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Fabrication of hierarchical anti-reflective structures using polystyrene sphere lithography on an as-cut p-Si substrate

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ABSTRACT

The broadband anti-reflective (AR) properties of hierarchical structures (HSs) have attracted considerable attention in recent years as a means to reduce Fresnel reflection in photovoltaic solar cell materials. This study employed polystyrene sphere lithography in conjunction with high density plasma dry etching in the fabrication of pure sub-wavelength structures and HSs on an as-cut p-Si substrate. Etching parameters, such as RF power, O_2, and etching time, were adjusted to alter the surface morphology. Experiment results demonstrate that the resulting hierarchical paraboloidal structures suppress average reflectance to below 0.5% across a spectral range of 500–1000 nm.

1. Introduction

Crystalline silicon (Si) remains the most common material used in photovoltaic cells [1]. Unfortunately, there is a considerable discrepancy in photoelectric conversion efficiency (PCE) between the performance of commercial Si-based solar cells [2] and what could theoretically be achieved. This difference can be attributed to Fresnel loss associated with a difference in the refractive indices of Si and air. This problem has conventionally been dealt with by reducing surface reflection through the application of anti-reflective (AR) thin films [5,6]; however, this approach is giving way to the fabrication of sub-wavelength structures (SWSs) featuring broadband anti-reflective (AR) properties [3,4]. A variety of structural profiles with excellent AR properties have been proposed, including nanopillars [7,8], nanoholes [9,10], and nanoconical [11]. In cases where the surface morphology presents a continuous change, such arrays can be viewed as a stack of multi-layer thin films, in which differences in the volume fraction of each layer produce gradual changes in the refractive index. The gradual change in refractive index from one layer to the next [12] reduces Fresnel reflection [13]. Previous studies have demonstrated that SWSs are able to suppress the surface reflection of photovoltaic solar cells over a wide range of frequencies as well as enhance their PCE [14]. Hierarchical structures (HSs) have recently been proposed [15] to further enhance AR performance. Park et al. [11] integrated polystyrene (PS) nanoisland coating on top of Si nano-conical-frustum (NCF) arrays, resulting in AR performance far exceeding that of sharp-tipped nanocone structures through improved impedance matching. Liu et al. [16] employed wet etching in conjunction with lift-off technology in the formation of a nanoporous Al coating on pyramids surface with inductively coupled plasma (ICP) dry etching to a pyramid-nanohole texture on the surfaces of silicon solar cells. The reflectance of that surface texture was below 4% at wavelengths ranging from 400 to 1000 nm, which is far lower than that of pyramids only or an array of nanoholes. The PCE of the resulting device (14.89%) is significantly higher than that of solar cells with a planar surface (12.18%), a surface with a nanohole array (13.27%), or pyramids only (14.49%).

High-efficiency black silicon solar cells have been developed to overcome surface recombination. In this approach, a thin conformal alumina film is deposited on the nanostructured front surface [17]. Its success illustrates the possibilities for the industrial production of black silicon solar cells. This study developed a rapid low-cost process involving colloidal lithography using PS spheres in conjunction with one-step high-density plasma (HDP) etching for the fabrication of hexagonal hierarchical (subwavelength-nano) AR structures on an as-cut p-Si substrate. Etching parameters, such as RF power, O_2, and etching time, were adjusted to fabricate a variety of surface morphologies. Finally, the AR properties of the structures were measured using a UV–vis-NIR spectrophotometer.

2. Experiments

PS spheres with diameter of 800 nm were synthesized using dispersion polymerization in an ethanol medium with 2, 2′-azobis(2-methylpropionitrile) (AIBN) as an initiator, styrene (St) as

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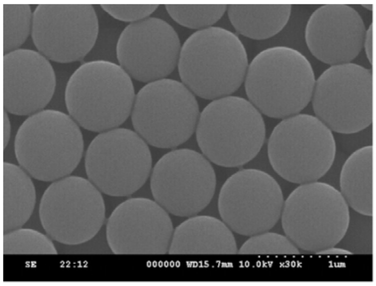

Material	Weight(g)
AIBN	0.181
St	9
PVP	27
Ethanol	47.5

Fig. 1. SEM image of PS spheres 800 nm in diameter and constituent chemicals.

a monomer, and polyvinylpyrrolidone (PVP) as a stabilizer. Polymerization was performed at 65 °C with an oscillation frequency of 400 rpm over a period of 10 h. The PS spheres were separated by centrifuge and washed using methanol and DI water. Finally, the PS spheres were obtained by drying the solution in a vacuum oven at 50 °C for 12 h, as shown in Fig. 1. The constituent chemicals and their corresponding quantities are presented in Fig. 1.

Fig. 2(a) presents a schematic representation of PS spheres on a 6-in.^{2} as-cut polycrystalline silicon (p-Si) substrate. The spheres were organized using the floating assembly method for use as an etching mask during the dry-etching process. In this study, the PS suspension was modified to enable assembly at the water-air interface. Upon completion, DI water was pumped using a peristaltic pump to enable to deposition of the PS spheres on the substrate. Compared to PS spheres assembled via spin coating, the floating assembly method helps to prevent nonuniformity in the thickness of PS suspension and dislocation of PS spheres resulting from poor coverage on a roughness surface substrate. To confirm whether the PS spheres were uniformly arranged on the surface of the unpolished substrate, measurements were taken at nine different positions using a scanning electron microscope (SEM), as shown in Fig. 2(b).

Fig. 3 illustrates the proposed fabrication process. HDP etcher (Unaxis GmbH, Nextral 860L) was used to produce cylindrical structures on the as-cut p-Si substrate under an RF power of 50 W for 5 min. The flow rate of SF_6, Ar, and O_2 were 50 sccm, 25 sccm and 25 sccm, respectively. The aim of this process was to obtain high structures for the following etching process [11]. Upon completion, the as-cut p-Si substrate and array of PS spheres were subjected to HDP etching, with the same Ar and SF_6 flow rates as those used for the etching of the cylindrical structures. The process pressure during etching was maintained at 25 mTorr. SWS arrays with profiles showing various surface structures were produced by adjusting the flow rate of O_2 as well as the RF power and etching time. The HSs were fabricated by increasing the etching time. Following the etching processes, the PS spheres were removed using RCA cleaning, whereupon the surface morphology of the structures was characterized using SEM. All dimensions in this study are the average values obtained from five measurements. Reflectance spectra were measured from 500 nm to 1000 nm using a UV–vis-NIR spectrophotometer at a near-normal incident angle of 8°.

3. Results and discussions

Fig. 4 presents SEM images of PS spheres organized on an as-cut 6-in.^{2} polycrystalline silicon (p-Si) substrate obtained in nine different positions. To ensure that the assembled PS spheres were organized as a monolayer, we reduced the diameter of the PS spheres to 700 nm through the application of O_2 plasma etching for 30 s. Clearly, the PS spheres were arranged uniformly in a hexagonal closely-packed monolayer arrangement, thereby demonstrating the feasibility of the floating assembly method for the application of PS spheres to non-planar substrate surfaces.

As mentioned above, structures with continuous surface profile provide a better AR property. In our previous study [18] using a monocrystalline silicon substrate, we showed how the flow rate of O_2 and etching time influence the height of the resulting structures as well as the overall surface morphology. Based on this experience, we sought in this study to fabricate pyramidal and paraboloidal structures on the as-cut p-Si substrate using HDP etching, as shown in Fig. 5. The etching parameter are summarized in Table 1. The diameter/height of the pyramidal and paraboloidal structures were approximately 800/700 nm.

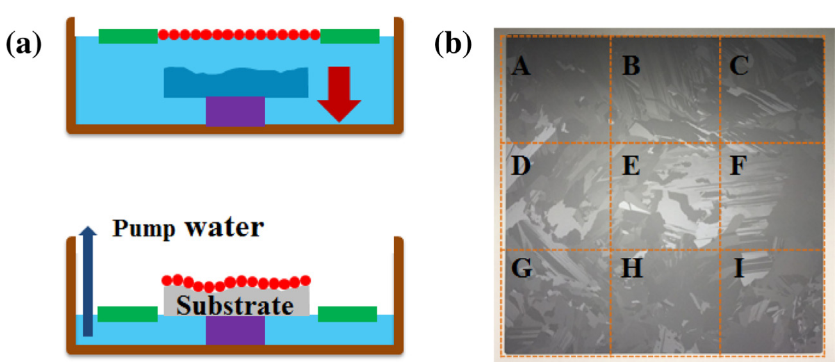

Fig. 2. (a) Schematic illustration of PS spheres organized on as-cut p-Si substrate; (b) photograph showing the nine positions from which SEM measurements were obtained.

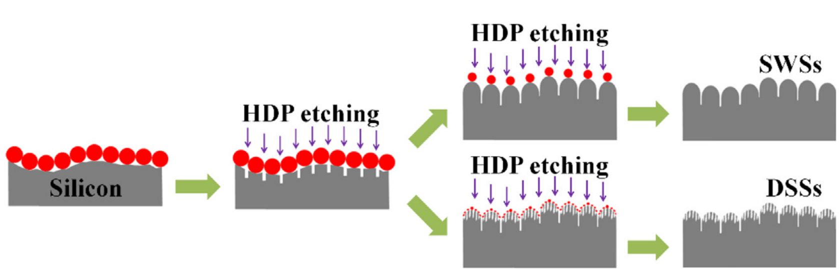

Fig. 3. Schematic illustration of HDP etching processes.