



Materials Characterization at Nano Scale: Importance and Implications

Avanish Kumar Srivastava

National Physical Laboratory (Council of Scientific and Industrial Research) New Delhi 110 012, INDIA

May 05, 2012

Seminar on Nano Technology The Indian Institute of Metals Delhi Chapter

Main Research Work

Growth, microstructure and properties evaluation of various metals & alloys and semiconducting nanostructures

Nucleation-growth mechanisms and phase transformations

In-situ image – spectrum interpretations

Various oxide nanostructures and phase formations

Evolution of optical bands and mechanical properties depending nano-scaled morphologies

Safe use of nanomaterials

Internal / External research projects in NPL (NWP, MNES, DST, CSIR, DST-NSF, DST-JSPS)

- Study of droplet dynamics and heat flow characteristics during spray atomization and deposition
- Bulk Aluminum alloy nSiC nano-composites
- Metal-induced crystallization of amorphous Si thin films
- Physico-chemical studies of metal and metal oxide Nanoparticles
- Development of Nano-structured Porous Materials
- Synthesis of Nanophase Luminiscent Materials & Devices
- Nanotubes of Carbon and Boron nitride
- Growth and characterization of Gold nano-particles as CRM
- Study of defect centres in nanomaterials for applications in sensors
- Custom Tailored Special Materials
- Establishment of high resolution TEM facility at NPL as an important part of Centre for Nanoscale Science

Future Research Projects

- Development of thermoelectric SiGe bulk nanocomposites with enhanced figure-of-merit for high temperature applications
- Pinning of flux lines by magnetic nanoparticles in high kappa superconductors
- Spintronics: Exploring Graphene
- Establishment of EELS to a new high resolution TEM facility

Significant contribution in the field of metal sciences and nanomaterials:

Grain microstructure, interface studies and phase formations in rapidly solidified and mechanically processed systems

Revelation of Multilayered thin films including spectroscopic evaluations on different topics: (i) Metal induced crystallization of amorphous Si and (ii) Al-Mn alloys multilayered thin films

Shape-selective growth, microstructure, spectroscopic and optical & mechanical response of bare & doped ZnO, CuO and Al₂O₃ nanostructures

Electron microscopy investigations on tungsten oxide, PEDOT and composite films with a novel microstructure for fast switching smart windows

Dynamics of Polymorphic Antimony Nanostructures: From Growth to Collapse, experimental and theoretical interpretations

A facile and novel synthesis of Ag-graphene based nanocomposites

Revelation of graphene-Au nano-composites for direct write deposition and electrical performance

Microstructure v/s Nanostructure

Gold atom -0.1nm C nanotube -0.1nm DNA -3nm	HIV virus HIV virus -100nm HIV virus	Hair ~100µm ~10mm
0.1nm 1nm 10nm	100nm 1µm 10µm	100µm 1mm 10mm
	Microstructure / Bulk	Nanostructure
Physics	Semi-classical	Quantum mechanical
Electron's nature	Particle-like	Wave-like
E or k-space	Continuous	Discrete
Current	Continuous	Quantized
Decision	Deterministic	Probabilistic
Fabrication	Micro-fabrication	Nano-fabrication
Surface to volume ratio	Small	Very large
Packing	Low	Very high

Carbon Nanotubes





Boron Nitride Nanotubes



Nano-materials

Metals Semiconductors Insulators Superconductors magnetic materials

Oxides Sulfides Nitrides Carbon

Methods for Synthesis of Nanomaterials



Techniques for Materials Characterization

Scanning Electron Microscopy Scanning Tunneling Microscopy, Atomic Force Microscopy **Transmission Electron Microscopy Energy-Dispersive X-Ray Spectroscopy Electron Energy-Loss Spectroscopy** Scanning Transmission Electron Microscopy **X-Ray Diffraction** X-Ray Photoelectron Spectroscopy Auger Electron Spectroscopy X-Ray Fluorescence Fourier Transform Infrared Spectroscopy Raman Spectroscopy **Secondary Ion Mass Spectrometry** Electron Paramagnetic Resonance **Cathodoluminescence Photoluminescence**

Solidification Morphology



Dependence of solidification morphology on temperature gradient G & interface velocity R, qualitative effect of increasing average cooling rate ε ave = GR is indicated by sloping arrow (Mehrabian1982)

Correlation between processing variables & microstructure length scales, characteristic lengths of physical processes (Trivedi, Kurz 1994)

Planar, Cellular, Dendritic, Eutectic

Dendrite/Cell tip radius, A Primary Spacing, A1

Secondary Spacing, λ_2 Eutectic Spacing, λ_{F}

General lengthscale : L

Crystal structure and Microstructure



Quasicrystals and related crystals in AI-Mn and AI-Fe based alloys







AI-Fe-V-Si alloy showing growth morphology of icosahedral phase surrounded by crystalline ring along 5-, 3and 2- fold axes



Formation of icosahedral phase surrounded by cubic silicide particles *Acta Materialia 1996* J. Mater. Res. 2001

Quasicrystals:

Nobel Prize in Chemistry – 2011 (5th October) Professor Daniel Shechtman, Israel Institute of Technology Date of birth: 24th January 1941, Observation: 5th April 1982

D.Shechtman, I.Blech, D.Gratias, J.W.Cahn, *Metallic Phase with Long-Range Orientational Order and No Translational Symmetry*, Physical Review Letters, 53, 12 November 1984







SAEDP along 5-fold rotational symmetry recorded from a single grain of the icosahedral phase

Stereographic projection of the symmetry elements of the icosahedral point group m35

Nanostructured bulk spray atomized and deposited AZ₃₁ magnesium alloy (Mg-2.8AI-0.84Zn-0.2Mn-0.15Si-0.007Cu-0.005Fe-0.004Ni in wt.%) Mater Sci Tech 2010



Orientation relationship between Mg₁₇Al₁₂ and Mg:

0.2 nm Intermetallic 0.25 nm Matrix

[1120]Mg // [111] Mg₁₇Al₁₂

hkl: 411, d=0.25 nm, cubic *hkl*: 1012, d=0.2 nm, hexagonal



Spray dynamics and heat flow characteristics



Synthesis and Characterization of Al-alloy/SiC_p nanocomposites employing high energy ball milling and spark plasma sintering



HRTEM images of spark plasma sintered Al-5083/10 wt.SiCp nanocomposite; (a) large number of nanocrystalline grains over entire matrix of Al-alloy and SiCp, (b) interface at atomic scale between Al alloy matrix and SiCp and (c) lattice imaging of Al alloy matrix





Oxide Nanostructures

Oxide nanomaterials like ZnO, CdO, TiO_2 , WO_3 , In_2O_3 , SnO_2 show enormous potential applications in device fabrications. Their properties can be tailored significantly by producing them at micro- and nano-scale in different morphologies.

ZnO (Zinc Oxide) CdO (Cadmium Oxide) CuO (Copper Oxide) TiO₂ (Titanium Oxide) WO₃ (Tungsten Oxide) Al₂O₃ (Alumina)

Application	CdO	WO ₃	ZrO ₂
Electronic devices	Used in photodiodes, phototransistors, photovoltaic cells, transparent electrodes,LCDs, IR detectors, cadmium plating baths, electrodes for storage batteries, phosphors etc.	Used in electrochromic windows or smart windows, flat panel displays, optical memory, writing reading erasing devices, electronic information displays, optical modulation displays, x-ray screen phosphors, fireproofing fabrics etc.	as a solid electrolyte, di- electrolyte, in transparent TFTs, nano-lithography, Precision valve balls & seats, Fuel cell membranes, High temperature induction furnace susceptors, Marine pump seals & shaft guides, Electric furnace heaters over 2000°C
Ceramics & coatings	Used in pigments and as ceramic glages, used in anti-reflection coatings.	Used in pigment in ceramics	In thermal barrier coatings, protective coatings for electronic devices, Powder compacting dies,
Sensing	Has potential applications in LPG sensors, formaldehyde sensors, ethanol sensor. Its composite has utility as CO sensor.	One of the best sensors for reducing gases such as NO ₂ ,CO and H ₂ ,also used in humidity and temperature sensors	Used in oxygen sensors, pollutant gases like Ammonia and CO can also be detected.
Catalysis	catalyst in ethanol dehydration, in chemo- regioselective reactions	Used as a photocatalyst in water splitting	In photocatalysis, as a general catalyst in knoevenagel condensation reactions
Bio-applications	Used as a nematocide	It has potential application in the detection of lipids and peptides	Its composites can be used in various biological load bearing applications

Application	ZnO	TiO ₂	CuO
Electronic devices	used in varistors, phosphors for CRT displays, electroluminescent panel displays,phosphors inside fluorescent tubes, field effect transistors, piezoelectric nanogenerators, in dye-sensitized solar cells	Used in capacitors, reflectors for incandescent lamps, semiconductors, bragg-stack style dielectric mirror, dye sensitized solar cells,memresistors, electronic data storage medium	Used as a major component in superconductive materials, as an anode material in Li ion batteries, magnetic storage devices, field emission sources,solar cell devices, optical switches
Ceramics & coatings	Used in UV protecting clear coats, antifungicide for paints, powder coating	Used in general pigments and coatings, UV protecting clear coats, automotive pigments, reinforcements for metal-matrix composites, porous membrane for gas filtration	Used as a pigment in ceramics to produce blue, green and red colours
sensing	ZnO nanorod based sensors can be used in ammonia, CO, hydrogen and UV detectors, ethanol sensors, Oxygen sensors,	In Oxygen sensors, hydrogen sensors	Used in hydrogen peroxide and glucose sensing, in H ₂ S sensors , NO ₂ sensors and in CO gas sensors
Catalysis	Used as a general catalyst in various reactions, as a visible light photocatalyst,	Used as a general catalyst in various reactions, as a photocatalyst and also as a catalyst support	Used as a catalyst in methanol synthesis , alkene oxidation, used as a photocatalyst
Bioapplication	Has potential applications as an antibacterial agent, bio-imaging on plant cells, intracellular potentiometric ion sensors, owing to its sensitivity towards tiny forces ZnO based pressure sensors can be produced and implanted in the body due to its biocompatibility, can be used as a glucose sensor, used in plasmid DNA delivery,	Its presence increases implant bioactivity and osteoblast adhesion of Ti and its alloys, enhances blood coagulation by reducing clotting time , acts as a biosensor for amperometric detection of glucose, enhances apatite formation, drug elution, cell activity and the nanotube arrays play important role in protein separation and drug delivery, TiO ₂ sol-gel has been used to detect large proteins like trypsinogen and also in the detection of insulin, can be used in the destruction of airborne pathogen	CuO based nanostructured surfaces can be functionalized to produce superhydrophobic interfaces for digital microfluidic systems for physical transfection of cells, has potential application as a biocidal agent,
others	Used in cosmetics like footcare, OTC optical and ointment,	Used in cosmetics such as sunscreens, moisturizers, lipstick,	Can be used as a crucial material for ink-jet printing



Nanostructured ZnO Tetrapods Patent: File Ref. No. 0773DEL2005 Dated 31st March, 2005

Nanoengg. Nanomanufac(2011) in press





 $[01\overline{1}0]$





First practical examination of Zn-O bond length of approximately 0.198 nm in real space Book Chapter: A. Mendez Vilas, Ed. Microscopy: Science, Technology, Applications and Education, Formatex Research Center, Spain (2010) vol. 3 No. 4, 1820-1823 Structural determination of Zn-O dumbbells in facetted nano-particles





Thermoluminescence

The thermally stimulated luminescence technique, commonly termed as thermoluminescence (TL). The ZnO is good for thermoluninescence dosimeters (TLD) applicable as environmental dosimetry, clinical dosimetry, inside nuclear reactors, during food sterilization and materials testing.



Induced TL spectra of an undoped ZnO sample at various temperatures. It shows a TL peak around 180°C around 600 nm. (a) TL spectrum integrated between 150 and 230 °C (b) spectrumtemperature diagram. TL intensity is displayed b false colors. © TL glow curve integrated between 560 and 640 nm, Optical Mater 2009

WO₃: crystal structure, microstructure and performance



Smarter liquid-crystal display

(J.Phys. D Appl. Phys. 44 (2011) 315404, NATURE India 23 August 2011)

Alumina nanoparticles to trap ionic impurities in ferroelectric liquid crystal (FLC) – based displays, which may improve display resolutions.

FLCs have good optical contrast, low turn-on voltage, memory effect and fast response. Impure ions can be efficiently trapped by Alumina nanoparticles for long durations. FLC materials free from ionic impurities have higher resolution and better contrast





Electrical resistance (R) of (a) pure and (b) 1 wt.% AL-NPs of size 20-30 nm doped KCFLC 7S material with frequency for aligned 4.2 μ m thick cells

Complex growth morphologies and characteristic optical bands of nanostructured CuO

CuO has a square planar coordination of Cu atom to neighboring O atoms and monoclinic crystal structure. With a narrow band gap (1.2 - 1.5 eV). uses as: p-type semiconductor, catalyst, gas sensing, crucial component in high temperature superconductors, pigment, electrode material in Liion battery and as nano-fluid



RSC Advances 2011



Thermal, luminescence and toxicity were correlated with the shapes of the particles for possible usage in nanofluid and optical devices in conjunction with their biological response. Flow cytometric (red fluorescence) quantification of dead *E. Coli* cells after CuO NP treatment; Q2 represents percent dead cells and Q4 represents percent live cells



Toxicity Evaluation of the CuO nanoparticles

MTT assay is well known method to assess the toxicity of the compound on cellular system under *in vitro* condition. In this assay, yellow tetrazolium MTT dye is reduced by succinate dehydrogenase enzymes produced by mitochondria of the metabolically active cells and form formazan crystal. The <u>spectrophotometric</u> quantification of the solubilized formazan corresponds to the viability of the cells. Our data demonstrates a statistically significant (p<0.05) cytotoxic effect of CuO NPs in CHO cells at concentrations 50 and 100 µg/ml after 3 hour exposure. MTT results demonstrated that mitochondrial succinate dehyrogenase activity was reduced to 79% and 38% (relative to 100% of control; pH 8.4) 94%, 45% (pH 10), 79%, 57% (pH 11.25) and 85%, 69% (pH 12) respectively at only the two higher concentrations (50 and 100 µg/ml) after 3 hour exposure





Dynamics of Polymorphic Nanostructures: From Growth to Collapse

F. Carlier,[†] S. Benrezzak,[†] Ph. Cahuzac,[†] N. Kebaïli,[†] A. Masson,[†] A. K. Srivastava,[‡]§ C. Colliex,[‡] and C. Bréchignac^{*,†}

Laboratoire Aimé Cotton CNRS, Bât. 505, Université Paris-Sud, 91405 Orsay Cedex, France, and Laboratoire de Physique des Solides (UMR CNRS 8502), Bât. 510, Université Paris-Sud, 91405 Orsay Cedex, France

Received April 6, 2006; Revised Manuscript Received June 28, 2006

[§] Permanent address: Division of Materials Characterization, National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110 012, India.

textile, t thread retic carinnings, process

Films from Clusters

In the "atom by atom" growth mode of inorganic films, strain induced by the substrate can largely control the final morphology, dictating outcomes



gas veloci-
ne convec-
observedSb₈₈ clusters added to
an Sb₃₀₀ fractal net-
work (yellow) produce
initially compact end
structures (red) that
flatten after further
gneticgas veloci-
an Sb₃₀₀ fractal net-
work (yellow) produce
initially compact end
structures (red) that
(deposition (cyan).

ranging from a smooth film to island formation. Carlier et al. have explored the consequences of delivering material to a surface as clusters rather than individual atoms. Beams of antimony clusters were tuned to peak at different average sizes—either 88 atoms (Sb_{aa}) or 300 atoms (Sb₃₀₀)—and then directed toward a graphite surface. Both types of cluster formed fractal structures on this ing the initially thick end groups to flatten out and spread along the graphite in two dimensions. The authors suggest that this transition is triggered because the strain accumulating in the compact end groups eventually exceeds the surface energy cost of producing a flatter but more crystalline structure. — PDS

Nano Lett. 6, 1875 (2006).

13 OCTOBER 2006VOL 314SCIENCESCIENCE

Impact Factor: 31.4

EDITORS'CHOICE

EDITED BY GILBERT CHIN AND JAKE YESTO



2006 Vol. 6, No. 9 1875–1879

Impact Factor: 12.2



100 particles with 7 steps

particles with 7

300 particles with 7 steps



Scanning Helium Ion Microscope







Morphological transformations from cellular to globular on individual nanoparticles of Al₂O₃



Schematic of helium ion microscope

राष्ट्रीय भौतिक प्रयोगशाला

He ion microscopy showing nanopatterning by
direct write depositionNano Scale Res Lett 2011

nm

Toxic potential of materials at the nanolavel (A.Nel, T.Xia, L.Madler and N.Li, <u>Science</u>, 311, 2006, 622)



Possible mechanisms by which nanomaterials interact with biological tissue. Examples illustrate the importance of material composition, electronic structure, bonded surface species (e.g., metal-containing), surface coatings (active or passive), and solubility, including the contribution of surface species and coatings and interactions with other environmental factors (e.g., UV activation)





Schematic of the coupling of terrestrial ecosystems and the hydrologic cycle via energy and water exchange and aerosol processing (Barth et al Bull Amer. Meter. Soc. 2005)

Structure of the ISO TC229

Specific tasks include developing standards for: terminology and nomenclature; metrology and instrumentation, including specifications for reference materials; test methodologies; modeling and simulation; and science-based health, safety, and environmental practices.

AIST



Opportunity from CHARGE

Detect deflections of electrons due to the presence of electric or magnetic fields, then we add electromagnetic information to the structural / crystallographic information

Electron wavefront modulation





Magnetic domains in perovskite A₂FeMoO₆





Lorentz TEM images of $Ca_{2}FeMoO_{6}$. (a) dark field image obtained by selecting the 002 spot. (b) Foucault image: white and black regions denote magnetic domains. © Fresnel image: white and black lines (indicated by white arrows) denote magnetic domain walls. Dashed lines in (a) - (c)are guides of grain boundaries. (d) The magnetization distribution obtained by the transport – of - intensity (TIE) method. The magnetizations are represented by white arrows. The TIE method was based on commercial software QPt with DM. Yu etal JMMM 2007

М	lost Importal	nt Recognitions /	Achievements	
Publications	Conferences	Chapters in Books	Invited lectures	Patent
140	105	04	45	01
Metallurgist of th	ne Year – 2011, N	Ainistry of Steel, Govern	nment of India	_
MRSI Medal – 2	011 for contributi	ons to the field of Mate	rials Science and Eng	gineering
Bharat Jyoti Award–2011, India International Friendship Society				
Kwan Im Thong Hood Award Travel Fellowship of Singapore				
INSA – KOSEF	Bilateral Internati	onal Exchange Program	n fellowship 2009	
BOYSCAST fellowship DST Government of India 2001, University of Paris				
External Expert to Bureau of Indian Standards, Nanotechnology Program				
Co-Chairman, Post Treatment Carbon Nanotubes, ICMAT 2011, Singapore				
Establishment of High Resolution TEM Facility, Centre for Nanoscale Science at NPL				
Visiting Scientis	t: UOP France,	FUD Germany, UO Japa	an, POSTECH South	Korea

High Resolution-TEM facility at NPL



Important specifications and key features

TEM Point Resolution	: 0.205 nm	
TEM Line Resolution	: 0.144 nm	
STEM resolution	: 0.17 nm	
EDAX resolution	: 136 eV	
• Fully integrated, optimized, easy-to-use interface		

• Extensive applications-software support

Interplanar spacings:

Golobid 2 nm 020 0.144 nm Ediffraction pattern; hkl: 0.12 nm 200, 020 are markedlectron 0.144 nm 0.12 nm

Beam induced movement of gold atoms on surface HR-TEM on TITAN with Image Cs-corrector @300kV



0.1nm

Image : B. Freitag , FEI

Movement of single atoms on surface can be monitored Atoms are activated by focusing the beam maximal on the area

In situ growth of Pt crystals on Titan probe Cs-corrector



Beam induced growth of Pt clusters in Cs-corrected-STEM The interaction of Pt clusters at the atomic level can be studied time resolved

Super Resolution Technology Map

SIM: Structured illumination microscopy; NSOM: Near field scanning optical microscopy; STED : Stimulated emission depletion microscopy; STROM : Stochastic optical reconstruction microscopy



<u>IMPORTANT REFERENCES / COLLABORATORS</u>

Professor S. K. Joshi Professor D. Chakravorty Professor T. R. Ramachandran Professor S. Ranganathan Professor K. Chattopadhyay Professor S. N. Ojha Professor E. S. Rajagopal Dr. Anil K. Gupta Professor Vikram Kumar Professor Sudhir Chandra Professor R. C. Budhani

Professor Christian Colliex Professor Kui Yu Zhang Professor H. A. Naseem Prof. Dr. -Ing. h.c. Hartmut Fuess Professor Shin Toyoda Professor Kijung Yong Professor Carlo S. Casari

I.I.T. Roorkee (UOR)	1986
I.I.T. Kanpur	1987
I.I.T. Kanpur	1988
I.I.Sc. Bangalore	1990
I.I.Sc. Bangalore	1990
I.T., B.H.U. Varanasi	1992
N. P. L. New Delhi	1996
N. P. L. New Delhi	1996
N. P. L. New Delhi	2003
I. I. T. Delhi	2004
N. P. L. New Delhi	2009
U.P.S. France	2001
U.O.R. France	2002
U.A.R.K. USA	2004
T.U.D. Germany	2006
O.U.S. Japan	2007
POSTECH Korea	2009
NEMAS Italy	2009



ZnO nanostructures on NPL new year greetings

Thank

You