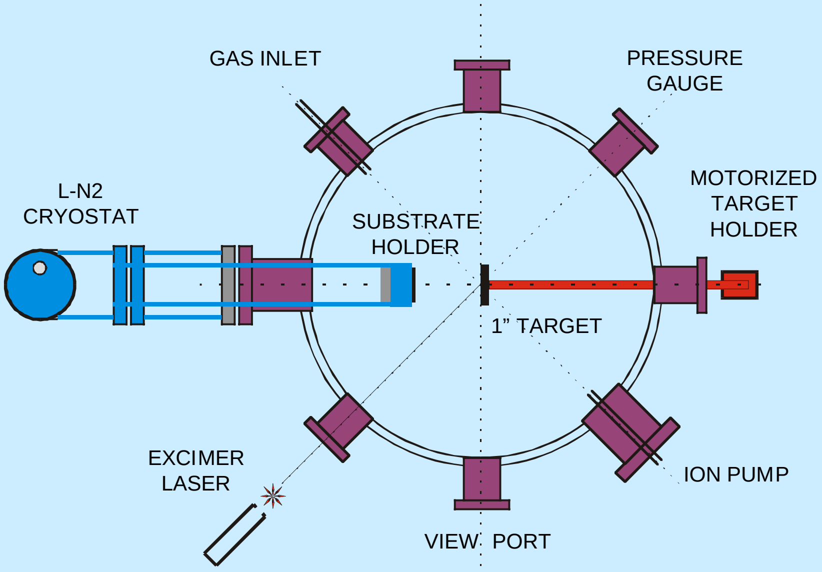
rotating axis seals in motors and HDD
ink-jet printers

☐ **MAGNETIC REFRIGERATION** (magnetocaloric effect)

adiabatic demagnetization using SPM particles

☐ **OPTICAL PROPERTIES** (stained glass)

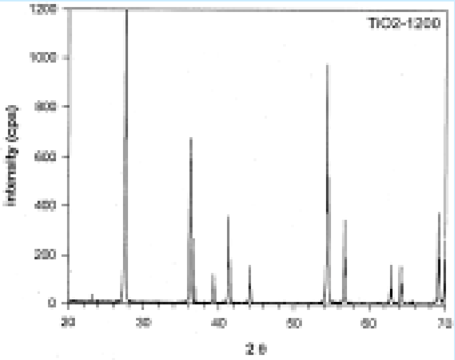
NANCRYSTALLINE FILMS BY LASER ABLATION



PROCESS PARAMETERS

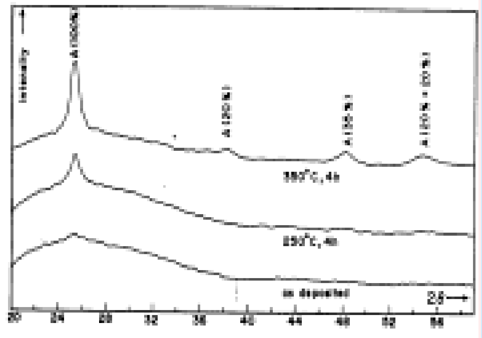
- **Laser: KrF Excimer, 248 nm**
- **Laser power: 0.5 – 0.6 J**
- **Rep rate / pulse width: 10 Hz / 25 ns**
- **Ambient gas: Oxygen**
- **Gas Pressure: 10 – 500 mTorr**
- **Substrate Temp.: 100 – 300 K**
- **System Geometry: T-S = 5 cm (oscillatory target scanner)**

NANO-TiO2 BY PLAD

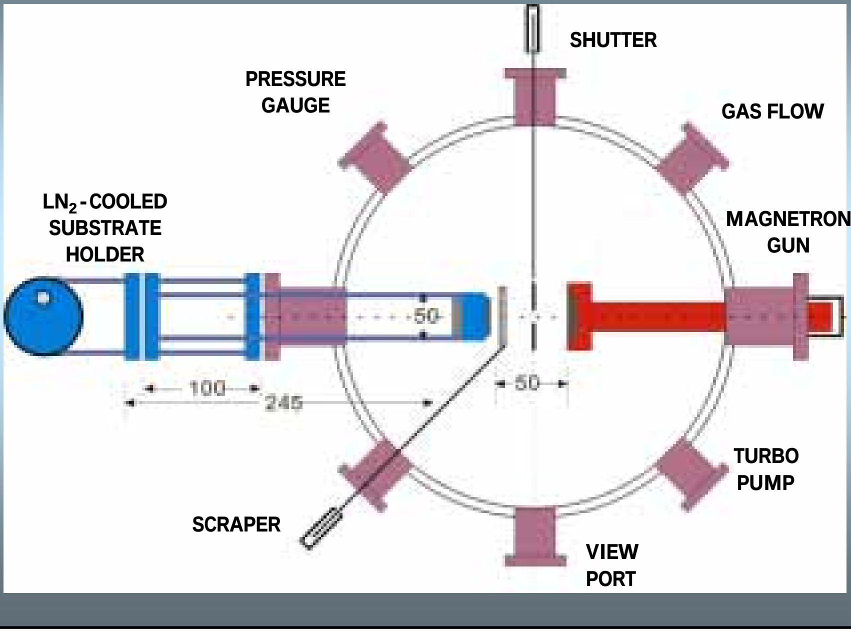


Target = Rutile (bulk)

Product = Anatase (nano)



SPUTTER SYNTHESIS OF NANOCRYSTALLINE FILMS

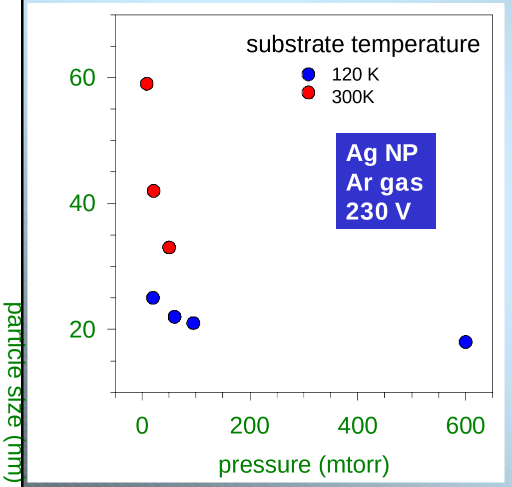


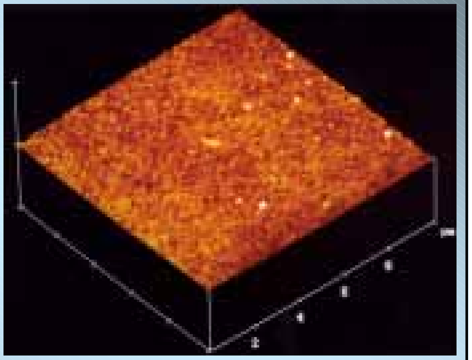
PROCESS PARAMETERS

- Sputtering Gas Pressure: 10 – 500 mTorr
- Substrate Temperature: 100 – 300 K
- Nature of Sputtering Gas: He, Ne, Ar, Kr, Xe

  (gas mixture for reactive sputtering)
- Sputtering Voltage: 100 – 300 V
- System Geometry: T-S = 5 cm

SIZE CONTROL

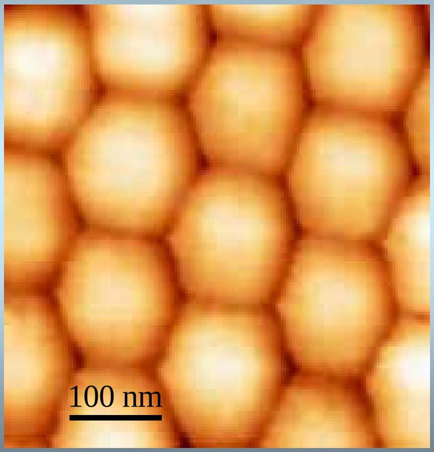




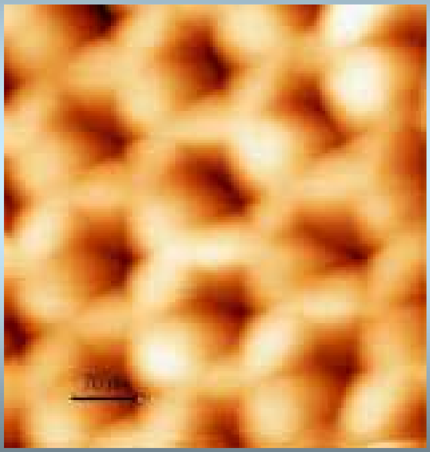
AFM: Ag NP / quartz

Manipulation and control at the nanoscale:

Nano-porous self-organized alumina templates
for application as photonic band-gap materials

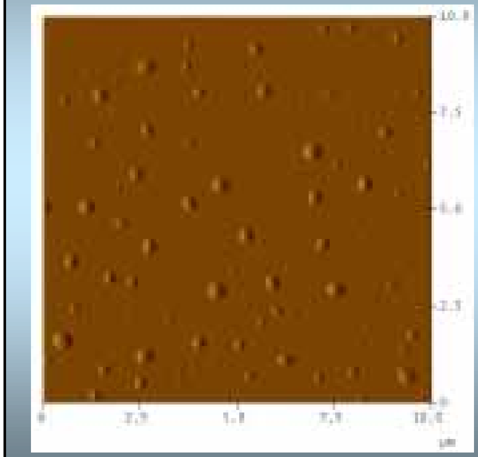


before opening of pores

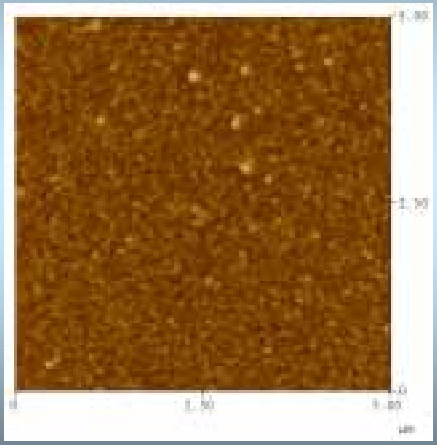


after opening of pores

Controlled sputter deposition through alumina template



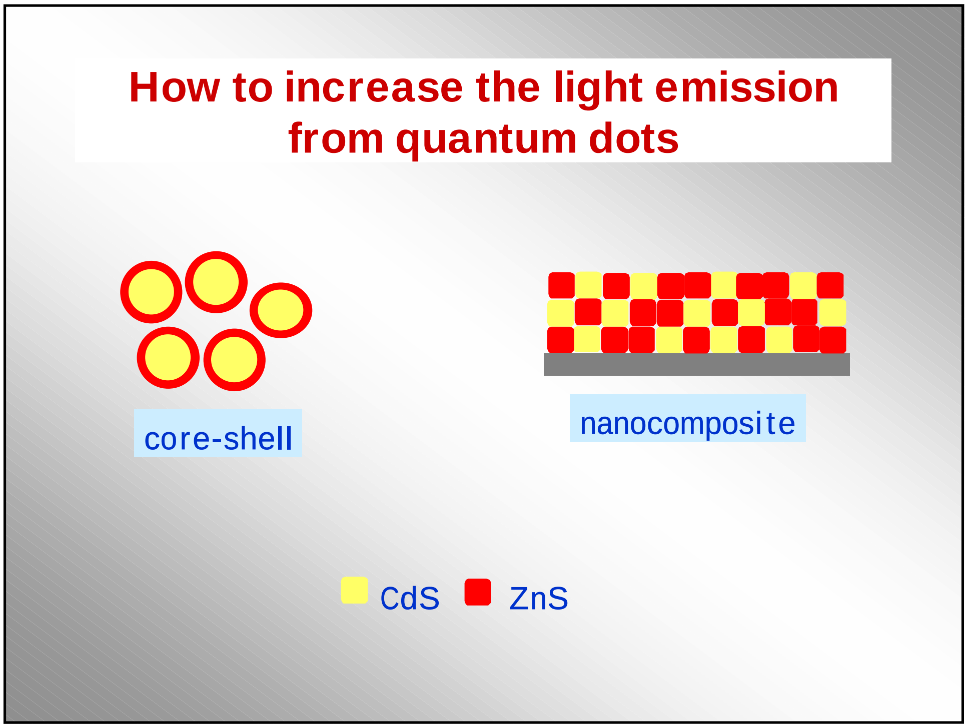
Cu on Si: templated region



Cu on Si: untemplated region

Application of nanocrystalline semiconductors: Problem issues

- Non-radiative decay channels → reduced QE for PL emission
- Surface electronic states need to be passivated
- Core shell structure
- Protein encapsulation
- Nanocomposite formation

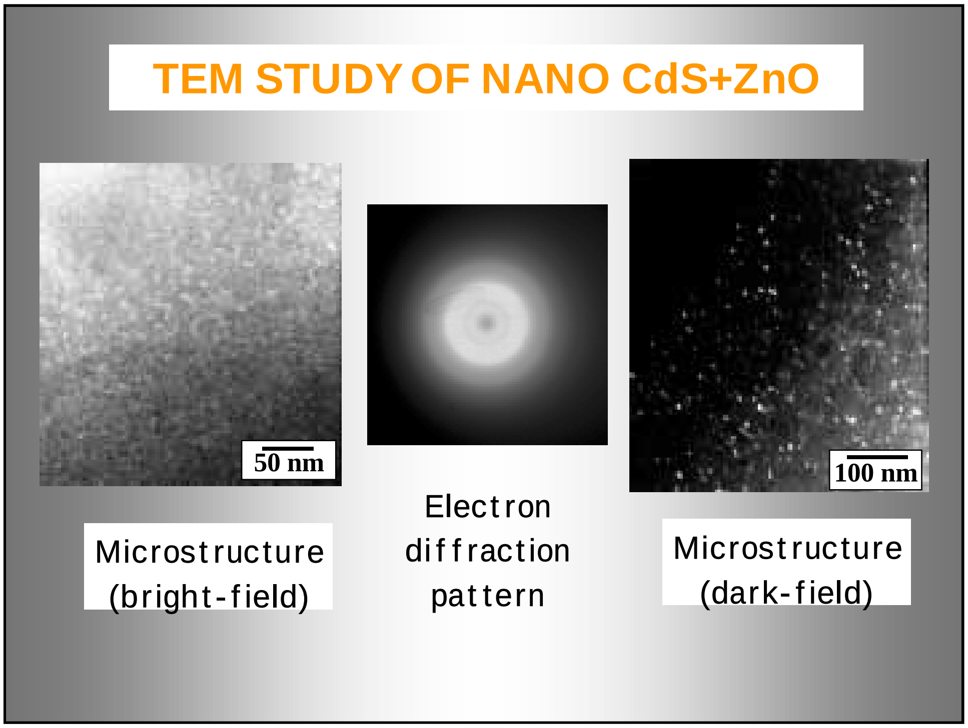


How to increase the light emission from quantum dots

core-shell

nanocomposite

🟨 CdS 🟥 ZnS



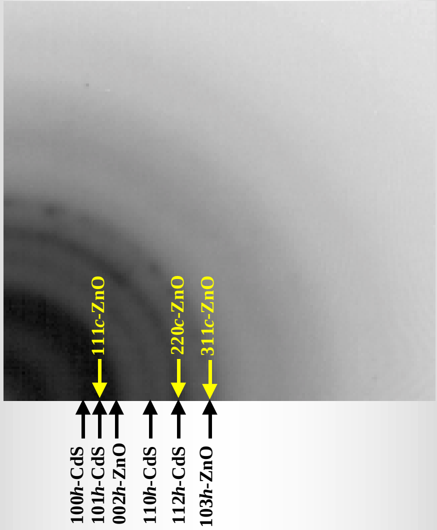
TEM STUDY OF NANO CdS+ZnO

Microstructure
(bright-field)

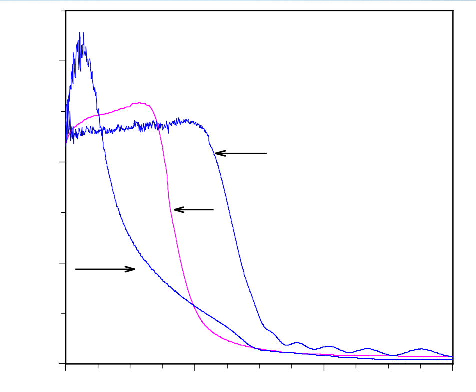
Electron
diffraction
pattern

Microstructure
(dark-field)

PHASE ANALYSIS USING TEM (DIFFRACTION MODE)



CdS-ZnO: LINEAR ABSORPTION SPECTRA

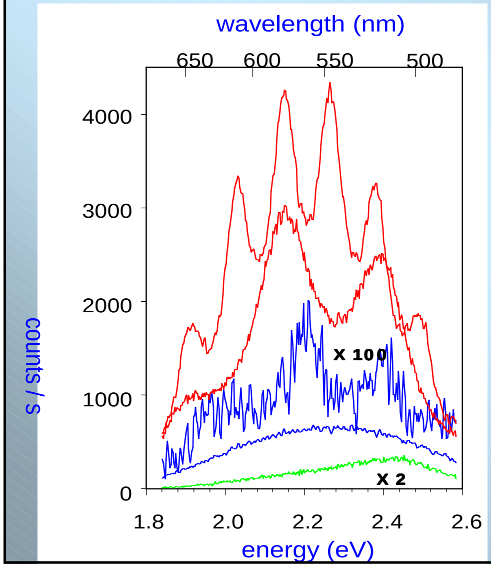


Bulk CdS: Eg = 2.4 eV
Bulk ZnO: Eg = 3.4 eV
Nano CZ: Eg = 2.8 eV
⇒ D = 2.8 nm

CdS+ZnO nanocomposite:

- ❍ restricted growth
- ❍ electronically passivate
- ❍ chemically passivated

PHOTOLUMINESCENCE EMISSION SPECTRA (λ_{ex}= 457.9nm)



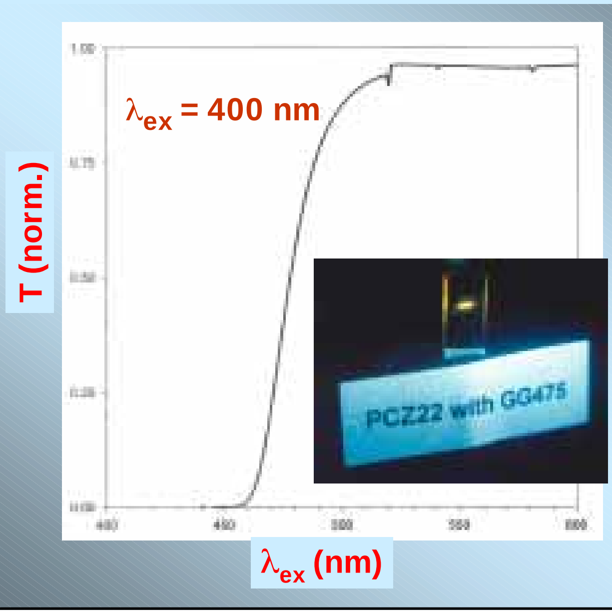
NANOCOMPOSITE:
Enhanced PL
Interference narrowing

Nano CdS-ZnO
t=1.8μm, D=2.8nm
t=0.9μm, D=2.8nm

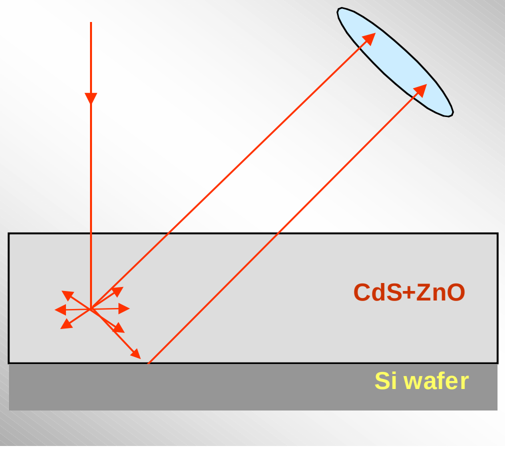
Nano-CdS
t=1.3μm, D=5.2nm
t=0.2μm, D=2.4nm

Nano-ZnO
t=0.9μm, D=3.0nm

PHOTOLUMINESCENCE FROM CdS+ZnO



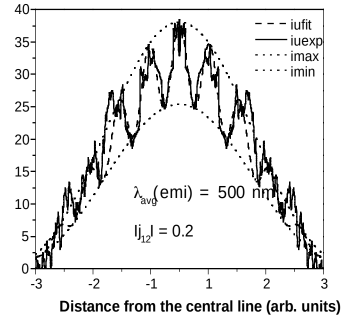
PHOTOLUMINESCENCE INTERFERENCE



COHERENT EMISSION FROM NANOPARTICLE ENSEMBLE !

COHERENCE OF PL EMISSION

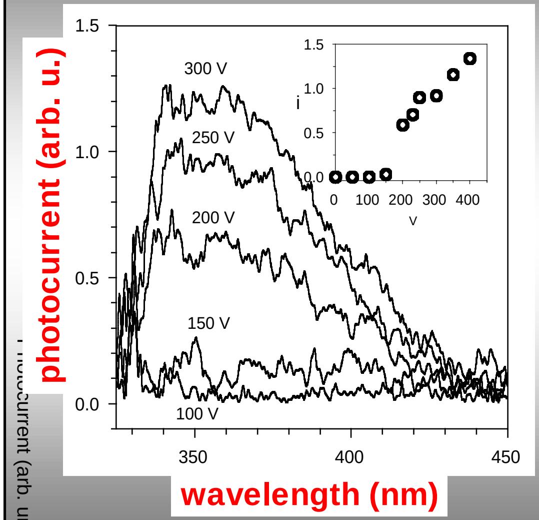
Young's Double Slit Expt.



Degree of Spatial Coherence = 0.2

IMPORTANCE: 1. Quantum information processing
2. Random lasing (repeated scattering from GB)

PHOTOCONDUCTIVITY DATA



I ∝ V (V > 150V)

Long-λ edge → E_g

Short-λ cut-off → Xe lamp spectrum

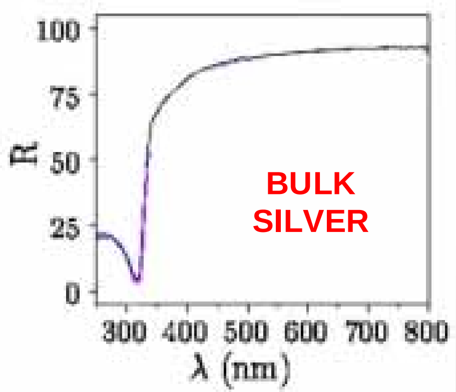
I_{max} = 13pA (355nm)

Breakdown at 450V

No saturation

Vasa, Taneja, Ayyub, Singh, Banerjee: J. Phys. Cond. Mat. 14 (2002) 281

Nanocrystalline Silver: Optical properties



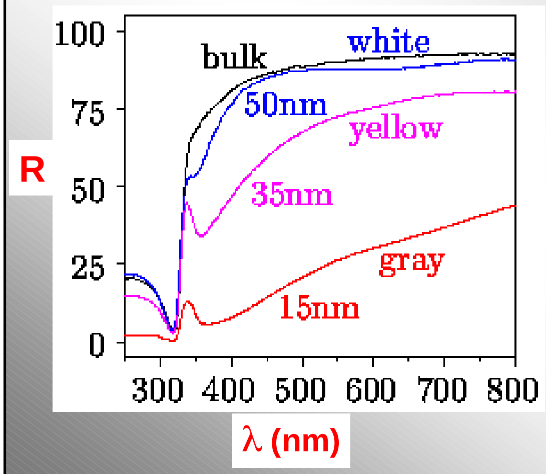
R is high when λ > 320 nm (below 3.2 eV)

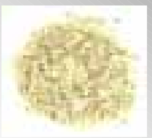
Sharp decrease at 320nm due to plasma resonance

Increase in R at low λ due to inter-band transitions

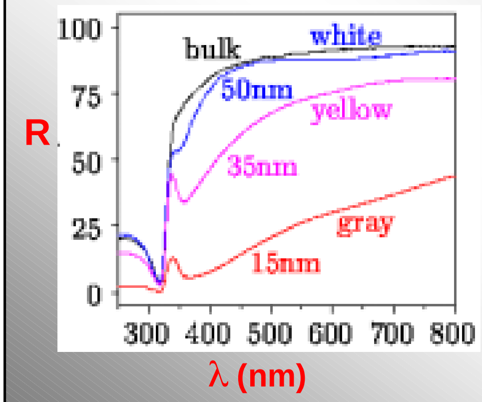
- ➔ **Colloidal metal particles known for thousand years**
- ➔ **Dense ensemble of metal NP: interparticle interactions**

Nanocrystalline Silver: Optical properties





Size dependence of optical properties



SPR peak in 50 nm sample

With decreasing size:

o R decreases for all λ, but decrease is λ – dependent

o SPR becomes more intense and broader, but no change in position

Taneja, Ayyub, Chandra: Phys. Rev. B 65 (2002) 245412

Production of X-rays by interaction of ultra-short lasers with metal surfaces

Intense Laser Field

Ionization of metal atoms

Acceleration of electrons in the plasma region

Bremsstrahlung + inner shell excitation

How are X-rays produced by laser light?

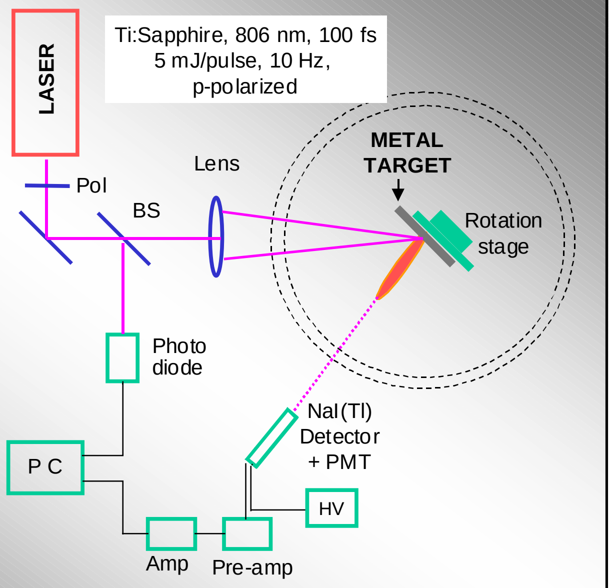
Enhanced X-ray emission from metal nanoparticles

POSSIBLE APPLICATIONS:

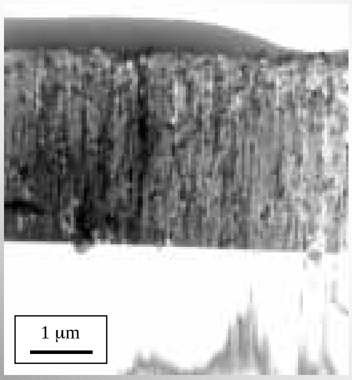
- Nano-lithography
- Chemical dynamics
- Time-resolved x-ray diffraction

Problem: Yield needs to be enhanced

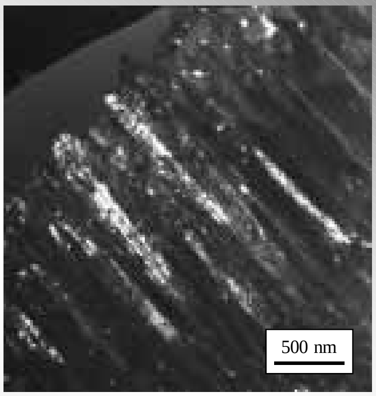
Experimental set-up



Nano-Cu/Si: Sectional TEM (low mag)



bright field



dark field

Bremsstrahlung emission from flat target and nanocrystalline target

$\theta = 10^{o}$, Ω = 720 μSr

I = 2.10^{15} Wcm^{-2} / pulse ⇒

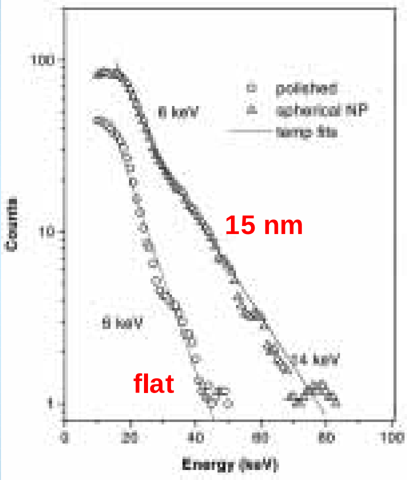
2mJ © 40 μm (spot size)

Total energy emitted / laser pulse:
(assume isotropic emission)

Polished Cu target = 2.2×10^{-12} J

Nano-Cu coated target = 1.0×10^{-11} J

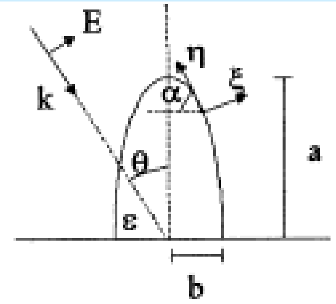
Hard X-ray emission is much higher



Model calculations

Nanoparticle metal target ⇒ collection of hemispheroids of permittivity ε, embedded on a flat substrate in vacuum.

Laser field (ampl. = E) incident at angle θ to the major axis.



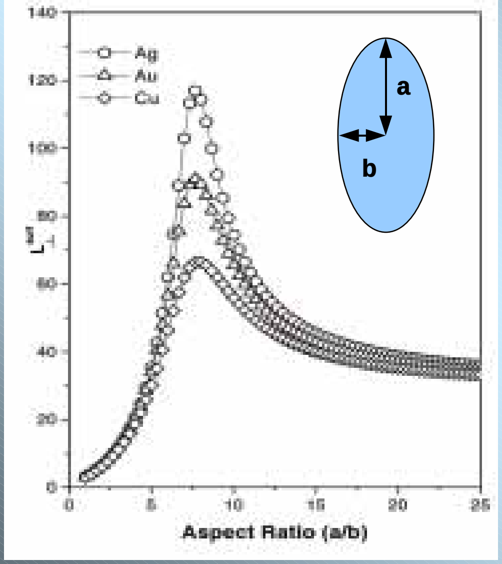
Electric field at **r** on the hemispheroid: $E(r) = E_L(\text{surf}) + E\cos\theta$

E_L(surf) is the enhanced local field at the surface, given in terms of the local field correction factors (cf. SHG, SERS, etc.)

Assume: $\varepsilon(\text{nano}) = \varepsilon'(\text{bulk}) + \mathbf{i}\,\varepsilon''(\text{bulk})\,(1 + \mathbf{l}/b)$ [**l** =mfp]

Int (0) / Int (in) ≈ 1.4 (α = $\mathbf{0^{0}}$, θ = $\mathbf{10^{0}}$)

Optimization of x-ray yield from nanoparticles



Field enhancement:

- ❍ Resonant with a/b
- ❍ Max for a/b = 8
- ❍ Max for nano-Ag

Bremsstrahlung emission from spherical and ellipsoidal Cu nanoparticles

$\theta = 45^o$, $\Omega = 22$ mSr

$I = 6.10^{14}$ Wcm^{-2} per pulse

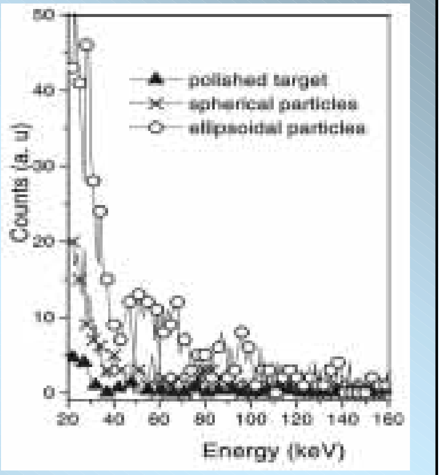
Total energy emitted / laser pulse:

Polished Cu target = 4.2×10^{-14} J

Spherical Cu NP = 1.4×10^{-13} J

Ellipsoidal Cu NP = 5.7×10^{-13} J

Ellipsoidal Cu NP yields 13-fold enhancement



Rajeev, Taneja, Ayyub, Sandhu, Kumar: Phys. Rev. Lett. 90 (2003) 115002

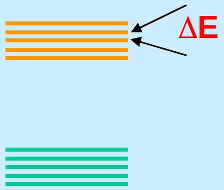
SIZE EFFECTS IN SUPERCONDUCTING Nb

Multiplicity of length scales:

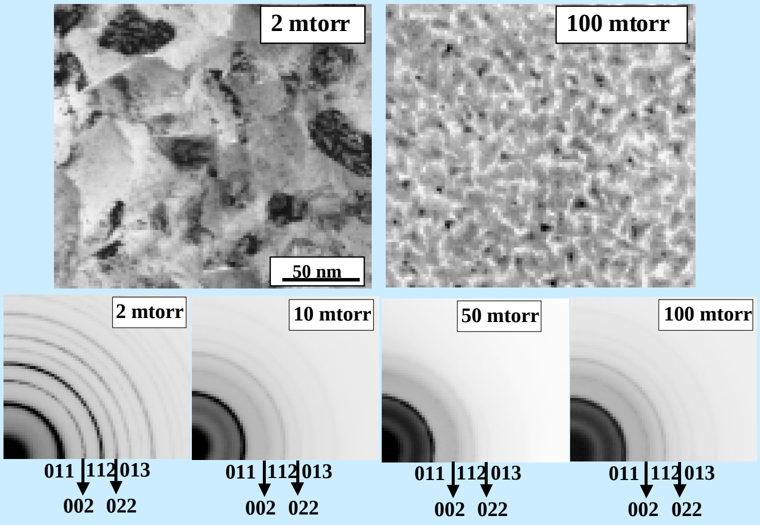
Ginzberg-Landau Coherence Length
Magnetic field penetration depth
Length scale corresponding to
ΔE ~ superconducting energy gap

+

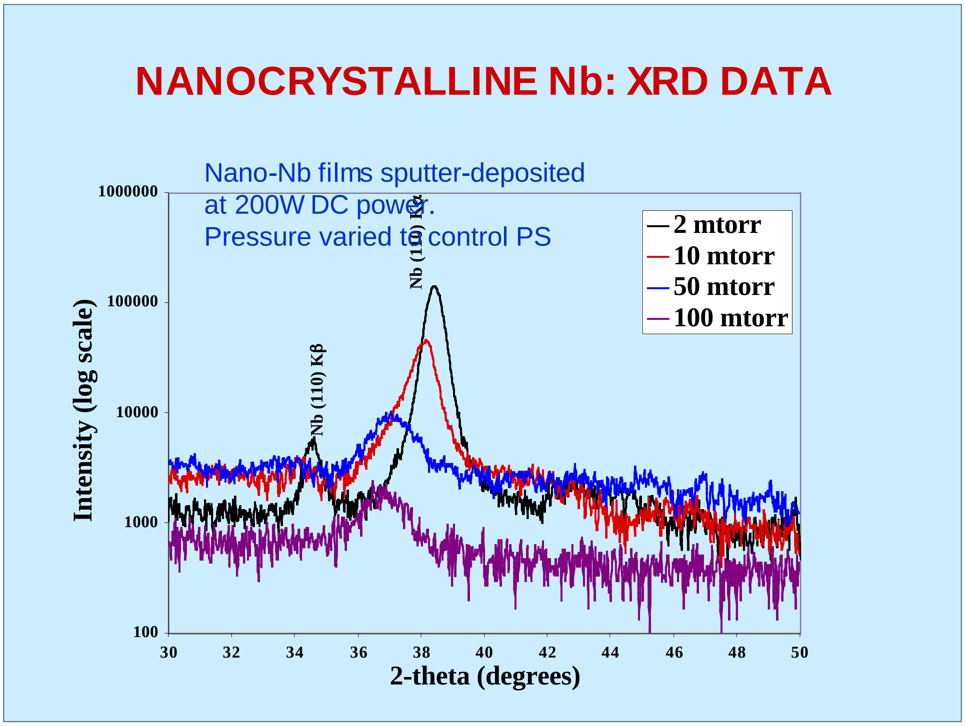
Size-induced structural distortions ?



NANOCRYSTALLINE Nb: TEM DATA

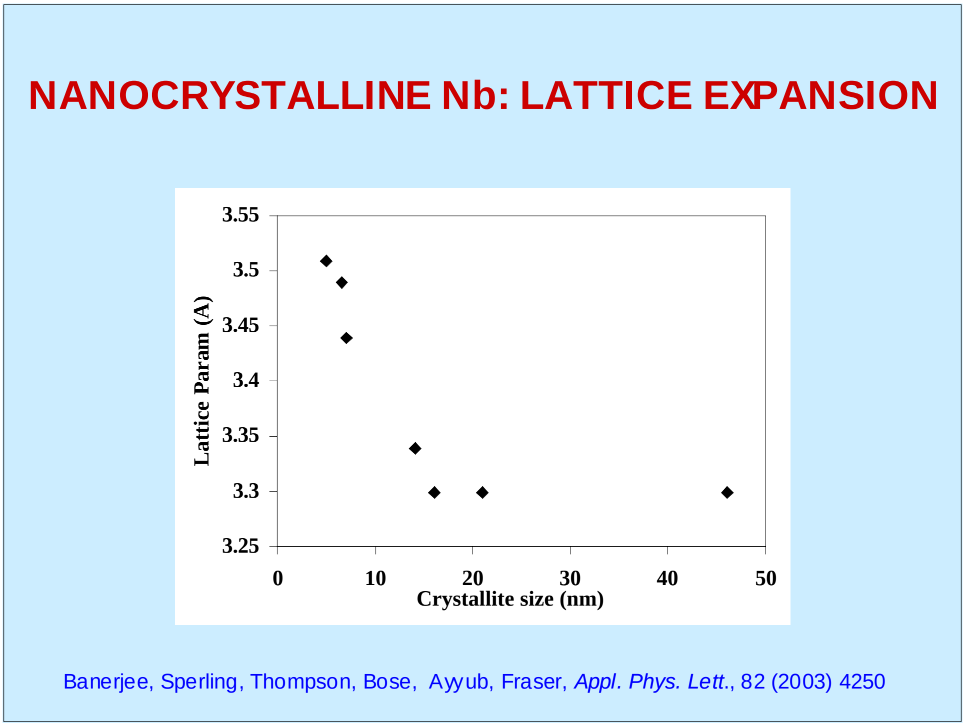


No change in cubic (bcc) symmetry with decreasing size



NANOCRYSTALLINE Nb: XRD DATA

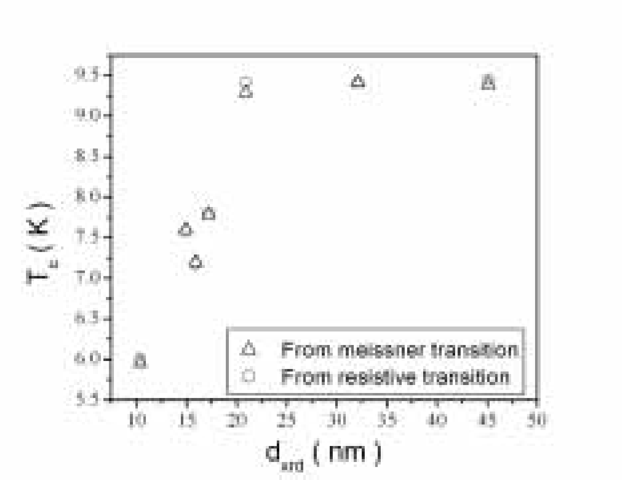
Nano-Nb films sputter-deposited
at 200W DC power.
Pressure varied to control PS



NANOCRYSTALLINE Nb: LATTICE EXPANSION

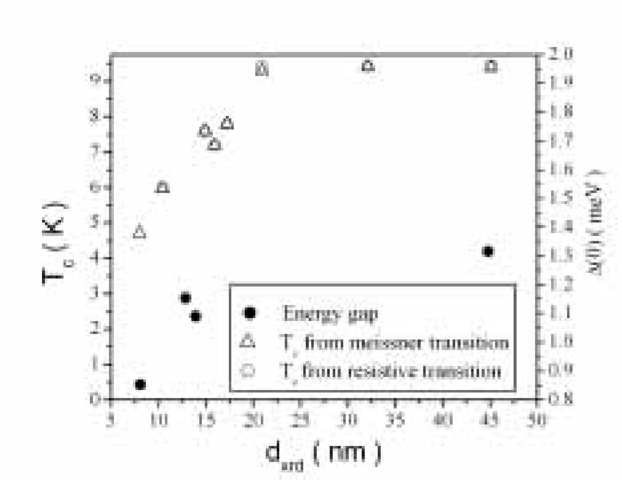
Banerjee, Sperling, Thompson, Bose, Ayyub, Fraser, *Appl. Phys. Lett.*, 82 (2003) 4250

NANOCRYSTALLINE Nb: Superconducting properties (T_C)

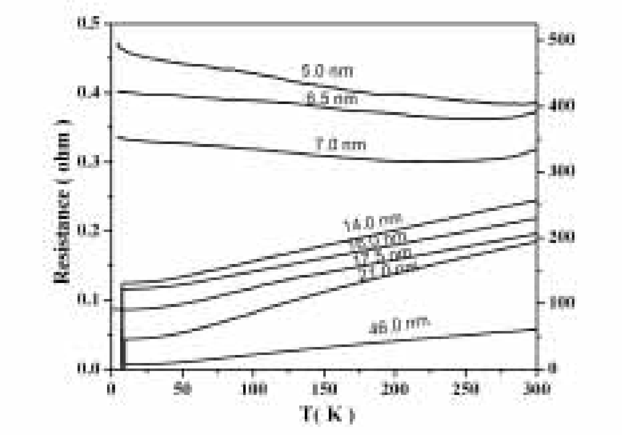


NANOCRYSTALLINE Nb: SC properties

(band gap from point contact spectroscopy)



NANOCRYSTALLINE Nb: SC properties
(size-induced metal-insulator transition)

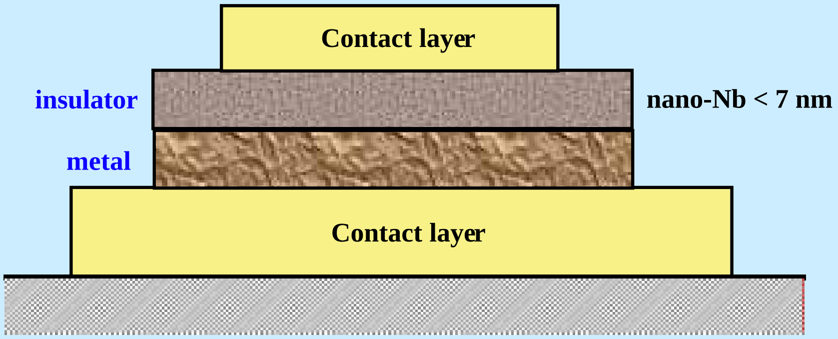


INSULATOR

METAL / SC

Critical PS
≈ 7nm

NANOCRYSTALLINE Nb: APPLICATION
Novel junctions and device structures


Contact layer

insulator

nano-Nb < 7 nm

metal

Contact layer

Novel metal-insulator junction with electronically abrupt but chemically continuous interface !

CONCLUSIONS

Size can be used to tune material properties and obtain novel crystallographic phases.

Nanocomposites provide an additional degree of freedom. Properties need not be linear combination of constituent phases.

CO–WORKERS

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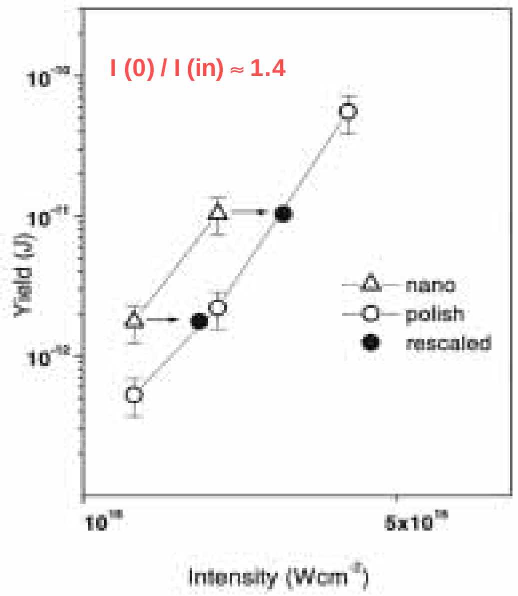
Rajarshi Banerjee (OSU)
Bhanu Pratap Singh (IIT-B)
Ramesh Chandra (Meerut)
Aneet Gupta (BARC)
Bijan Rao (VCU)

Rescaled integrated emission vs. laser intensity



I (0) / I (in) ≈ 1.4

Emission from
NP-coated surface
≡
Emission from
polished surface

with rescaled
(enhanced) intensity