

Investigating antireflection properties of hybrid silicon nanostructures comprising rod-like nanopores and nano-textured surface

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Abstract:

In the present work, we have fabricated hybrid silicon (Si) nanostructures comprising vertical rod-like nanopores and nano-textured surface by employing silver nanoparticle metal assisted chemical etching (MACE) method at room temperature. The as-received p-type Upgraded Metallurgical grade (UMG) Si wafers were chemical polished prior to investigating the etching effects at the metal nanoparticle semiconductor interface. The influence of metal nanoparticle concentration on the formation of hybrid nanostructures were investigated systematically. The synthesized porous vertical nano rods of Si were examined using reflectance spectroscopy, Raman spectroscopy and scanning electron microscopy. Depending on the surface morphology, the hybrid structures exhibited constant 10% average reflectance in the UV-Visible spectral region or average 7.5% reflectance in 200-400nm wavelength range.

Key words: rod-like nanoporous structure, nano-textured surface, metal assisted chemical etching, graded hybrid nanostructures, reflectance spectroscopy.

Introduction:

In recent years, demand for clean and renewable energy has drawn attention towards solar cells. The majority of them are silicon (Si) based due to their relatively low cost and high efficiency. Current Si solar cells has not reached their theoretical efficiency limit, mainly due to optical losses. A key to come closer to this limit is to maximize the absorption of incident photons and reduce surface reflectance. To reduce surface reflectance, anti-reflection (AR) coatings has to be incorporated. That is commonly done by forming destructive interference of incident light. However, the frequently used quarter-wave AR coatings are efficient only over a narrow range of wavelengths and incident angles [1]. It is also needed to enhance photon collection efficiency using light trapping by surface textures. Surface texturing in dimensions smaller than the wavelength of incident light (nanoscale) can provide efficient AR functionality and effective light trapping as nanoscale textured Si surface has a gradually varying refractive index resulting in low reflectivity and correspondingly high absorption of visible light [2]. In addition, one-dimensional (1D) nanostructures, such as nanowires (NWs) and nanopores (NPs), may have the potential to yield high-efficient photovoltaic cells, due to their unique light trapping characteristics involving multiple scattering of incident waves and antireflection from the visible to the near-infrared region given by their structural geometry [3,4]. Among different fabrication methods for NWs and NPs, metal assisted chemical etching (MACE) is one of the simplest and least expensive methods [5,6]. Jiang et.al [7] fabricated vertical rod-like NPs with diameters about 50–90 nm and depth of 500 nm on silicon surface by the MACE method. The nanostructured silicon exhibited more than 90 % absorption of incident light at UV-visible wavelengths and on average 10 % for wavelengths longer than 1,170 nm (up to 2000 nm). In addition, conduction within the nanostructures was found to be similar to that in unstructured silicon but with a negative temperature coefficient of resistance (TCR) dominated by hopping mechanism. Chen et.al investigated the AR properties of distributed rod-like NPs, NW arrays and graded NP/NW hybrid structures fabricated by the MACE method and demonstrated reflectance below 2.5 % for 300 - 900 nm spectral range [8]. So far, Si solar cell based on 1D NW structures exhibit lower power conversion efficiencies than conventional cells due to the enhanced photo-carrier recombination associated with the nanostructures [9].

In this work, anti-reflection properties of graded-hybrid structure comprising vertical rod-like NPs and nano-textured surface were studied. The influence of metal catalyst concentration (by varying the diluent concentration) on graded nanostructure formation in low-cost upgraded metallurgical grade silicon through the MACE method were investigated.

Experimental method:

As-sawn monocrystalline silicon wafers with a thickness of about 225 μm and a resistivity of 1-3 $\Omega\text{-cm}$ were used in this experiment. The wafers are SiC-slurry sawn and made using upgraded metallurgical grade (UMG) feedstock. The surface polishing (CP5) and pre-treatment was carried out by adapting the procedure followed in our previous work [10]. Different molar concentration of AgNO_3 solution: 2mM, 1mM, 0.6mM, 0.5mM and 0.4mM were prepared by varying the diluent volume (7 mg AgNO_3 in 20 ml, 40 ml, 60 ml and 80 ml of water, respectively) for the preparation of Si nanostructures. In the first step, silver (Ag) nanoparticles were coated on the CP5 polished Si wafers by immersing in 3.6 ml of HF (45 %) with various concentrations of AgNO_3 aqueous solution for one minute. The excess Ag^+ ions present in the surface were washed with double distilled (DD) water. In the second-step, the Ag nanoparticle deposited Si wafers were immersed in HF etching solution (20ml of DD water 3.6 ml of HF (45%) and 0.6 ml of H_2O_2) for 45 minutes. Then, the samples were transferred into an aqueous HNO_3 solution (3:1) for at least 1 h to remove the residual Ag nanoparticles.

Results and Discussion

Scanning electron microscopy (SEM) analysis

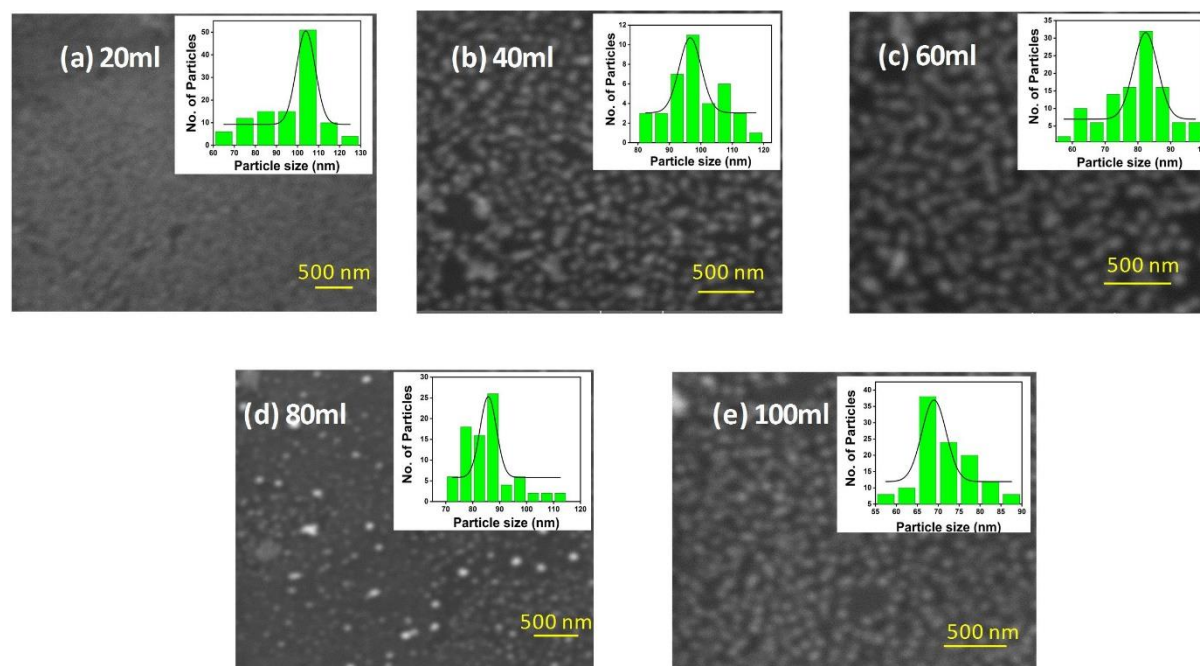


Fig.1 Areal distribution of Ag nanoparticles deposited on Si by varying the AgNO₃ concentration by dissolving 7 mg AgNO₃ in 20ml to 100 ml of DD water and the insert shows corresponding particle size distribution of Ag nanoparticles.

Figure 1 shows the top view SEM images of Ag nanoparticles deposited on the Si substrates by varying the AgNO₃ molar concentration at room temperature. The self assembled Ag nanoparticles have spherical shape and the areal density of the particles tends to decrease with decreasing molar concentrations of the solutions. For 2mM to 0.6 mM molar solutions, two or three particles tend to cluster together, while at lower molar concentrations, the Ag nanoparticles are isolated. The corresponding variation in the size of the Ag nanoparticles are calculated using image J software and the particle size distribution are calculated and represented in insert of fig.1. The average Ag nanoparticle size for each molar concentration is provided in Table I.

Figure 2 shows the surface view of MACE treated Si surface by varying the AgNO₃ molar concentration by dissolving 7 mg AgNO₃ in 20ml to 100 ml of DD water respectively. For all the samples (figs. 2(a-e)), black spots/holes can be observed, which represent the formation of vertical rod-like NPs. Sample prepared with 2mM AgNO₃ solution (20ml) demonstrate very rough surface along with observation of many nanocrystals. Further decreasing the molar concentration to 1mM (40ml) increases the surface roughness but reduces the number of observed nanocrystals. It should be noted that, the average Ag nanoparticles were 105 and 95 nm for 2mM and 1mM concentration, respectively; meaning that the areal distribution of Ag nanoparticle decreases for the 1mM sample. The sample with 0.6 mM solution demonstrates decrease in surface roughness and re-appearance of networked nanocrystals on the surface along with widely distributed NPs. However, the sample prepared with 0.5 mM exhibits a similar Ag particle size to that of the 0.6 mM sample; demonstrate increase in surface roughness. Reducing the molar concentration to 0.4 mM decreases the surface roughness. The NP diameter for each sample is calculated and the corresponding size

distribution is presented in the insets of Fig. 2. The average NP diameter for each sample is available in Table I.

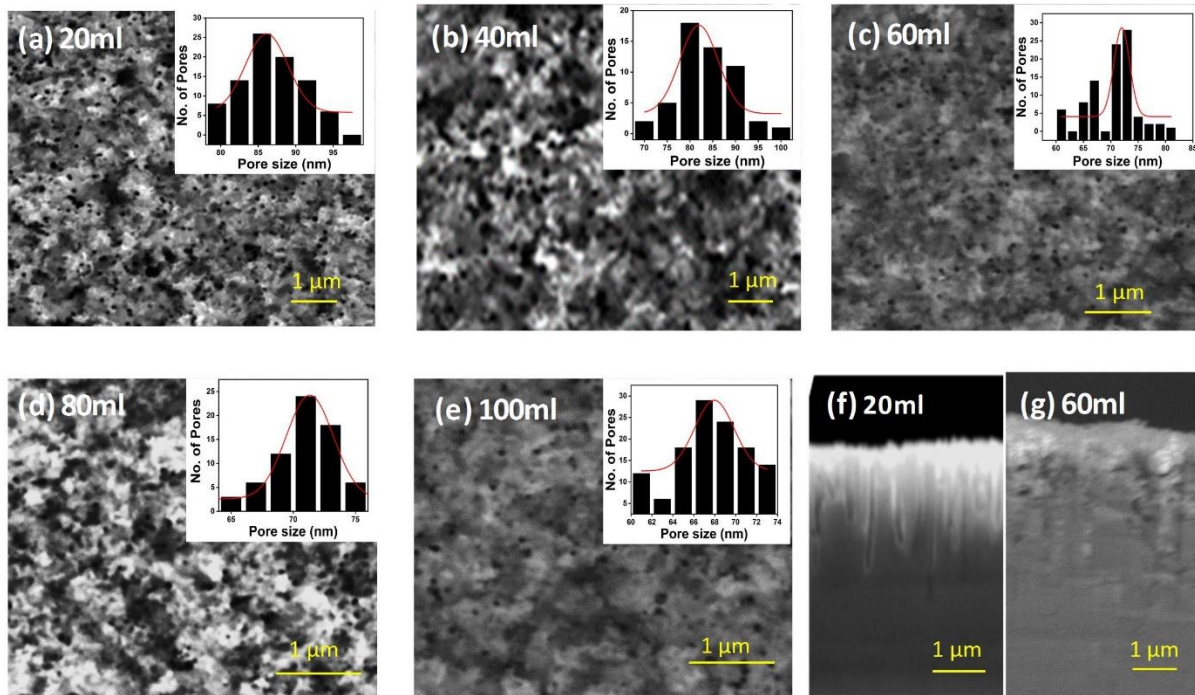


Fig. 2: Surface view of prepared p-Si by varying the AgNO_3 concentration (a) 20ml - 2 mM, (b) 40ml - 1 mM (c) 60ml - 0.6 mM, (d) 80ml - 0.5 mM and (e) 20ml - 0.4 mM, insert is the pore size distribution image of sample. Cross sectional image demonstrating vertical rod-like nanopores for (f) 20 ml and (g) 60 ml samples.

The cross-sectional SEM images of Fig 2(f) and (g) demonstrates the formation of vertical rod-like nanoporous structures in Si prepared by dissolving 7 mg AgNO_3 in 20ml & 60 ml of DD water. One can observe that pore formation occurs along the [100] crystallographic direction, indicating that the MACE of crystalline Si in HF-solution is strongly crystallographic oriented; which agrees with the various results in the literature [11,12]. In this work, the duration of etching is kept constant for about 45 minutes for all the samples. The diameter of the individual pore does not vary significantly with Ag particle size, whereas the depth shows a huge variation. The depth of the NPs prepared from 2mM and 0.6mM AgNO_3 solution reveal typical dimensions of 1 to 2.0 μm . The variation in the depth is attributed to the individual Ag NPs size, surface wettability and HF concentration dependent etch rates. The silver contamination in the MACE method is well known and are easily removed from the pores by washing the samples in HNO_3 as shown in cross sectional image [10].

Raman Analysis:

Figure 3 shows the Raman scattering spectra of nanostructured Si prepared by a two-step MACE method along with CP5 polished silicon as reference. A very sharp and intense Raman line at 521.4 cm^{-1} with a full width at half maximum (FWHM) of 3.40 cm^{-1} was observed in the Raman spectrum for reference CP5 polished Si. This peak corresponds to the degenerate zone-centre optical phonon mode of bulk crystalline Si. Si samples etched with 2mM and 1mM AgNO_3 solution, exhibit a broad characteristic Raman peak red-shifted to 520.84 cm^{-1} and 520.32 cm^{-1} , respectively, which corresponds to the T_{2g} Raman active mode [13]. Asymmetrical broadening and frequency shifts are usually observed in nanocrystalline structures and related to phonon confinement effects by nanocrystallite boundaries [14]. This

observation correlates very well with the surface morphology observed in SEM analysis. However, increasing the dilution from 60 to 100 ml samples exhibit Raman characteristics similar to that of reference Si indicating disappearance of nanocrystals. Table 1 provides the information on the characteristic Raman peak shifts and variation in intensity for all samples compared to reference; the Lorentzian fit was adopted for Raman spectra analysis [15].

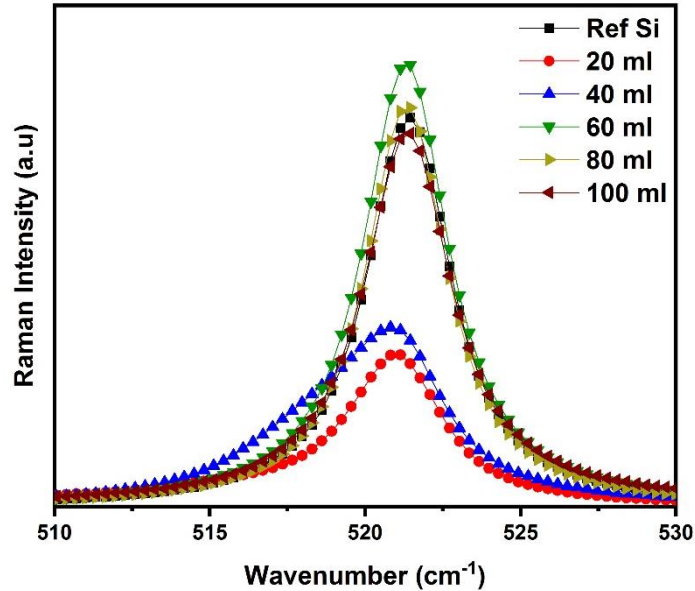


Fig. 3: Raman spectra of nanostructured Si formed by varying the AgNO_3 concentration by dissolving 7 mg AgNO_3 in 20ml to 100 ml of DD water (2mM to 0.4 mM, respectively)

Table 1: Lorentzian fit results for ref-Si along with hybrid nanostructured Si

Sample	Area cm^2	Centre cm^{-1}	Width cm^{-1}	Height (a.u)	Average Ag particle Size (nm)	Average pore diameter (nm)
Ref	276549.84	521.40	3.20	54882.57	-	-
20 ml	131395.31	520.84	4.05	20631.90	103.96 ± 2.41	85.11 ± 1.68
40 ml	200372.57	520.32	5.15	24742.56	94.62 ± 1.13	87.91 ± 1.31
60 ml	318570.19	521.31	3.25	62389.22	85.77 ± 1.53	71.32 ± 1.16
80 ml	275678.59	521.33	3.10	56510.33	82.35 ± 0.77	72.01 ± 1.39
100 ml	275322.11	521.37	3.36	52029.32	69.06 ± 1.36	67.96 ± 1.57

UV-Visible spectroscopy

Figure 4 shows the reflectance spectra of hybrid nanostructured Si employing the two-step MACE method by varying the molar concentration of AgNO_3 solution. The chemically etched samples exhibited a hybrid nanostructure encompassing vertical rod-like nanopores and nano-textured surface. For comparison, the reflectance spectra of CP5 polished reference Si was also provided in Fig. 4. Reference Si show a maximum reflectance of 55% at 260 nm with average 25% reflectance in the visible region. Compared to the reference Si, all the MACE treated samples has reduced reflectance and this can be attributed to the hybrid nanostructure on the Si surface. The minimum reflectance in the vertical rod-like nanoporous Si structure can

be supported by enhanced absorption in Si due to the multiple reflection of light and ratio of trapped photons in the pore [16]. Reduction in reflectance is mainly due to the formation of gradient refractive index between c-Si and the air due to the presence of hybrid NPs and nano-textured surface (hierarchical structures). This structure disturbs Fresnel reflection on a bare crystalline Si surface. As a result, the hybrid Si nanostructure significantly reduces the reflection of the incident light. Samples with 20 and 60 ml exhibit similar reflectance spectra with average 7.5% reflectance in UV spectral region and increased reflectance in visible spectral region; even though the AgNO_3 molar concentration was reduced from 2 mM to 0.6 mM. However, they exhibit similar surface morphology decorated with nanocrystals with the exception of different areal distribution of NPs. Surprisingly, 40 ml and 80 ml samples exhibit similar reflectance characteristics with average 10 % reflectance in the UV-Visible region. Further dilution of the AgNO_3 solution to 100 ml exhibit reflectance characteristics similar to that of 20ml and 60 ml diluted samples. It should be noted from SEM analysis that 40 & 80 ml exhibit relatively high surface roughness compared to that of other hybrid nanostructured samples. These observations suggest that presence of nanocrystals on the surface decrease the reflectance in the UV region, while higher surface roughness decrease the reflectance in the visible region.

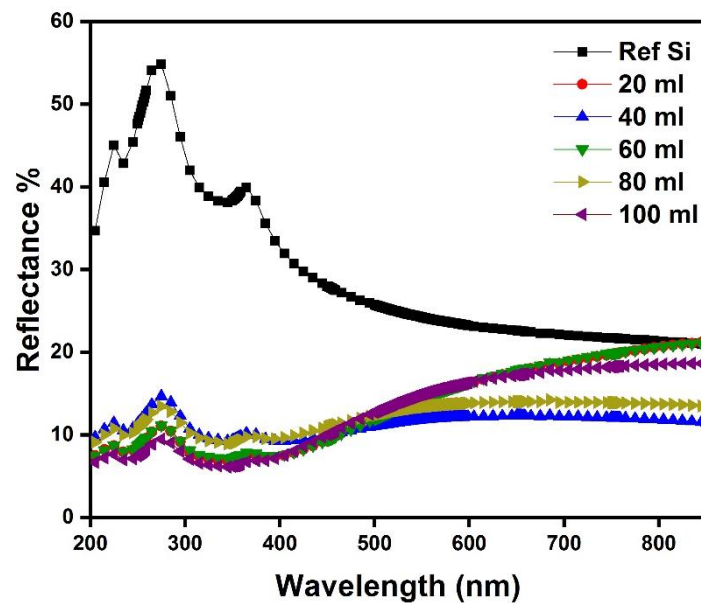


Fig. 4: Reflectance spectrum of ref-Si along with nanostructured Si formed by varying the AgNO_3 concentration by dissolving 7 mg AgNO_3 in 20ml to 100 ml of DD water

Conclusion

Preparation of hybrid Si nanostructures encompassing vertical rod-like nanopores with nano-textured surface employing simple and low-cost MACE method was investigated. The influence of AgNO_3 molar concentration realized by variation in dilution; such as 20, 40, 60, 80 and 100 ml of DD water, on hybrid structure formation was explored. The hybrid nanostructures were characterized by various tools to analyze the optical, structural and morphological properties. All the samples demonstrated formation of hybrid nanostructures on Si wafer surface. The diameter of the nanopores (NP) followed the trend of Ag nanoparticle size distribution, however with different pore depths for all the samples attributed to surface

wettability, Ag nanoparticle size and HF concentration dependent etch rate. Raman analysis confirmed formation of nanocrystals for high molar concentrations, while properties similar to that of bulk Si for low AgNO₃ molar concentration. From the optical results, the minimum surface reflectance in the UV region was observed for samples decorated with nanocrystals on the surface, while higher surface roughness decreased the reflectance in the visible spectral region. The present work suggests that an optimum low reflectance across the entire UV-visible spectral region can be achieved in hybrid nanostructures overcoming the recombination problems in 1D nanostructured Si; making it an especially sustainable candidate for antireflection coatings on silicon solar cells.

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