Fabrication and Characterization of Plasmonic Au Nanoparticles on ITO coated glass sheets

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Abstract

Noble metal nanoparticles are the topic of profound interest on account of their exceptional optical properties contrary to their bulk counterparts. We report here the fabrication of sputter-deposited Au nanoparticles on ITO (Sn doped Indium Oxide) coated glass substrate. The effect of varying annealing parameters viz. time and temperature in conjunction with varying thickness parameters have been thoroughly investigated. Prepared thin films were characterized using FE-SEM (Field emission scanning electron microscope), RBS (Rutherford backscattering) measurement, and optical absorbance spectroscopy. The role of annealing temperature and time duration on the evolution of Au nanoparticles is discussed. At low temperature, film dewetting has been observed while at high temperature and longer duration of annealing leads to particle dissolution for the greater thickness of 5 nm and 8 nm in the case of Au thin films. According to the study, 5 nm thickness Au thin film which was annealed at 500°C for 90 min exhibited maximum SPR (surface plasmon resonance) effect.

1. Introduction

Plasmonic metal nanoparticles of noble metals such as Au, Ag, Cu are of great interest because of their unique optical, electrical, and their subsequent application in chemical sensors, biosensors, photonic devices, resistive random access memory (RRAM) and DNA engineering, etc. due to their unique property of surface plasmon resonance (SPR). However, the SPR properties of these nanoparticles depend upon their size, shape as well as dielectric constant of the medium [1]. Altering the shape and size of nanostructures in the form of nanorings, nanorods, and nanospheres is quite tricky to get desired SPR properties and requires the use of various chemical and physical methods [2]. The effect of the annealing process for the evolution of Au nanorings at the surface of ITO was reported by Runo et al. [3]. The size of nanoparticles and their distribution depend upon the environment in which they are grown. A recent report by Meischein et al. shows the effect on the size distribution of Ag, Au, and Cu in different ionic liquids [4]. On a similar note, the role of viscosity of ionic liquids surface in controlling the size of Au nanoparticles deposited by sputtering has been reported in the literature [5–6]. In addition to this, the effect of annealing temperature and the atmosphere was investigated by M. Bechelany and they observed the transformation of the honeycomb mask of Au nanoparticles deposited by sputtering into the hexagonal arrays [7]. Mishra et al investigated the effect of annealing temperature and annealing conditions on the formation of Au nanorings on the quartz substrate. In another report, a systematic investigation was made on tuning localized surface plasmon resonance (LSPR) properties of Au nanoparticles embedded in the ZnO matrix with varying temperatures from 200°C to 600°C. The redshift in LSPR was observed with increasing annealing temperature on account of the agglomeration of Au nanoparticles. The process of diffusion of small Au nanocrystals during the annealing was responsible for the growth of Au nanoparticles. In another examination, the formation of silver nano cups on the surface of quartz using ultra-thin silver film and their subsequent annealing in an inert environment was also investigated by Mishra et al. The atomic force microscopy (AFM) measurements show the presence of unsymmetric islands in the as-deposited film while annealing at 900°C in Ar environment shows the
evolution of nano cup type structure. Ostwald ripening and buckling phenomena were responsible for their evolution because of the existence of a metastable state during the process of annealing [8–10].
Pannu et al. demonstrated the formation of Au nanoparticles on graphene substrate by the way of varying thin film thickness which was annealed at 400°C. The formation of Au nanoparticles with optimum thickness was responsible for engineering strain in graphene nanosheets which in turn alters the semiconducting properties [11]. The formation of Ag nanorings was illustrated by Mohapatra et al. The nano rings are formed by atom beam co-sputtering method through self-assembly of Ag nanoparticles embedded in the silica matrix. The study reveals that the change in ring dimensions is due to a change in surface diffusivity of Ag nanoparticles in different substrates that is carbon and silica substrates [12]. Khan et al. adopted the glancing angle deposition method to develop aligned nanodots on a rippled silica substrate. Low energy ion beam irradiation was used to fabricate the rippled silica substrates. An atomistic simulation was performed on the annealing and deposition process by using Monte-Carlo techniques to develop aligned nanodots. The study reveals that the rippled silica template/transparent substrate could be of great interest to obtain aligned metal nanoparticles with narrow size distribution for application in biosensing [13]. Singhal et al. reported the formation of Au-C$_{60}$ nanocomposite by thermal co-evaporation followed by thermal annealing treatment from 150°C to 300°C. Evolution of broad SPR peak was observed at 250°C and with the rise in temperature, blue shift in SPR peak was realized due to transformation of C$_{60}$ fullerene matrix into amorphous carbon [14]. All the reports discussed above confirm the significant role of annealing parameters and the substrate on the plasmonic properties of metal nanoparticles.

ITO (Sn doped indium oxide) coated glass substrates are most commonly used to prepare thin films for their application in resistive random access memory (RRAM), solar cell electrodes, photoelectrochemical water splitting studies, etc [15–17]. The authors have prepared Au nanoparticles by various routes such as electrodeposition, and citrate reduction method and examined their role in enhancing photoelectrochemical response for hydrogen generation for metal oxides viz. Fe$_2$O$_3$ and BiVO$_4$/Fe$_2$O$_3$ heterojunction respectively [17–18]. The motivation behind the present investigation is to get the optimum thickness, and annealing parameters to derive maximum SPR effect by adopting the sputtering method to deposit Au nanoparticles on ITO coated glass substrates. The parameters so obtained were utilized to prepare thin films of Au/TiO$_2$ which were further irradiated with 500 keV Ar$^{2+}$ ion beams for their application in PEC water splitting for hydrogen generation and the results have been reported by the authors [19].

The present work reports the highlights of the effect of film thickness, annealing temperature and time on the evolution of Au nanoparticles on ITO coated glass substrate deposited by the sputtering method. Various sets of samples prepared under the present investigation are shown below in Fig. 1.

The absorbance spectrum of all 27 samples along with FE-SEM imaging was performed. The thickness of the sample was confirmed by RBS measurements.
2. Experimental

Au thin films were deposited under inert conditions using Q150T-S, Quoram Technologies, a high vacuum turbo pumped sputter coater system available at Inter-University Accelerator Center, New Delhi. Plasma in the deposition chamber was created using Ar gas under vacuum conditions and by increasing time of deposition time from 10 to 50 seconds to deposit three different thicknesses of 2 nm, 5 nm, and 8 nm on cleaned ITO coated glass substrates. The as-deposited thin films were then annealed for different time duration (30 min, 60 min, and 90 min) and at each annealing temperature viz. 400°C, 500°C, and 600°C in an inert N₂ atmosphere.

Thin films so obtained were characterized by FE-SEM instrument (MIRA II LMH from TESCAN), and RBS measurements were performed with 2 MeV He⁺ ion beam from 1.7 MV tandem accelerator facilities available at Inter University Accelerator Center, New Delhi, and UV-visible absorbance spectroscopy was performed by double beam UV-Visible spectrometer, UV-1800, Shimadzu, Japan available at DEI, Dayalbagh, Agra.

3. Results And Discussion

3.1. Microscopic Imaging

The particle size distribution of all the samples was determined from FE-SEM images. The Image J software was used to get the average particle size of particles. A typical FE-SEM image of plane/pristine ITO glass substrate is given below in Fig. 2.

Figure 3–5 (a-i), show the FESEM image for various annealing time and temperature is shown for all three different thicknesses. The inset of FE-SEM micrographs shows the particle size distribution.

In the case of a 2 nm thick Au film, the average particle size lies in the range of 24–34 nm. From the particle size distribution shown in Fig. 6, with an increase in time and temperature for annealing, the particle size tends to increase. A similar trend of increase in particle size with a rise in temperature rise on SiO₂ substrate was reported by Kwon et al which is showing an increasing trend [6].

As can be seen in Fig. 4–5 for 5 nm and 8 nm thickness at the lowest annealing temperature of 400°C, dewetting was observed. An increase in annealing time for 5 nm thick Au film at 500°C led to an increase in particle size from 77 nm to 83 nm. At 600°C, 78 nm to 94 nm increase in particle size was observed by increasing annealing time. When the duration was raised to 90 min, particle fragmentation was observed indicating that high temperature and time for annealing are responsible for the dissolution of particles at the surface.

At the highest thickness, i.e., 8 nm taken in the present study, dewetting was observed at the lowest temperature of 400°C. On increasing annealing temperature to 500°C, the particle size of 171 nm and 170 nm was obtained at 60 min and 90 min annealing time while for 30 min annealing time average particle
size was 256 nm showing agglomeration of Au nanoparticles. On further increasing annealing temperature up to 600°C, particle dissolution was observed showing a reduction in particle size.

### 3.2. Optical Measurements

To confirm the effect of annealing on sputter-deposited nanoparticles, the absorbance spectra of plane ITO sheet and as-deposited films were recorded and are presented in Fig. 7. It is clearly visible from the figure that the absorbance spectra of as-deposited Au thin films match well with the plane ITO which confirms the absence of nanoparticles formation that was responsible for the SPR peak.

Figure 8 (a-c), shows absorbance spectra for 2 nm thick film. The broad absorbance is visible on account of the variable size of particles up to 500°C. At a high temperature of 600°C, maximum absorbance was attained at 90 min annealing time which shows direct relation with increasing particle size.

In the case of 5 nm thick films, absorbance at low temperature does not show SPR due to dewetting of films (Fig. 8 (d)). At 500°C and 600°C, maximum intensity SPR peaks are visible at 90 min and 60 min annealing time respectively and the SPR peak intensity shows direct dependency on the particle size of nanoparticles so formed (Fig. 8 (e-f)).

Likewise for 8 nm thick film, dewetting was prominent at a low annealing temperature of 400°C. At high temperatures, particle size shows harmony with the calculated average particle size. The shift in SPR peak towards higher wavelength was observed due to the bigger sized Au nanoparticles and in addition to this reduced absorbance is a result of prevalent light scattering by larger size Au particles.

From the UV-vis spectroscopy, it is clear that for 2 nm and 8 nm thick Au thin films, no clear signature of SPR is as such visible thus for 5 nm thick Au film (annealed at 500°C and 600°C) was taken to see the dependence of surface plasmon resonance peak position on average particle size. For 5 nm thick Au film annealed at 400°C, film dewetting was prominent. At 500°C with an increase in annealing time, particle size increases and SPR peak is shifting towards higher wavelength i.e., redshift is visible. On increasing annealing temperature to 600°C, the red shift in SPR peak is observed up to 60 min annealing time but for 90 min annealing particle size reduces from 94 nm (60 min annealing) to 86 nm on account of particle dissolution which results in a shift of SPR peak from 633 nm to 629 nm. This can also be inferred that high annealing temperature does not influence SPR peak position at large with increasing annealing time.

### 3.3. Rutherford Backscattering (RBS) Measurements

The thickness of Au thin film samples was estimated by RBS measurements. The obtained data were simulated to reveal the thickness information by SIMNRA software. The recorded spectrum is shown in Fig. 10 which confirms the presence of Au at channel no. 1800 and the calculated thickness values are provided below in Table I.


**TABLE I. Thickness of Au thin films by SIMNRA simulation.**

| Film Identity | Areal Concentration | Film Thickness |
|---------------|---------------------|----------------|
| 2 nm, 500°C, 60 min | 17×10¹⁵ atoms/cm² | 2.8 nm         |
| 5 nm, 500°C, 90 min  | 41×10¹⁵ atoms/cm² | 6.9 nm         |
| 8 nm, 400°C, 30 min  | 63×10¹⁵ atoms/cm² | 10.6 nm        |

### 4. Conclusion

The investigation on annealing of Au thin films with different thicknesses for different time durations revealed that 5 nm thickness annealed at 500°C temperature for 90 min duration offers the best SPR effect. Besides this, it was also observed that dewetting of films occurs at low annealing temperature while increased temperature and annealing time leads to particles fragmentation. The study was aimed to obtain suitable conditions to use these nanoparticles as visible-light sensitizers.

### Declarations

**Authors Contribution**

**Anuradha Verma**: Conceptualization, Methodology, Writing- Original draft preparation, Investigation  
**Sakshi Saxena**: Data curation, Editing, Formal analysis. **Neeraj Kumar Biswas**: Visualization, Data Curation.  
**Anupam Srivastav**: Conceptualization, Visualization. **Uday Bhan Singh**: Software, Validation.  
**Saif A Khan**: Visualization, Data Curation. **Devesh Kumar Avasthi**: Supervision, Writing- Reviewing and Editing, Conceptualization, Validation  
**Sahab Dass**: Supervision, Research Activity Planning, Writing-Reviewing and Editing.

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**Funding Declaration**

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**Data Availability**

The data used to support the findings of this study are included within the article and no additional source data are required.

**Competing Interests Statement**
The authors declare that they have no financial and non-financial competing interests.

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Figures

Figure 1
Schematic presentation of samples prepared by adopting different thickness and annealing parameters.

Figure 2
FE-SEM micrograph of plane ITO substrate

Figure 3
FE-SEM micrographs of 2 nm thick Au film annealed for different time duration at varied annealing temperatures.

Figure 4
FE-SEM micrographs of 5 nm thick Au film annealed for different time duration at varied annealing temperatures.

Figure 5
FE-SEM micrographs of 8 nm thick Au film annealed for different time duration at varied annealing temperatures.

Figure 6
Average particle size distribution of (a) 2 nm (b) 5 nm and (c) 8 nm thick films recorded at varying annealing parameters.

Figure 7
Absorbance spectra of plane ITO along with as-deposited thin films.

Figure 8

Absorbance spectra of Au thin films (a-c) 2 nm Au thin films annealed at 400°C, 500°C, and 600°C for different time duration (d-f) 5 nm Au thin films annealed at 400°C, 500°C, and 600°C for different time duration (g-i) 8 nm Au thin films annealed at 400°C, 500°C and 600°C for different time duration at varied annealing temperatures.

Figure 9

SPR peak versus average particle size distribution plot for 5 nm thick Au film annealed at 500°C and 600°C.

Figure 10

RBS spectrum of Au thin films