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"Nanostructuring by electrons, photons and ions" Special Issue Published online by the VBRI press in 2013

Nano science and engineering by ionizing radiations

Dear Reader,

The properties of materials at the nano scale critically depend on their size and shape, thus opening a new exciting area of nanotechnology. Its main thrust is to create novel functional materials with their unique physical, chemical and biological properties. The field of engineering of materials with desired properties is seeing a revolution as it becomes feasible to fabricate nanoscale building blocks having precisely controlled size and composition. Ionizing radiation (photon, electron and ion beams) have provided immense possibilities for engineering the desired properties of materials and are now emerging as indispensible tools for mesoscopic structuring [**1-5**]. The field of materials engineering through nano approach has demonstrated tremendous potential in the development of different types of novel materials with new characteristics and functions. The aim of nano engineering with photon, electron and ion beams is to control the nano scale structure of materials to optimize their properties and functionality.

Acquiring the ability to direct and control matter all the way down to molecular, atomic, and electronic levels will require fundamental and new knowledge in several critical areas. The research is inherently multidisciplinary and requires sustained efforts in many disciplines underpinning basic energy science research: chemistry, condensed matter, materials physics, engineering, biology, etc. The dual advances of temporal and spatial resolution promised by tools like lasers and accelerators ideally match various challenges. Femtosecond time resolution has opened up a new territory where atomic motion can be followed in real time and electronic excitations / decay processes can be followed over time. Coherent imaging with short-wavelength radiation will make it possible to access the nanometer length scale, where intrinsic quantum behaviour becomes dominant. Performing spectroscopy on individual nanometer-scale objects rather than on conglomerates will eliminate the blurring of energy levels induced by particle size and shape distributions and reveal the energetics of single functional unit.

In this context, a DAE-BRNS Theme Meeting on Emerging Trends in Applications of Lasers and Accelerators in Nanomaterials (ETALAN-2011) was jointly organized by the Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai and the Indian Society for Radiation and Photochemical Sciences (ISRAPS) during October 20-21, 2011 at BARC, Mumbai. Another conference on 'Nanostructuring by ion beams' was organized by Inter University Accelerator Centre (IUAC) at Allahabad University from 17th to 19th October, 2011. The purpose of these meetings was to identify challenges and opportunities in cross-cutting areas of experiments, theory and modeling in nano science and engineering and to investigate the growing and promising role of lasers and accelerators in meeting those challenges. It was jointly decided by the organizers to publish this special issue based on some of the invited talks and contributed papers presented in these meetings covering the research in nano science and engineering with photon, electron and ion employing lasers and accelerators, after reviewing the contributions.

Conventionally, lasers, ion and electron beams have shown their powerful applications in the processing of bulk materials for quite long, such as laser cutting, drilling, welding, alloying, and nanostructuring the surface etc. With the thrust in nanomaterials research, the scope has been greatly expanded: nanomaterial generation, fabrication of nanostructures, the modification of the size, shape, phase, morphology and composition of the produced nanomaterials through the control of various process parameters. All these are crucial for the improvement of various performances, and hence applications of nanomaterials in optoelectronics, medical diagnostics, catalysis, sensors and so on. Finally, the methods developed are simple, quick, one step and green. A common feature of ionizing radiation (photon, electron and ions) is the ability to deposit a huge energy density in the materials when they are incident on materials. At its extreme, laser with high power >10^{19} W/cm^2 is capable of producing eletrons and ions upto hundreds of MeV [**6, 7**], whereas high energy heavy ions of energy > MeV per nucleon, creates an ion track [**8**] i.e., a cyllindrical zone of radius typically upto 10 nm different from the surrounding, in insulating materials.

This special issue is devoted on the above aspects and also the physical/chemical process during photon, electron beam and ion beam interaction with material. The main aim of this effort is to provide the readers a broad overview about the ongoing research activities in the forefront of this field. This issue includes 21 research articles on a broad range of topics related to the role of photons, electrons and ion beams in nanomaterials.

Applications of laser beams

When a laser beam impinges on a material, laser energy is first absorbed by free electrons. The absorbed energy then propagates through the electron subsystem and is transferred to the lattice [**1-3**]. Three characteristic time scales are: T_e - the electron cooling time, which is of the order of 1 ps; T_i - the lattice heating time; and T_l - the duration of the laser pulse. T_e and T_i are proportional to their heat capacity divided by the same constant and the heat capacity of electron is much less than that of the

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lattice; therefore, $T_e << T_i$. Three cases occur when T_l is in different ranges.

(i) Case one: T_l >1ms>> T_i >> T_e, where T_l is of millisecond or infinite (continuous wave laser). The typical time scale is much larger than the electron-lattice energy coupling time, and the primary material removal mechanism melts with molten metal ejected by an assisting gas jet if metal is the target material. Classical heat transfer laws are fully appropriate in modeling these machining processes. Laser cutting is the most common process in this time region and used for steel, nonferrous metals, and nonmetals. The typical laser system in this time scale is a 10.6 micron CO_2 laser, which has power of a few KW and intensity of 1 – 2MW/ cm^2.

(ii) Case two: T_l > 1 ns>> T_i >> T_e, where T_l is of nanosecond scale. In this case, the electron absorbing the laser energy has enough time to be transferred to the lattice (for energy transfer to lattice), the electron and the lattice can reach thermal equilibrium, and the main energy loss is the heat conduction into the solid target. Material is first melted, and when the beam is strong enough, evaporation occurs from the liquid state. Laser drilling, grooving, marking, or scribing is typical processes in this regime, where slight melting is followed by quick evaporation. Also the heat affected zone (HAZ) is usually smaller than that of the CW laser processing. However, the existence of a melting layer makes precise material removal difficult. In this time scale, the typical laser used is the Q-switched solid state laser, such as a Nd:YAG laser, which has tripled frequency (355 nm), and with intensity of 100 -200 J/cm^2. The materials used are often nonferrous metals such as Cu and Al and alloys because of their good absorptivity at the UV wavelength.

Case three: $T_l << T_e << T_i$, where T_l is of the femtosecond scale, and laser pulse duration is shorter than the electron cooling time. Electrons are heated instantly, and then in about 1 ps, electrons transfer their energy to their positive lattice ions. When this energy intensity is high enough, which is often true for ultrafast pulsed lasers, those ions get energy high enough to break the bonding of the lattice structure. They break off instantly without having time to transfer their energy to their neighboring lattice ions; thus, direct solid-vapour transition occurs. Heat conduction into the target can be neglected; the heat affected zone is greatly reduced. For melting-free ablation to be possible, two conditions must be met: ultra-short pulse duration and high enough pulse energy. Since direct solid-vapour transition can be achieved, all processes such as cutting, drilling, grooving, marking, or scribing can be used in this time region, and precise material removal is possible. In this time scale, the typical laser used is Ti:sapphire laser with wavelength 780 nm and intensity from 0.1-10 J/cm^2. Almost all materials such as metals, alloys, polymers, and ceramics can be removed at this time scale, and the absorptivity is wavelength independent. Thus, the thermal aspects such as internal thermal transport, melting, vapourization, thermodynamic phase equilibrium, and electron-lattice energy coupling in laser material processing need to be modeled quite differently under different cases, which will ultimately affect subsequent process outcomes.

Contribution based on lasers

- R. Kuladeep et al. in their studies on 'Synthesis, characterization and nonlinear optical properties of laser-induced Au colloidal nanoparticles' have synthesized Gold (Au) colloidal nanoparticles (NPs) by direct irradiation of gold precursor ($HAuCl_4$) solution in polyvinyl alcohol (PVA) matrix using nanosecond laser pulses (532 nm) at different irradiation fluences and exposure times.
- K. I. Gnanasekar et al. in their paper titled 'Sensor grade nanostructured thin films of multicomponent semiconducting oxide materials by pulsed laser deposition' presented the fabrication of high quality sensor grade nanostructured thin films of multicomponent semiconducting oxide sensors with superior sensitivity for monitoring trace levels of pollutant gases like NO_x, NH_3, H_2 etc., in the ambient by pulsed laser deposition technique.
- Nandita Maiti et al. in their studies on "Surface-enhanced Raman scattering (SERS) spectroscopy for trace level detection of chlorogenic acid' have produced substrates in the form of silver-coated films with an average size of about 16 nm particles by reducing silver nitrate by neat formamide. Then these substrates were used in SERS investigation for the trace-level detection of chlorogenic acid (CGA) adsorbed on them.
- Suman Rana et al. in their investigations on 'Microstructural investigation of lipid solubilized microemulsions using laser light scattering' have found out that oil in water microemulsion using Tween-80 (T-80) as a surfactant and isopropyl myristate (IPM) as an oil phase could be utilized for the preparation of Solid Lipid Nanoparticles (SLN). They have evaluated the microstrucrure of such microemulsions using laser light scattering.
- Rajesh V. Nair et al. in their paper titled 'Inhibition and enhancement of spontaneous emission using photonic band gap structures' have experimentally demonstrated the inhibition and enhancement of spontaneous emission of dye molecules embedded in a nanophotonic structure.
- Pratap. K. Sahoo in his paper on 'Nano slit and dot array pattern of Au on SiO_2 substrates using laser beam lithography' has fabricated 2D grating structure and periodic nano hole and dot arrays with structure size of 50-100 nm and pitch of 200-300 nm on SiO_2 substrate using two laser beam interference lithography.
- Sucharita Sinha et al. in their studies on 'Self-assembled microcones generated on solid surface through pulsed laser irradiation' have presented results on surface micro-structuring via nanosecond pulsed laser irradiation of titanium and stainless steel cathode samples.

Contribution based on electron beam

- Nilanjal Misra et al. in their investigation on 'Comparative study of gamma, electron beam, and synchrotron X-ray irradiation method for synthesis of silver nanoparticles in PVP' have discussed one-pot synthesis method for preparation of silver nanoparticles in aqueous poly (vinyl pyrrolidone) (PVP) solution by synchrotron X-ray radiation. They have also carried out

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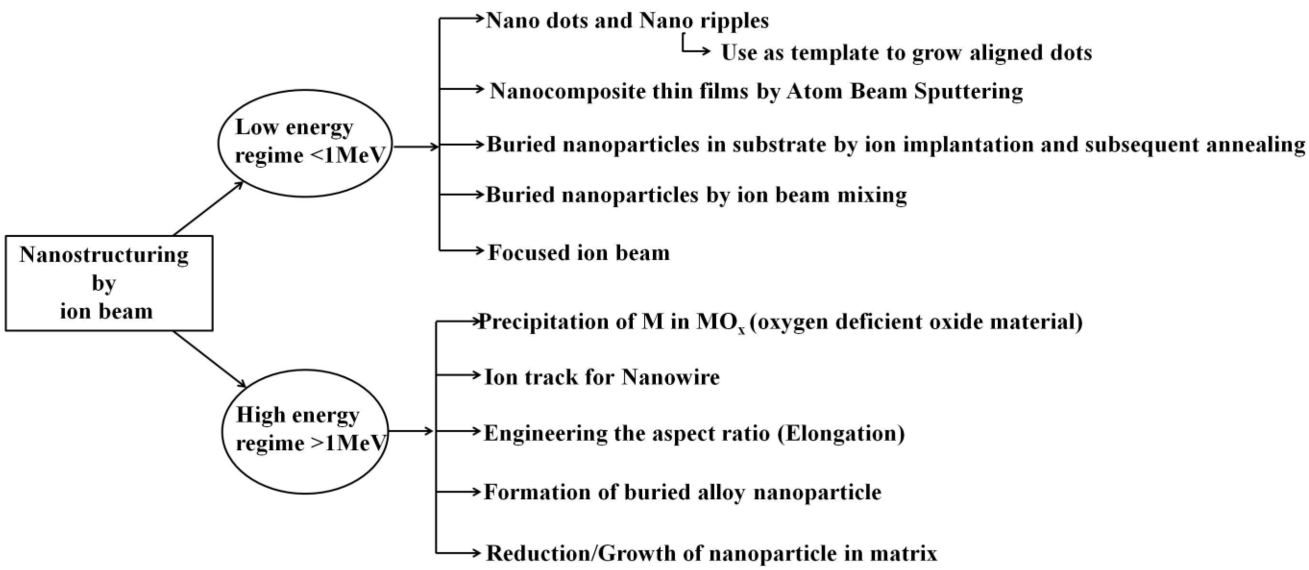

Fig. 1. Different possibilities of synthesis and engineering of the nanostructures by ion beam in low energy and high energy regime.

comparative study to know the effectiveness of this synthesis method with that of gamma and electron beam-irradiation methods.

- Shalini Singh et al. in their work on 'Shape evolution of CdSe nanomaterials in microheterogenous media' achieved synthesis of CdSe nanomaterials through the green chemistry as well as the radiation-chemical route using 7 MeV electron beam from a linear electron accelerator (LINAC). The shape of the nanomaterial was found to evolve from isotropic spherical to anisotropic rod-like structures in microemulsions with lower water content.
- Chethan Pai et al. in their paper titled 'Effect of electron beam irradiation on photoluminescence properties of Thioglycolic acid (TGA) capped CdTe nanoparticles' presented irradiation effects of 8 MeV electrons on photoluminescence properties of thioglycolic acid (TGA) capped CdTe quantum Dots (QD).
- Mohapatra et al. demonstrated the electron irradiation induced shape transition in elongated gold nanoparticles burried in silica matrix in an in-situ TEM experiment.

Applications of ion beams

Ion beams, depending on the energy regime, can play different roles in materials science such as synthesis, modification and characterizations. Energetic ions have shown their excellent potential in engineering the desired properties of the materials. The ion beams deposit a large energy density in the material driving it far from equilibrium, resulting in unusual and unexpected effects on materials. The incident ion interacts with the target and looses its energy along its path before stopping. At low energies (up to a few MeVs) the energy loss is dominated by elastic collisions with the nuclei, referred as the nuclear energy loss. The recoils produced by elastic collisions can further cause elastic collisions resulting in collision cascade resulting in creation of defects, sputtering, radiation enhanced diffusion etc. At higher energies (a few to hundreds of MeVs) the energy loss is dominated by inelastic collisions leading to excitation/ionization of target electrons, referred as electronic energy loss. In this energy regime the incident ion is capable of creating columnar defect along its path, which is referred as ion track. The ion track diameter can be upto 10 nm or so where as the incident ion size is typically 0.3 nm. Accelerated ion beams provide large flexibility as a tool for modifying materials properties due to large variation in their energies (from a few eVs to GeVs), fluences (from 10^5 ions cm^{-2} to 10^{14} ions cm^{-2}).

There are various possibilities of synthesis and engineering the nanostructuring by low energy as well as high energy ion beams as depicted in figure 1. Some of the aspects out of various possibilities are discussed under low energy ion beams and high energy ion beams in this special issue. The considered low energy regime is typically below 1 MeV where ion and matter collisions are dominantly elastic and the high energy ion beam region is typically above 1 MeV per nucleon where the energy loss of incident ions in materials is prominently via inelastic collisions. Heavy ions with energy above 1 MeV per nuclean have velocities comparable or more than the Bohr electron velocity and is referred as swift heavy ions.

Low energy ion beams

(i) Creation of nanoripples and nanodots at surfaces

Ion beam can induce self-organized nanostructures at surface in a manner similar to the patterns in sand produced by winds in deserts. The formation of ripples and nano dots on surfaces after irradiation with a few hundred eV to a few keV is observed in different materials such as Si, InP, GaAs, SiC etc. The basic mechanism involves surface roughening by sputtering and smoothening by diffusion process. The direction of ripples can be tailored either perpendicular or parallel to the ion beam direction in the surface plane by varying the incidence angle. The atom beam induced ripples on silicon surface have been used as substrate to deposit aligned gold nanodots on them [**9**]. In this issue, a few examples in this category are:

- Sarathlal et al. studied the dependence of nanoripples at Si wafer on the azimuthal angle (of incident Ar ions).

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- Sulania et al. created nanostructures at Ge wafer by 1.5 keV atom beam.
- Jai Prakash et al. synthesized Ag nanoparticles on polymer surface by 150 keV Ar ion irradiation of Ag thin film deposited on polymer.

(ii) Synthesis of embedded nanocomposite by atom beam co-sputtering

A unique way of synthesizing embedded nanostructure in silica and other matrices by atom beam cosputtering has been demonstrated at IUAC [**10, 11**]. The problem of charging in insulator sputter targets is taken care of by use of neutral atom beams instead of ion beams.

- Hardeep et al. used atom beam co-sputtering techniques for synthesis of FeCo nanoparticles embedded in silica.

High energy ion beams

(i) Synthesis of embedded nanowires in fullerenes

Specific feature of nanometric cyllindrical shape of ion track can be utilized for synthesis of nanowires because of its resemblance with nanowire.

- Singhal et al. utilized this special feature for synthesis of conducting nanowires in $C_{70.}$

(ii) Ion tracks and biomedical applications

Tracks in polymers are produced by high energy heavy ions, which are cylinders of modified materials within nanometer dimensions. The ion tracks can be etched chemically to form narrow cyllindrical holes of diameter from a few tens of nanometer to a few micrometers.

- Rattan et al. used etched ion track for fabricating stimulii responsive membranes through graft copolymerization.

(iii) Polymer/organic nanostructures

- Kumar et al. studied the structural, optical and conformational modifications in conducting polymer nanostructures. Salient feature was the transformation of benzenoid structure of PANI nanofibres to quinoid structure by SHI irradiation.
- Sarath Chandra et al. reported ion induced modification in Fe doped nanosize hydroxyapatite and enhanced bioactivity of the SHI irradiated samples.

(iv) Engineering of aspect ratio of metal nanoparticles

Atom beam sputtering set up has been used to make Au-silica nanocomposite thin films. The elongation of Au nanoparticles occurs along the beam direction in Au silica NC thin films after irradiation with Au ions has been demonstrated [**12**].

In the area of modification of existing nanostructures by ion beams there are following two articles.

- Vijay Kumar et al. showed the narrowing down of crystallite size of nanocrystalline film as a result of SHI irradiation.
- Vinod Kumar et al. studied the structural and optical properties of the SHI irradiated nanocrystalline doped and undoped ZnO thin films.

It is anticipated that this special issue not only presents to the readers a cross-section of the current on-going research activities worldwide in nano science and engineering with photon, electron and ion beam employing lasers and accelerators but also serves as guide line about their future research endeavours and developments. We thank all the authors for their contributions and referees to review the manuscripts. We are pleased for the opportunity to present this special issue of *Advanced Materials Letters*.

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Guest Editors

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Devesh Kumar Avasthi is Group Leader for materials science and radiation biology at Inter University Accelerator Centre, (formerly known as Nuclear Science Centre), New Delhi. He did Ph. D. from Panjab University, Chandigarh in 1982. After serving in Defence Laboratory for about three years, he joined Nuclear Science Centre in 1986, an inter university accelerator based facility. He implemented elastic recoil detection analysis (ERDA) technique for light element depth profiling. Later a gaseous telescope detector was designed, fabricated and installed to enhance the capabilities of ERDA, which was used for electronic sputtering measurements. The most recent developments have been an atom beam sputtering set up for synthesis of nanocomposite thin films, in-situ ERDA, In-situ XRD, in-situ QMA in beam line. His main interest is ion beams for analysis, modification of materials, synthesis and engineering the nanostructures by ion beams. Currently the interest has been creation and modification of nanostructures by ion beams. He had major research projects under 'Intensifying

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Research in High Priority Area' scheme and currently a project under 'Nano Mission' funded by Department of Science and Technology, Government of India. Dr. Avasthi had several international collaborations with research groups in Munich, Stuttgart, Kiel (Germany), Orsay (France), Padova (Italy), NCSU Raleigh (USA) and Tsukuba (Japan). He is a member of international committee for the conferences on 'Ion Beam Analysis' and 'Swift Heavy Ion in Matter'. He has several conference proceedings as editor and four hundred research papers to his credit.

Sisir K. Sarkar is presently the Head, Radiation & Photochemistry Division, BARC. He did his post-doctoral work at Columbia University, New York. He has worked extensively as visiting scientist at the P.N.Lebedev Physical Institute & Institute of Spectroscopy, Russia, Kyoto Institute of Technology, Japan, Institute of Chemical Process Fundamentals, Czech Republic, University of Paris-sud, France and University of Heidelberg, Germany with various laser systems including Free Electron Laser. He has published more than 350 papers. He is Senior Professor at Homi Bhabha National Institute and Fellow of Maharashtra Academy of Sciences. His research interest includes radiation & photochemistry with lasers and accelerators, chemical dynamics, spectroscopy and laser development.

Ambuj Tripathi has done his Ph.D. from University of Allahabad and had joined Inter University Accelerator Centre, New Delhi as scientist in 1988 where he is presently working as scientist 'G'. He played a key role in setting up of materials science beamline and many in-situ/on-line experimental facilities and is presently in-charge for Materials Science Beamline facilities and SPM/SEM Lab. He has published more than 100 research papers in international refereed journals and has contributed 3 book chapters besides being guest editor for special issues of Radiation Effects and Defects and Advance Materials Letters journals. His areas of interest are Ion beam induced surface modification of carbon based materials (such as HOPG, fullerenes and CNTs) and other surfaces and synthesis/ characterization of embedded and surface nanostructures.

Tulsi Mukherjee is presently the Director, Chemistry Group, BARC. He has been involved in the front-line research areas of chemical sciences for last four decades. He was Visiting Scientist at various places like Paterson Institute for Cancer Research, Christie Hospital, Manchester, UK, University of Leipzig, Hahn-Meitner Institute, Jacob University, Bremen, Germany, University of Paris Sud, France, Shanghai Institute of Applied Physics, China, Osaka Univ, Tokyo Univ, Waseda Univ, RIKEN, NIMS, AIST, Japan. He has many awards to his credit namely Homi Bhabha Gold Medal, Dr P.K. Bose Memorial Award, Indian Nuclear Society Award, ICS Acharya P C Ray Memorial Lifetime Award, Da-Ichi Fellow, ICT, Mumbai etc. He is currently Distinguished Scientist, DAE and Senior Professor, Homi Bhabha National Institute. He is Fellow, National Academy of Sciences and Maharashtra Academy of Sciences. He has published 330 papers in international journals of high repute. His Research interest is: Radiation & Photochemistry, Laser-based Chemistry, Time-resolved fluorescence spectroscopy, Ultrafast Dynamics, Nanoparticles and Drugs & Antioxidants.

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