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Morphology and optical properties of sputter deposited silver nanoparticles on plain, textured and antireflection layer coated textured silicon

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ABSTRACT

Silver nanoparticles (Ag NPs) are prepared on plain silicon (P-Si), textured silicon (T-Si), and silicon nitride coated textured silicon (Si_3N_4/T-Si) substrates using magnetron sputtering powered with RF and pulsed DC followed by thermal annealing at different temperatures. The Ag NPs size, shape and concentration are very sensitive to the silicon topology, material (Si/Si_3N_4), sputter power (DC/RF), and annealing temperature. In Ag NPs morphology study, we observed that P-Si favors bigger NPs growth compared to T-Si and Si_3N_4/T-Si substrates due to the variation in the silicon topography, and RF powered sputtering favors bigger NPs size compared to pulsed DC powered sputtering due to variation in the deposition rate. We have not observed much variation in Ag NPs sizes between T-Si and Si_3N_4/T-Si substrates. The light trapping in P-Si, T-Si and Si_3N_4/T-Si substrates after integrating Ag NPs are investigated using total reflectance and transmittance measurements. The excited Ag NPs' surface plasmon resonances led to the wavelength dependent enhancement in light absorption as well as reflection in the polychromatic spectrum. Maximum reflectance reduction (~8%) observed from T-Si integrated with Ag NPs, due to the simultaneous light interaction with textured micron scale Si and nano-scale Ag, in the entire wavelength region.

1. Introduction

In a solar cell, one of the basic processes for conversion of sun light into electrical energy is the absorption of incident photons. Depending on the properties of absorbing semiconductor and cell structure, certain optical losses are associated with each photovoltaic material. In case of silicon (Si) solar cells, the reflection losses are more than 30% for polished Si in the entire polychromatic spectrum. To overcome these optical losses, light trapping techniques like surface texturing and antireflection coatings have been developed [1,2]. Emerging branch of plasmonics from nanophotonics is also providing some promising solutions for light trapping/management using metal nanoparticles (NPs) in photovoltaics. Absorption enhancement in solar cells can be attained by using either near-field or far-field effects of metal NPs depending on the cell structure [3]. For Si solar cells, far-field effects play a vital role in enhancing the path length of incident photons [4].

These sub-wavelength metal NPs interacts with the incident light in a different way than the bulk material, due to the increased surface to volume ratio. The collective oscillations of metal NPs' free electrons after light incidence lead to surface plasmon resonances (SPRs), and these resonance wavelength positions are function of NPs sizes, shapes, concentration, and dielectric environment [5–8]. Among different plasmonic materials for enhancing the absorption process, Ag NPs are best suited for Si solar cells because of their high scattering efficiency in the visible region of the spectrum, and also due to low parasitic absorption losses. Recently, we reported a broadband absorption enhancement by depositing Ag NPs on front side of polished Si using thermal evaporation technique [9]. A few reports are also available, in which metal NPs deposited on the textured silicon for increasing the coupling of incident light into the silicon [10–12]. Further, Spinelli et al. also investigated the Ag NPs growth on Si_3N_4 as an antireflection layer on silicon surface, and demonstrated better light in-coupling to a Si over a broad spectral range [13].

In this work, our interest is to understand further the Ag NPs growth on various silicon morphologies using sputtering

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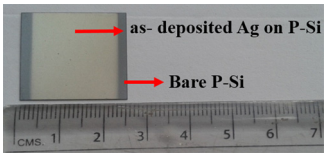

Fig. 1. Photograph of as-deposited Ag thin film on plain silicon.

deposition with different power sources. Noble metal NPs can be fabricated by using different techniques like e-beam lithography, sputtering, evaporation methods and also by simple chemical routes [9–24]. Sputtering (ions collision dislodges particles from the target material) is one of the most popular methods of physical vapor deposition (PVD) for the large area uniform deposition, and it is viable integration tool for any large area plasmonics based device fabrication. In the present study, we used radio frequency and pulsed direct current powered magnetron sputtering for growing Ag NPs on silicon, and tried to understand the NPs size distribution and concentration. We have investigated the optical properties of Ag NPs deposited on three different types of substrates like: (1) on plain chemically polished silicon (P-Si), (2) textured silicon (T-Si), and (3) silicon nitride coated textured silicon (Si_3N_4/T-Si).

2. Experimental details

Ultra-thin silver (Ag) films are deposited simultaneously on P-Si, T-Si and Si_3N_4/T-Si substrates using radio frequency (RF) and pulsed direct current (DC) powered magnetron sputtering system. Silicon substrates are p-type with the (1 0 0) orientation having thicknesses of 200 μm. The texturization was done using alkali anisotropic etching to get random pyramid surface of texture size of ~1–10 μm, which provides the large surface area to the Ag NPs. The antireflection Si_3N_4 layer thickness is ~75 nm. Prior to the sputter deposition of Ag thin films, all the substrates are cleaned with soapy water, and then sequentially ultra-sonicated for 10 min each in deionized water, acetone, and propanol. Magnetron sputtering system has the option for large area uniform deposition on silicon wafers with 2 in. × 6 in. rectangular silver target (99.99% pure) as the cathode. The distance between the cathode and substrate is around 10 cm. Initially, the sputter chamber was evacuated to a base pressure of 6.0×10^{-6} mbar and then depositions were carried out onto the above mentioned substrates for 60 s at a constant working pressure of 2×10^{-2} mbar in argon gas environment (gas flow rate = 15 sccm) with the RF power of 20 W. In case of pulsed DC magnetron sputtering, the depositions were carried out under a bias voltage of 300 V and 0.5 A current with argon assisted plasma operated at argon gas flow rate of 15 sccm. The Ag film deposition time for all these samples is 60 s. As deposited Ag film thickness is ~12 nm in the case pulsed DC power, whereas the thickness is around 8–10 nm for RF power. The area of the silicon wafer is $2.5 \times 2.5\ cm^2$. The optical image of as-deposited Ag thin films on P-Si is shown in Fig. 1, the deposited Ag film is almost uniform in the entire area.

The post-deposition annealing was performed for all these samples to get Ag NPs of various sizes and concentrations at different temperatures like; 200 °C, 300 °C and 400 °C in nitrogen environment for 1 h. The Ag NPs prepared on P-Si; and T-Si substrates after annealing at 200 °C, 300 °C and 400 °C named as P2, P3 and P4; and T2, T3 and T4, respectively, and on the Si_3N_4 coated T-Si substrates with annealing at 300 °C and 400 °C named as S3 and S4 samples. Further, we have also added _RF or _PDC to these names for distinguishing between different power modes of plasma generation, i.e. RF and pulsed DC for Ag discontinuous film deposition, respectively. Bare P-Si, bare T-Si and bare Si_3N_4/T-Si (without Ag NPs) samples are named as P0, T0 and S0, respectively.

Optical properties of Ag NPs were investigated using Perkin Elmer Lambda 1050 UV–vis–NIR spectrophotometer, the attachment of 150 mm integrating sphere was used for measuring the total reflectance (specular and diffuse) and total transmittance from the Ag NPs coated on silicon substrates in the broad wavelength range from 300 to 1100 nm. A Carl Zeiss Scanning Electron Microscope (SEM), and Quanta 3D FEI field emission scanning electron microscope (FESEM) were used to study the surface morphology of Ag nanostructures. The average size of Ag NPs is calculated by using Image toolbar software. The Ag particles sizes from plain and textured silicon surfaces are measured by taking horizontal axis as a reference.

3. Results and discussions

3.1. RF sputtering

3.1.1. Growth of Ag NPs on P-Si, T-Si and Si_3N_4/T-Si substrates

Fig. 2(a–i) shows SEM images of Ag NPs prepared simultaneously on P-Si, T-Si and Si_3N_4/T-Si substrates from Ag discontinuous thin films deposited using RF sputtering, followed by thermal annealing at 200 °C, 300 °C and 400 °C. As we increase the annealing temperature from 200 °C to 300 °C, it is observed that the NPs size increases, surface coverage decreases (inter-particle distance between the Ag NPs increases), and also NPs shape becomes more spherical on P-Si, T-Si and Si_3N_4/T-Si substrates. Further increase in the annealing temperature from 300 °C to 400 °C led to the increase in particles sizes with irregular shapes along with decrease in particle density. From Fig. 2(a, d and g), one can observe dense and small sized NPs from samples P2_RF, T2_RF and S2_RF, it is difficult to quantify the size of Ag NPs. For sample P3_RF, the average particle size is ~90 nm with the standard deviation of ~14 nm (histogram not shown), but, for sample T3_RF and S3_RF we are unable to measure NPs size distribution because of large surface coverage on a slanting textured surface. Inset of Fig. 2(c, f and i) shows NPs size histogram corresponding to samples P4_RF, T4_RF and S4_RF, respectively. The Ag NPs of P4_RF sample has an average size of 160 nm, while samples T4_RF and S4_RF have an average size of 120 nm and 130 nm, respectively, with a large deviation in their sizes.

Usually ultra-thin films are metastable in as-deposited form, and upon annealing, they will undergo solid state dewetting (sometimes termed agglomeration) to form arrays of islands, this can happen well below the film's melting temperature, so, no material is lost during the annealing process. The driving force for solid state dewetting process is the minimization of total energy of free surface of discontinuous film, substrate, and film-substrate interface [20]. The surface mobility of Ag atoms/islands is proportional to the annealing temperature, so, at sufficiently high temperature, the surface diffusion lengths will be higher than the inter-particles distances, allowing their agglomeration leading to the formation of bigger particles. At relatively high temperatures, large atomic diffusion allows the formation of uniform round shaped NPs, since it tends to minimize the particles surface tension [11].

The first observation from these sputtered films is that the average size of Ag NPs on P-Si samples is bigger than compared to grown on T-Si and Si_3N_4/T-Si samples. The size difference of Ag NPs on plain and textured silicon substrates is due to the difference in the surface morphologies. Growth of metal NPs on textured surface is very much depends upon the textured dimensions (size, depth, mesa and period) and also on the relative thickness of the metal film [22–24]. Our samples textured size (~1–10 μm) is large, during the annealing process, the dewetting process can be different on flat surfaces compared to ruptures on the pit edges, which resulting multiple NPs of relatively smaller size with shape variation compared to plain silicon surface. The second observation is the shape