Chapter 3

Fabrication of Nanoparticles of Noble Metals viz. Gold and Silver and their Surface Plasmon Resonance Studies
In this chapter, we shall present the fabrication of nanoparticles of noble metals *viz.* gold (Au) and silver (Ag) using high fluence ions of these metals generated by hot and dense plasma obtained in modified DPF device. Further, these nanoparticles are studied for their morphological, structural and plasmonic properties.

### 3.1. Introduction

Fine particles (of nm dimensions) of noble metals have been of interest to us since time immemorial for their intense bright colors. It was Faraday who had pointed out that the origin of these bright colors is due to the presence of fine metal particles [1]. In present day context, metal nanoparticles exhibit surface plasmon resonance (SPR) which has been discussed in section 1.4 of chapter 1. Nanoparticles of gold and silver exhibit SPR in visible region. This resonance is attributed to the collective oscillations of free electrons in response to an incident electromagnetic radiation. The resonance is characterized by maximum extinction cross section which is the addition of absorption and scattering cross sections and enhancement of electric field intensity in the vicinity of the nanoparticles [2]. Gold nanodots ~ 10 nm show strong absorption but negligible scattering while larger gold nanoparticles show scattering which is about several order of magnitude larger. When the size of the nanoparticles is very small as compared to the wavelength of the incident light, the dipole contribution to the absorption dominates. Moreover, the spectral position of SPR depends on size, shape, interparticle distance and dielectric properties of the metal nanostructures in combination with the surrounding matrix. The SPR wavelength red shifts predominantly with increase in size of metal nanostructures. Spherical nanostructures have only one SPR peak whereas nanorods have two SPR peaks corresponding to oscillation of free electrons along and perpendicular to the axis of the rods. When the dielectric constant of the surrounding matrix increases, there is redshift in the resonance wavelength [3]. Metal nanoparticles in assembly show optical properties different from those of isolated nanoparticle. This is due to coupling of plasmon oscillations in metal nanoparticle assembly which results in an enhanced electric field that falls off with distance. The near field coupling of the plasmons results redshift of the surface plasmon resonance wavelength of the assembly of the nanoparticles. This coupling induced red shift increases with decrease in the
interparticle distance and with increase in the number of the nanoparticles in the assembly [4,5]. The enhancement of electric field at SPR wavelength can increase Raman scattering cross sections which is known as surface enhanced Raman scattering (SERS). This plasmonic enhancement of Raman scattering can be tailored with size, shape and composition of the nanoparticle.

Gold and silver nanoparticles exhibit strong absorption and scattering at the resonance wavelength. Moreover, the ability of metal nanoparticles to link with biological systems has widened their applicability in medical applications. For instance, the plasmonic properties of gold and silver nanostructures can be utilized for diagnostics and therapy of cancer. The strong scattering at the resonance wavelength has been used in optical imaging and labeling of the bio-systems. Gold nanoparticles conjugated antibodies can selectively target the cancerous cells by photo-thermal heating [6] at the plasmon frequency (or wavelength). This causes destruction of cancer cells at much lower laser energy resulting in minimal harm to the healthy cells which is a very important issue. Furthermore, the resonance wavelength in near infra-red allows in-vivo imaging and photo-thermal treatment. Moreover, different geometries of nanoparticles offer high sensitivity in addition to tunability of the plasmon peak [7]. The use of metal nanoparticles is interesting as they offer strong optical signal as compared to radioactive dye used conventionally and are not susceptible to photo-bleaching [8]. Gold nanoparticles are found to enhance the catalytic activity in the oxidation of carbon monoxide [9]. The dependence of SPR on the interparticle distance of metal nanoparticles has been exploited for probing distance in biomolecules. The red shift of surface plasmon resonance peak in a functionalized metal nanoparticles that forms an assembly in the presence of bioanalyte has been used in sensing biomolecule such as DNA [10], glucose [11], biomarkers for Alzheimer’s disease [12], etc. Haes et al. [12] have used silver nanoparticle fabricated by nanosphere lithography which is conjugated with amyloid-β (Aβ) oligomer specific antibodies to determine the presence of amyloid-β derived diffusible ligands (ADDLs), a biomarker for Alzheimer’s disease. The use of silver nanoparticles in the diagnostics of Alzheimer’s disease offers a ray of hope for the therapy of this disease which is yet to find its cure. The dependence of resonance wavelength on the dielectric constant of the surrounding in combination with
the metal nanoparticles has been exploited for optical sensing of chemical and biomolecular analytes. Silver nanoparticles have antimicrobial effect due to high affinity of silver ions towards proteins, enzymes, DNA, RNA, etc. which can interfere with microbial processes [13]. The gold and silver nanostructures on silicon heterostructures or similar materials are also known to increase light absorption and hence efficiency of solar conversion in photovoltaic cells [14, 15]. Losurdo et al. [14] have integrated gold nanoparticles in n-type a-Si:H/p-type c-Si heterojunction solar cells and found that the absorption of light increases due to surface plasmon resonance thereby improving the efficiency of the solar cells [14]. Pillai et al. [15] have investigated the suitability of SPR of silver nanoparticles for enhancing the absorbance of silicon solar cells and reported significant enhancement of absorption.

Nanofabrication techniques have great influence on the size and shape of nanostructures. Moreover, growth of metal nanoparticles of controlled size and homogeneity onto a substrate has always been a challenge. Most of the chemical methods used for fabrication of gold and silver nanoparticles are based on reduction reactions of metal salts. The synthesis method of nanoparticles in solution in general requires the components such as metal precursor, reducing agent and stabilizing agent. One of the earlier chemical method for obtaining gold nanoparticles in colloidal solution is the Turkevich method [16]. The method is based on reduction of gold hydrochlorate solution by sodium citrate at 100 °C. One of the common method for synthesis is Lee-Meisal method [17] in which silver nitrate is reduced with sodium citrate. This method produced a wide distribution of size. Another common method is Creighton method [18]. Serra et al. [19] had prepared silver nanoparticles using soft solution technique starting with silver nitrate in ethanol solution and an aqueous solution of polyvinyl alcohol (PVA). Silver nanoparticles embedded in a SiO$_2$ matrix were synthesized by sol-gel technique [20]. The silver-doped gel was first annealed in air and finally annealed in hydrogen ambient at 20 ºC to 1200 ºC. The annealing resulted in formation of silver nanoparticles. Noroozi et al. [21] had fabricated silver nanoparticles by reduction of Ag$^+$ in a water medium using polyvinylpyrrolidone (PVP) as the stabilizing agent. A microwave oven was used to irradiate silver solutions for 20 s, 40 s, 60 s and 90 s. Formation of spherical and dendritic silver nanostructures was observed in TEM images.
In these methods, the presence of chemical contaminants is a main concern even if choice of precursors, reducing agent as well as surfactants is made judiciously. These processes are complex and slow. However, fabrication of metal nanostructures by plasma methods such as dc sputtering [22], RF sputtering [23,24] including laser ablation deposition [25,26] etc. overcome these shortcomings. Sangpour et al. [23] reported the formation of gold nanoparticles using RF magnetron reactive sputtered gold film on quartz substrate and post annealing at different temperatures. The as-deposited films did not show any SPR, characteristic of gold nanoparticles while the films annealed at 400 ºC, 600 ºC and 800 ºC in hydrogen atmosphere showed SPR peaks. Ko et al. [26] have explored the ablation of self assembled monolayer gold nanoparticle film on polyimide layer using a Nd:YAG laser of nanosecond pulse. They prepared a nanoparticle film by spin coating gold nanoparticles suspended in alpha terpenol on polyimide film which was subsequently dried at 120 ºC. Bruno et al. [27] had used two step sputtering method to fabricate gold nanoparticles on silicon. In the first step, they had created Au nanoparticles seeds on the silicon surface by sputtering followed by annealing. Finally, another sputtering was carried out in order to enlarge Au seeds. Tsuji et al. [28] had prepared colloidal solutions of silver nanoparticles by ablation with 1064 nm, 532 nm and 355 nm laser. The size of the silver nanoparticles became smaller from 29 nm to 12 nm with decreasing laser energy fluence. Ashkarran [29] had reported the synthesis of colloidal silver nanoparticles using electrical arc discharge between titanium electrodes in silver nitrate solution. It was observed that with high arc current, the gold nanoparticles contained titanium impurities.

Most of the plasma methods [22-24,26,27] of fabricating metal nanoparticles employ post-deposition heat treatment or ion irradiation. However, metal nanoparticles are obtained without heating or biasing the substrate or post deposition annealing or ion irradiation of the deposited material by making use of high fluence and highly energetic ions generated by hot and dense plasma such as found in modified dense plasma focus (DPF) [30,31] device. This method has also been adopted for nanofabrication of many other materials [31-33].
3.2. Nanofabrication of gold and silver

We make use of metal ions generated by hot and dense plasma such as found in DPF device for fabrication of gold and silver nanostructures. The schematic of Mather type DPF device [34] with suitable modifications [30,31] is given in fig. 2.18 of chapter 2. The experimental set up for fabrication is similar for both metals, except that different anode is used for each metal which is fixed inside its top portion. The details of the formation of focused plasma as well as experimental setup for nanofabrication are described in sections 2.3 and 2.5 of chapter 2. Formation of focused plasma (density ~ $10^{26}$ m$^{-3}$ and temperature ~ 1-2 keV) is indicated as a spike in voltage probe signal shown in fig. 2.17 of chapter 2 and is referred to as a “DPF shot”. Ion fluence produced in each shot of focused plasma is of the order of $10^{18-19}$ m$^{-2}$ [35].

The fabrication of metal nanoparticles can be understood as follows: The hot and dense argon plasma ionizes the metal (gold/silver) disc present inside the top of anode. These highly energetic metal ions along with argon ions move vertically upward in a fountain like structure due to the large electric fields generated by instabilities and are accelerated. In the post focus phase, these high fluence and highly energetic ions lose their energies on hitting the substrate which results in heating the substrate locally and, on cooling down ultimately get deposited in the form of nanostructures.

Gold nanostructures are fabricated on different substrates using gold ions generated by hot, dense and strongly non equilibrium plasma produced in modified DPF device. The typical distance between the substrate and the top of anode is fixed at 4.0 cm for optimum nanofabrication. The substrates used in the experiment are glass, indium tin oxide (ITO) coated glass and quartz which are ultra-sonicated prior to deposition. The number of DPF shots for fabrication of nanostructures is one and two. The surface morphology of the gold nanostructures is investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The samples for TEM measurement were prepared by dispersing the fabricated gold nanostructures in a solution of ethanol and few drops of the dispersed gold solution were put onto a copper grid covered with thin film of carbon. The structural results using high resolution X-ray diffraction (HRXRD) and selected area electron diffraction (SAED) are presented. We have studied the plasmonic properties of gold nanostructures obtained on different substrates using UV-Visible spectroscopy.
Silver nanoparticles are fabricated on glass substrate using energetic and high fluence ions by hot, dense and extremely non equilibrium plasma. The distance between the glass substrate on which nanofabrication is to be done and the top of anode is varied as 4.0 cm, 5.0 cm and 6.0 cm. Silver nanoparticles obtained with one DPF shot are analyzed for their surface morphology using SEM. Their structural properties are studied using HRXRD. We have also investigated optical properties with the help of UV-visible spectroscopy for silver nanoparticles.

In the following sections, the morphological, structural and optical properties are presented separately for each metal nanostructures viz. gold and silver.

3.3. Results of fabricated gold nanostructures

3.3.1. Surface morphology

The surface morphology of gold nanostructures is carried out using Scanning Electron Microscope Model FEI Quanta 200F. Gold nanostructures obtained on glass substrate using single shot of gold ions have nanodots (diameter ranging from 8 nm to 19 nm) and nanorods (diameter ranging from 12 nm to 17 nm) as shown in the SEM image in fig. 3.1 (a). In order to obtain size distribution, we measure size of more than 100 nanoparticles from SEM images using ImageJ software. A bar chart (size distribution) is plotted between counts and size of the nanoparticles and is fitted with Gaussian profile(s) using Origin 6.1. The Gaussian profile of the distribution yields mean size as well as full width at half maximum (FWHM). The size distribution of nanodots as shown in fig. 3.1 (b) whose FWHM is about 4 nm gives a mean size of about 14 nm. The diameter distribution of nanorods in fig. 3.1 (c) yields a mean diameter of 14 nm.

The surface morphology of gold nanostructures is investigated using FEI Tecnai G² T30, U-TWIN with a Gatan CCD camera. TEM image for single gold ions shot on glass substrate shown in fig 3.2 (a) has nanodots and nanorods which are in conformity with the results observed in SEM shown in fig. 3.1 (a). The nanorods have diameter in the range 13-18 nm and length in the range 80-125 nm. The HRTEM of the gold nanostructures in fig. 3.2 (b) shows nanodots of about 4 nm.
The morphological properties with two shots of gold ions on glass are further studied. Both nanodots and nanorods are observed in SEM image shown in fig.3.3 (a). The size distribution of nanodots in fig. 3.3 (b) obtained from SEM image shows FWHM of about 7 nm and has a mean diameter of 32 nm. However, fewer nanorods were observed in this case as compared to that of single shot of gold ions. This may possibly be due to breaking of nanorods when hit by highly energetic gold ions of second shot. The broken nanorods can be seen in TEM image shown in fig. 3.4 (a). Fig. 3.4 (b) shows the HRTEM of gold nanostructures obtained with two gold ions shots indicating presence of small dot like structures.

Gold nanostructures on ITO-coated glass substrate shown in fig. 3.5 (a) have sparse distribution of gold nanodots with mean diameter of 31 nm obtained from the size distribution as shown in fig. 3.5 (b) having a FWHM of about 8 nm. On increasing the number of shots to two, it can be seen in the SEM image in fig. 3.6 (a) that gold nanodots are more densely populated with two shots of gold ions as compared to single shot of gold ions. Further, the size distribution of nanodots as shown in fig. 3.6 (b) having a FWHM of about 14 nm yields a mean diameter of about 44 nm.

We have analyzed the morphology of gold nanostructures on quartz substrate obtained with one, two and three shots of gold ions using SEM and TEM. Fig. 3.7 (a) shows SEM image for gold ions deposited with one shot. Gold nanodots are observed in the SEM image in fig. 3.7 (a). The size distribution of nanodots with FWHM of 6 nm as shown in fig. 3.7 (b) yields a mean size of 20 nm. TEM image as shown in fig. 3.7 (c) has nanodots which are in conformity with the SEM results. However, gold ions with two shots yield nanodots of increased size as observed in the SEM image of fig. 3.8 (a) as compared to that of single gold ions shot as shown in fig 3.7 (a). The size distribution shown in fig. 3.8 (b) has FWHM of about 12 nm and a mean size of ~ 29 nm. TEM image in fig.3.8 (c) shows a typical gold nanodots having size of ~ 34 nm. On further increasing the number of shots to three, the mean size of nanodots observed in the SEM image as shown in fig. 3.9 (a) is found to be increased to 45 nm. The size distribution as shown in fig. 3.9 (b) has FWHM of about 14 nm.
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Fig. 3.1: (a) SEM image of gold nanostructures on glass with one shot of gold ions, (b) size distribution of nanodots and (c) diameter distribution of nanorods.
Fig. 3.2: (a) TEM and (b) HRTEM images of gold nanostructures formed with one shot of gold ions.
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Fig. 3.3: (a) SEM image of gold nanostructures obtained on glass with two shots of gold ions and (b) size distribution of nanodots therein.
Fig. 3.4: (a) TEM and (b) HRTEM images of gold nanostructures obtained with two shots of gold ions.
Fig. 3.5: (a) SEM image of gold nanodots obtained on ITO coated glass with one shot of gold ions and (b) their size distribution.
Fig. 3.6: (a) SEM image of gold nanodots obtained on ITO coated glass with two shots of gold ions and (b) their size distribution.
Fig. 3.7: (a) SEM image of gold nanodots obtained on quartz with one shot of gold ions, (b) their size distribution and (c) corresponding TEM image.
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Fig. 3.8: (a) SEM image of gold nanodots obtained on quartz with two shots of gold ions, (b) their size distribution and (c) corresponding TEM image.
Fig. 3.9: (a) SEM image of gold nanodots obtained on quartz with three shots of gold ions and (b) their size distribution.
The FWHM and mean diameter of nanodots obtained on glass, ITO coated glass and quartz with two shots of gold ions are bigger as compared to that of nanodots obtained with one shot. Gold nanodots and nanorods are obtained on glass substrates whereas only nanodots are observed on ITO-coated glass and quartz substrates. For one shot, mean size of nanodots on glass (fig. 3.1) is lesser than those of nanodots on ITO-coated glass (fig. 3.5) and quartz (fig. 3.7) substrates. We conclude that the morphology as well as size of gold nanodots is different on different substrates though fabricated under same experimental conditions. The formation of larger nanodots is explained as follows: Hitting the gold nanostructures deposited with one shot by energetic gold ions of second shot resulted in melting and subsequent rearrangement of gold nanostructures leading to increase in both FWHM and mean size of nanodots on glass, ITO coated glass and quartz. It may be noted that gold nanodots obtained in the present experiment are more uniform as indicated by sharper size distribution curve (signified by narrower FWHM) than the nanostructures obtained by Sangpour et al. [23] using RF reactive magnetron sputtering and by Kawakami et al. [25] using laser ablation deposition.

### 3.3.2. Structure of gold nanostructures

For studying the structure of gold ions deposited on glass, ITO coated glass and quartz substrates, we carry out HRXRD and SAED. HRXRD patterns of nanostructures are obtained using D8 DISCOVER diffractometer with Cu Ka radiation.

Fig. 3.10 (a) and 3.10 (b) show HRXRD patterns of nanostructures fabricated on glass substrates using one and two shots of gold ions respectively. Nanostructures are found to possess crystalline planes of face-centered cubic (fcc) gold in HRXRD. The 2θ values along with their planes and the mean grain size ‘d’ estimated using Debye-Scherrer’s equation, \( d = \frac{0.9\lambda}{\beta \cos \theta} \) \( [\lambda \text{ is the wavelength of X-ray radiation, } \beta \text{ is the FWHM in } \theta \text{ is the diffraction angle}] \) are given in table 3.1. We may note from fig. 3.10 that HRXRD intensities show increase with increase in the number of shots of gold ions from one to two. The estimated mean grain size is found to increase when the number of shots of gold ions is increased from one to two. This is in conformity with the increase in mean size obtained from SEM results. Fig. 3.10 (c) and 3.10 (d) show SAED
patterns for gold nanostructures obtained from one and two shots respectively. The pattern shows hexagonal array of spots confirming the crystalline nature of the nanostructures. The d-values are found to be 0.2405 nm, 0.2072 nm, 0.150 nm and 0.1280 nm which correspond to (111), (200), (220) and (311) planes respectively of gold having fcc structure. These planes are in conformity with the HRXRD results.

Fig. 3.11 shows HRXRD patterns for gold nanoparticles obtained on ITO-coated glass substrates. The HRXRD pattern in fig. 3.11 (a) for one shot of gold ions shows only one peak whereas the pattern shown in fig. 3.11 (b) for nanodots obtained with two shots of gold ions have three peaks. The presence of only one peak for one shot can be interpreted due to sparse distribution of the nanoparticles. The 2θ values along with their planes and the mean size estimated using Debye-Scherrer’s equation are tabulated in table 3.2. On increasing the number of shots from one to two, intensity increase indicating a better crystallinity in the nanoparticles obtained with two gold ions shot. Further the mean size also increases which is in conformity with the SEM results.

Fig. 3.12 shows HRXRD patterns for gold ions deposited on quartz substrates. The HRXRD patterns confirm crystalline nature of the nanoparticles. The 2θ values of HRXRD peaks along with their planes and the mean grain size estimated using Debye-Scherrer’s equation are listed in table 3.3. The intensity of peak as well as the mean size of gold nanodots is found to increase with increase in the number of gold ions shots from one to two. SAED pattern showing arrays of bright spots is presented in fig. 3.12 (c). The spots can be indexed to (111), (200), (220) and (311) planes of face centered cubic gold confirming the nanocrystalline nature of the gold particles.

HRXRD spectra of gold nanostructures obtained with single and double shots on glass in fig. 3.10 and quartz substrate in fig. 3.12 show similar planes of cubic gold. However, single gold ions shot on ITO coated glass substrate in fig. 3.11 shows only one plane of cubic gold as compared to three planes in nanoparticles obtained with two shots of gold ions. The intensity of the HRXRD peaks is higher as compared to that of one shot of gold ions. The mean grain size of gold nanostructures (on all the substrates) estimated using Debye Scherrer’s equation is found to increase as the number of shot is increased from one to two.
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Fig. 3.10: HRXRD of nanostructures with (a) one and (b) two shots of gold ions on glass and SAED micrographs of nanostructures with (c) one and (d) two shots.

**Table 3.1:** $2\theta$ values in the HRXRD and mean grain size of nanoparticles nanostructures obtained on glass.

<table>
<thead>
<tr>
<th>Number of gold ions shot</th>
<th>$2\theta$ (°)</th>
<th>Mean grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One</td>
<td>38.08</td>
<td>44.16</td>
</tr>
<tr>
<td>Two</td>
<td>38.22</td>
<td>44.48</td>
</tr>
<tr>
<td>hkl plane of cubic gold</td>
<td>(111)</td>
<td>(200)</td>
</tr>
</tbody>
</table>
Fig. 3.11: HRXRD of gold nanoparticles with (a) one and (b) two shots of gold ions on ITO-coated glass substrate.

Table 3.2: 2θ values in the HRXRD and mean grain size of nanoparticles obtained on ITO glass.

<table>
<thead>
<tr>
<th>Number of gold ions shot</th>
<th>2θ (º)</th>
<th>Mean grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One</td>
<td>38.36</td>
<td>10</td>
</tr>
<tr>
<td>Two</td>
<td>38.06</td>
<td>44.36 64.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>hkl plane of cubic gold</td>
<td>(111)</td>
<td>(200) (220)</td>
</tr>
</tbody>
</table>
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Fig. 3.12: XRD of gold nanoparticles with (a) one and (b) two DPF shots on quartz, and (c) SAED micrograph of nanoparticles on quartz substrate.

Table 3.3: 2θ values in the HRXRD and mean grain size of nanoparticles obtained on quartz.

<table>
<thead>
<tr>
<th>Number of gold ions shot</th>
<th>2θ (°)</th>
<th>Mean grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One</td>
<td>38.66</td>
<td>44.90</td>
</tr>
<tr>
<td>Two</td>
<td>38.50</td>
<td>44.75</td>
</tr>
<tr>
<td>hkl plane of cubic gold</td>
<td>(111)</td>
<td>(200)</td>
</tr>
</tbody>
</table>
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The crystallinity inferred from the number as well as intensity of XRD peak observed in the present experiment is better as compared to that observed for gold nanostructures fabricated using RF reactive magnetron co-sputtering and heat treatment [36].

3.3.3. Surface plasmonic properties

UV-visible absorption spectra and SPR studies are carried out using a Perkin Elmer Lambda 35 UV visible spectrometer.

Fig. 3.13 shows absorption spectra for gold nanostructures formed with one and two shots of gold ions on glass substrates. Gold nanostructures fabricated with single shot have SPR peak at 561 nm in the absorption spectra shown in fig. 3.13 (a) whereas nanostructures fabricated with two shots show SPR peak at 588 nm in the absorption spectra shown in fig. 3.13 (b). We observe a red shift of SPR peak with increase in the number of shots. The red shift can be attributed to decrease in the interparticle distance of the gold nanoparticles. Rechberger et al. [5] had also found that with decreasing interparticle distance of gold nanoparticle pairs the SPR shifts to longer wavelength. Moreover, the increase of mean size of gold nanostructures also results in redshift of SPR peak.

Fig. 3.14 (a) shows absorption spectra of nanoparticles obtained on ITO-coated glass substrate with single shot. The spectra show peaks at 545 nm and 378 nm. The peak at 545 nm in fig. 3.14 (a) is attributed to SPR of gold nanoparticles whereas 378 nm corresponds to the absorbance of ITO substrate. However, nanoparticles obtained on ITO coated glass substrate with two shots have two absorption peaks at 580 nm and 370 nm in the absorption spectra as shown in fig. 3.14 (b). The peak at 580 nm corresponds to SPR of gold nanoparticles and peak at 370 nm corresponding to ITO-coated glass substrate. We observe a red shift in SPR peak with increase in the mean size of gold nanodots. The intensity of SPR for nanoparticles obtained with two shots is found to be more than that of nanodots obtained with one shot.
UV-Vis absorption spectra for nanoparticles obtained on quartz substrate with one to five shots of gold ions are shown in fig. 3.15. The spectra for nanoparticles obtained with one, two, three, four and five shots show SPR peaks at 527 nm, 537 nm, 540 nm, 542 nm and 542 nm respectively. A red shift in SPR peak is observed with increase in the number of shots from one to three. The red shift of SPR peak is attributed to the size effect as the mean size of nanodots increases with increase in the number of shots from one to three but no apparent change in the interparticle distance. This red shift in SPR has also been reported by Wang et al. [36]. However on further increasing the number of shots from three to five, there is no appreciable shift of SPR peak. No shift in the SPR peak is possibly due to formation of gold nanostructured thin film rather than nanodots. The spectral width of SPR of nanoparticles obtained with single shot is more than that of nanoparticles obtained with two shots. Moreover, we observe decrease in absorbance of nanoparticles on increasing the number of shots from three to five. This can be interpreted due to formation of film like structures instead of distinct nanodots, resulted in dampening of the SPR absorbance. We observe that in all the substrates, the SPR peaks red shift when the number of shots is increased. The red shift of SPR peaks of gold nanostructures on glass and ITO-coated glass substrates is attributed to the decrease in interparticle distance resulting in increased interaction. Such a red shift dependence on decrease in interparticle distance has been reported by Rechberger et al. [5]. However, nanoparticles on quartz substrate do not have any visible change in interparticle distance but in mean size of nanoparticles with increase in the number of shots. We relate the red shift of SPR peak with increase in the mean size of nanoparticles. The red shift in SPR with increase in the mean size of nanoparticles has also been reported by Link et al. [37]. The observed SPR peaks of gold nanostructures are red shifted from that of colloidal gold nanostructures [37]. This shift is possibly due to substrate effect. We also note that the absorption peaks are blue shifted from that reported by Zhou et al. [22] for gold nanostructures fabricated on carbon film by sputtering and irradiation with focused ion beam and by Ballarin et al. [24] for gold nanostructures fabricated on ITO electrode by RF sputtering.
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Fig. 3.13: Absorption spectra of gold nanostructures with (a) one and (b) two shots of gold ions deposited on glass substrates.

Fig. 3.14: Absorption spectra of gold nanoparticles with (a) one and (b) two shots of gold ions deposited on ITO coated glass substrates.
Fig. 3.15: Absorption spectra of gold nanostructures with (a) one, (b) two, (c) three, (d) four and (e) five shots of gold ions on quartz substrates.
3.4. Results of fabricated silver nanoparticles

3.4.1. SEM results

The surface morphology of silver ions deposited on glass substrates placed at 4.0 cm, 5.0 cm and 6.0 cm is analyzed using SEM. Fig. 3.16 shows SEM images for one shot of silver ions on substrate placed at 4.0 cm from the top of anode. Nanoparticles consisting of nanodots and nanocapsules are observed in the SEM images. The nanoparticles are uniformly distributed and a typical interparticle separation shown by arrowhead in fig. 3.16 (b) is about 109 nm. Size distribution is obtained by measuring size of about 150 nanoparticles. The size distribution as shown in fig. 3.17 is wide ranging from 15-85 nm and yields two mean sizes of 20 nm and 60 nm. Silver ions deposited on glass substrate placed at 5.0 cm have nanodots and nanocapsules in SEM image as shown in fig. 3.18 (a) and (b). Nanoparticles are denser than one obtained at 4.0 cm. A typical interparticle distance between the nanoparticles as shown by the arrowhead in fig. 3.18 (b) is of 90 nm. The mean size of nanodots obtained from the size distribution as shown in fig. 3.19 is about 40 nm. SEM image shown in fig. 3.20 for silver ions deposited on substrate placed at 6.0 cm from the top of anode has nanodots and nanocapsules. A typical interparticle distance joining any two random neighboring nanoparticles as shown by arrowheads in fig. 3.20 (b) is about 83 nm. The size distribution of nanoparticles as shown in fig. 3.21 yields a mean size of 47 nm. The nanoparticles are denser as compared to nanoparticles obtained earlier at 4.0 and 5.0 cm from the top of anode. The interparticle separation decreases on increasing the distance at which fabrication of nanoparticles is carried out. It is observed that the mean sizes of nanoparticles remain almost same. The size range obtained is wider than that reported by Pyatenko et al. [38] wherein the size of silver nanoparticles is in the range of 5-15 nm. They found that size of the nanoparticle increases with increase in spot size of the laser and found particle agglomerates with spot size of 1.5 mm. The mean size observed in the present experiment is comparable to those reported by Tsuji et al. [28] for colloidal silver nanoparticles by laser ablation deposition and by Ashkarran [29] for colloidal silver nanoparticles using electrical arc discharge. The silver nanoparticles obtained were minimal with 15 A arc current.
Fig. 3.16: SEM images with (a) 1,00,000 and (b) 2,00,000 magnifications of silver nanoparticles on glass substrate placed at 4.0 cm.
Fig. 3.17: Size distribution of silver nanoparticles on substrate placed at 4.0 cm.
Fig. 3.18: SEM images with (a) 100000 and (b) 200000 magnifications of silver nanoparticles on glass substrate placed at 5.0 cm.
Fig. 3.19: Size distribution of silver nanoparticles on substrate placed at 5.0 cm.
Fig. 3.20: SEM images with (a) 1,00,000 and (b) 2,00,000 magnifications of silver nanoparticles on glass substrate placed at 5.0 cm.
Fig. 3.21: Size distribution of silver nanoparticles on substrate placed at 6.0 cm.
3.4.2. X-ray diffraction studies

The X-ray diffraction technique used for obtaining the high resolution XRD is D8 Discover X-ray diffractometer with Cu Kα radiation. XRD analysis of silver ions deposited with one shot on glass substrates is discussed.

For silver nanoparticles obtained at a distance of 4.0 cm, HRXRD pattern is shown in fig. 3.22. The pattern has peaks at 2θ equals 38.04°, 44.30° and 64.44° which correspond to (111), (200) and (220) planes of crystalline silver having fcc structure. Using Debye-Scherrer equation, the mean crystallite size of the nanoparticles is estimated to be 29 nm. Fig. 3.23 shows HRXRD pattern for silver nanoparticles obtained at 5.0 cm. The pattern show peaks at 2θ equals 37.90°, 44.24° and 64.20° which correspond to (111), (200) and (220) planes of fcc silver. The intensity of the HRXRD peak is reduced when the substrate distance is increased from 4.0 cm to 5.0 cm. The mean size of the crystallite estimated from Debye-Scherrer’s equation is 26 nm. HRXRD in fig. 3.24 for silver nanoparticles obtained at 6.0 cm show peaks at 2θ equals 37.90° and 64.36° which correspond to (111) and (220) planes of fcc silver whereas a weak peak at 2θ equals 44.14° corresponding to (200) plane of fcc silver is also observed.

Fig. 3.22: HRXRD of silver nanoparticles on glass substrate placed at 4.0 cm.
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Fig. 3.23: HRXRD of silver nanoparticles on glass substrate placed at 5.0 cm.

Fig. 3.24: HRXRD of silver nanoparticles on glass substrate placed at 6.0 cm.
The mean size obtained from Debye-Scherrer’s equation is found to be about 26 nm. The hump in the HRXRD pattern is because of glass substrate. On comparison with the peak intensities in HRXRD patterns of silver nanoparticles shown in fig. 3.22, fig. 3.23 and fig. 3.24, the crystallinity of the nanoparticles decreases with increase in substrate distance from 4.0 cm to 6.0 cm from the top of anode.

### 3.4.3. Absorption spectroscopy

The surface plasmonic properties of silver ions deposited on glass substrate are analyzed using UV-visible absorption spectroscopy. Fig. 3.25 shows absorption spectra of silver nanoparticles on glass placed at 4.0 cm from the top of anode and the spectra show peak at 420 nm due to surface plasmon resonance of silver nanoparticles. The bandwidth of SPR peak is found to be 110 nm. The wide bandwidth is due to large distribution of size of silver nanoparticles observed in SEM results. Fig. 3.26 shows the absorption spectra of silver nanoparticles obtained at 5.0 cm from the top of anode. The spectra have a SPR peak at 426 nm whose bandwidth is about 90 nm. The bandwidth is relatively smaller than that observed for nanoparticles obtained at 4.0 cm.

![Absorption spectra of silver nanoparticles on glass substrate placed at 4.0 cm.](image)

**Fig. 3.25:** Absorption spectra of silver nanoparticles on glass substrate placed at 4.0 cm.
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Fig. 3.26: Absorption spectra of silver nanoparticles on glass substrate placed at 5.0 cm.

Fig. 3.27: Absorption spectra of silver nanoparticles on glass substrate placed at 6.0 cm.
The decrease in bandwidth is in accordance with the observed decrease in size distribution of nanoparticles at 5.0 cm as compared to that of nanoparticles at 4.0 cm. A small red shift of SPR peak at 428 nm is observed in the absorption spectra shown in fig. 3.27 when substrate distance in increased from 5.0 cm to 6.0 cm from the top of anode. The red shift of SPR peak from 420 nm to 428 nm is possibly due to decrease in interparticle distance indicating strong interaction. The redshift with decrease in interparticle distance has also been reported by Cao et al. [39] for silver nanoparticles. The SPR peak observed in our experiment is redshifted and intense than the plasmonic peak at 410 nm reported by Ashkarran et al. [29] for silver nanoparticles. The intense SPR peak in our case can be explained due to presence of large number of silver nanoparticles (fig. 3.16, fig. 3.18 and fig. 3.20) as compared to small amount silver nanoparticles reported by Ashkarran et al. [29] SPR peaks observed in our experiment is blue shifted from those observed by Donnelly et al. [40] for ultrathin nanostructured film of silver prepared by pulsed laser deposition. The blueshift is due to presence of distinct silver nanoparticles in our experiment as compared to nanostructured film as reported by Donnelly et al. [40].
References

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