150 MeV Au ion induced modification of Si nanoparticles prepared by laser ablation

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A B S T R A C T

We have investigated in detail the effects of 150 MeV Au ions irradiation on Si nanoparticles (NPs) synthesized by picosecond laser ablation of single crystal Si wafers in acetone. The formation of Si NPs was confirmed by Raman spectroscopy, transmission electron microscopy (TEM) and field emission scanning electron microscope (FESEM) measurements. The size distribution of synthesized NPs was found to be in the range of few nm to 80 nm. These samples were then irradiated with 150 MeV Au ions at various fluences ranging from $1 \times 10^{13}$ to $1 \times 10^{14}$ ions/cm$^2$. The effects of ion irradiation on the size and shape of Si NPs were further investigated using TEM, FESEM and micro Raman spectroscopy. From TEM data, we have noticed the reduction in size of NPs with increasing ion irradiation fluence. Furthermore with the increasing fluence we also observed the nucleation of 6–9 nm NPs in the vicinity of bigger NPs where there were no such NPs before ion irradiation. The increase in the FWHM of the Raman peak and its shift towards lower wave number side also suggests that the decrease in NP size is a result of increase in the fluence of irradiation.

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1. Introduction

Silicon (Si) is the second most commonly occurring element in the earth's crust, after oxygen and it is extensively used in solar energy applications. More than 90% of the world's solar photovoltaic modules in the market today are manufactured using Si [1]. Therefore, bulk/nano silicon based studies are important for various practical applications. It is also well known that the Si is a standard material in semiconductor industry and devices. Since it is an indirect band gap material, for a long time it has been considered incompatible for optoelectronic and photonic applications. Recent research efforts have concentrated on the studies of nanocrystalline Si based devices due to their photoluminescence (PL) properties observed in early nineties [2,3]. The research on Si nanoparticles (NPs) has received substantial attention due to their potential applications in diverse fields [4,5]. The use of embedded NPs or quantum dots in a matrix of silicon oxide [6], nitride [7], or carbide [8] has many potential applications in third generation tandem solar cell designs [9], optoelectronics and biomedical areas [10,11]. Out of many available methods for the synthesis of Si NPs Laser ablation/irradiation has emerged as one of the versatile methods to prepare NPs from solid targets in either gas or liquid media [12]. The laser generated plasma formed during ablation and confined within the liquid media is an ideal environment to promote non-equilibrium processes, which in turn facilitates the formation of nano-scale structures [13]. The size and shape of the NPs depend on the conditions of the laser ablation such as energy, time of ablation, and the solvents used during the process. Herein, we have synthesized Si-NPs by picosecond (ps) laser ablation of Si wafer in acetone. The Si NPs thus obtained, were used to understand the effects of swift heavy ion (SHI) irradiation at various fluences. The studies based on the SHI irradiation of semiconductor nanostructures have attracted researchers due to its versatility and its use in tuning the material properties at the nanoscale site selectively [14–17]. Kachurin et al. [18] have reported the growth of light emitting Si quantum dots in Silica layers by first low energy implantation and then followed by SHI irradiation. Chaudhari et al. [19] have carried out studies of SHI induced growth of nanocrystalline Si in silicon oxide. Both the above mentioned works have reported the PL properties of nanocrystals (NCs) in silicon oxide matrix. Anatova et al. [20] have studied the high energy irradiation induced modification of the structural, electrical and PL properties of Si NCs embedded in a SiO$_2$ matrix. SiO$_2$ phase separation into Si and SiO$_2$ was observed under 50 MeV Cu ion irradiation [21] and
120 MeV Ni ion irradiation [22]. These results were attributed to the phase separation in the ion tracks by the process of spinodal decomposition. SHI irradiation induced modification on structural and optical properties of the nanocrystalline Si–H films have also been reported very recently [23] and these results have been investigated by using X-ray diffraction and optical absorption measurements. To the best of our knowledge, there are no reports available directly observed using TEM in understanding the effects of SHI irradiation on already synthesized free Si NPs. Here, our aim is to study the effects of 150 MeV Au ions irradiation on the size and shape of Si NPs obtained by using ps laser ablation of Si wafer in acetone. The fluence dependence on the size and shape of the Si NPs was studied using TEM, which has not been investigated earlier. The samples have been characterized by micro Raman spectroscopy, transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) before and after 150 MeV Au ions irradiation for understanding the modifications such as nucleation of smaller size NPs in the vicinities of bigger NPs induced by SHI irradiation.

2. Experimental details

The ps laser ablation study has been performed using a chirped pulse amplified (CPA) Ti: sapphire laser system (LEGEND, Coherent) delivering nearly bandwidth limited laser pulses (~2 ps, 1 kHz repetition rate) at 800 nm. Complete details of laser ablation experiments are reported in our earlier publications [24,25]. Briefly, the target was placed in a Pyrex cell and covered by a layer of acetone. The targets were placed normal to the input laser pulses on a motorized X–Y stage, which was controlled by ESP 300 (Newport, USA) motion controller. The stages were translated so as to produce line patterns on the substrates with a separation of ~50 μm. The wafer used in this study was a boron doped p-type Si(1 0 0) of resistivity 10 Ω-cm. The Raman measurements were carried out with HR 800 Horiba Jobin Yvon model, at room temperature using 514.5 nm line of an Ar+ laser as an excitation source. The morphology of the laser ablated wafer was studied using FESEM (Carl Zeiss, FEG, Ultra 55). The images of Si NPs have been obtained by using advanced TEM (Tecnai 20 G2 STwin) with electron-accelerating voltage of 200 kV. The ablated liquid was drop casted on to TEM grids and Si or glass substrates for TEM and FESEM measurements, respectively. FESEM measurements were also performed on the irradiated/ablated Si wafer. The laser ablated Si wafers and the drop casted TEM grids were directly used for SHI irradiation with 150 MeV Au ions at room temperature using the accelerator facilities available at IUAC, New Delhi. The fluence was varied from 1 × 10^{13} to 1 × 10^{14} ions/cm². The range and the electronic energy loss associated with the 150 MeV Au ions in Si/SiO2 are calculated using the simulation code SRIM [26] and listed in Table 1.

3. Results and discussion

3.1. Raman results

Raman scattering measurements provide an evidence for the presence of Si NPs in our samples. Fig. 1 shows the room temperature Raman spectra of the laser ablated Si NPs in acetone (dropcasted on glass plate). The sharp peak at 521 cm⁻¹ corresponds to the bulk Si and it is due to the optical phonon modes of the Si substrate and it is symmetric near 521 cm⁻¹ [27]. However, the spectrum obtained from laser irradiated area has an asymmetric peak near 517 cm⁻¹. This peak is more asymmetric towards lower wavenumber side. According to the confinement effects of optical phonons in low dimensional structures, the asymmetry in the Raman peak together with the increase in FWHM confirms the formation of NPs at the irradiated site. The broad peak centered near 480 cm⁻¹ indicates the amorphous nature of the Si wafer at the laser ablated area [28]. This peak also corresponds to the SiO2 vibrational modes. This also suggests that in the proximity of amorphized area on Si wafer, the NPs were oxidized indicating the formation of SiO2. The size of the Si NPs can be estimated from the shift in the peak position from the bulk value and width of the peak [29]. The inset of the Fig. 1 shows the Raman spectra of the Si NPs in acetone which strongly confirms the presence of the Si NPs after the laser ablation.

![Fig. 1. Micro-Raman spectra of laser ablated Si and normal Si wafers. Inset shows the micro-Raman spectra of the Si NPs in acetone (dropcasted on glass plate).](image)

![Fig. 2. Micro-Raman spectra of the laser ablated Si NPs on Si wafer with (at different fluences) and without 150 MeV Au ions irradiation.](image)

<table>
<thead>
<tr>
<th>Incident ion</th>
<th>Energy (MeV)</th>
<th>Electronic energy loss (keV/nm)</th>
<th>Nuclear energy loss (keV/nm)</th>
<th>Range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>SiO2 150 16.31 14.43</td>
<td>SiO2 0.182 SiO2 0.179</td>
<td>Si 17 18.5</td>
</tr>
</tbody>
</table>

Table 1

The range and the electronic energy loss of 150 MeV ions in Si and SiO2.
The Raman spectra of the 150 MeV Au ions irradiated samples at various fluences are shown in Fig. 2 along with the one related to un-irradiated Si NPs. The samples used for ion irradiation are the laser ablated Si wafer samples. The data clearly indicates that the Raman spectra is similar to the one obtained from the laser ablated area of Si wafer. All the spectra have the peak position centered at 517 cm\(^{-1}\) and a broad shoulder towards the lower wave number side (asymmetry). It was also observed that with the increase in irradiation fluence, the FWHM of the peak increased signifying that the NP size decreased\[30\]. The broadening of the peak at 521 cm\(^{-1}\) after 150 MeV Au ion irradiation and the significant increase of the peak width at 480 cm\(^{-1}\) further suggests that amorphization of the laser ablated Si wafer took place upon ion irradiation. The values of peak position, shift in the peak position from its bulk value and FWHM of the peak are summarized in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Sample with irradiation fluence</th>
<th>Peak position (cm(^{-1}))</th>
<th>Shift in peak position from its bulk value (cm(^{-1}))</th>
<th>FWHM of the peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si wafer</td>
<td>521</td>
<td>-</td>
<td>3.31</td>
</tr>
<tr>
<td>2</td>
<td>Laser ablated Si</td>
<td>517.5</td>
<td>3.5</td>
<td>4.44</td>
</tr>
<tr>
<td>3</td>
<td>150 MeV Au 1E13</td>
<td>516.6</td>
<td>4.5</td>
<td>4.26</td>
</tr>
<tr>
<td>4</td>
<td>150 MeV Au 3E13</td>
<td>516</td>
<td>5</td>
<td>5.39</td>
</tr>
<tr>
<td>5</td>
<td>150 MeV Au 1E14</td>
<td>516</td>
<td>5</td>
<td>5.93</td>
</tr>
</tbody>
</table>

3.2. FESEM study of ablated Si-wafer

Fig. 3 shows the corresponding FESEM image of the dropcasted solution on glass plate [Fig. 3(a)] and laser ablated spot of single crystalline Si wafer [Fig. 3(b)]. It is evident from these images that the formation of Si NPs at the laser irradiated area of the wafer and in the liquid. Obviously, such nanoparticles were not present in unablated Si wafers. The density of these particles is also very high in ablated samples. Moreover, these particles were found to be self organized and aligned along the pattern formed in laser irradiation spot similar to laser induced periodic surface structures [31,32] and in the direction of incident laser beam. It may be seen from these images that the particle size varied from 40 to 100 nm in acetone. Similar kind of particle distribution was observed in other liquids such as water and methanol. However, the growth in different liquids is observed to be different. Spherical and isolated particles were observed in the sample prepared in acetone whereas the particles prepared in methanol/water were found to agglomerate over a period of time [33]. In the present investigations we focus mainly on the irradiation effects on Si NPs synthesized by laser ablation in acetone. The Si NPs obtained were then irradiated with 150 MeV Au ions at different fluences. Fig. 4 shows the FESEM surface microstructures of the 150 MeV Au irradiated Si wafer at \(1 \times 10^{13}\) and \(3 \times 10^{13}\) ions/cm\(^2\) fluence. From these images no significant changes were seen on the laser ablated area of Si wafers with the increase in fluence of ion irradiation, but the formation of smaller size Si NPs is clearly noticed. The decrease in Si NP size was also visible from the images of irradiated samples.
3.3. TEM study of Si-nanoparticles

Fig. 5 depicts the TEM images of the Si NPs obtained by laser ablation of Si wafer in acetone. The solution was centrifuged on carbon coated copper grids and analyzed using TEM operated at 200 keV. These TEM images further confirm the formation of well dispersed spherical NPs in acetone drop-casted on TEM grid. The estimated size of these spherical NPs was also in the same range.

![TEM images of the as prepared Si NPs in acetone by laser ablation of Si wafer](image1)

![TEM images of the 150 MeV Au ions irradiated Si NPs at fluences](image2)
as those observed for ablated Si-wafers (by using FESEM). The particles are observed to be clear with considerably sharp edges.

Selective area electron diffraction (SAED) patterns, shown in Fig. 7(a), reveal the polycrystalline nature of the Si NPs. The size distribution of the as-prepared Si NPs in acetone is given in Fig. 8(a). It indicates that the average NP size in the as-prepared sample was \( \approx 42 \) nm and there were not many NPs in the size range 6–9 nm and especially in the vicinities of the bigger NPs as observed from the TEM images.

The Si NPs on carbon coated Cu grids were also directly used for 150 MeV Au ions irradiation at different fluences along with the laser ablated Si wafers. These irradiated Si NPs on TEM grids were used directly for the TEM studies to see the modifications induced by 150 MeV Au ion irradiation. Fig. 6(a)–(c) depict the TEM images of these 150 MeV Au irradiated Si NPs at fluences of (a) \( 1 \times 10^{13} \) (b) \( 3 \times 10^{13} \) and (c) \( 1 \times 10^{14} \) ions/cm\(^2\) respectively. It is clearly observed from the images that irradiation created a hazy outline around the NPs consisting of a high density of smaller NPs. Hence we observe irradiation induced growth of relatively small NPs in the vicinity of bigger NPs. With the increase in the fluence of irradiation, the density of smaller NPs increased and from the SAED pattern, it was observed that the particles were amorphized due to heavy ion irradiation [see Fig. 7(b)]. The size distributions of various fluence irradiated Si NPs are depicted in Fig. 8(b) and (c). The data clearly indicates that the average NP size was reduced with the increase in fluence of irradiation. The average NP size measured from the TEM images of the various fluence irradiated samples are summarized in Table 3. With the increase in fluence of irradiation, a decrease in NP size was observed.

**Table 3**

Variation of Si NP size with ion irradiation fluence of 150 MeV Au ion irradiation.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Sample with irradiation fluence</th>
<th>Average NP diameter/size (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si NPs pristine</td>
<td>42</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>150 MeV Au 1E13</td>
<td>38</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>150 MeV Au 3E13</td>
<td>31</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>150 MeV Au 1E14</td>
<td>24</td>
<td>11</td>
</tr>
</tbody>
</table>

Fig. 9 shows the TEM images of bigger Si NP (\( \geq 100 \) nm) irradiated with 150 MeV Au ions at \( 1 \times 10^{13}, 3 \times 10^{13} \) and \( 1 \times 10^{14} \) ions/cm\(^2\) fluences. It was observed that in the pristine sample (see Fig. 5) such NPs are clear with considerably sharper edges. With the increase in fluence of irradiation, it was observed that smaller size NPs of the size 6–9 nm were formed around the big NPs. This is due to the breaking of Si atoms as a result of irradiation from bonding and these separated Si atoms got nucleated to form such type of Si NPs. This type of formation increases with the increasing fluence of irradiation. The same was observed from the TEM images and corresponding size distribution also shows the formation of these NPs of the order 6–9 nm with the fluence of irradiation. Furthermore, the FWHM of the size distribution also decreased and became sharp with the increase in irradiation fluence. It suggests that the formation and the nucleation of Si NPs around the surroundings of bigger NPs increased. As indicated by Raman measurements the broad peak at 480 cm\(^{-1}\) is due to the amorphization and also due to the formation of silicon oxide. These data point out that as a result of ion irradiation, the edges of the bigger NPs which are already oxidized, are getting modified with the deposited...
electronic energy and the Si atoms were removed from their bonding, got dissolved into the oxide matrix and formed as smaller NPs by agglomeration of Si atoms. The details of the smaller NPs and their FWHM of the size distribution are given in Table 4.

The electronic energy loss of 150 MeV Au ions in Si is 14.43 keV/nm. The momentary rise in the temperature during the irradiation may heat the sample to 1500 °C with this deposited energy. This temperature is sufficient for breaking the bonds between Si atoms to make them free with tendency of large displacements. With the increase in fluence of irradiation, these liberated atoms can join by diffusion and form new bonds to initiate the nucleation of smaller NPs in the surroundings of the bigger NPs as a result of irradiation. During irradiation process, the crystalline Si NPs also become amorphous. The amorphization of the Si with lower incident ion energies at higher fluences was studied by many groups [34,35]. In these studies, thermal spike created due to large electronic energy deposition and following

![Fig. 9. TEM image of the large Si NPs irradiated with 150 MeV Au ions at fluences (a) 1 × 10^{13}, (b) 3 × 10^{13} and (c) 1 × 10^{14} ions/cm² and (d–f) are the respective size distribution histograms.](image)

### Table 4
Formation of Si NPs with smaller size upon ion irradiation of bigger NPs at various fluences of 150 MeV Au ion irradiation.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Sample with irradiation fluence</th>
<th>Average NP diameter/size (nm)</th>
<th>Standard deviation (nm)</th>
<th>FWHM of size distribution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si NPs pristine</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>150 MeV Au 1E13</td>
<td>7</td>
<td>2.3</td>
<td>4.76</td>
</tr>
<tr>
<td>3</td>
<td>150 MeV Au 3E13</td>
<td>7</td>
<td>1.8</td>
<td>3.63</td>
</tr>
<tr>
<td>4</td>
<td>150 MeV Au 1E14</td>
<td>9</td>
<td>1</td>
<td>2.15</td>
</tr>
</tbody>
</table>
rapid cooling causes the amorphization in these materials during ion irradiation. Here, the medium and high fluence of the energetic irradiating ions plays an important role in the modification and the formation of satellite NPs around the bigger NPs. The formation of smaller NPs in the vicinity of bigger NPs is due to the breaking of the bonding between Si atoms and the deposited energy density which is sufficient for the diffusion of the Si atoms to move in the oxidized network to form smaller Si NPs. These small NPs grow at the expense of larger ones. At the same time an overall reduction in the size of the bigger NPs is observed. Therefore, the growth struggle of NPs by interaction due to diffusion leads to a mono-disperse size distribution of NPs. From the TEM images it was observed that the mean NP diameter was \(9 \text{ nm} \) with a FWHM of \(\approx 7 \text{ nm}\) [see Fig. 9(b)].

With the increase in fluence, it was observed that the evolution of the smaller NPs was more in the vicinity of bigger NPs. The mean size of Si NPs increased and was observed that the evolution of the smaller NPs was more in the vicinity of bigger NPs. The mean size of Si NPs increased and the FWHM of the size distribution decreased with increasing fluence which is sufficient for the diffusion of the Si atoms to move in the oxidized network to form smaller Si NPs. These small NPs grow at the expense of larger ones. At the same time an overall reduction in the size of the bigger NPs is observed. Therefore, the growth struggle of NPs by interaction due to diffusion leads to a mono-disperse size distribution of NPs. From the TEM images it was observed that the mean NP diameter was \(9 \text{ nm} \) with a FWHM of \(\approx 7 \text{ nm}\) [see Fig. 9(b)].

These results support that ion beam irradiation of nanostructures is a controlled nanostructuring tool and one can use this technique effectively for the modification of nanostructures site selectively.

4. Conclusions

We have studied the effects of high energy heavy ion irradiation on Si NPs synthesized using ps laser ablation of single crystal silicon in acetone. The presence of Si-NPs in acetone and on the laser ablated area of the Si wafer was confirmed by Raman, TEM, and FESEM measurements. The tuning of size and shape of these NPs using 150 MeV Au ion irradiation of various fluences was observed along with the formation of smaller NPs around the vicinities of bigger NPs. With the increase in fluence, it was observed that the average particle size was reduced on a whole and growth of 6–9 nm NPs in the surroundings of bigger NPs was observed. As a result of irradiation it was also observed that the Si NPs are amorphized with the deposition of electronic energy by the irradiating ion at the higher fluences. By tuning the ion irradiation parameters such as energy deposition, fluence of irradiation etc. controlled shaping of these Si NPs can be achieved. The NPs synthesized in other liquids such as water, methanol are also being used to understand the behavior of modification of size and shape under SHI irradiation.

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References