CHAPTER – 7

Nanosphere Lithography enabled self-aligned nanopatterns for Plasmonic Solar Cells

The Conventional deposition techniques like PECVD, thermal evaporation and sputtering are used to grow continuous thin films and they need to be subjected to additional processing like conventional lithography to create two-dimensional (2-D) structures, which are expensive. However, if direct 2-D patterns have to be created with intended shape and size patterns, techniques like Nanosphere lithography (NSL), electron beam lithography or Nanoimprint lithography are used for the creation of features with nanometer range resolution. Further these process call for an ultra-clean environment such as Class 1000 or Class 100 for the creation of dense arrays of nanostructures with high dimensional tolerances at the nanoscale for exploring the plasmonic coupling effects. However, applications in the domain like large area flexible microelectronics and large area photovoltaic modules involve thin film technology and literally there is a need for role to role fabrication on the inexpensive substrates. Under such an environment, NSL offers the feasibility of a more affordable and scalable option with provision for precision. Hence for demonstrating the feasibility of fabricating nano-metal structure patterns (NP)s in a controlled way in an academic environment NSL experiments were carried out, for possible use in plasmonics a-Si:H TFSC.

7.1. Process of Nanosphere Lithographic Technique

The promising and inexpensive NSL fabrication technique for producing a regular and homogenous array of NPs combines the advantages of both bottom-up and top-down fabrication techniques [194] without having high initial equipment costs. A simple and high throughput NSL nanofabrication technique is capable of producing a large variety of nanostructures and patterned nanoparticle arrays on any given substrate. The study of NP pattern formation using NSL technique was performed on a polished silicon substrate and a TCO coated glass substrate. The polished Si and TCO surface were coated with suspension constituting of Polystyrene Spheres (PS) and left for drying to obtain a single layer triangular closely packed NP structures. The PS spread surface act as mask for as grown NP structures of metals. After metallization, the mask is lifted off by
subjecting the substrate to ultrasonic agitation in an appropriate solvent resulting in an ordered array of nanopatterns on the substrate. Various diameters of PS spheres in the range of 350nm-400nm were used for creating self-aligned pattern mask for the growth of Nickel and Titanium NPs.

7.1.1. *Monolayer Distribution of Polystyrene Spheres on the Substrates*

The polystyrene balls act like a monolayer self-assembled mask to pattern the desired metallic material. The self-organization of colloidal suspension can be obtained with dip coating due to the associated capillary force and controlled evaporation. A closely packed colloidal crystal mask (CCM) of a single or double layer is formed after drying i.e ultrasonic agitation, which is further used for patterning the required material. The size of polystyrene balls determines the size and shape of the sputtered material.

*Figure 7.1. Process steps to create nanostructures through Nanosphere lithographic technique [194]*
In our study, powdered form of PS sphere is used to create CCM for varying nanometer size arrays. The colloidal solution constitutes of Sodium Dodecyl Sulphate (SDS), powdered polystyrene spheres, distilled water ($\text{H}_2\text{O}$) and Methanol ($\text{CH}_3\text{OH}$). The liquid form of PS sphere exhibits spontaneous property to form self-assembled periodic arrays developing a lithographic mask for nanosphere array creation. The Soap contains molecules such as SDS, which has both hydrophilic and hydrophobic components. When these molecules are dispersed in the polar solvent such as $\text{CH}_3\text{OH}$ and distilled water ($\text{H}_2\text{O}$) they form Micelle structures which contain hydrophobic spaces when the PS spheres are dispersed into this solution. The sphere occupies the hydrophobic spaces of the micelle structure resulting in uniform distribution of PS spheres in the colloidal solution and can be used to form monolayers of a uniformly distributed array of nanospheres. The cleaned ITO coated glass substrates were immersed in a colloidal suspension and pulled out at a slow pace. This dip coating method of the substrate into the colloidal suspension is further allowed to dry to avoid agglomeration of PS spheres. The initial steps of mask formation are as shown in Fig.7.1.

![Image](image.png)

**Figure 7.2.** AFM images depicting uniform distribution of polystyrene balls on the ITO coated glass in (a) 2.5 sq μm area, (b) 4.5 sq μm area

The process of PS sphere injection on to the surface is carried out using a fine nozzle pipette and dispersed on the distilled water inside which substrate surface to be coated is immersed. Then the substrate is slowly lifted up, allowing PS layer on the water surface to settle on it, without disturbing the distribution. It is then allowed to dry in the clean laminar test-bench environment to have self-aligned PS spheres distributed on to the surface. The AFM images of the surface are captured through NSOM to view the pattern of PS nanosphere assembly on the Si substrate as
shown in Fig.7.2. The AFM images taken using tapping mode confirms the uniform distribution of the PS spread across the Si surface.

7.1.2. Deposition of Metal to form Self aligned Nanopatterns

The next step for metal pattern generation is equipped with sputtering of intended metal on to the self-assembled surface of the ITO coated glass substrate and Si Substrate. The material sputtered on to the surface also gets deposited in the intermediate space between PS spheres. Further, the substrate is processed for ultrasonic agitation with intention of detaching the PS spheres from the surface. The left over metal on the Si or ITO substrate would be self-aligned nano-metal structured patterns.

![AFM images showing (a) holes after peeling of polystyrene balls from the silicon surface, (b) generated triangular shaped nickel nano-metal structure patterns](image)

Figure 7.3. AFM images showing (a) holes after peeling of polystyrene balls from the silicon surface, (b) generated triangular shaped nickel nano-metal structure patterns

To clearly depict the generated patterns and also to be able to estimate the count of patterns the polished Silicon substrates were used. Shown in Fig.7.3 (a) are the array of hexagonal holes after removal of PS sphere balls by the ultrasonic agitation. The remaining pattern is that of the nickel taking up shape in the nanoscale dimensions. The obtained triangular patterns are as shown in Fig.7.3 (b) for the sputtered nickel pattern. The NSOM captured AFM images portray the pattern of nickel nanoparticles formed. Similarly, the patterns are obtained for Titanium on the other substrate. In an area of 1cm² x 1cm², a total of over 60,000 triangular nanopatterns were generated, demonstrating cost-effective NP generation for plasmonic applications in an academic
environment. However to actually study the plasmonics effect or the influence on the spectral behaviour the NP structures grown on the TCO substrates are studied.

7.2. Study of Plasmonic Effects for Solar Cell applications

To illustrate the feasibility of plasmonic effect for use in any optoelectronics device and in the case of a-Si:H TFSC in the direction of the incident light at the interface between TCO and semiconductor, periodic NPs are generated on TCO coated glass using NSL technique. The basic a-Si:H TFSC are good absorbents of the blue part and poor absorbents of the near-red part of the solar spectrum.

![Nanosphere lithography synthesis procedure for generating nano-metal structure pattern arrays on ITO coated glass](image)

Figure 7.4. Nanosphere lithography synthesis procedure for generating nano-metal structure pattern arrays on ITO coated glass

The main purpose of introducing the NPs on the front surface is to enhance the device absorption range. The blue part of incident radiations are directly absorbed in the a-Si:H layers and the introduced NPs scatter unabsorbed red light back into the device for absorption during the second pass of radiations. The material defined resonance frequency of NP varies with the material choice as presented in chapter 6, by using different metals or metal nitrides NP structures. The simulation data indicated that by using the appropriate material it is possible to tailor the range or
choice of spectral region for absorption enhancement or associated transmission. To illustrate the plasmonic resonance phenomenon and the spectral enhancement feasibility, nickel and titanium NPs were generated on the ITO coated glass. Fig.7.4 summarizes the synthesis procedure followed for any metal pattern generation or NP formation on ITO coated glass and used in the present study to create Ni and Ti nanopattern structures.

7.2.1. Influence of Plasmonic Metal Nanostructures on Optical Properties

The feasibility of plasmonic NP nanostructures and their influence on the optical properties on the front interface, in terms of enhanced absorption or associated transmission behavioral change in the spectral range of interest is demonstrated. As mentioned earlier the NP patterns were created using NSL on TCO substrates. The transmission and absorption spectra of the substrates NP enabled TCO substrate and the bare TCO substrate were studied using UV-VIS spectrometer.

![Absorbance spectra for Ni and Ti nanostructures](image)

**Figure 7.5.** Study of absorption on glass substrate with Nickel and Titanium nanopatterns created using Nanosphere Lithographic technique

Shown in Fig.7.5 is the absorbance spectra for the incident spectrum in the range of 300-800 nm denoting the visible spectrum part on uncoated TCO and varying NP structured Ni films. For the structures with Nickel nanostructures there is a minor jump in the absorption at the incident wavelength of around 430nm and for structures with Titanium nanostructures, major absorption enhancement is seen at an incident wavelength of 450nm. The magnitude of device absorption is higher with Titanium nanostructures when compared to Nickel nanostructures signifying that the absorption range and the magnitude are specific and dependent on the choice of metal. It may also
been seen that there is a slight shift in the peak from blue to green in the case of Ti NP structures, demonstrating the absorption range being spread across the visible part of the spectrum and possible selective capability creation using NP on the front side from where the light is incident in the case of solar cell or any other optoelectronic device or sensor. The obtained experimental data are similar to the simulated results mentioned in section 6.3 of chapter 6. The obtained transmission curves of various thickness of Nickel nanopatterns illustrate the transmission shift into the TCO coated glass substrate as captured in Fig. 7.6. The evenly deposited triangular shaped nanopatterns lead to an enhanced transmission in the wavelength range of 300-1000nm as compared to the base TCO substrate highlighting the influence of the NP structures.

![Figure 7.6. Influence of triangular shaped nanopatterns on transmission pattern shift with ITO coated glass as a substrate](image)

The main focus of the work is to demonstrate the design and indigenous fabrication of plasmonic structured photovoltaic device feasibility including development of process and characterization facility in an affordable manner. Within the scope of this work a wide range of nanomaterials and sizes and shapes associated with the same have also been simulated and studied. So that one could understand the feasibility of tailoring an optoelectronic device and the absorption region or the spread of the spectrum absorption capability based on the application. The whole of design, analysis, characterization and validation of the single junction a-Si:H TFSC is done in an academic environment. The proof of plasmonics concept has been experimentally illustrated into
TFSC which is relatively matching to the simulated results. The chosen nickel and titanium NPs have given us the required shift in the resonance for the spread of absorption of incident radiations range into the device. In case of nickel and titanium, the maximum absorption into the ITO coated glass is in range of 400-500nm with relatively higher absorption in titanium NPs compared to nickel NPs. The obtained transmission curves and maximum peaks are similar to the results obtained through simulation. The obtained absorption spectra with nickel nanoparticles are similar to the other published data [195-197]. Similarly, the obtained absorption spectra for the Titanium NPs match to the earlier published data [198]. The current work as compared to published work has lower efficiency, but as the simulation was done based on the developed materials the simulation results match the fabricated device performance. Having demonstrated the indigenous capability of plasmonic device, a detailed study with optimized nanoparticle sizes with Titanium and Nickel, as also the other metal and metal nitride nanoparticles come under the future scope of study and beyond the scope of one PhD work.

**Summary:** Presented in this chapter is a demonstration of simple and cost-effective way of creation of nano-metal patterns on any substrate, as the experiments have been shown on the glass, TCO and Si substrates. For exact precise estimation of the patterned nano-metal structures polished Si substrates were used. The data suggests that nearly 60000 triangular metal patterns can be fabricated over a 1 sq. cm$^2$ area, with each triangular structure having dimensions between 200nm at the base and ~300 nm for the sides. The transmission data shows that there is a marked enhancement in transmission indicating the influence of the NP structures and plasmonic effects which is similar to the simulated data. Thus demonstrated is the feasibility of fabrication of plasmonic structures. The ability to selectively choose NP structures over a wide desired spectral range for a-S:H solar cell has been shown in chapter 6, which is one of the first time of its kind, covering a wide spectrum of metals and metal nitrides for plasmonic applications.