Nanostructuring Methods for Enhancing Light Absorption Rate of Si-Based Photovoltaic Devices: A Review

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KEYWORDS: Photovoltaic device, Light absorption, Vapor-liquid-solid, Solution-liquid-solid, Reactive ion etching, Metal assisted chemical etching

In recent years, there has been growing consideration of renewable energy especially photovoltaic devices. A silicon (Si) based solar cell is the most popularly and frequently considered among the photovoltaic devices, but its bulk thickness issue lowers the performance and hinders widespread application due to the material cost. Also, this thick nature causes difference in length between minority carrier diffusion and sufficient light absorption. To mitigate the issues there have been many recent studies on Si photovoltaic devices adopting nanostructuring strategies to enhance the performance. Therefore, we report two different approaches on recent nanostructuring techniques for photovoltaic devices; bottom-up and top-down processes, which are composed of vapor-liquid-solid, solution-liquid-solid, reactive ion etching with Langmuir Blodgett and metal assisted chemical etching. Those fabrication processes enable the fabrication of nanostructures with a highly ordered and alignment structures leading to enhance the light absorption and have an appropriate thickness of Si substrate regressing Auger recombination. The fabricated nanowire and nanocone array structures outperform existing results with light absorption exceeding 90%.

Manuscript received: November 28, 2013 / Accepted: December 26, 2013 (Invited Paper)

1. Introduction

Many studies have been focused on energy conversion devices utilizing renewable energy sources such as hydrogen, solar, geothermal, wind, and biofuels.¹⁻⁵ Among those renewable energy systems, photovoltaics (PV) may be the most attractive solution for the replacement of fossil fuel due to zero emissions, environment-friendliness and infinite reserves. Since first discovery of the photovoltaic effects, less research and trials for the commercialization of the PV has been conducted until the appearance of the silicon (Si) based solar cell.^{6,7} Though the initially invented Si based PV had a only ~4% of efficiency of converting sun light into electricity, by the help of continual research efforts, the efficiency has significantly increased up to near the theoretical value of the single junction Si-PV.^{7,8}

Indeed, despite discordance of band gap energy between the Si (1.1 eV) and the optimal value (1.4 eV) for single junction solar cell, Si has been considered as a promising material for PV, particularly

crystalline Si-PV.^{9,10} The Si is second abundant element in earth and has non-toxicity, enabling to wide utilize in PV industry. It is also attractive point for using Si-PV that the surface of Si substrate can be easily passivated by thermal oxidation for prevention of surface recombination. However, the crystalline Si-PV should have 10~1000 μm of the thickness for absorption of photons in various wavelengths due to its indirect band gap, and therefore, electron and hole pairs are readily recombined via Auger recombination in surface of Si-PV, as shown in Fig. 1(a).^{1,11,12} This bulky thickness of Si significantly drives up the fabrication cost of Si-PV devices. Also, it accounts for ~40% of the total fabrication cost and this hinders growth of the solar cell commercialization for industrial use.¹³ Therefore, many strategies have been conducted to overcome the fabrication cost issue in silicon based solar cell such as using other materials having direct band gap for example cadmium telluride (CdTe). Especially, cadmium telluride (CdTe), gallium arsenide (GaAs), indium phosphide (InP), copper indium gallium selenide (CIGS) and their alloys and ternaries/

quaternaries compounds have been considered as the most promising materials for PV. However, these materials are much expensive and phase diagram is also quite complicate to fabricate in a large scale production. Therefore, the development of the doping techniques for hydrogenated amorphous silicon (a-Si:H) has received great attention since it has higher absorptivity than bulky Si based solar cell by help of thin film process with conventional thin film deposition techniques.^{14,15} This high absorption of light in a varied spectrum resulted from the high structural disorder in the material allowing all optical transition, while the disorder simultaneously served as core part of recombination which highly reduces the carrier lifetime.^{10,14} However, during the deposition of a-Si:H, 10% of the hydrogen incorporated greatly reduced the density of disorder, so it is considered that a-Si:H is the most suitable materials itself for substrate of thin film solar cells as well as substrate for nanostructure.¹⁴ Although a-Si:H solar cells are subject to the Staebler-Wronski effect, which is caused by light-induced degradation related to a creation of defect acting as non-radiative recombination centers, it is also partially overcome by reducing the thickness of the a-Si:H layer in solar cells.^{1,14,16}

However, as in the case of the a-Si:H thin film solar cells, it has no chance to have less than 1 μm of thickness in order to absorb sufficient light spectrum unlike the minority carrier diffusion length has the typical length of the 300 nm.¹⁷ This difference of the length for sufficient light absorption and diffusion length causes significant reduction of the Si-PV power generation due to a lack of light absorption and the loss of the carrier collection in the electrodes.^{17,18} For this reason, many researchers try to narrow this gap and then nanostructure (i.e. nanorod, nanowire, nanocone, and nanohole) is considered as a solution. This strategy is

mostly helpful to enhance light absorption in various wavelengths and increase the diffusion length of photons in Si-PV.^{19,20} As shown in Fig. 1(b), the nanowire, commonly has 1~50 μm of height and 10~500 nm of diameter, allows to the sufficient thickness of the light absorption for thin film Si-PV, while simultaneously offering a relatively short path of the carrier collection which means the efficient collection of carrier with short minority carrier diffusion length.¹⁸ In addition, compared to the technique achieving more light absorption for conventional planar Si-PV, thin film Si-PV with nanostructure has more advantages than antireflection coating (ARC) which is only able to decrease the reflection with a specific incident angel of the sun light and wavelength.¹⁷

In this paper, we report recent fabrication process of thin film Si-PV with one-dimensional nanostructures specialized in enhancing light absorption. Among the nanostructures, nanowire and nanocone are the most considered structures due to highly ordered arrays leading to enhanced light absorption.

2. Fabrication of Nanostructures

In general, fabrication approaches can be divided into two on nanostructures for thin film Si-PV: deposition (bottom-up) and etching (top-down) methods. The thin film Si-PV strongly requires nanostructured scattering part using nanowires, nanorods, and nanocones. To fabricate the nanostructures for Si-PV, we therefore discuss the conventional fabrication process such as vapor-liquid-solid (VLS), solution-liquid-solid (SLS), metal assisted chemical etching, and reactive ion etching.

2.1 Bottom-Up Method

Lieber et al. reported a new method based on bottom-up approach for silicon nanowire synthesis.²¹⁻²⁵ VLS has been introduced and developed to combine with high techniques: annealing in reactive atmosphere, laser ablation and evaporation.²⁶⁻³² These techniques can generate nanoscale catalytic droplets with precise size control, high yielding rate, and purity.

The VLS process usually requires a thin gold film which is deposited on Si substrate via physical vapor deposition technique. The size and density of the Si nanowires are defined by the density and size of Au nanoparticles that can be controlled by the sputtering conditions and the thickness of the Au film. As shown in Fig. 2, VLS process has used about 1~10 nm thickness of Au film which is deposited by sputtering or evaporation. Then, thermal annealing process of the

Fig. 1 (a) The conventional bulk Si-PV leading to Auger recombination in surface and have relatively long path of diffusion length, (b) The Si-PV with nanostructure have relatively short path of diffusion length and enhanced light absorption in wide region of wavelength

Fig. 2 Schematic of Si nanowire growth process, (a) Au thin film is deposited on substrate by PVD, (b) Au-Si droplets are by thermal annealing and (c) Si nanowires grow from the reaction of SiCl_4 and H_2 vapor Phases

deposited Au film creates Au-Si alloy droplets which have a lower melting temperature compared to each composition material. Therefore, Si-Au alloy droplet can form a liquid type when the temperature is higher than the eutectic point (363°C). SiCl_4 and hydrogen vapor adsorbs onto the Au-Si alloy liquid surface and react gaseous mixture reaction ($\text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl}$) with catalytic assistance. As a result of the reaction, Si and hydrogen chloride are created and Si diffuses into Au-Si alloy droplet. Subsequently, one dimensional crystalline nanowire is grown by a liquid metal alloy droplet. Si atoms are nucleated at the liquid-solid interface which leads to axial crystal growth by Si supersaturated liquid alloy droplet. Then, Si nucleation raises a droplet on the surface to promote nanowire growth.³³⁻⁴⁰

The solution-liquid-solid (SLS) growth mechanism shows similarities with the VLS process. Buhro et al. developed SLS method for synthesis of nanowire at a relatively lower temperature than the VLS method. Unlike the VLS method, SLS can create metal nanowires and lower the fabrication cost even in a large scale production. Moreover, SLS facilitates using metal catalyst with a low melting temperature, and the desired material can be created by decomposition of organometallic precursors in solution.

The production principle of Si nanowire using SLS method takes place as follows: metal catalyst (Au) and silicon precursor such as diphenylsilane are distributed with hexane when heated and pressurized above the critical point. Then, uniformly distributed alkanethiol-capped Au single crystals take on nucleation sites for Si nanowire growth. When the concentration of Au is higher than Si over 18.6 mol% at the temperature of eutectic point, Au is formed in an alloy phase with the solid Si in an equilibrium state. As a result, Si atoms are melted in the Au nanocrystals until the supersaturation, and uniform nanowire is formed by Si protruding from the Au-Si alloy particles.^{41,42}

2.2 Top-Down Method

The lithography uses close-packed nano spheres as a masking structure which allows it to fabricate various sizes of nanopillars and cones with controllable spacing.⁴³⁻⁴⁴ Although spin coating method has been widely used, it provides relatively poor coverage and is difficult to create a close-packed monolayer on the desired substrate. Since the Langmuir Blodgett (LB) method provides precise control to form the close-packed monolayer of nanoscale particles in a relatively large area, the LB method has been used for the fabrication of a close-packed monolayer of spherical nano particles. The fabrication process of LB is described in Fig. 3. The

Fig. 3 The process of LB of (a) the dispersed silica particles are randomly located, (b) the close-packed array of silica particles are obtained using bar, (c) the substrate are submerged in distilled water, (d) then silica particles are stuck on substrate retaining the close-packed array

synthesized nanoscale silica particles are dispersed on the surface of distilled water in the trough. Then, using compression bars a close-packed monolayer of silica particles can be formed while measuring the surface tension. Sequentially, a desired substrate is submerged in distilled water and is pulled out at a constant speed.

Due to capillary force and convective flow as the water evaporates, the particles follow the substrate and form a close-packed monolayer. After the particle transfer using LB method, combinatorial (physical and chemical) etching steps are required to fabricate the nanostructures. Reactive ion etching (RIE) is one of the dry etching methods having precise controllability and selectivity.⁴⁵ This etching method is assisted by plasma to ionize and dissociate the gas molecules to chemically reactive ions. Then, the substrate can be placed on the bottom electrode which is negatively charged. The reactive ions diffuse to the substrate by d.c. driven electric force and absorption occurs on the substrate. The ionic chemicals react with the substrate, then are desorbed. Since the chemical products resulting in the reaction are volatile, they can be removed after the reaction. Lastly, the desorbed products are then pumped out.

For the fabrication of silicon nanopillars or nanocones, fluorine based or chlorine based gases are used. For example, if SF_6 gas is used, the plasma generates F^+ , SF_5^+ and F^- . The radicals (F^+) diffuse with d.c. biased condition, reacts with Si atoms during the absorption and reaction process, and then produces SiF_4 which is volatile and allows it to be removed. The intensity of plasma influences the directionality of etching. Therefore, isotropic etching usually requires moderate RF power while anisotropic etching needs strong plasma density.⁴⁶ Figure 4 shows the actual images of homemade silica particles on the silicon substrate deposited by LB method (Fig. 4(a)) and the nanocone structures having various shapes created by RIE method (Fig. 4(b) and (c)).

Recently, a number of researchers focused on LB method for solar cell fabrication to create a light absorption structure and layer.^{17,47} In some literature, LB and RIE were used for fabrication of nanopillar and nanocone arrays. As shown in Fig. 5, the process of making nanocone has several steps. First of all, the surface of the synthesized particles

Fig. 4 FE-SEM images of (a) silica mask after RIE etching, (b) nanocones and silica particles, and (c) fabricated nanocones after HF etching of silica mask

Fig. 5 The fabrication steps of nanocone structure. (a) On silicon wafer, (b) silica particles are dispersed via LB, and etched by selective and isotropic RIE, (c) The nanopillars can be made by anisotropic etching, (d) Then, the nanocones can be fabricated by isotropic RIE using SF_6 , (e) Lastly, the etch-mask can be removed by buffered oxide etching¹⁷

was modified with aminopropyl methyl-diethoxysilane to avoid agglomeration by giving positively charged amine groups and this gives repulsive force between each particle. Then, on a silicon wafer (Fig. 5(a)), close-packed monolayer of silica particles were created by LB method (Fig. 5(b)).

Silica particles have the diameter from few tens of nanometers to few microns. After the deposition of silica particles, selective and isotropic RIE was conducted to reduce the size of silica particles (Fig. 5(c)). In this step, the particle size can be controlled as well as the spacing between the particles. The RIE was performed with a gas mixture of O_2 and CHF_3 . Then, the silicon wafer was etched to form nanopillars by Cl_2 based anisotropic RIE etching which has selectivity to Si wafer (Fig. 5(d)). The height of the pillars can be controlled by adjusting the etching time of this RIE process. For the fabrication of nanocones, the anisotropic and isotropic etching was performed to make a sharp tip of nanocone arrays (Fig. 5. (e)). Due to the silica particles, there is a difference in gas diffusion rate at the top and the bottom of the pillars. That is the mechanism of fabricating the cone structures. The last step is removal of remaining the silica particles by buffered oxide etching.

Another method of the top-down nanostructuring is metal assisted chemical etching (MacEtching) which is intrinsically a wet etching method to fabricate Si nanostructures. Since Li et al. first adopted the noble metal (e.g. Au, Pt, Au/Pd alloy) as a catalyst in etching process MacEtching had growing concerns of etching techniques in the last decade.⁴⁸ MacEtching has several advantages over other etching methods such as RIE, electrochemical etching, and anodic etching. Huang et al. well defined the merit of metal assisted chemical etching.⁴⁹ It has a simple process, low fabrication cost, no limitation of the size of structures, the possibility to control the orientation of structures in a given substrate, flexibility of geometry in cross-sections, and fine crystalline quality.

MacEtching utilizes the characteristic of anisotropy in the etching process. The etching rate of Si which has the catalyst material on top is much faster than the etching rate of Si itself in the solution mixture of hydrogen peroxide and hydrofluoric acid. By using this characteristic, high aspect ratio nanowire or nanopillar structures can be achieved while the height of the structure is dependent on the etching time. Fig. 6 shows the schematic and the detailed process of metal assisted etching. Noble metal catalyst particles or a layer are deposited on the Si substrate by conventional metal deposition techniques. Then, the sample is put in the liquid solution of H_2O_2/HF mixture. Consequently, due to the catalytic reaction between the metal and the substrate, Si beneath the noble metal is etched much faster than Si without catalyst and the process keeps going on until the sample is taken out from the solution. (Fig. 6 (b)). The un-etched part of the Si substrate is the final nanostructures. In this process, a noble metal contact area is employed as partial cathodic areas in which occurs reduction of oxidants (e.g. H_2O_2).

Subsequently, the hole (h^+) is generated as a byproduct of reduction and transferred to the interface between noble metal and Si substrate. Finally, the Si substrate is oxidized and transforms into an ionic state which is dissolved in an acid solution (e.g. HF).^{49,50}

The reaction of MacEtching was presented by Chartier et al. who proposed mixed reaction.⁵¹ The overall reaction is:

Where n is the number of holes in dissolved Si atom with cathodic and anodic reaction.

One of the main features of the fabrication methods is that the capability of creating ordered nanostructures and controllability of the geometry such as the size or diameter, and spacing between fabricated nanostructures. It can be decided by the pattern of deposited noble metal particles or structure of the metal film created on the Si substrate. There are several methods for making patterns or local arrays on Si substrates. The most highly ordered arrays are obtained by template-based masking method such as self-assembly of a monolayer using polystyrene (PS) spherical particles. Huang et al. firstly adopted the PS spheres as a masking material and created noble metal film structure on the Si substrate. Detailed process of this method is well presented in Huang's early report.⁵² They created a close-packed monolayer of PS spheres and gave some spacing between the spheres by dry etching technique. By using a thermal evaporation, the highly ordered honey comb pattern of a noble metal film was deposited through the spacing between the PS spheres. After removing the PS spheres, MacEtching was performed and the patterned noble metal sank in vertically remaining the un-etched Si substrate as a nanowire array. Another report by Huang et al. concerns with template-based etching method using anodic aluminum oxide (AAO) as a mask as well as polystyrene composite.⁵³

AAO membrane/polystyrene composite was located on Si substrate and then polystyrene which served as a stabilizer was removed through the oxygen plasma. Subsequently, Si substrate was patterned in hexagonal geometry via RIE process and RCA solution which able to remove AAO from the patterned Si substrate. By using sputtering, the noble metal was deposited as a catalyst, then, vertically aligned Si nanowires were obtained through the metal assisted chemical etching.

Fig. 6 The principle of metal assisted chemical etching, (a) catalyst is deposited on the substrate then H_2O_2/HF gases are applied, (b) substrate beneath the catalyst contacted area is etched into vertically and remain substrate exists as a nanostructure⁶⁴

3. Result Structures and Enhanced Absorption Rate

3.1 Nanowire Structures (Bottom-Up Method)

In Si-PV, n-type silicon nanowires are grown by chemical vapor deposition (CVD) via the Au catalyzed the bottom-up method on p-type silicon substrate.

These nanostructures help to increase performance and have antireflection properties by multiple reflections. It is expected to enhance light absorption and short circuit current.⁵⁵⁻⁵⁷ Cabarrocas et al. reported ultra-thin Sn layers that were evaporated on top of the substrate and applied H₂ plasma treatment at 180°C to form Sn catalyst droplet.⁵⁹ Droplets act as catalyst to facilitate the growth of Si nanowires at total gas pressure of 600 mTorr and RF power density of 50 mW/cm². Si nanowires which have a diameter of around 80 nm and enhanced strong light trapping capability more than 90% within 1.7 μ m Si in 300 to 700 nm of wavelength range. Moreover, the density of Si nanowires played an important role in light absorption because higher light absorption was detected as density of Si nanowires increases.^{58,59} Falk et al. demonstrated the sputtered Au layer which has thickness of 2 nm and heated the sample to 700°C for making catalytic droplet. As a result of this experiment, nanowires were fabricated with the mean diameter of 80 nm, and these nanowires demonstrated more than 90% enhancement of light absorption within 1.5 μ m Si in the wavelength region below 1000 nm. In the case of a planar sample, the absorption drops to as low as 55% at 400 nm and 70% in the 600 nm wavelength region.⁶⁰ Christiansen et al. reported their experiment that the nanowires grown on glass substrate have a length of 3-6 μ m and diameter in range of 20-100 nm. A strong broadband optical absorption can be observed in the relatively thin Si nanowire films. This phenomenon can be attributed to the significant reduction of the reflectance and the strong light trapping of the nanowires.⁶¹

3.2 Nanopillar and Nanocone Arrays (Top-Down Method)

The nanocone and nanopillar structures can be customized through the whole process. Zhu et al. recently published a paper concerned with nanostructures for PV.¹⁷ The PV device performances of fabricated nanopillar and nanocone arrays were compared with that of the thin film a-Si:H PV device. The surface of thin film a-Si:H looks very smooth and shiny since most of the absorbed light is reflected.

On the other hand, the nanopillar and nanocone arrays have darker

surfaces. Especially, the nanocone arrays look almost black and the surface was very rough. For a quantitative measurement, they performed absolute hemispherical measurement with an integrating sphere. In addition, the Maxwell equation with rigorous coupled-wave analysis was used for numerical comparison. The results show that 90% of light absorption within 1.0 μ m Si for nanocone arrays which is the highest among three samples. Nanopillar arrays and thin film have 70% and 45% within 1.0 μ m Si, respectively. When the incidence angle is increasing, the light absorption of all three samples is decreasing, but the nano-cone arrays still have the highest values due to the characteristic cone shaped structure. Lal et al. fabricated an ordered Si nano-conical-frustum array structure by lithography techniques. The feature of nanocone like nanostructure is height of 3.5 μ m and top radius of 170 nm, bottom radius of 400 nm. Due to the higher light trapping ability of conical structure, absorption of the ordered Si arrays is exhibited about 99% over wavelengths 400-1100 nm.⁶²

In the case of the MacEtching, nanostructure for photovoltaic using Si nanowire was reported by Najar et al.⁶³ This paper reported photovoltaic device with porous Si nanowire created by MacEtching. After thorough cleaning, Si wafer was dipped into aqueous HF/AgNO₃ solution for Ag-deposition which affects the Si with porous surface and it was rinsed with distilled water to remove residual silver ions. Then Si wafer was transferred to the HF-H₂O₂ solution bath for etching process. The fabricated porous Si nanowire with length of 31 μ m and diameter of ~150 nm was reported as less than 0.1% of reflectance for various wavelengths and indicated that the fabricated nanowire is able to drastically decrease the reflectance for enhancing solar cell performance. All of the earlier published results of enhancing absorption rates in Si-PV as suggested in this paper are well organized in Table 1.

4. Conclusions

Recent approaches and results of fabricating various nanostructures for solar cells are discussed in this report. To overcome bulky thickness problem of crystalline Si, thin film Si based solar cell such as a-Si:H was considered. However, the mismatch of the length between minority carrier diffusion length and sufficient absorption thickness has caused other issues lowering the performance. To compensate this gap, various nanostructures were employed in solar cell fabrication. Two most popularly used nanostructure fabrication methods are introduced and categorized in this paper; VLS, SLS as a bottom-up and RIE, MacEtching as a top-down method. VLS and SLS grow the silicon structure beneath the catalyst on Si substrate at the nucleation in liquid-solid interface. These methods are capable of conformal growth of Si nanowires in large-area platform, while having no chance to control the growing direction due to non-uniform orientation and difficulty in fabricating ordered array structure. RIE is employed for the Si based substrate with a masking material to have a certain cone shaped structure which comes from the diffusion limit of the bottom structure. This difference of etching rate caused by masking material affects the etching of Si substrate with different geometry of structures. Therefore remained Si structures can be nanostructures with nanowire and tapered geometry. MacEtching is a wet etching method having intrinsic and anisotropic characteristic. This method utilizes the different etching rate

Table 1 Summary of nanostructure fabrication and light absorption rate

Author	Published date	Process method	Structure	Absorption
Cabarrocas et al. ⁵⁹	2013	VLS	Nanowire	90% within 1.7 μ m Si
Falk et al. ⁶⁰	2013	VLS	Nanowire	90% within 1.5 μ m Si
Zhu et al. ¹⁷	2009	RIE	Nanocone	90% within 1.0 μ m Si
Zhu et al. ¹⁷	2009	RIE	Nanopillar	70% within 1.0 μ m Si
Lal et al. ⁶²	2010	Litho-graphy	Nano-conical-frustum	99% within 3.5 μ m Si
Najar et al. ⁶³	2012	Mac-Etching	Nanowire	99.9% within 31 μ m Si

of catalyst/substrate interface and the substrate itself in a certain solution mixture. Like the RIE, template-based structures are considered as a mask for MacEtching in order to obtain highly ordered arrays of nanowires. Therefore, the fabricated nanostructures are employing to enhance light absorption locating the nanostructure in surface of the solar cells. Thus, many researches have reported repeatedly that such nanostructures significantly contribute to increase light absorption in various wavelength regions.

ACKNOWLEDGEMENT

Y.B.K. and S.W.H. is grateful to the National Research Foundation (NRF) of the Korean Ministry of Education, Science, and Technology (MEST) (Grant No. 2012R1A1A1014689) for its financial support.

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