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Rapid and Facile One Step Fabrication of Wafer Scale Silicon Hierarchical Structures with High Broadband Anti-Reflection Property

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Abstract: Nanostructured Silicon surfaces are highly acclaimed for its unique properties like superhydrophobicity and high anti-reflection. Hierarchical nanostructures with a combination of micro- and nano- structures with much larger surface area can be of more appealing to enhance the surface and optical properties. In this context, we propose rapid and facile one-step electroless method of realizing hierarchical structures on Silicon surface covering the entire wafer area in comparison to the existing two-step methods. A complete wafer could be textured within 3 to 5 minutes time span. Moreover, this process is not dependent on the orientation or doping concentration of Silicon. Diffused optical reflectance measurement on the hierarchical structured Silicon (Si) showed a broadband enhanced anti-reflection property (R% ~ 2.4%; 300 nm to 1400 nm) with wide prospects in opto-electronic applications. Utilization of the hierarchical structured Si as a template for soft imprinting transparent polymer layers and its further use as solar encapsulant is also demonstrated.

Keywords: silicon; optical property; anti-reflection; hierarchical structure; electroless deposition

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1. Introduction

Nanostructuring of Silicon surface has perceived exponential growth over time due to its high demanding properties like superhydrophobicity and high anti-reflection [1–3]. Especially hierarchical structures (combination of micro- and nano- structures) on Silicon with significantly increased surface area has demonstrated enhanced optical and surface wettability properties, making it highly suitable for applications like self-cleaning, solar cell, photoluminescence, contamination prevention, etc [3–5]. Various techniques like vapour-liquid-solid (VLS), reactive ion etching (RIE), electrochemical etching and wet anisotropic electroless etching have been optimised for micro- and nanostructuring over Silicon surface [5–9]. Methods like VLS and RIE are expensive and complicated. Wet electrochemical and electroless etching processes are simpler, however, electrochemical etching gives a non-uniform porous structure. Electroless anisotropic etching can be performed when specific orientation (100) of crystalline Si is used that gives rise to pyramidal shaped microstructures. Electroless nanotexturing of Si wafers using metal assisted etching has also been reported which is a rapid process [4,10]. There are several reports where wet chemical anisotropic etching (in potassium hydroxide (KOH) bath) and metal assisted etching process have been combined to realize hierarchical structures on Silicon [2,3,11]. One of these literature demonstrated superhydrophobicity with water contact angle (WCA) as high as 166^0 on the Si hierarchical structures using conventional KOH etching combined with Gold nanoparticle assisted etching followed by treatment with perfluorooctyl trichlorosilane (PFTOS) [2]. However, the self-assembled monolayer (SAM) of PFTOS may not render the superhydrophobicity as SAM is quite affected by environmental conditions. Another literature, where hierarchical Si structures have been prepared using similar methods has shown WCA 165^0 and a high broadband anti-reflection of 4% [3]. Broadband anti-reflection property has also been demonstrated in another literature using wet chemical anisotropic etching of n-type (100) Si followed by Nickel (Ni) nanoparticle assisted chemical etching. Authors demonstrated 5% reflectance within 300 nm to 1100 nm wavelength [12]. Yet another literature demonstrated fabrication of crystalline silicon solar cells with hierarchical textured surface consisting of micropyramids using wet anisotropic etching of p-type Si followed by nanotexturing using silver nanoparticles. Here authors demonstrated 3% reflectance over 300 nm to 900 nm wavelength indicative of improved absorption of sunlight by the solar cell. Overall, an improved short wavelength spectral response and enhanced solar cell efficiency was observed for the hierarchical structured crystalline solar cell [11].

In this work, we propose an extremely fast and facile electroless method of fabricating hierarchical structures on Silicon wafer covering a large area. Unlike all other literatures on fabrication of hierarchical structure on Si using two-scale texturing process (i.e. conventional wet anisotropic etching followed by metal nanoparticle assisted wet etching); we demonstrate a one-step nanotexturing on the unpolished side of a commercial Si wafer. The unpolished side of a commercial Silicon wafer having grooved square shaped microstructures was used as the base to further nanotexture its surface using a known silver (Ag) nanoparticle assisted etching process. Major benefits of this proposed method is that complete wafer can be textured within 3 to 5 minutes time span and is not dependent on the orientation or doping concentration of Si. Using the proposed method of fabrication of hierarchical textured Si surface, we could significantly reduce the reflectance to 2.4% over a broad wavelength of 300 nm to 1400 nm. These hierarchical Si structures can be efficiently used to enhance solar cell efficiency as mentioned in a previous literature as well.

We have also demonstrated soft imprinting of thin PDMS layer from the hierarchical structured Si template and its prospects for utilization as efficient solar encapsulant. Materials with high optical transmittance, low moisture permeability, high temperature sustainability and self-cleaning property are considered to be excellent candidates for solar encapsulation. Hierarchical structured PDMS has already shown its prospects for efficient solar encapsulation in our previous studies [13,14]. In this study we propose another structural variation in the hierarchical texturing of PDMS layer by mimicking from a one-step processed hierarchical Si surface.

2. Materials and Methods

2.1. Materials

Single side polished (100) plane n-type Si wafer (Vinkarola), Hydrofluoric acid (Merck), Nitric acid (Merck), Silver Nitrate (Merck), DI water (HPLC; 18 MΩ cm), Sylgard 184 PDMS kit, hexane (Merck), and 1-Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Sigma Aldrich). All chemicals and salts used were Analytical grade.

Equipment used for characterization – Scanning electron microscope (Zeiss EVO 18 448), UV-vis-NIR spectrophotometer (Shimadzu UV spectrophotometer-2600), Canon digital camera (IXUS 185) for optical images.

2.2. Methodology

Si wafers were cleaned using standard RCA cleaning protocol and stored inside a vacuum desiccator till further experiments were conducted. The initial phase of experiment involves deposition of Ag nanoparticles by electroless metal deposition as published elsewhere [3]. In brief, a mixed solution of 0.01M of silver nitrate ($AgNO_3$) and 4.6M hydrofluoric acid (HF) was prepared at room temperature. The deposition of Ag nanoparticles was performed in dark with variable time intervals of 30s, 60s, 90s and 120s. The wafers were gently cleaned and dried and next step of etching. Further, the Si wafers with deposited Ag nanoparticles were etched in a solution of Hydrofluric acid (HF), Hydrogen peroxide (H_2O_2) and DI water mixed in a volume ratio of 1:5:10 at room temperature. Etching was performed for three different time durations for 5s, 10s, and 20s at dark condition. The etched samples were then washed thoroughly in DI water and further dipped in neat Nitric acid (HNO_3) for removing the Ag nanoparticles deposited on the Si surface (rear side). After repeated washing in DI water (ultrasonication), the etched Si samples were dried and stored for further analysis.

PDMS pre-polymer and curing agent was mixed in a ratio of 10:1 w/w and degassed to remove the bubbles generated during mixing process. The mixture was then diluted in hexane with 1:1 v/v and spins coated onto the etched Si wafers and cured at 150° for 10 mins. Cured PDMS polymer layer was then peeled-off from the Si surface. Dilution was necessary to lower the viscosity of the PDMS pre-polymer mix so as to ensure its capillary filling inside the pores of the etched Si. Before spin coating the PDMS pore-polymer mix, the etched Si wafer was treated with a self-assembled monolayer (SAM) of 1-Trichloro (1H,1H,2H,2H-perfluorooctyl) silane to make the surface superhydrophobic so that cured PDMS could be peeled off easily off the etched Si surface.

Characterization like Scanning Electron Microscopy and UV-vis spectrophotometry were performed for surface and optical analysis.

3. Results

3.1. Structural Analysis

The scanning electron micrograph (SEM) image in Figure 1a shows the rear morphological archietecture of Si. The rear side of Si comprises of grooved square shaped microstructures with an average dimension of 32 μm × 25 μm. A magnified morphological profile of the rear side of Si is shown in Figure 1b. This rear side of the Si wafer was further used to realize hierarchical texturing on its surface using only one-step experimentation.

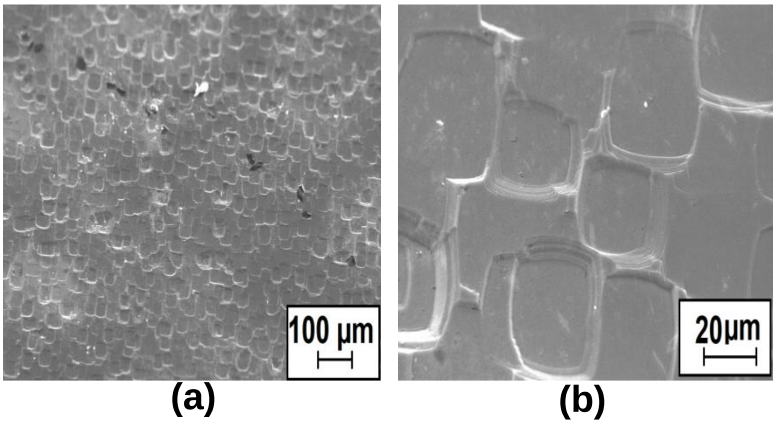

Figure 1. SEM image showing rear morphological archietecture of polished Si (a) lower magnification (**b**) higher magnification.

Different time intervals of 30s, 60s, 90s and 120s were used to deposit Ag nanoparticles on the rear side of the Si wafer to optimize large area uniformity, surface wettability and optical performance of the hierarchical textured Si. Electroless metal deposition performed for 60s gave a high uniformity throughout the sample with moderate inter-particle spacing and was further used to perform metal assisted etching on the Si surface. The SEM image of the rear side of Si wafer after 60s immersion in the metallization bath ($AgNO_3$ + HF) is shown in Figure 2. Average dimension of the Ag nanoparticles were measured to be 100 nm to 150 nm as can be observed in Figure 2b with higher magnification. Ag nanoparticle deposition performed for a time span of 30s caused minimum surface area coverage on Si, whereas, deposition for 90s and 120s resulted in vigorous growth of Ag nanoparticles that limited the exposed Si surface that could be utilized for further etching. Moreover, at 90s and 120s deposition time, Ag nanoparticles looked agglomerated which eventually led to their physical detachment from Si wafer surface.

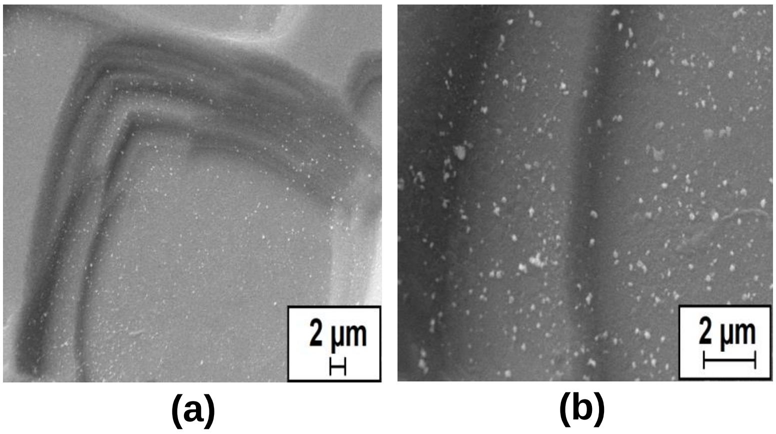

Figure 2. SEM image showing Ag nanoparticles deposited for time span of 60 seconds (**a**) lower magnification (**b**) higher magnification.

3.2. Optical Peformance

The effect of Ag nanoparticles deposition on Si and Ag assisted chemical etching of Si on anti-reflection property of the rear side of Si wafer was studied by measuring the diffused reflectance spectrum in wavelength range of 300 nm to 1400 nm. Figure 3 shows the reflectance spectra of rear side of Si wafer with Ag nanoparticles deposited for time duration of 60s, 90s and 120s. Figure 3 indicates that for deposition time higher than 60s, a significant increase in reflectance is observed (11% for 90s and 13% for 120s) in comparison to 60s deposition time where the average reflectance is only 2%. The appearance of increasing reflectance value with respect to increasing deposition time probably attributes to particle agglomeration and detachment as mentioned the Materials & Methods section. Based on these results, chemical etching on the Si wafer was further performed on the sample with Ag nanoparticles deposited for 60s.

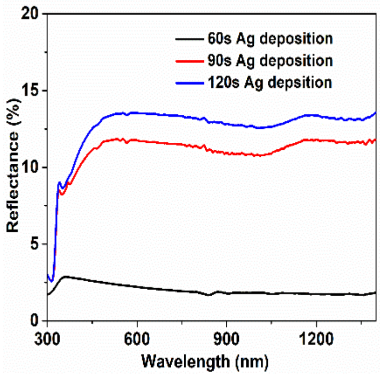

Figure 3. Reflectance spectrum of rear side of Si wafer with Ag nanoparticle deposited for various time intervals.

Figure 4 shows the reflectance spectrum of the chemically etched rear surface of Si wafer with Ag nanoparticles (60s deposition) for time durations of 5s, 10s and 20s. The graph reveals that reflectance of all the etched Si surfaces is certainly significantly less than of a plain polished Si (R% ~ 47%) and also less than the rear side microstructured Si surface (R% ~ 10%). Further it is observed that reflectance increases with increase in the etch time from 5s to 20s. Average reflectance observed with chemical etching for 20s is ~5% whereas for 5s chemical etching reflectance is ~2.4% within a wavelength of 300 nm to 1400 nm.

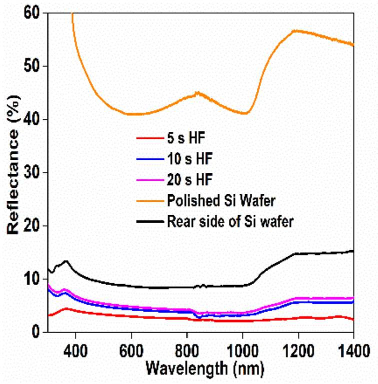

Figure 4. Reflectance spectrum of rear sided Si wafer post chemical etching at various time intervals.

3.3. PDMS Layer Mimicked from Hierarchical Si Template

The as prepared hierarchical Si wafer was treated with a SAM layer of 1-Trichloro(1H,1H,2H,2H-perfluorooctyl) silane to make it superhydrophobic. This step ensured an easy peeling of the cured PDMS layer from the textured Si template. The optical image of the imprinted PDMS layer is shown in Figure 5. PDMS layer was imprinted from the Si surface etched for 5s as it demonstrated minimum reflectance (Figure 4). A low reflectance of ~6% and high transmittance of 90% over a wavelength of 300 nm to 1400 nm could be observed (Figure 6). We also imprinted PDMS from the Si surface deposited with Ag nanoparticles for 60s and interestingly a lower reflectance/higher transmittance was observed (Figure 6). The nanotexturing on the latter sample is expected to have a concave nanodimpled impression on the microstructured PDMS whereas the previous sample is expected to have convex nanotexturing. SEM analysis of these textured PDMS surface is in process along with surface wettability tests. Overall, it is indicated that PDMS imprinted from the textured Si surfaces as proposed in the current study can be well utilized to prepare hierarchical PDMS layer suitable for solar encapsulation.

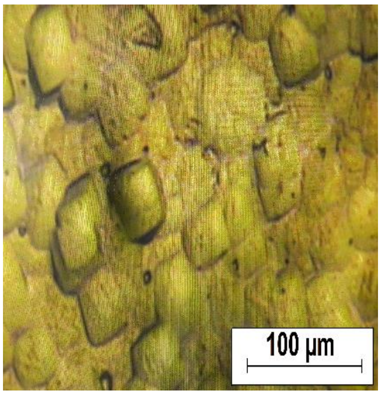

Figure 5. Optical image of soft imprinted PDMS surface from hierarchical Si.

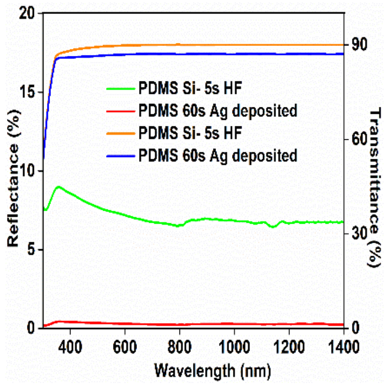

Figure 6. Transmittance and Reflectance spectra of hierarchical structured PDMS.

4. Discussion

By Following a one step process, only nanotexturing of rear Si surface resulted in hierarchical structures with an average reflectance as low as 2.4%. Whereas earlier literature on developing hierarchical Si structures employed conventional two step method using a doped (100) polished side of Si [11,12]. Here, hierarchical texturing on the Si surface is not dependent on its doping type or orientation. By avoiding the conventional wet anisotropic etching process for generating micropyramidal Si surface, we have significantly reduced the time required for preparation of the hierarchical Si surface. Almost 30 min to 75 min of time has been reported by other literatures to prepare the microstructures on Si [3,11,12]. Moreover, one-step surface texturing also avoids the use of high temperature bath (65°C–85°C) as required in conventional wet anisotropic etching process using alkali solution. The nanotexturing demonstrated here using Ag nanoparticles assisted etching can also be replaced with Ni nanoparticles as reported in other literatures [12] that can further reduce the cost of fabrication of hierarchical Si surface.

5. Conclusions

An extremely fast and facile one-scale texturing process has been demonstrated to generate hierarchical Si structures on a wafer scale. Overall, less time duration, less chemicals and room temperature preparation condition makes this process much more superior and cost-effective than already published literatures with similar goal. High broadband anti-reflection combined with self-cleaning property makes the hierarchical Si surface promising for optical and opto-electronic applications. Further, its utilization as a template for preparing one-step negative or two-step positive imprints on transparent polymer materials can be extremely beneficial for application as solar encapsulants.

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