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Nanostructuring by Energetic Ion Beams

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Nanostructuring by Energetic Ion Beams

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Abstract. Development of nanostructured materials has become of wide interest due to their exotic properties and interesting physics aspects. Energetic ions play a crucial role in the development of nano materials. Ions of different energy regimes have different roles in growth of nano particles. Low energy ions (typically up to a (kiloelectronvolt) keV) in plasma, have been in use for growth of nano particle thin films. Low energy ions (typically a few hundred (kiloelectronvolt) keV) from ion implanters are used for growth of nano particles in a matrix. High energy heavy ions (swift heavy ions) have been in use in recent years for growth of nanostructures and also for modifying nanostructures. Highly charged slow moving ions and focused ion beams too, have potential for creating nanostructures. Out of these several possible roles of energetic ions, there have been developments at NSC Delhi in growth of nanostructures by RF plasma, low energy ions and swift heavy.

1. Introduction

Nanotechnology has become very popular and attracting field of research due to the possibilities of a wide range of promising futuristic applications. Physicists find it interesting as systems of confined low dimensions, representing a picture of quantum mechanically confined potentials, where the confining dimension is represented by the size of nanostructures. The ability of altering the properties (physical, electronic, optical, etc.) by merely changing the size of the nano particles makes it extremely suitable for a variety of applications. Most common and economical approach of generating nanostructures is the chemical rout, where the precipitation in a solution is arrested by capping the particles when they are in the region of suitable nano dimensions. If such a process is not arrested, one gets a colloidal solution and then precipitation in form of insoluble matter getting settled in the solution. One can produce powder and thin films of nano particles embedded in certain matrices by chemical routes. In most of the applications, one requires thin films in a suitable matrix, which is sometimes not achievable by a chemical route. There are other routes of creating nano structures like vapor phase condensation, thermal co-deposition, arc discharge, RF plasma sputtering, RF plasma co-sputtering, ion beam co-sputtering, ion implantation, other ion beam based methods, pulsed laser deposition etc. Two basic approaches in synthesis of nanostructures are the bottom up and top to down. In the bottom up

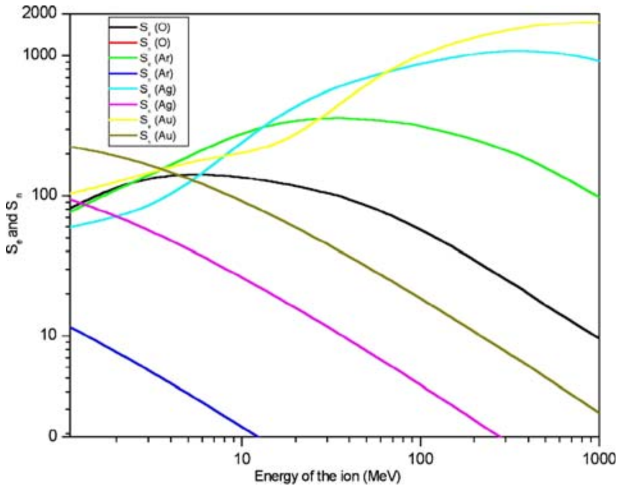

Figure 1. The electronic and nuclear energy losses for O, Ar and Au ions as calculated by TRIM. The values of S_e and S_n are in eV/A. The curves show that (1) the S_e at higher energies (about 100 MeV or higher) is always higher (two orders of magnitude or more) than S_n and (2) the value of S_e can be varied from about a few tens of eV/A to about 2 keV/A.

approach the atoms are brought together to form particles of nano dimension whereas in the top–down approach, the large size grains are broken to form nano size particles. In the ion beam based methods, mostly the bottom up approach is used.

In the present article, the methods related to energetic ions only, are discussed for synthesis of nanostructures. It is therefore essential to have some basic idea of ion–matter interaction.

During the passage through the material, energetic ions loose energy, which is quantitatively governed by the ion mass and its energy. Energy loss in the material can be either by elastic collisions or by in-elastic collisions. A typical curve for the energy loss in elastic collisions (nuclear stopping) and that in in-elastic collisions (electronic stopping) is given in Figure 1 as estimated by TRIM code [1]. Important features to be noted in these curves is that (1) the electronic energy loss dominates at high energies (>100 kiloelectronvolt (keV)/nucleon) and nuclear energy loss dominates at the low energies (<10 kiloelectronvolt (keV)/nucleon) and (2) ions of mass have higher energy losses (nuclear as well as electronic). It will be shown in the present article that the energetic ions have different types of role in nanostructure synthesis depending on the ion energies. This can be divided in three energy regimes e.g., (1) very low energies up to a few kiloelectronvolt (keV) suitable for sputtering purpose (2) energies from tens of kiloelectronvolt (keV) to a few megaelectronvolt (MeV)

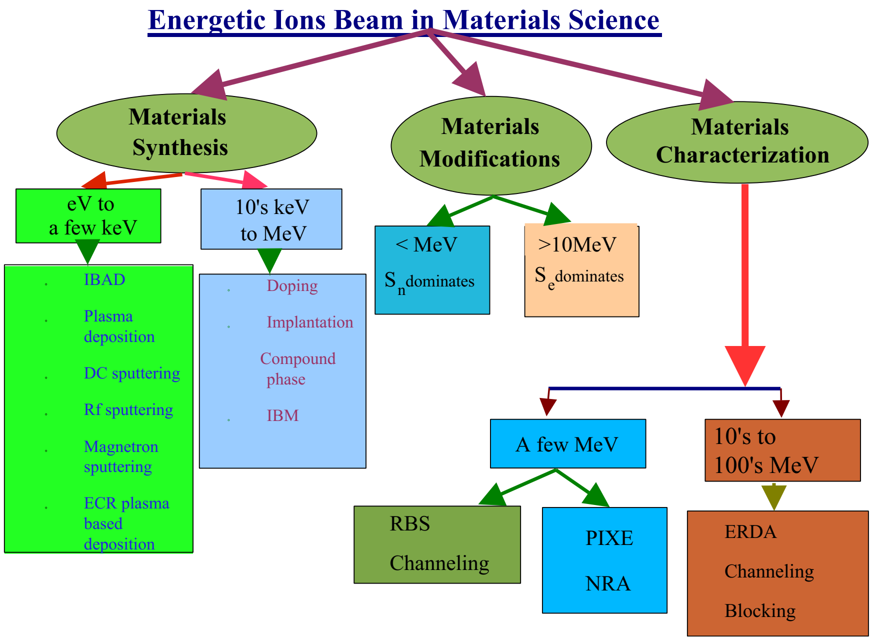

Figure 2. Schematic view to show the role of energetic ions in materials science in synthesis, modification and characterization of materials. A few electronvolts (eV) to a few kiloelectronvolts (keV) energy ions from ion sources or from plasmas play a crucial role in making thin films. IBAD stands for Ion Beam Assisted Deposition, which is a good tool to deposit films free from voids as compared to other conventional methods. ECR stands for Electron Cyclotron Plasma. The ECR source are popular due to their capability of providing high charge state of ions and high ion current. Low energy of 10 keV to about a MeV ions revolutionalized the field of semiconductor technology for doping semiconductors. IBM represents Ion Beam Mixing, a technique to produce compound phase by ion irradiation. These energies from ion implanters also find application in compound phase formation. Modification of materials have been shown both by S_n and S_e. Work on latter is mostly from mid eighties onwards. Rutherford backscattering (*RBS*), channeling, proton induced X-ray emission (*PIXE*), nuclear reaction activation analysis (*NRA*), elastic recoil detection analysis (*ERDA*), blocking etc. have been widely used characterization tools of ion beams.

and (3) energies (>1 megaelectronvolt (MeV)/nucleon), where electronic energy loss is dominant.

Energetic ions in general are of use to materials science as given in Figure 2. in different energy regions. They play a crucial roles in the synthesis, modification and characterization of materials. In the field of nano materials, the energetic ions are of use for synthesis and modification. The important issues in nano materials are the (1) control of the size of particles and (2) and the size distribution. This being a review will give a brief account of various aspects of the ion beam related to synthesis and modification of nano materials and the

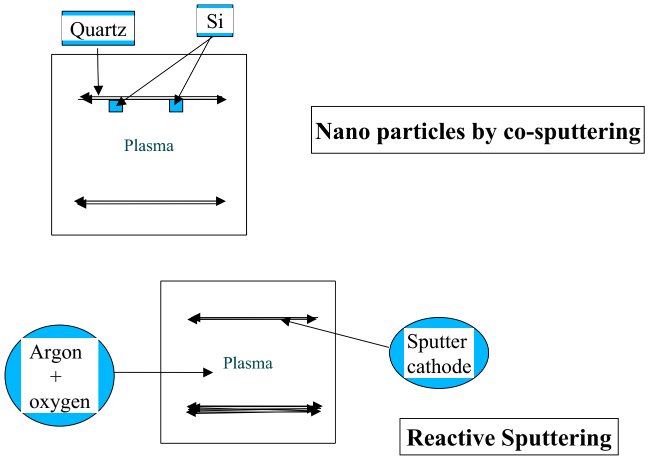

Figure 3. Schematic of (a) RF reactive sputtering and (b) RF co-sputtering. The Argon and oxygen gas ratios are controlled by mass flow controllers. The electrode at the bottom side is used to keep the substrate at which the film is to be deposited.

issues of control of size and size distribution will be discussed with examples of the work at NSC [3–7] and elsewhere [8–13].

2. RF sputtering and co-sputtering

Sputtering is a phenomenon of erosion of solids under ion impingement. Erosion of solids can be in the form of neutral atoms, ions, clusters etc. In contrast to thermal evaporation, where the vapors/atoms arrive at the substrate (for growth of film) with a typical energy of a fraction of an electronvolt (eV), the sputtered atoms arrive at the substrate with an energy of a few electronvolt (eV). This helps in the atomic motions/surface diffusion for better growth of the film and in the nucleation and growth of the nano particles in a matrix. A RF sputtering/co-sputtering set up (schematic as shown in Figure 3) has a sputtering cathode housed in a vacuum chamber, grounded electrode, RF power amplifier, matching network, mass flow controller, and a vacuum system. The substrate on which the nano particles in a matrix are grown in the form of a film is kept on the grounded electrode. The process of sputtering or co-sputtering can also be performed by an ion source or an atom source.

2.1. GROWTH OF NANO PARTICLES OF NITRIDE AND OXIDES OF COPPER BY REACTIVE SPUTTERING

An indigenous RF sputtering unit has been set up [2] at NSC. It has been used for reactive sputtering for the growth of copper nitride [3] and copper oxides [4].

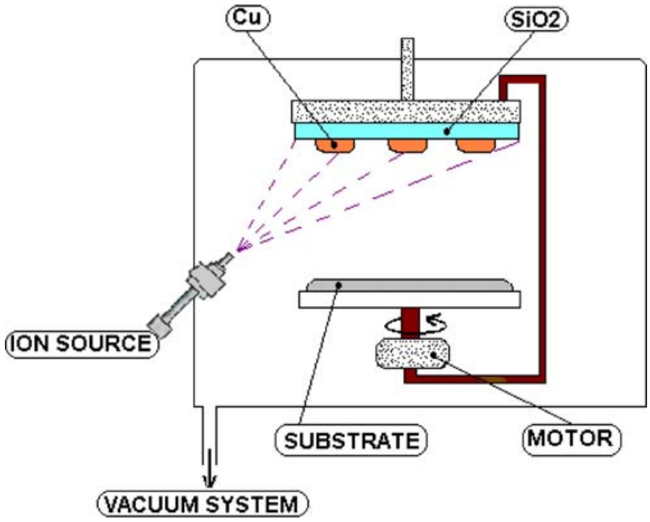

Figure 4. A sketch of atom beam sputtering. An ion source (in present case an atom source) is mounted in the chamber. Gas and electrical connections are provided by appropriate feedthroughs. The atoms from source strike the metal and silica, which sputter and get deposited on the substrate. The substrate is rotated by a motor for uniform deposition.

The operating pressure for copper nitride was 50 mtorr and the gas flow of N_2 was 15 sccm. RF power used was 100 W. Grain size of the copper nitride grown was 10 to 50 nm depending on the substrate temperature. More details of the deposition and characterization by XRD, ERDA and UV–Vis absorption spectroscopy are given in the work by Ghosh *et al*. [3].

The operating pressure for two oxides was 50 mtorr and oxygen gas flow was 7.5 sccm. RF power used was 200 W. The films were characterized for the size by atomic force microscopy and the X-ray diffraction. The later gives the average size distribution determined by the Scherer formula using the width of XRD peak. Average grain size of 10 to 45 nm was obtained depending on the substrate temperature [4].

In the above two examples, oxygen and nitrogen gases do the sputtering as well as provide the reactive environment of plasma for the formation of oxides and nitrides respectively.

2.2. GROWTH OF NANO PARTICLES IN A MATRIX BY RF CO-SPUTTERING

The experimental set up in this method remains the same except the sputtering cathode, which in this case is a disc of a dielectric matrix (for example silica) with a few pieces of the material (whose nano particles are to be formed) glued to the disc. These are spatially distributed uniformly for growth of uniform particle density. It is advisable to have substrate rotation during the deposition. Nanoparticles of ZnO in an SiO2 matrix by RF co-sputtering have been prepared at NSC [5].

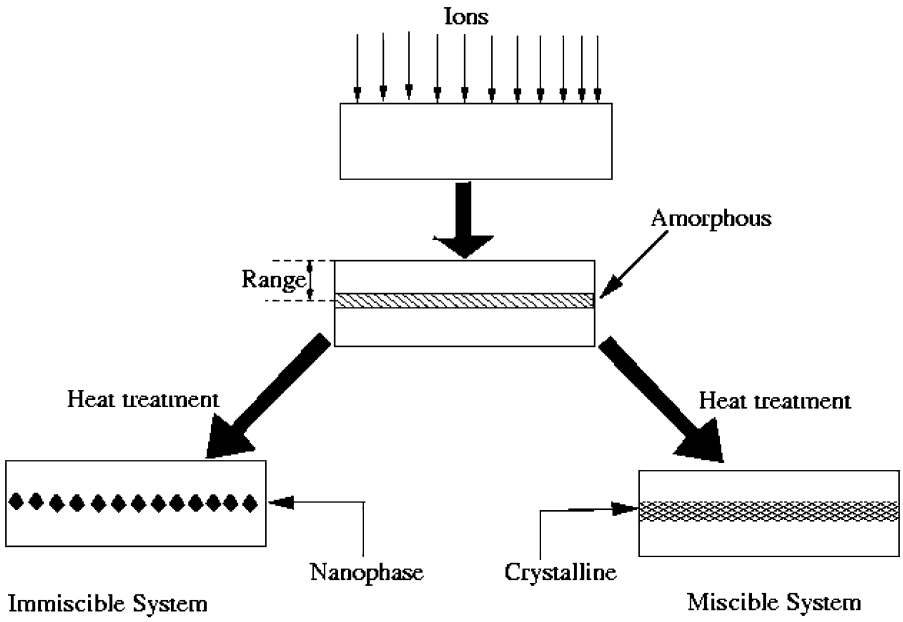

Figure 5. Schematic of creating nano particles buried in a matrix by ion implantation and subsequent annealing. Implanted species on subsequent annealing result in a crystalline phase (in case of a missible system) or in nano particles (in case of im-miscible system).

2.3. GROWTH OF Cu METAL CLUSTERS IN SILICA BY ATOM BEAM CO-SPUTTERING

A fast atom source is used to sputter the metal and silica simultaneously to obtain the embedded Ag and Cu particles in a silica matrix. The atom beam sputtering set up has recently been assembled at NSC. An atom source is preferred to an ion source to get rid of the problem of space charge near the insulating sputtering cathode. The characterizations of these metal particles embedded in silica matrix are in progress by UV–vis absorption spectroscopy, which reveals the surface plasmon resonance peak, a characteristic of metal particles in an insulating matrix. This aspect is briefed in Section 4.4 (Figure 4).

3. Nano particles by low energy ion irradiation

3.1. EMBEDDED Si NANO PARTICLES IN SILICA BY ION IMPLANTATION

Low energy ions typically up to a few tens of kiloelectronvolt (keV) to hundreds of kiloelectron (keV) are employed to implant the ions whose nano particles are to be formed in the substrate (in which the particles are to be embedded). The condition for such a process is that the implanted ion should not make a phase or compound with the substrate material. Energy of the ions decides the mean depth at which particles are embedded. A schematic of the process shown in Figure 5, gives in brief the route to form nano particles by ion implantation and subsequent annealing. In a recent work by Tanuja *et al*. [7], Si nano crystal in silica matrix are grown by implantation of 100 keV Si in silica and subsequent annealing. These samples of Si nano crystals in silica were characterized by photo luminescence. Normally size distribution achieved by this method is rather wide. The efforts are going on to achieve a narrower size distribution by SHI irradiation. It is expected that each SHI will produce a defected zone of certain diameter and therefore Si nano particle size will be narrowed down to the diameter of the track during annealing of SHI irradiated, Si implanted samples.

3.2. FORMATION OF C DOTS

Carbon dots are shown to be formed by irradiation of Si based polymers (Methyltriethoxysiulane) by 3 MeV Au ions. These were characterized by high resolution transmission electron microscopy. It was shown that the dot size (typically 5 nm) is decreasing with the increase of the fluence [8]. The irradiated films exhibit photo luminescence at 2.1 eV and is maximum at the fluence of 10^{14} ions/cm^2. It was also shown that the size of the particles were dependent on the fluence.

4. Swift heavy ions (SHI) in nanostructuring

4.1. GENERATION OF ALIGNED C CLUSTERS IN NANO SIZE CYLINDERS

It was shown by Pivin *et al*. [8] and Seki *et al*. [9] that the irradiation of Si based polymers by swift heavy ions creates C clusters all along the ion path in the entire sub-micron thick film. The cylinders were however filled only up to 60% or so with the clusters [9]. If this filling can be increased to 100% it will be like a quantum wire. Irradiation by 100 MeV Au ions, using the NSC Delhi Pelletron facility, was performed on the polycarbosilane (PCS) and Allylhydridopolycarbosilane (HP CS). TEM and EFTEM revealed the alignment of carbon clusters all along the ion path. Photoluminescence observed in these samples was more or less the same as in the case of low energy ion irradiation (3 MeV Au ions).

4.2. CREATION OF UNIFORM SIZE DISTRIBUTION OF NANO PARTICLES

It has been shown by Valentine *et al*. [10] that a more uniform size distribution can be achieved by the use of 30 MeV Si ions. Normally Cu and copper oxide nano particles in glass matrix are obtained by annealing of the glass containing Cu. If the system is irradiated before annealing a better size distribution is achieved. This was correlated to the electronic energy loss estimated by TRIM. As the ions penetrates the material they loose energy and therefore the electronic energy loss changes at different depths. It was shown by cross sectional TEM that such a phenomenon takes place up to a certain depth which indicates the role of electronic energy loss, in achieving better size distribution as compared to the conventional tools. It suggests that there is a threshold of electronic energy loss above which it helps in achieving a better size distribution.

4.3. CONDUCTING C RODS IN DIAMOND LIKE CARBON

The irradiation of diamond like carbon (DLC) film leads to the increase in conductivity. It is therefore expected that all along each ion track created by individual ion impact will have higher conductivity than the surrounding. It is therefore possible to generate conducting C rods or nano wires in the DLC matrix by high energy heavy ion irradiation of DLC film as demonstrated recently [11]. The DLC films were irradiated by 350 MeV and 1 GeV Au ions and the resistance measurement at the ions' impacts is carried out by scanning force microscopy. It gave a significant increase in conductivity, revealed by the large current flowing from the scanning force microscopy tip to the substrate via the ion path in the film. There is depletion of H along the ion path and structural modifications making the zone along the ion path more like graphite, which is cause of the high conductivity along the ion path. Possibility of creating conducting carbon tracks in fullerene matrix is planned at NSC by swift heavy ion irradiation of thin fullerene films.

4.4. EFFECT OF SHI IRRADIATION ON METAL PARTICLES IN INSULATING MATRIX

Metal nano particles in an insulating transparent matrix like silica have the property of absorbing visible light in a narrow band owing to a surface plasmon resonance. The collective motion of free electrons in the particle induced by the oscillating electric field vector of incident electromagnetic wave is called as surface plasmons. The resonance frequency of the spherical metal nano particles depends on the size of the particles and the dielectric constants of the particle and the surrounding medium. In cases of metal nano particles in an insulating transparent matrix, the UV–Vis spectroscopy becomes an excellent tool to characterize the nano particles by surface plasmon resonance. There are possibilities of interacting nanoparticles for miniature waveguides [12]. The effect of SHI on metal nano particles is of interest (1) to understand the ion and low dimension matter (2) to look into the details of modification to probe the possibilities of engineering the nano structures.

4.4.1. *Growth of Au particle size under SHI irradiation*

Au nano particles were grown in a Teflon matrix by tandem deposition [13]. Size of Au particles (in as deposited film) was not spherical as investigated by TEM.

The samples were prepared specially on TEM grids [13] for the ease of characterization. The samples on TEM grids were irradiated by 100 MeV Au ion beam at different fluences. It was observed [14] that the shape of particles became spherical and the size starts growing with fluence. The formation of perfect spherical particles indicates the possibility of the existence of a transiently molten state, as in the molten state the metal will like to have spherical shape like a liquid drop. In general the average size (about 9 nm before irradiation) of the particle became about 14 nm after irradiation. It shows that the particles coalesce together to form a bigger particle under SHI irradiation.

4.4.2. *Effect of SHI irradiation on Ag particles in insulating matrix*

Ag nano particles were also made in the similar way as stated above on TEM grids and were irradiated at different fluences. The TEM study of the irradiated samples indicated different type of behavior as observed in Au particle case. The average size of particles is reduced slightly. It appeared that there is loss of Ag content which is attributed to the electronic sputtering of Ag particles. Smaller the size of particle, greater is the confinement of electrons [15–17] (produced in the wake of passage of incident high energy ion) within the particle, which causes higher temperature rise resulting in transient molten state during which the metal atoms escape.

Randomly distributed Ag particles in silica matrix are shown [18] to be aligned along the beam direction as a result of 30 MeV Si ion irradiation. This was investigated by plan-view TEM. This is an excellent approach to align the existing particles in a matrix.

In an another experiment Ag particles were grown in silica by magnetron co-sputtering and then the response of irradiation of 100 MeV Ag was studied [19]. It was observed that the Ag atoms were released from the clusters as a result of irradiation indicating dissolution of clusters in silica. This conclusion was based on the decreasing integral intensity of the plasmon resonance peak with the fluence. The decrease in particle size in the work by Biswas *et al.* is also consistent with the present observation. It is apparent that the matrix in which the particles are existing also plays a role in deciding the effect of swift heavy ions on the nano particles. In this work, the aspect of aligning of the clusters along the beam direction was not studied, which requires cross sectional TEM.

4.5. EFFECT OF SHI ON COPPER OXIDE NANO PARTICLES

Copper oxide nano particles were prepared by the activated reactive evaporation method [20]. The effect of large electronic excitation (24 keV/nm) generated by 120 MeV Ag ions was examined by X-ray diffraction, Raman spectroscopy and photoluminescence [21]. The XRD revealed that the pristine films were having both the phases CuO and Cu_2O and the irradiation induced a phase change from CuO to Cu_2O. It is most likely due to release of oxygen. The crystalline quality of the films appeared to have improved with irradiation. It was observed that the PL intensity increased in the irradiated sample, which was attributed to the removal of surface states. This observation is similar to the results [22, 23] of 1 MeV proton irradiation of CdS nanoparticles, where the irradiation leads to increase of the PL intensity which was attributed to the removal of surface states.

4.6. EFFECT OF SHI ON SEMICONDUCTOR NANO PARTICLES IN POLYMER MATRIX

Nano particles of ZnO in polyvinyl alcohol matrix were prepared and irradiated by 100 MeV Cl ions. It was observed [24] that the particle size increased from about 1 nm for a pristine sample to 4 nm at the fluence of 5×10^{12} ions/cm^2. The size went up sharply at the fluence of 10^{13} ions/cm^2. The characterizations were performed by UV–Vis absorption spectroscopy and electron microscopy.

4.7. SHI INDUCED FORMATION OF Si NANO PARTICLES

Thin films of SiOx were irradiated with swift heavy ions [25], as a result of which the formation of Si nano crystals was reported. This was investigated by PL and TEM. The irradiation causes evolution of oxygen from the film. The possible reaction due to SHI was formation of Si nano crystal with SiO_2 accompanied by release of oxygen. This could be explained on the basis of the occurrence of transient temperature spike during which a molten state is created all along the ion path, resulting in release of oxygen and the formation of Si nanocrystals. Creation of such latent tracks in the insulating matrix is already known.

5. Future promising aspects of ion beams in nanostructuring

There is a variety of possibilities, in which energetic ions can play a crucial role in the engineering of nanomaterials. Most of these possibilities are touched upon as stated in above sections. A key issue is presently to generate the nano dots in a regular pattern. A possibility in this direction is to use focused ion beams of nano dimensions (current state of art is beams of 10 to 20 nm size) for creation of defects in a regular pattern and then growing quantum dots on these defected zones. Since the defected regions are excellent nucleation sites, this is likely to produce nanostructure as desired. The nano beam will also play a crucial role in characterization of nano particles, where the composition and structure can be probed at a nano scale. Another interesting way of achieving nanostructures at a surface is by irradiation of highly charged ions, which is not discussed in this article.

6. Conclusion

The present article gives a very brief overview of the interesting aspects of ions in different energy regimes for nano structuring, with examples of the work carried out at NSC. The ion energies from a few tens of electronvolt (eV) (in atom sputtering and RF sputtering) to a few hundred megaelectronvolt (MeV) are presented in context of synthesis and modification of nano-structures.

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