CHAPTER 5

SWIFT HEAVY ION ENGINEERING OF NANOPARTICLES

Synthesis of nanoparticles/nanostructures with controlled size, shape and size distribution is major requirement in nanoscience and nanotechnology. Swift heavy ion irradiation has been proven to be the unique tool for controlled engineering of nanomaterials under appropriate selection of different parameters. This chapter has been divided into three sections. First section describes the reduction of gold nanoparticles under SHI irradiation. Controlled growth of gold nanoparticles under SHI irradiation, confirmed by an in-situ X-ray diffraction is briefed in second section. Elongation of gold nanoparticles along the ion beam direction is described in section three. The aspect ratio of elongated nanoparticles has been observed to depend on ion beam parameters. A summary of engineering of nanoparticles using swift heavy ions is discussed in the end.
5.1 Introduction to SHI Engineering of Nanoparticles

Noble metal nanoparticles (NPs) embedded in dielectric matrices exhibit interesting physical and chemical properties. These properties strongly depend on the size and shape of nanoparticles and the dielectric properties of the matrix in which they are embedded. Elongated metal nanoparticles show two surface plasmon resonance (SPR) bands due to transverse and longitudinal modes of charge density oscillations when excited by electromagnetic radiation. The controlled synthesis of nanoparticles with desired size and shape provides a unique way to tailor the properties of nanomaterials for different applications. Several physical and chemical techniques have been employed for synthesizing the nanostructures, but control over size and shape and reproducibility have always been the major issues and challenge for the scientific community. The control of size, shape and size distribution of NPs is investigated under swift heavy ion (SHI) irradiation.

SHI irradiation of the metal-nanoparticles has been proved to be the unique tool for controlled engineering of size and shape of nanomaterials [1-6]. As MeV ions pass through the nanocomposite system, they deposit large amount of electronic energy within a localized volume, which leads to the modification of nanomaterials [7]. SHI ions create cylindrical ion tracks [8, 9] with size in nanometric dimensions, when pass through insulating materials, and the material present within the track can be engineered. Spatial selectivity and controlled energy deposition are the unique features of swift heavy ions. Ion beam irradiation of nanoparticles embedded in insulating matrix can result in dissolution [10-12] and growth of nanoparticles [4], which can be controlled by ion beam parameters (dE/dx and fluence) and size and interparticle separation of nanoparticles. Size distribution of nanoparticles can also be modified by SHI irradiation. The passage of SHI ions also results in elongation of nanoparticles along the ion beam direction. The aspect ratio of elongated nanoparticles has been observed to be depending on the product of electronic energy loss and ion beam fluence. Thus SHI ions have proven to be the unique tool for engineering of nanomaterials. In this chapter we will discuss the dissolution, growth and elongation of gold nanoparticles embedded in silica matrix under...
SHI irradiation in terms of (i) dE/dx, (ii) fluence, (iii) size of nanoparticles and (iv) interparticle spacing.

5.2 SHI Induced Size Reduction of Gold Nanoparticles

Gold nanoparticles embedded in silica matrix, prepared by thermal co-evaporation and subsequent annealing, were irradiated with swift heavy ions. Optical absorption and TEM studies of pristine and irradiated samples confirmed the reduction of Au NPs after ion irradiation but the size distribution becomes relatively narrower that of pristine sample.

5.2.1 Experimental Details

Au and silica were co-evaporated inside a high vacuum chamber using resistive heating and an electron gun respectively [10]. The vacuum of \( \sim 5 \times 10^{-7} \) torr inside the chamber was maintained by a diffusion pump and a rotary pump. The vacuum during deposition was \( \sim 10^{-6} \) torr. Thin films with thickness \( \sim 30 \) nm were deposited on quartz and silicon substrates as monitored by a quartz crystal thickness monitor. Rutherford backscattering spectroscopy (RBS) measurement was performed using 2.4 MeV He ions at Orsay, France. RBS analysis of the Au-SiO\(_2\) as deposited films confirmed the existence of gold with atomic fraction of 5.3% in nanocomposite film as analyzed by RUMP simulation [13] of the RBS data. The deposited films were annealed at 900ºC in an argon environment for 30 minutes. The Au-silica nanocomposite film was irradiated with 90MeV Ni ions at a fluence of \( 1 \times 10^{13} \) ions/cm\(^2\) at IUAC, New Delhi. UV-visible absorption spectra of pristine and irradiated samples were recorded using a dual beam spectrophotometer Hitachi U3300 in the spectral range 400 – 750 nm. TEM measurements were carried out at 200 keV using the JEOL 2010 UHR TEM facility at Institute of Physics, Bhubaneswar.

5.2.2 Results and Discussions

5.2.2.1 Optical Absorption Studies

Optical absorption spectra corresponding to pristine and irradiated Au-silica nanocomposite (NC) film is shown in Fig. 5.1. The surface plasmon resonance peak around 525 nm clearly indicates the presence of nanoparticles in pristine sample. The
decrease in full width at half maximum (FWHM) and reduction in intensity of SPR after irradiation with 90MeV Ni ions at fluence $1 \times 10^{13}$ ions/cm$^2$ in case of irradiated samples confirm the reduction of gold nanoparticles.

![Optical absorption spectra](image)

**FIG. 5.1**: Optical absorption spectra of pre and post irradiated Au-silica NC film.

### 5.2.2.2 Transmission Electron Microscopy Results

TEM micrographs of Au-silica nanocomposite sample on TEM grid before and after 90MeV Ni ion irradiation are shown in Fig. 5.2 (a) and (b). The size distributions corresponding to TEM images 5.2 (a) and (b) are shown in Fig. 5(c) and 5(d) respectively. The micrograph corresponding to pristine sample reveals the average size of nanoparticles $\sim$ 10.1 nm. Size distribution corresponding to pristine sample reveals the presence of gold nanoparticles with average size (diameter) $\sim$10.1 nm. However the size distribution corresponding to irradiated sample, shown in Fig. 5(d), clearly shows the presence of gold nanoparticles with average size around 8.8 nm. Thus the TEM results clearly indicate the reduction of Au nanoparticles. In order to have better statistics of nanoparticle size distribution, 10 frames from different sections of each TEM grid were analyzed. In 10 sections of pristine sample, total number of gold nanoparticles was $\sim$ 1060 which reduced to a number 640 after SHI irradiation. Thus TEM results confirm the
reduction of size of nanoparticles with a reduction of nanoparticles density under SHI irradiation, which is due to the dissolution of gold atoms into silica matrix. Size distributions of pristine and irradiated samples reveal an interesting feature narrowing the size distribution.

FIG. 5.2 (a to d): Transmission electron microscopy image of (a) pristine and (b) irradiated Au-silica nanocomposites. The size distributions corresponding to TEM images (a) and (b) are shown in (c) and (d) respectively.

The observed reduction of Au NPs under SHI irradiation is in good agreement with increase in FWHM and decrease in SPR intensity in optical absorption result. The average interparticle separation was calculated theoretically using RBS data which revealed the average interparticle distance (surface to surface) to be around ~14.2 nm.

The passage of swift heavy ions creates nanodimensional cylindrical ion tracks in silica and the Au NPs and silica present within the track goes into molten state due to thermal spike for short duration (~10^{-12}s). During the transient molten state (temperature spike) the gold atoms migrate from surface of molten gold nanoparticle and dissolve in the
surrounding molten silica, which is called dissolution. Since interparticle separation is this case is quite large (~14.2 nm), the migrated atoms dissolve into silica matrix leading to the reduction of size of nanoparticles.

5.3 SHI Induced Growth of Au Nanoparticles: An in situ- XRD Study

The growth kinetics of Au NPs was studied under 90 MeV Ni ion irradiation by in-situ X-ray diffraction [4]. In-situ XRD technique was preferred to study the growth kinetics of NPs because generally there are variations from sample to sample in synthesis of nanoparticles in a matrix and the effect of ion irradiation is dependent on the initial or virgin state of the sample. Therefore it is desirable that the ion fluence dependence study should be performed on the same sample. The incidence angle \( 1^\circ - 2^\circ \) in the grazing incidence XRD experiments cannot be perfectly reproduced in case of different samples, as it depends on the gluing of the sample on the holder. The in-situ XRD facility [14], recently commissioned at IUAC allows studying the XRD of the same sample at various ion fluences to understand the influence of SHI on average size of Au NPs in silica.

5.3.1 Experimental Details

Thin films of silica (thickness ~ 140nm) having Au NPs embedded in it, were deposited on quartz and TEM grid by atom beam co-sputtering [15-17]. RBS was used for the quantification of gold fraction in SiO\(_2\) [section 5.2.1]. The Bruker D8 Advance diffractometer, after suitable modification, is integrated with a vacuum chamber connected to the beamline of the accelerator [14]. The Au-silica nanocomposite of silica embedded with Au NPs on quartz substrates was irradiated with 90 MeV Ni ions [4]. The mean projected range for 90MeV Ni ions in silica is ~18.5 μm (much larger than the film thickness) and the electronic and nuclear stopping powers are 7.2 and 0.01 keV/nm respectively [15]. The irradiation fluence was varied from \( 1 \times 10^{13} \) to \( 1 \times 10^{14} \) ions cm\(^{-2}\) using 15UD Pelletron accelerator. Vacuum inside the XRD chamber was ~ \( 10^{-5} \) torr during irradiation. Sample was irradiated at normal beam incidence. The XRD spectra of the sample were recorded after every fluence of 2 x \( 10^{13} \) ions cm\(^{-2}\) using a position sensitive, Vantec detector with angular increment of 0.02°. The use of Vantec detector (due to its position sensitivity) makes the data acquisition sixty times faster than the conventional
NaI detector, which is desirable for in-situ measurement. UV-visible absorption spectra of pristine and irradiated samples were recorded using Hitachi U3300 spectrophotometer. Planer and cross-sectional-TEM measurements were carried out using a JEOL JEM-3010 300 kV machine with a LaB\textsubscript{6} electron source at University of Chicago.

5.3.2 Results and Discussions

5.3.2.1 RBS and X-ray Diffraction Results

RBS spectrum of co-sputtered Au-SiO\textsubscript{2} nanocomposite film is shown in Fig. 5.3. RUMP analysis [13] of RBS data confirmed the presence of Au with atomic fraction of \(\sim 19.6\%\) in nanocomposite film with equivalent thickness of silica film \(\sim 140\) nm.

![RBS spectrum of the as-deposited sample.](image)

The XRD spectra of pristine and irradiated samples (shown in Fig. 5.4) at different fluences clearly indicate the growth of Au nanoparticles with ion beam fluence. A continuous decrease in FWHM of the FCC (111) peak for gold in XRD spectra is observed with increase in fluence. Initially there is a rapid growth (almost linearly) of nanoparticles with fluence (Fig. 5.5) but beyond a critical fluence the growth rate is decreased. The average size of the nanoparticles was estimated using Scherrer's formula.
FIG. 5.4: X-ray diffraction spectra of pristine and irradiated sample.

FIG. 5.5: Variation of nanoparticles size and lattice constant with ion fluence. The growth of nanoparticles occurs rapidly up to ~7 nm with increase in fluence up to $4 \times 10^{13}$ ions cm$^{-2}$, beyond which the growth rate decreases with fluence.
Optical absorption results of irradiated sample at highest fluence showed a decrease in full width at half maximum and a corresponding red shift (~22nm) in SPR peak position as compared to pristine sample. The decrease (~22nm) in FWHM and red shift also indicate the growth of gold nanoparticles.

5.3.2.2 Transmission Electron Microscopy Studies
SHI irradiation induced growth of Au NPs was confirmed by the TEM measurements of the pristine and irradiated samples. Fig. 5.6 (a) and (b) show TEM micrographs of pristine and irradiated samples respectively. The TEM results clearly show the growth of Au nanoparticles from a pristine Au nanoparticles size of about 5.7 nm to about 9 nm that occurred at the highest fluence in agreement with XRD results.

![TEM micrographs](image)

**FIG. 5.6:** TEM micrographs of silica films containing Au nanoparticles before (a) and after irradiation (b) suggesting a growth of the Au nanoparticles upon irradiation. Figure (a) shows the TEM image of pristine sample and (b) shows the TEM micrograph for sample irradiated with 90 MeV Ni ions at a fluence of 1x10^{14} ions cm^{-2}. TEM measurements were performed on pristine and irradiated Au-silica nanocomposite film deposited on TEM grids.

The size distributions of gold nanoparticles corresponding to pristine and irradiated sample are shown in Fig. 5.7 (a) and (b) respectively. The average size of nanoparticles in
case of pristine sample is around ~5.7 nm however it is ~9 nm in case irradiated sample after a fluence of 1x10^{14} ions/cm^2. Thus the observed results from TEM analysis are in good agreement with the observations and interpretations made from in-situ X-ray diffraction data on the Au nanoparticles growth. Cross-sectional transmission electron microscopy results of irradiated Au-silica nanocomposite film, which was used for in-situ XRD experiment also revealed the presence of Au nanoparticles with average size of ~9 nm with narrower size distribution.

![Size distribution of Au NPs embedded in silica matrix before (a) and after 90 MeV Ni ions at a fluence of 1x10^{14} ions cm^{-2}.](image)

FIG. 5.7: Size distribution of Au NPs embedded in silica matrix before (a) and after 90 MeV Ni ions at a fluence of 1x10^{14} ions cm^{-2}.

The passage of 90 MeV Ni ions through thin silica film containing the Au NPs deposits the electronic energy, (S_e), of 7.2 keV/nm as estimated by SRIM. These nanocomposite thin films were synthesized by atom beam co-sputtering and the pristine film is likely to have particles with a certain size distribution along with some gold atoms in atomic state itself. The calculated interparticle separation from RBS data is ~2.1 nm which is very small as compared to that observed in case of Au nanoparticles synthesized by thermal evaporation and subsequent annealing. Thus in present case when gold silica nanocomposite film is irradiated by swift heavy ions, dissolution of gold atoms occurs into silica due to thermal spike. Since the interparticle separation is very small in present case, the dissolved atomic gold species further agglomerate with other nanoparticles resulting in growth. It is known from the work done by Meftah [8] and Toulemonde et al
[9] that a $S_x$ loss of $\sim 7$ keV/nm in silica creates the track diameter of $\sim 7$ nm in silica. We therefore expect that 90 MeV Ni ions in present case create the track of diameter about $7 \text{ nm}$. The material within the ion tracks goes to molten state due to thermal spike produced by ion for a short duration of time ($\sim 10^{-12}s$). The diffusion of Au atoms and smaller particles to bigger particles leads to ripening of Au nanoparticles in the latent track around ion path. The diffusion of clusters [19] and atomic species [20] within the ion track has been shown in recent experiments. Normally it is expected that the growth of particles should not exceed the track diameter, whereas in the present case the particle growth is observed to be occurring with fluence beyond the track diameter. This can be explained by the fact that the temperature of silica in annular region around ion track is $1000^\circ C (\sim 10^{-12}s)$ within a diameter of 14 nm, (Fig. 5.8) [9], which is sufficient for the melting of Au nanoparticles transiently.

![Graph](image)

**FIG. 5.8:** Variation of lattice temperature with radius of molten zone, [Thermal spike calculation for 90 MeV Ni ions in silica by Toulemonde et al. (9)].

Since it is known [21, 22] that the melting point (Fig. 5.9) of Au nanoparticles is less than that of bulk value (Fig. 5.9) of $1060^\circ C$, and for a Au NP with diameter 4 nm, it is around $\sim 700^\circ C$. Therefore it is expected that the silica of the annular region (of diameter $\sim 14$
nm) around the ion track has temperature high enough to melt the Au nanoparticles. During the transient melt phase of Au, further diffusion of Au occurs in the silica. The high temperature of silica leads to Ostwald ripening of Au nanoparticles. As the fluence increases, the overlapping of latent tracks occurs, which leads to further agglomeration of Au nanoparticles due to enhanced diffusivity within overlapped ion tracks. It is clear from the Fig. 5.5, that up to track diameter of ~7 nm a rapid growth of Au nanoparticles occurred with increase in fluence which is due to the enhanced diffusivity of Au within the ion track because both Au and silica are in transient molten state. However, beyond the core of ion track, the rate of growth of nanoparticles is slowed down due to decreased diffusivity of molten Au in silica in solid state. The Au nanoparticles are still in molten state as their melting temperature is lower than bulk value. The growth in size up to about 9 nm with fluence has been observed and is shown in Fig. 5.5.

![Graph showing melting point vs. particle diameter](image.png)

**FIG. 5.9:** Reduction of melting point with a decrease in size of Au NPs, showing both theoretical [23] and experimental [24] for Au NPs encapsulated in silica [24].

In-situ XRD spectra (Fig. 5.4) shows a regular shift in the diffraction peak of the Au (111) towards larger angle with increase in fluence, which indicates a decrease in lattice constant as shown in Fig. 5.5. This decrease could be attributed to the decrease in surface
tension [25] of Au nanoparticles with the increase in size. It is well known that the surface effect is significant for small size nanoparticles. As the particles size increases, the surface effect and hence the surface tension decreases, which leads to decrease in lattice constant at higher fluences.

5.4 Swift Heavy Ion Induced Elongation of Au Nanoparticles

In this experiment, we synthesized elongated Au nanoparticles (NPs) parallel to each other, embedded in silica matrix using SHI irradiation. The Au-silica nanocomposite samples, synthesized by RF-co-sputtering and subsequent annealing, were irradiated by 120 MeV Au ions at different fluences to induce elongation. Optical absorption study of irradiated film showed a clear splitting of surface plasmon bands corresponding to transverse and longitudinal modes of charge density oscillations. TEM investigations of pristine and irradiated samples revealed an elongation (aspect ratio ~ 3.5) in Au NPs occurred as a result of irradiation.

5.4.1 Experimental Details

Thin films of silica containing Au were deposited on silica substrates by RF-magnetron sputtering [5] (at Bulgaria) in an Ar atmosphere (5Pa) of a silica target on which Au sheets were placed in the maximum erosion zone. The films were annealed in Ar: 5% H₂ atmosphere for 1h at 950°C for promoting the growth of Au particles. RBS was used for quantification of gold fraction in silica. The measured thickness of films found by fitting the RBS spectra with RUMP code [13] was of 200 nm and the mean Au fraction of 15 at.% ± 1 at. % with depth. No loss of Au by evaporation or diffusion inside the substrate was observed after annealing at 950°C for 1h. Annealed films were irradiated with 120 MeV Au ions delivered by 15 UD pelletron at IUAC, New Delhi. The samples were irradiated with an ion beam 45° off normal at fluence of 3x10¹³ ions-cm⁻². The electronic (Sₑ) and nuclear (Sₙ) stopping powers of these ions were calculated with SRIM program [18] and were found to be ~ 14.1 keV/ nm and ~ 0.2 keV/nm respectively with ion range of ~16 μm. Optical absorption spectra were recorded with linearly polarized light along two perpendicular directions, one being the projection of the ion beam in the surface plane (noted //) and the other being in transverse direction being noted ⊥). Cross-sections
of the pristine and irradiated sample were observed by TEM, using the high resolution Philips CM 20 FEG field emission electron microscope of Max Planck Institute, Halle.

5.3.2 Results and Discussion

5.4.2.1 Transmission Electron Microscopy Studies

Cross-sectional TEM (X-TEM) image of pristine sample, shown in Fig. 5.10(a) clearly reveals the existence of spherically shaped nanoparticles with average size (diameter) ~ 13.5 nm as evident from size histogram shown in Fig. 5.10(b).

![X-TEM image of pristine film and NP size distribution](image)

**FIG. 5.10(a)** X-TEM image of pristine film and (b) corresponding NP size distribution.

Fig. 5.11 (a) shows the X- TEM image of sample irradiated with 120 MeV Au ions at fluence (\(\phi\)) \(3 \times 10^{13}\) ions-cm\(^{-2}\) with the ion beam 45° off normal. Clearly after irradiation, elongation of Au NPs occurs along ion beam direction forming prolate shaped particles.

The major axis length is ~ 25 nm while the minor is ~ 10 nm as evident from Fig. 5.11 (b and c). The average aspect ratio of the elongated nanoparticles is 2.5. Correcting for the 45° projection of the TEM image with respect to the ion beam direction, the actual aspect ratio is ~ 3.5. However it can also be clearly observed from TEM image of irradiated samples that a few NPs with size below 13 nm remain spherical even after irradiation.
FIG. 5.11 (a) X-TEM image of an irradiated film at 45° beam incident normal.

FIG. 5.11 (b and c): Size distribution of major (b) and minor (c) axis lengths of elongated nanoparticles after irradiation at 45° beam incident normal.

Fig. 5.12 shows the average size of Au NPs (average of major and minor axis lengths) after irradiation. It is clear from Fig. 5.12, that ion irradiation leads to a relatively narrower size distribution. There is not much growth along the oblate axis (perpendicular direction). Due to the modification induced by ion beam, the nanoparticles expand along ion beam direction and thus transform spherical particles to prolate shaped particles.
It is noticed that when the longitudinal separation between the spherical nanoparticles was small, the end of prolate spheroid join together and thus formation of a large prolate spheroid like a nanorod with large aspect ratio occurs. A close perusal of the TEM image of the irradiated sample suggests that the ion beam induced elongation occurs beyond a threshold size of nanoparticles and below which nanoparticles grow. A nominal growth in smaller particles with ion irradiation is observed due to Ostwald ripening induced by large electronic energy deposition. The growth of Au NPs from 4 to 9 nm by electronic excitation (induced by ion irradiation) using an in-situ XRD experiment has been explained in section 5.2.

5.4.2.2 Optical Absorption Results

Optical absorption spectra of pristine and irradiated samples are shown in Fig. 5.13. The pristine sample shows a clear SPR absorption band at $\sim 2.44$ eV as expected from the Au nanoparticles in pristine sample. Optical absorption spectra for irradiated sample were recorded with polarized light parallel ($//\parallel$) and perpendicular ($\perp\perp$) to the ion incident direction. The significant red shift ($\sim 0.17$ eV) in SPR peak position of Au nanoparticles along parallel direction reveals the elongation of Au nanoparticles. However, insignificant shift in SPR band along perpendicular direction indicates a small
compaction in the direction perpendicular to ion beam.

![Absorption spectra of pristine and irradiated sample with polarized light.](image)

FIG. 5.13: Absorption spectra of pristine and irradiated sample with polarized light.

The passage of 120 MeV Au ions through thin silica film containing the Au nanoparticles deposits the electronic energy, \( (S_e) \), of 14.1 keV/nm. It is known from the work done by Meftah and Toulemonde et al. [8, 9] that an electronic energy loss of ~14 keV/nm in silica creates the track diameter of ~10 nm in silica. Hence 120 MeV Au ions in present case create the track of diameter about 10 nm. Each individual Au ion impact in silica leads to the formation of thermal spike (duration ~ 10^{-12} s). There are two possible mechanisms of elongation of nanoparticles along the track. Both of them are discussed here and one of them is ruled out on the basis of experimental observations.

Each individual Au ion impact in silica leads to the formation of thermal spike (duration ~ 10^{-12} s), which results in plastic flow of silica. This plastic flow induces an in-plane stress perpendicular to the ion beam direction. The stress change is attributed to radiation-induced plastic flow, which serves to relieve stress in the material and also the stress relaxation is accompanied by an increase in the density. The combined effect of all ion impacts on planer Au-silica nanocomposites film builds up a larger pressure on nanoparticles which results in its elongation along the ion track.
If the elongation of nanoparticles along the ion track is due to the pressure effect, smaller gold nanoparticles must have elongated, which has not been observed as evident from Fig. 5.10(a). It can be clearly seen that the gold nanoparticles with size less than track diameter remains spherical after ion irradiation however a nominal growth of nanoparticles occurs in agreement with earlier in-situ XRD experiment. Hence pressure effect is not only the mechanism, which is completely responsible for elongation of nanoparticles. Thus a new mechanism called dissolution re-precipitation mechanism may be responsible for elongation process under ion irradiation. It is well established that growth of nanoparticles under MeV ion irradiation is due to the dissolution-reprecipitation mechanism because of thermal spike model. When an atom present at the surface of nanoparticle receives energy larger than its binding energy, it dissolves into the matrix and further combines with other neighboring nanoparticle resulting in growth of nanoparticle provided the distance between the neighboring nanoparticles is smaller than the diffusion length of migrated atoms. When swift heavy ions pass through the nanocomposite film, it results in dissolution of smaller nanoparticles present within the track. These dissolved nanoparticles are reprecipitated on the bigger nanoparticles present within the track, resulting in formation of elongated nanoparticles (Fig. 5.14). A schematic of formation of elongated nanoparticle after swift heavy ion (SHI) irradiation is shown in Fig. 5.14. However few nanoparticles of smaller size still remain spherical, with a nominal growth in their size. The exact mechanism of growth or reduction and elongation of particles is still an open question, which demands for more experiments with different particle size and interparticle separation to be performed.

**FIG. 5.14:** Schematic of formation of elongated nanoparticle based on dissolution-reprecipitation mechanism after swift heavy ion irradiation.
5.5 Summary of Nano-engineering by Swift Heavy Ions

Swift heavy ion induced engineering of metal nanoparticles embedded in silica can be understood in terms of nanoparticle size, interparticle separation and ion beam parameters (electronic energy loss and fluence). It has been observed that SHI irradiation of gold-silica nanocomposites can result in reduction or growth or elongation of Au nanoparticles. We have estimated the interparticle spacing theoretically using the RBS data. The detailed summary of SHI induced modification of gold–silica nanocomposite films under SHI ion irradiation are summarized in table 5.1.

Table 5.1: Nano-engineering by swift heavy ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. Metal Fraction at. %</th>
<th>Avg. particle size (nm)</th>
<th>Avg. IPS* (Sur-Sur) (nm)</th>
<th>Method of synthesis</th>
<th>Energy deposited (S_e#)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-SiO₂</td>
<td>5%</td>
<td>10.1</td>
<td>14.2</td>
<td>Thermal co-evaporation followed by annealing</td>
<td>(7.2)x (1x10¹⁵)</td>
<td>Reduction</td>
</tr>
<tr>
<td>Au-SiO₂</td>
<td>20%</td>
<td>4.0</td>
<td>2.1</td>
<td>Atom Beam Co-sputtering</td>
<td>(7.2) x(1x10¹⁴)</td>
<td>Growth</td>
</tr>
<tr>
<td>Au-SiO₂</td>
<td>16%</td>
<td>12.8</td>
<td>8.3</td>
<td>RF Co-sputtering followed by annealing</td>
<td>(14.1)x (3x10¹⁵)</td>
<td>Elongation</td>
</tr>
</tbody>
</table>

*(IPS-interparticle separation from surface to surface)*

Table 5.1 presents a summary of swift heavy ion induced engineering of nanomaterials. In case of Au-silica nanocomposite with metal fraction ~5% (prepared by thermal co-evaporation and subsequent annealing), the average size of Au nanoparticles is ~10.1 nm and the average interparticle separation (IPS) from surface to surface is ~14.2 nm. 90MeV Ni irradiation of this Au-silica nanocomposites results in reduction of Au NPs. Since average IPS in this is case is large, the migrated gold species are dissolved in silica and could not involved in reprecipitation.
In case of Au-SiO₂ nanocomposite with gold fraction 20%, the average size of nanoparticles ~4 nm and the average IPS (surface to surface) is ~2.1 nm. Since this film was prepared by atom beam co-sputtering was not annealed, the pristine film is likely to have gold nanoparticles along with smaller gold clusters as well as Au atoms. The average IPS in this case is smaller than the size of the particle. When this film is irradiated with 90MeV Ni ions, growth of nanoparticles occurs by dissolution of gold atoms from smaller particles and reprecipitation of dissolved atoms on the bigger nanoparticles. The presence of Au atomic species in pristine film also contributes in growth of nanoparticles under swift heavy ion irradiation due to molten state diffusivity.

In case of Au-SiO₂ nanocomposite, with gold fraction (16.1%) prepared by RF co-sputtering and subsequent annealing, the average size of gold nanoparticles is around ~12.8 nm with a broad distribution. The interparticle separation (surface to surface) in this case is around ~8.3 nm. 120MeV Au ion irradiation of these nanocomposites results in formation of elongated nanoparticles with an aspect ratio ~ 3.5. The formation of elongated nanoparticles occurs because of dissolution of smaller nanoparticles and subsequently reprecipitation of dissolved atoms on the larger nanoparticles within the ion track. The amount of elongation has been observed to be dependent on the product of electronic energy loss and ion beam fluence (Sₑ x ϕ). Elongation of spherical gold nanoparticles with diameter 14 nm surrounded by thick silica shell under 30MeV Se ions has been reported by Roorda et al. [2]. The aspect ratio of nanoparticles achieved in the irradiation at a fluence (ϕ) of 2x10¹⁴ ions-cm⁻² and Sₑ = 6.2 keV/nm was ~ 8.4, whereas the aspect ratio in the present experiment is ~ 3.5 for irradiation parameters of Sₑ = 14.1 keV/nm, ϕ = 3x10¹³ ions-cm⁻². It is clear from the above data on aspect ratio and ion beam parameters that when the product of Sₑ x ϕ changes by ~3 times, the aspect ratio also changes by a similar factor.

Thus the above study suggests that size and shape of nanoparticles can be engineered by swift heavy ion irradiation by appropriate selection of ion beam parameters.
References