

# **Nano-Materials and Nano-Technology**

*(Lecture delivered on 24th Jan. 2003)*

**Prof. K. L. CHOPRA**

**Former Director**

**Indian Institute of Technology, New Delhi-110016**

---



Prof Kasturi Lal Chopra was born at Chahal Kalan, Punjab (Now Pakistan) in 1933. He did his matriculation from DAV in 1948 and secured 1st position. After, completion of his Masters in Physics in 1954 from Delhi University he took his Ph.D in Low Temperature Physics as World University Service Fellow from University of British Columbia, Canada. After that he was post doctoral fellow at Royal Military college, Canada and then Max Planck guest scientist at the Mtz Haber Institute, Berlin. He took the assignment as group leader at Philco-food scientific laboratory, Blue Bell and then at Ledgemont Laboratory, Kennecott Copper corp., USA. He joined IIT Delhi in 1970 as a senior professor to head the physics department and there he established school of solid state physics. He founded Thin Film Laboratory, a unique collection of facilities in one lab and is considered one of the top thin film laboratory in Asia. After serving IIT Delhi for 17 years as senior Professor; Head, Physics and Energy Department; Dean, Post graduate studies; and Industrial Research & Development, he took over as Director IIT Kharagpur. He was there for 2 terms of his Directorship till 1997. He established another important Microscience Laboratory in the department of physics at IIT Kharagpur. Later he joined IIT Delhi as IREDA Chair Professor, Govt. of India.

He has guided more than 60 Ph.D theses and have 5 US patents and published over 450 papers and have authored and co-authored books on "Thin Film Phenomena", "Thin film device application", "Thin Film Solar Cells". Several published papers are classical citations and "Thin Film Phenomena" continues for the last 30 years considered as "bible" of the field. He has served on the editorial boards of several international journals and has been consultant to many international industries.

He is an elected fellow of America Physical Society, Indian National Science Academy, Indian Academy of Sciences and Indian Academy of Engineering. He has delivered several memorial lectures and is recipient of several awards: Bhatnagar prize (Physics), Bhatnagar award (Energy), FICCI award (Science & Technology), Bhasin award (Energy), Bhabha award (Applied sciences), INSA Krishnan Memorial Lecture award, Distinguished Material Scientist (MRSI) award.

## *The excerpts of the lecture delivered by Prof. K. L. Chopra*

Nano, a Greek word, means dwarf. Science has, however, given this dwarf a numerical value of "one billionth". A nanometer is thus one billionth of a meter, or  $10\text{\AA}$ . As a very general definition, materials/structures with one or more physical dimensions having the size of some nanometers are now called nano-materials/ nano-structures. The processes utilized to create such materials/structures, and technologies to exploit these to fabricate devices with/ without integration with suitable micro/macro dimension materials/ structures /devices are termed as nano-technologies. With increasing use of the word NANO in popular science and consumer applications, sub-micron size materials and devices are also loosely included in the nano-categories.

Nano-materials are low dimensional materials which are classified by physicists as zero, one, or two dimensional, depending on whether three, two, or one dimensions are small enough in size (which is of course relative to the size of the probe entities) so that classical laws of physics are not applicable with confidence. Some typical examples of low dimensional materials and devices are listed in the following:

- 2-D : Thin films, Thin foils, Multilayers/ Superlattices, Planar interfaces, Surfaces, Grain Boundaries, Quantum wells, Langmuir-Blodgett Films
- 1-D : Whiskers, Fibres, Nano-tubes, Quantum wires, Long Chain molecules
- 0-D : Quantum Dot, Nano-powder, Colloids, Aerogel

The structure of the surface of any material differs markedly from that of the bulk. The same is true of grain boundaries and interfacial regions between grains. Both cases are nano-metric in dimensions and are good examples of nano-materials. Indeed, Surface Science dealing with such phenomena as adsorption, desorption, wetting, catalysis, passivation, tribology, epitaxial growth, etc. is a good example of Nano-Science. The curiosity of understanding how matter is created by the nano-metric size building blocks of atoms /molecules/ions has been a challenge for researchers in the field of two dimensional, thin films for over a century. With dramatic developments in ultra high vacuum technology, computer controlled very precise monitoring and digital imaging techniques, and with the advent in 1980's and 90's of nano-analytical TEM and SEM related techniques, and with the availability of

reprographic and lithographic processes at nano-metric scale, it has been possible to literally see the interacting atoms in the process of creating matter. Further, the creation of matter and its tailoring and engineering at a nano-metric scale in different dimensions is now common place. Interestingly, unprecedented advances in understanding and handling of DNA and RNA, the live molecular machines of nano-metric size, have led to simultaneous interest in rapid development of nano-bioengineering. Consequently, a wide diversity of nano-materials and nano-technologies are emerging and, in some cases, converging synergetically.

## SYNTHESIS TECHNIQUES

Creation or synthesis of nano-materials can be achieved by a large no. of some very old techniques which are extensions of thin-film technologies, and some new ones. Depending on the common characteristics, these techniques are listed in the following:

- *Physical* : Rapid thermal evaporation sublimation in a controlled ambient poor vacuum, Laser ablation, Direct Atomic Beam writing
- *Plasma Processes* : High rate glow discharge/ion beam/microwave sputter deposition, Arc evaporation, Plasma enhanced chemical vapour deposition, Cluster beam deposition, Plasma etching
- *Mechanical* : Ball milling, Plastic Deformation, Atomic Force microscopy
- *Electrochemical* : Nano-plating, Pulsed electro-deposition, Electrophoresis, Rapid Anodization, Faraday microprobe
- *Chemical* : Spray Pyrolysis, Hydrolysis, Pyrophoric, Co-precipitation, Colloidal, Sono-chemical, Laser CVD, Surface chemical-conversion, Sol-Gel, Aero and Xero-Gel, Chemical Solution/ Bath deposition, Self assembly processes, Chemical Force microprobe
- *Lithographic/ Reprographic* : Deep UV/X-ray /e-Beam /Ion-beam lithographies, Plasma/ Ion etching, Dry lithography/ reprography using chalcogenide films, Chemical and Soft lithographies
- *Electrostatic* : STM based tip-field dependent mass transfer techniques
- *Magnetic* : Magnetic Force microprobe

Each technique has its own unique characteristics which depend on numerous operating parameters. To appreciate this point, it is instructive

to look at the basic processes preceding thin film formation as given below in Fig. 1.

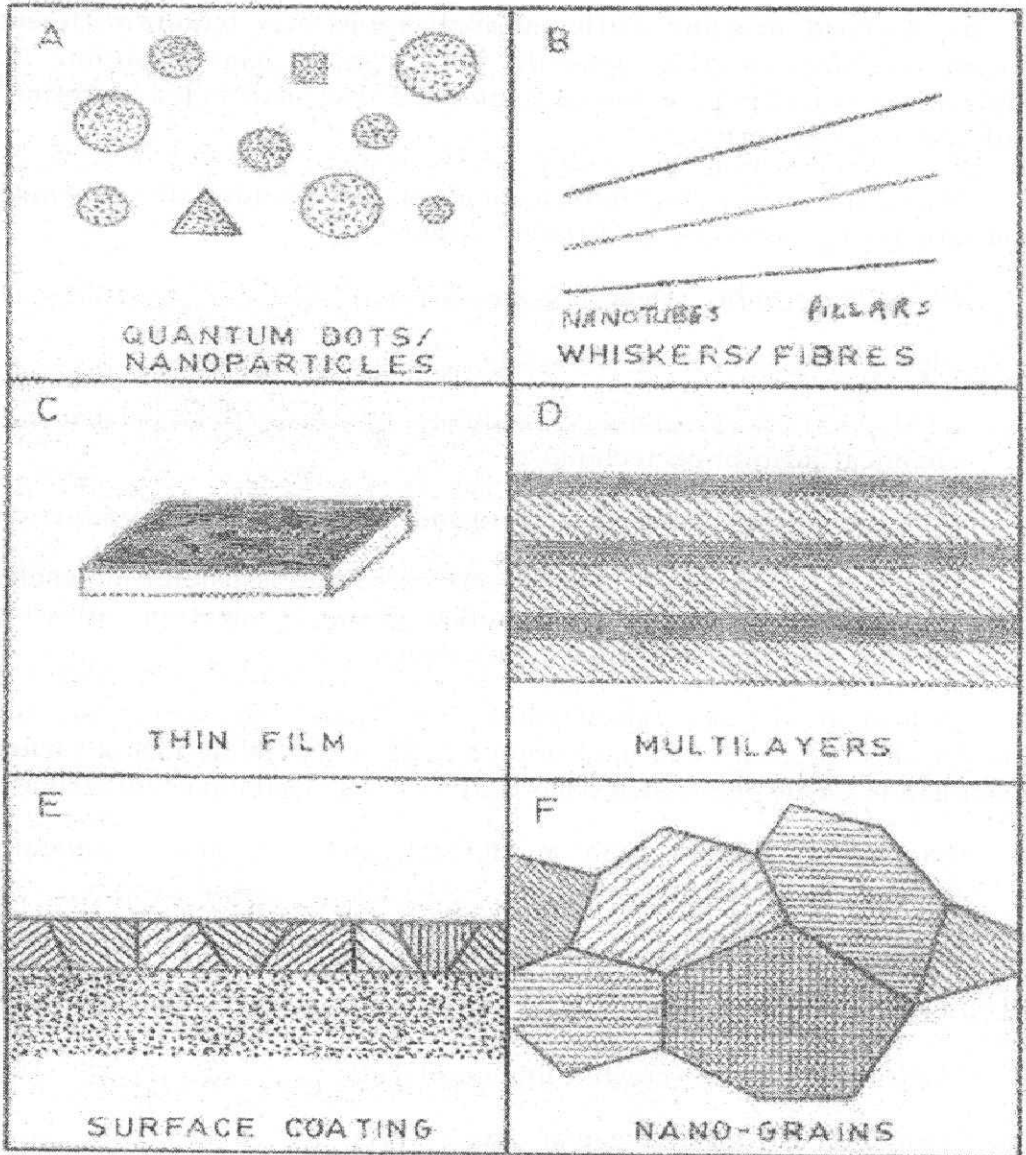


Fig. 1 : Block diagram of processes underlying the nucleation and growth of thin films

Each step allows the possibility of modifying the size, shape and their distribution. Depending on techniques and materials, cap-shaped, spherical, whiskers, discs, hollow tubes etc. can be obtained. Some techniques, particularly chemical, make it possible to prepare nano-

materials and nano-composites in large commercial quantities. On the other hand, scanning nano-probe techniques (STM, AFM, and numerous variants) allow controlled formation of atomic scale holes, hills, valleys, or any designed structure. Different applications may require different shapes and sizes of nano-materials. For example, nano-electronic IC applications would require cloned shapes and sizes distributed uniformly with a density at least  $10^{12}$ .

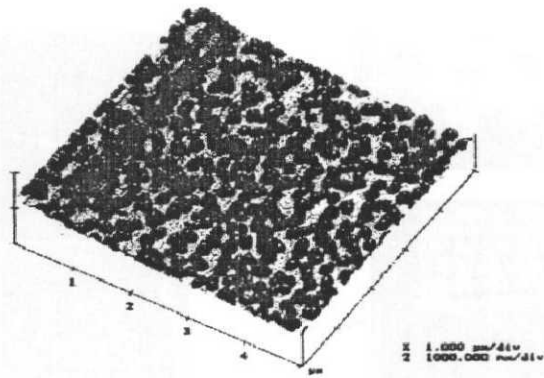
Micro and nano-lithographic techniques, listed below, allow shaping and structuring materials in different forms.

- *Photolithography* : Deep UV and X-ray
- Electron and Ion beam lithography
- STM/ AFM based scanning probe lithography using field/ mechanical/ chemical adsorption techniques
- Soft lithography using special organic molecules for reproduction
- Chemical lithography using nano-structured self-assembled molecules (e.g., thiol) by carefully controlled chemical reaction, allowing contact printing, imprinting, embossing, etc.

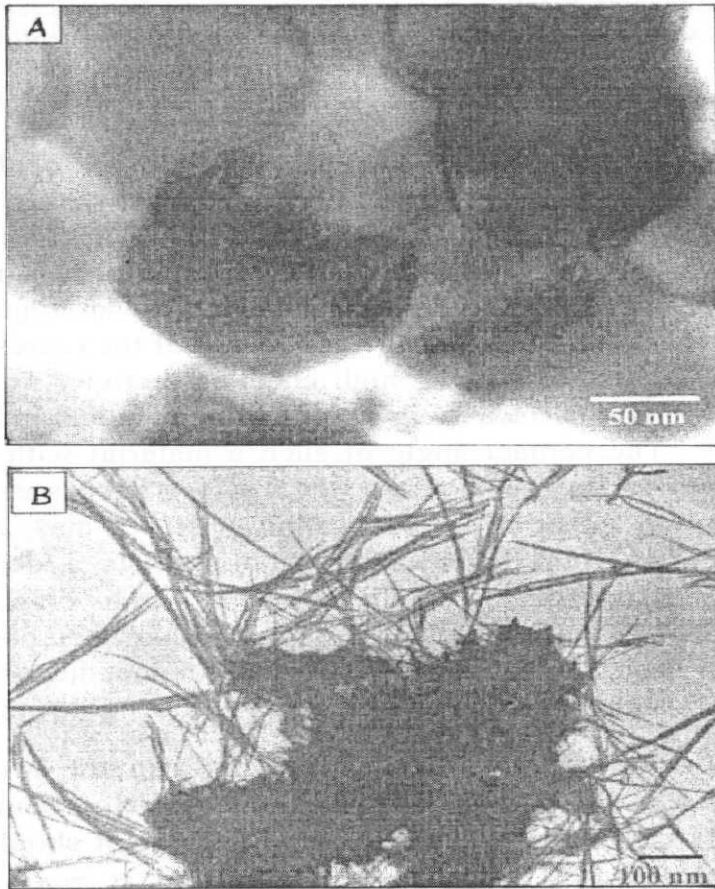
A host of so-called self-assembly techniques using clever but well known ideas of controlled nucleation and growth of materials are being exploited to create engineered nano-materials. The techniques utilized are:

- Nucleation centers such as defects, steps, ledges, chemically active/ sensitized sites
- Selective surface chemical reactions
- Chemical writing with beams of photons, electrons, or ions
- Sensitized patterns created lithographically
- Langmuir-Blodget molecular mono layers

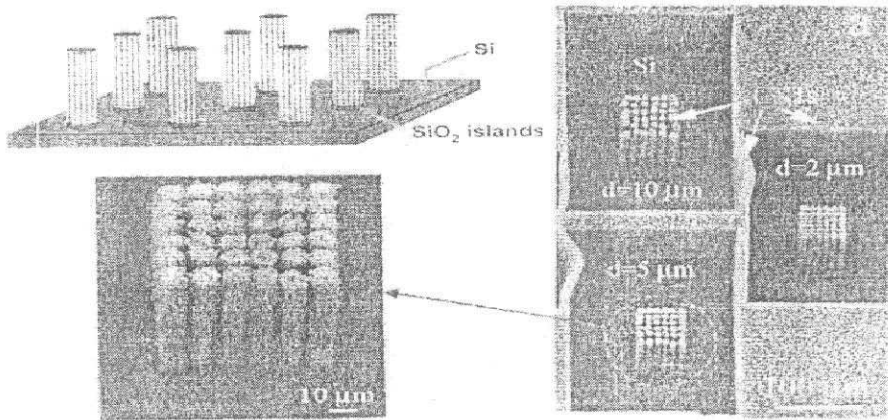
Some examples, taken from our work at IIT Delhi and Kharagpur, of nano-materials such as Cup prepared by activated reactive evaporation, and Y-Ba-Cu-O prepared by a pyrophoric process are shown in figures 2 and 3. An example of carbon nano-tubes grown selectively by a plasma CVD process on  $\text{SiO}_2$  island-created lithographically on Si substrate is shown in Fig. 4.



*Fig. 2 : An AFM picture of  $\text{Cu}_2\text{O}$  nano-particle prepared by an activated reactive evaporation process*



*Fig. 3 : Electron micrographs of nano-particles of YBCO prepared by pyrophoric process (A). and nano-whiskers of YBCO prepared from the polymerized citrate precursor (B)*



*Fig. 4 : Scanning Electron micrograph of plasma CVD processed carbon nano-tubes grown selectively on SiO<sub>2</sub> islands created lithographically on Si substrate*

## SOME PROPERTIES

With decreasing size, the surface to volume ratio of the material increases. At nano-metric sizes, surface is the dominant material. For example, a 20Å diameter spherical particle has 60% of its atoms on the surface. Being a discontinuity, surface gives rise to unsatisfied and dangling bonds. The apparent physical density of an aggregate powder of such particles would be a small fraction that of the corresponding bulk material. Large surface area of high chemical activity due to dangling bonds implies a large surface energy with serious chemical and metallurgical consequences. The contact angle of such a material with its own bulk material will invariably be non-zero which affects processes of nucleation and growth of a material created ab-initio. If we may apply laws of thermodynamics, Gibbs-Thomson relation predicts a decrease of the melting point, proportional to the surface energy and inversely proportional to the size. Such reduction of the melting point has been observed in thin films and nano-particles of metals, insulators, semiconductors and polymer chains. Fig. 5 shows such an effect observed on gold nano-particles.

The lowering of the melting point, as also the lowering of the activation energy for surface diffusion, the sintering characteristics of such powders are modified drastically. In general, it should be possible to achieve sintering at lower temperatures and at much higher rates. Fig. 6 shows data for the size dependent sintering of yttrium-barium-copper-oxide nano-powder. It is an excellent example of achieving pressureless sintering of this technologically important material at



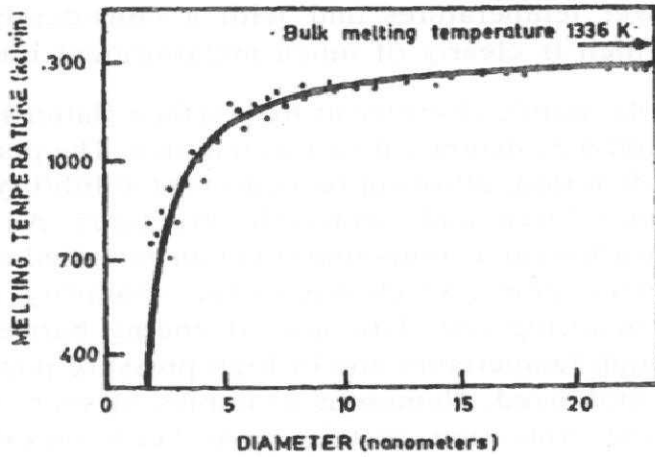


Fig. 5 : Size dependence of the melting point of gold clusters

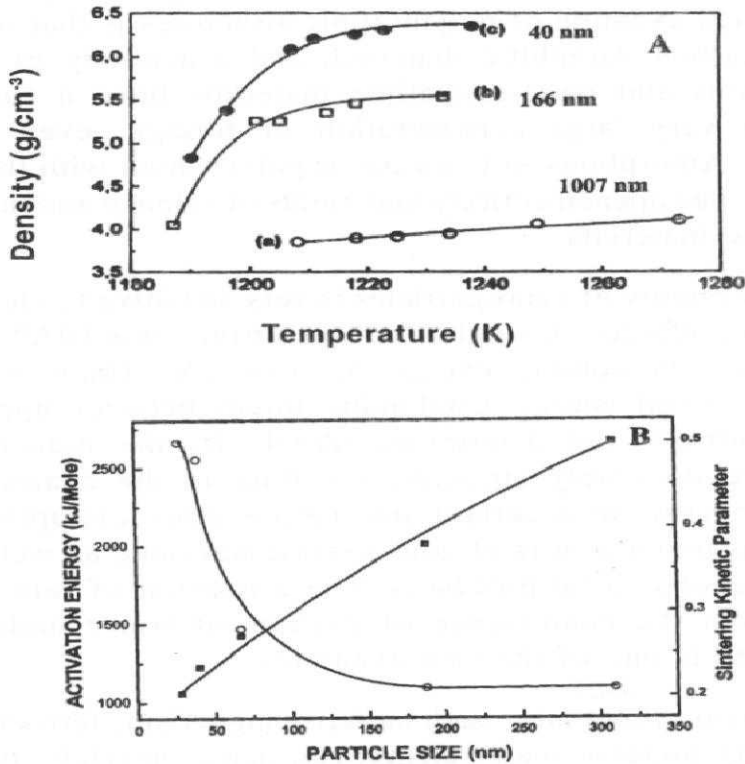


Fig. 6: Pressureless sintering characteristics of YBCO nano-powder showing the size dependence of apparent density of sintered material with sintering temperatures (A), and the activation energy & sintering kinetic parameter of the process, (B).

relatively much lower temperatures and with a considerably reduced activation energy which is clearly of much metallurgical interest.

The considerable atomic disorder at the surface flattens the energy versus positional coordinate diagram for a given lattice. The phase diagram becomes fuzzy and distorted, allowing relaxation of solubility of foreign atoms, and formation of new and metastable structures. As a result, it is possible to prepare alloys and compounds over an extended composition range, often even with atoms which have little solubility in the host lattice. Because of lowering and flattening of energy barriers between metastable phases, high temperature and/or high pressure phases of such materials are easily stabilized. Numerous examples of such a behaviour in chalcogenides and transition metals have been reported in the literature. As an example-chromium films exhibit five different structures. Some general but empirical rules for the formation of the metastable phases have been enunciated by the author. Among the most dramatic and widely studied example of polymorphic structures is that of carbon, in amorphous carbon, Graphitic diamond, and a diversity of fullerene forms. Amorphous and nano-crystalline materials have a capacity to accommodate a very large concentration of foreign, even normally insoluble atoms. Amorphous Si is a case in point which with the help of several additives has opened entirely new fields of science and technology of optoelectronic materials.

The surface energy of nano-particles is very sensitive to electrostatic and magnetostatic effects. A single electron sitting on a  $10\text{\AA}$  spherical particle enhances its volume energy by 1.44 eV which is a large contribution to its self energy. Coulombic forces between approaching charged nano-particles are determined largely by the induced image forces which are invariably attractive resulting in the coalescence of such particles to grow to a certain size before other disruptive forces take over. This phenomenon is of considerable nuisance as well interest in associated manufacturing processes. The formation of rain droplets, for example, from the coalescence of clusters of water molecules in upper atmosphere is one of the best examples.

All ferroic processes, such as ferromagnetism, ferroelectricity, and ferroelasticity undergo major changes in nano-materials. In case of magnetic materials, spins can be aligned and pinned at the surface or at the interface between two nanostructures, resulting in a giant magnetoresistance (GMR) effect due to enhanced scattering of conduction electrons. This GMR phenomenon observed in nano-powders, thin films

and multi layers has given birth to a new field of spin-electronics, or Spintronix which has already found applications in magnetic reading heads. Fig. 7 shows the GMR result for a Cu/Co multilayer structure and modification of its temperature dependence behaviour. As the size becomes comparable to the mean free path (mfp) of electrons and the corresponding deBroglie wavelength, we expect a host of mfp and quantization effects in a variety of electron and photon transport processes. Size dependent increase of band gap, relaxation of selection rules for optical transitions due to disorder, surface plasmon excitation, hot and ballistic transport of electrons, quantised thermal conductivity, etc. are only a few of the exciting effects which are being studied extensively in nano-materials in the form of quantum dots, quantum wires, quantum wells, superlattices, tailored grain boundaries, etc.

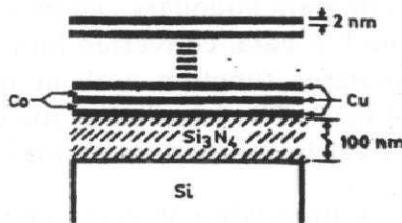
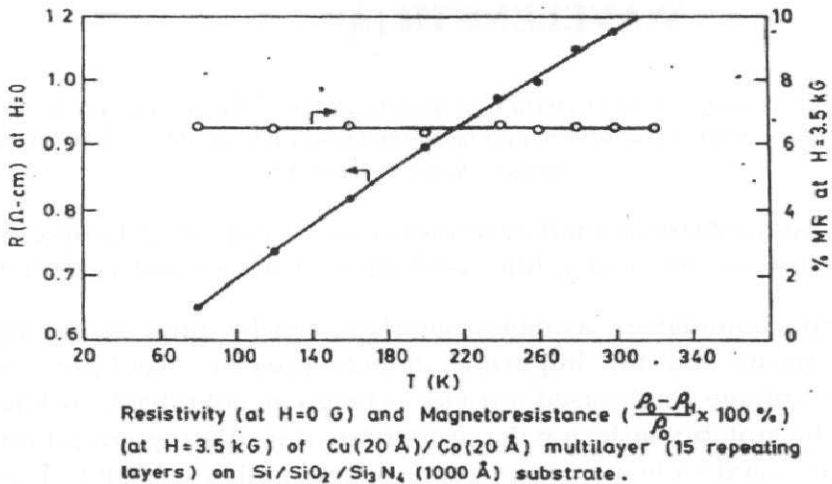


Fig. 7 : Temperature dependence of the zero field resistivity and magnetoresistance at 3.5kG of 20 layers of Cu (20Å)/Co (20Å) on Si/SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> substrate

Before the advent of superlattices, we used the same concept in our work to deposit nano-metric thin films of two materials alternatively in the form of multi layers of a certain periodicity, as shown in Fig. 8, to

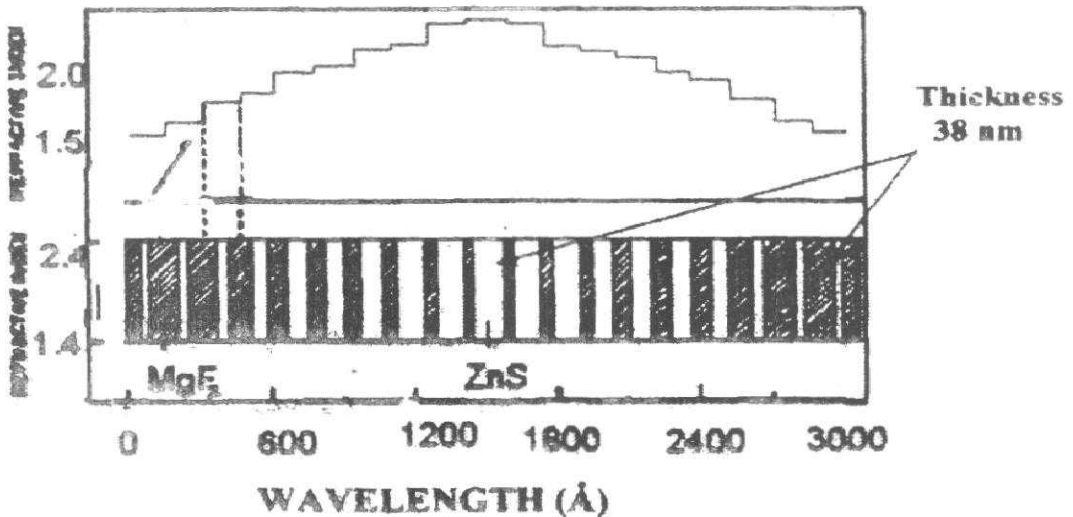


Fig. 8 : Reflectivity Vs wavelength of a graded index 35 layer interference filter, each layer consisting of alternating nano-thickness ZnS and MgF<sub>2</sub> films as per design shown in the figure

obtain a tailored rise and fall of refractive index, repeated 35 times to obtain a superstructure to yield a high performance wide band optical filter.

Grain boundaries, as nano-materials, can be quite active depending on the grains and the impurities/defects present. We have developed variable voltage ZnO based varistors (behaving like back to back Zener diodes) by suitably tailoring the properties of insulating grain boundaries/interfaces sandwiched between conducting grains of ZnO so that it is essentially a no. of MIM structures stringed together. Just how electronically active each grain boundary can be is illustrated by our STM study of ZnO films. The I-V data, converted into a suitable form to yield directly the density-of-states function both at the grain and the grain boundary is shown in Fig. 9. The location of the conduction and valence bands and the Fermi level in the two cases makes the point clear.

Chemists have been modifying surfaces chemically for a very long time. Anodized and colored aluminum have been manufactured for a long time. Rapid anodization can be used to drill nano-sized holes in Al surface as shown in Fig. 10. The holes can be filled up with colored dyes, or metal/metal oxide powder. We have used this technique to obtain 98% solar absorptance for solar-thermal applications. By converting surface chemically into a mixture of nano-size particles, high optical absorptance



Fig 9 : Current-voltage characteristics of an STM nano-probe on a ZnO film grain and on the grain boundary between two grains. The positions of the energy bands and the Fermi level are indicated

due to Photon trapping and multiple-reflections has been achieved on such metal surfaces as Cu, Mo, SS, Ni, etc.

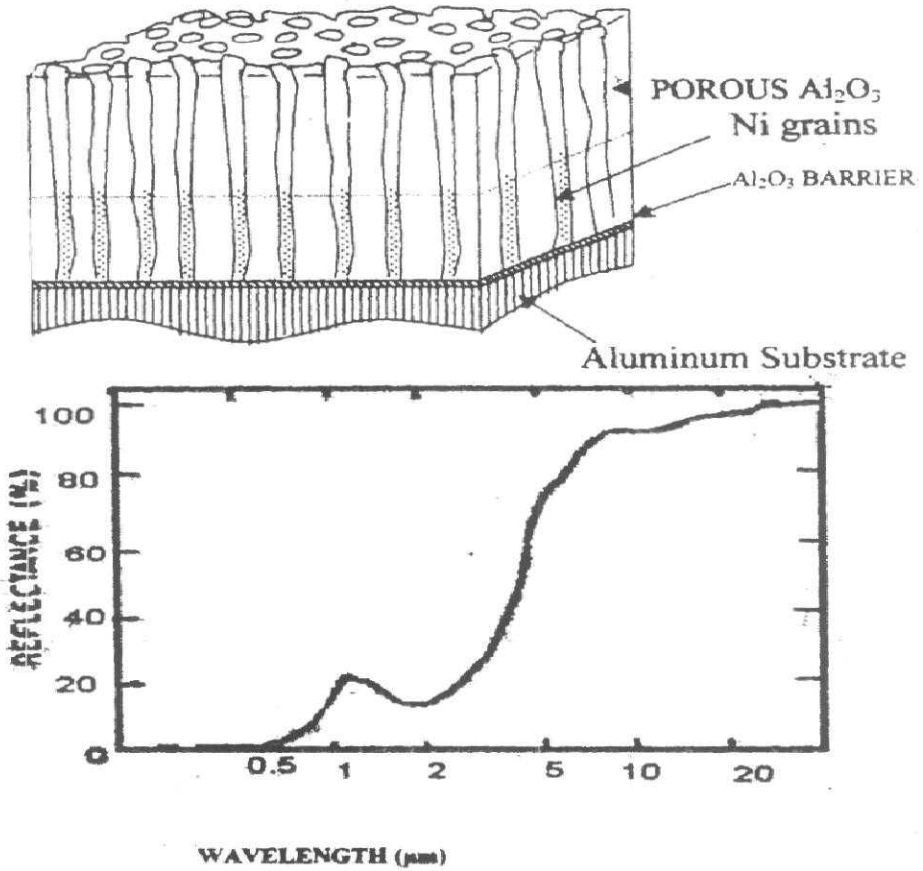


Fig 10 : Cross-section of anodized porous Al surface showing nano-tubes filled with Ni and the corresponding reflectance of the highly absorbing surface for solar spectrum

## NANO-SCIENCE CHALLENGES

The dominance of size and surface related effects is not well understood in terms of our existing and conventional knowledge. Nano-science, therefore, presents a new interdisciplinary challenge. Some of these challenges are summarized as follows:

- Thermodynamics & Structure : Size dependence of free energy, modified phase diagrams, nano-mixing, extended solubility, metastability, polymorphism, critical phenomena, activation processes
- Microstructure : Nano-scale inhomogenities, grain boundary dominated effects

- *Surface Effects* : Highly active and reactive surface dependent diffusion, absorption, adsorption, catalytic, protective and corrosion effects
- *Mechanical Effects* : Defect-defect interaction dependent mechanical properties such as adhesion, tribology, wear and tear, adhesion, hardness, elasticity
- *Ferroic Processes* : Size dependence of cooperative phenomena of super-conductivity, ferroelectricity, ferromagnetism, and ferroelasticity, domain structure and dynamics, surface pinning effects
- *Optical Transport* : Modification of E-k diagram, relaxation of selection rules, optical constants, surface plasmons and excitons
- *Electron Transport* : Mean free path and quantization effects, ballistic transport, hot electron transport, electro migration effects, electrostatic charge and discharge effects, grain boundary electronics

## SOME APPLICATIONS

Nano-materials and nanotechnologies have been exploited by chemists, thin-film scientists, cosmetic manufacturers, metallurgists, microelectronics and optical component manufacturers for several decades. In the age of GREEN technologies meant to conserve material, energy and environment, these technologies are indeed very promising. Some of the well known applications are :

- Tooth Paste
- Cosmetics
- Paints, including electroluminescent paints
- Pharma products
- Metal surface finish
- Ultra-thin metal foils
- Decorative coatings
- Photo and electro-chromic devices
- Composite ceramic sensors
- Nano-silica in rubber tyres
- Solar selective coatings

- Varistors
- Flexible, machinable and high performance dispersion phase composite ceramics
- Thin film solar cells

A lot of scientific excitement, however, lies in the applications of nano-technologies in the areas of integrated circuits, photonics, mech-o-nics, MEMs, bio-medical and bio-engineering. As for nano-electronics, the smaller the device, more efficient, effective, intelligent, faster, more densely packed and cheaper it is. And, this is the major driving force in the field to demonstrate single electron transistor, single atom laser, molecular switch/transistor, bio-electronics, quantum computing components, quantum meteorology of unprecedented precision for time, current and voltage, NEMs, nano-robots, bio-nanotech sensors, etc.

### SOME NANO LANDMARKS

- 3.5 Billion Yrs. : Nano-size-bio-machines evolved
- 19th Century : Supramolecular Chemistry-empirical
- 1950s : Zeolites with nano-size pores
- 1960s : Nano-size nucleated atom clusters seen by Transmission Electron Microscope (TEM)
- 1974 : Submicron technology named "Nanotechnology" by Tanaguchi
- 1970-80s : Atomic lattices and nano clusters observed in high resolution TEM. Submicron lithography ushered in.
- 1970s-80s : Artificial lattices; Quantum dots; Quantum wires; Lipid nano-spheres
- 1985 : Coulomb Island/ Blockade (Likharev et al.)
- 1987 : Single Electron Transistor (Fulton & Dolan)
- 1987 : Single atoms and 3D nano clusters, and DNA seen in STM
- 1989 : STM used to move Xenon atoms (Eigler)
- 1991 : Carbon nano-tubes (Iijima)
- 1998 : Carbon nanotube transistor (Dekker)



- 1999 : Single molecule switch (Tour & Reed)
- 1999 : Single atom laser, Nano mechanical resonators, levers & sensors
- ...Onwards... : with Bio-Nanotech- nano robot, shells, bridges, barcodes, magtags, sensors....

## CONCLUDING REMARKS

- The availability of precise controls and computerized automation of equipment, and the advent of nano-analytical instrumentation of a wide variety enabling in-situ and ex-situ monitoring and analysis have propelled the development of the science and technology of living and non-living matter on an atomic and molecular scale. Besides a few new ones, a lot of old material synthesis techniques have been upgraded for the purpose.
- The science of nano-sized materials deviates considerably from that of corresponding macroscopic materials. Nano-sciences of physics, chemistry, metallurgy, and biology are emerging frontiers.
- Nano-materials can be tailored and engineered with suitable tools and processes.
- Commercial viability of nano-devices, in most cases, would ultimately depend on how economically these can be produced and integrated with micro/macro materials and devices.
- In general, the existing so-called nano-technologies are enabling technologies. Convergence and/or integration of some or all of the technologies such as nano-mechanics, nano-optics, nano-electronics, and nano-biology would be required to fulfill the dream of useful and viable nano-devices of future.
- Small is GREEN and Mean Beautiful and Bountiful.

## ACKNOWLEDGEMENT

Most of the work reported in this paper is based on the work done and published over three decades with my Ph D students in the Thin Film Laboratory at I.I.T. Delhi and the Microscience Laboratory at I.I.T. Kharagpur. While standing gratefully on the shoulders of my research students, I am happy to dedicate this paper, abbreviated considerably from my talk delivered at N.M.L., Jamshedpur to the Diamond Jubilee of the CSIR and offer my best wishes for a bright future for the CSIR family.