Potential of quasi-inverted pyramid with both efficient light trapping and sufficient wettability for ultrathin *c*-Si/PEDOT:PSS hybrid solar cells

Quntao Tang[a], Honglie Shen[a,*], Hanyu Yao[a], Kai Gao[b], Ye Jiang[a], Chaofan Zheng[a], Wangyang Yang[a], Yufang Li[a], Youwen Liu[b], Lei Zhang[c]

[a] *College of Materials Science and Technology, Jiangsu Key Laboratory of Materials and Technology for Energy Conversion, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China*
[b] *College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, PR China*
[c] *Department of Physics, Changshu Institute of Technology, Changshu 215500, PR China*

ARTICLE INFO

ABSTRACT

In this paper, a simple and cost-effective wet chemical method is presented to form quasi-inverted pyramids (QIP) on ultrathin *c*-Si for efficient light trapping and sufficient wettability. The QIP is fabricated by a well-known two-step Ag assisted chemical etching method followed by a post nanostructure rebuilding (NSR) process. The variation of [Ag$^+$] realizes the modulation of QIP size from sub-micro scale to micro scale. The comparable average absorptance value of 50 μm *c*-Si with double-sided QIP fabricated under 0.5 mM [Ag$^+$] (QIP-50) to that of 182 μm *c*-Si with double-sided conventional micro-scale pyramid in the spectral range of 300 – 1100 nm demonstrates an over 3.6-fold reduction in material usage. In comparison with nanopores-structured light-trapping configuration, the QIP-50 possesses much smaller specific surface area of ~2.39, which alleviates the surface recombination losses. After wet oxidation treatment, the water contact angle (WCA) of QIP-50 (35.73°) can achieve a comparable value to that of wet oxidized polished wafer (33.30°), demonstrating sufficient wettability of the QIP for high efficiency ultrathin *c*-Si/PEDOT:PSS hybrid solar cells. The finding of QIP with both efficient light trapping and superior wettability provides a new opportunity to improve the performance of ultrathin *c*-Si/PEDOT:PSS hybrid solar cells with a simple process at low cost.

1. Introduction

Until now, 160–200 μm thick bulk crystalline silicon (*c*-Si) solar cells still hold 87% of the PV market due to their advantages including material abundance, non-toxicity and mature fabrication technology [1]. However, the *c*-Si material, including the wafer and the kerfloss, still accounts for more than 25% solar cell module cost, which urges the inexpensive production of ultrathin *c*-Si (≤50 μm) solar cells to accelerate the cost reduction in PV application [2]. Simultaneously, ultrathin *c*-Si solar cells allows the possible use of silicon with lower quality and shorter carrier diffusion length, indicating another aspect of cost reduction [3]. Furthermore, ultrathin *c*-Si can introduce new features including flexibility and light weight, expanding the application scope of the energy-generating products. Most importantly, ultrathin *c*-Si solar cells have potentially higher open circuit voltage (V_{oc}) and efficiency limits imposed by Auger recombination compared with bulk wafers [4], making ultrathin *c*-Si highly attractive for high performance flexible solar cells. However, one big challenge accom-

panied with the thickness reduction is the insufficient light absorption due to the indirect bandgap of *c*-Si [5], which limits the efficiency enhancement of solar cells if no suitable surface light-trapping structures are developed.

The state-of-the-art surface texture for commercial bulk *c*-Si solar cells is to produce randomly positioned micro-scale pyramids [6] which is obviously unsuitable for ultrathin *c*-Si for its comparable characteristic size (3–10 μm) to ultrathin *c*-Si thickness (≤50 μm). The conventional micro-scale pyramid texture tends to behave like hidden cracks to lower the yield of ultrathin *c*-Si solar cells. Therefore, significant effort has been made to enhance light absorption without sacrificing the yield by nanoscale structures including nanowires [7,8], nanoholes [9,10], nanobowls [11] and inverted nanopyramids [12] and so forth. Of all these structures, inverted nanopyramids are mostly adopted for its excellent anti-reflection property and small specific surface area (only 1.7 times compared to flat surface), and thus high efficiency silicon solar cells can be obtained by the increase of light absorption and easy surface passivation. Theoretically, an incoming ray of light typically

---

* Corresponding author.
  E-mail address: hlshen@nuaa.edu.cn (H. Shen).

experiences not only one downward reflectance but usually three before reflecting away from the inverted pyramid (IP), giving even lower reflectance losses and hence higher absorption than upright pyramid textures [13]. Indeed, IP based c-Si solar cells have achieved an efficiency of 24.7%, demonstrating the superiority of inverted pyramid texture [14]. However, the usually used techniques including lithography [15] and laser processes [16,17] for producing such structures is costly and time-consuming, which hinders its further implement in mass production. Recently, a cost-effective and efficient approach called metal-assisted chemical etching (MACE) method has been developed to avoid the above disadvantages for industrial mass production. Moreover, a lot of research groups including our group have successfully realized the fabrication of sub-micro scale inverted pyramid textured bulk silicon cells by MACE method, the efficiencies of which have exceeded that of conventional pyramid textured solar cells in the same period [18,19]. As a result, the fabrication of sub-micro scale structures with excellent anti-reflectance performance through a mask-less wet chemical etching method is desirable for ultrathin c-Si solar cells.

Another issue with the ultrathin c-Si solar cell is the bowing phenomenon that gives rise to problems during module production with handing and wafer mounting. As the conventional silicon solar cells use aluminium (Al) layer as the back side field (BSF), bowing phenomenon always happens on ultrathin c-Si solar cell due to the different thermal coefficients of the expansion of Al and Si [20], as a result of which non-Al BSF based ultrathin c-Si solar cell accompanied with low temperature fabrication procedure are desirable. Besides, a planar technology is preferred to reduce the yield loss due to the easy crack of ultrathin c-Si solar cell during fabrication process. As a result, a lot of research groups focus on Si/organic (especially PEDOT:PSS) hybrid solar cells that inherit the advantages of low temperature process and planar fabrication procedure [21,22]. Specifically, by a simple spin-coating process at room temperature followed by a short-time annealing at low temperature, conjugated PEDOT:PSS is uniformly coated on the c-Si substrate and thus the functional heterojunction is formed. Additionally, efficient surface texture including nanopillars [23] and nanowires [24] have been designed to enhance the light harvesting and thus to increase photocurrent density (J_{sc}) of c-Si/PEDOT:PSS hybrid solar cells. Since the non-diffusion process is adopted to form the junctions, the severe Auger recombination caused by diffusion on nanostructure textured surfaces can be eliminated. However, the insufficient wettability of the textured c-Si surface, especially the nanowires [25] or nanoholes [26], always leads to a bad surface coverage of PEDOT:PSS layer and severe recombination [27], and also the deep and dense nature of the above nanostructures makes the intimate contact between the nanostructure surface and the PEDOT:PSS difficult, resulting in the deterioration of the cell's performance. Therefore, surface textures with superior light trapping ability, low specific surface area and excellent wettability are desired for the efficient fabrication of high efficiency ultrathin c-Si/PEDOT:PSS hybrid solar cells.

In this paper, we developed a rational method to realize the controllable fabrication of quasi-inverted pyramid (QIP) from sub-micro scale to micro scale on c-Si through a mask-less wet chemical method, which was of great significance for the mass production of QIP based c-Si solar cells. The QIP was fabricated by a well-known two-step Ag assisted chemical etching method followed by a post nanostructure rebuilding (NSR) process. The size of the obtained QIP was controlled by modulating the AgNO$_3$ concentration during Ag deposition process, and the QIP size could be adjusted from 794 nm to 1101 nm accompanied with the reduction of its specific surface area (S_A) from ~3.29 to ~1.89 along with increasing the AgNO$_3$ concentration from 0.25 mM to 0.75 mM. Based on the 15 min NSR treated BS structure fabricated under 0.5 mM [Ag$^+$], the obtained 50 μm c-Si with double-sided surface QIP can achieve an average absorptance value comparable to that of 182 μm c-Si with double-sided surface conventional micro-scale

pyramid in the spectral range of 300–1100 nm, amounting to an over 3.6-fold reduction in material usage. Simultaneously, a time-dependent experiment was conducted to investigate the role of NSR treatment played in the QIP formation process. Furthermore, the cross-section E-field intensity spatial distributions was simulated to understand how light was trapped in these QIP nanostructures by finite-difference-frequency-domain (FDTD) analysis. Finally, the comparable water contact angle (WCA) of wet oxidized QIP (15 min NSR treated BS structure fabricated under 0.5 mM [Ag$^+$]) to that of wet oxidized polished wafer demonstrated the sufficient wettability of the QIP for high efficiency ultrathin c-Si/PEDOT:PSS hybrid solar cells.

2. Experimental details

2.1. Reagents

Silver nitrate (AgNO$_3$, 99.99%), hydrofluoric acid (HF, 50%), hydrogen peroxide (H$_2$O$_2$, 30%) and ammonia (NH$_3$·H$_2$O, 30%) were all purchased from Nanjing Chemical Reagent Co., Ltd. All the reagents were used without further purification.

2.2. Wafer cleaning

Commercially available n-type (100) Czochralski (CZ) Si wafers (resistivity, 1–5 Ω cm) with a thickness of 200 ± 10 μm were cut to 2 × 2 cm^2 and ultrasonically cleaned in acetone, ethanol and deionized (DI) water successively for 10 min each, and then dipped into 5 wt% HF aqueous solution to remove the oxide layer formed on the surface for further use.

2.3. Wafer thinning

In order to evaluate the light trapping ability of the obtained QIP, n-type (100) Czochralski (CZ) Si wafers (resistivity, 1–5 Ω cm) with different thickness ranging from 182 μm to 43 μm are used as the substrates. Wafer thickness is controlled by NaOH solution etching of 200 ± 10 μm wafers at 90 °C for different time. The etching rate is about 75 μm/h.

2.4. Preparation of quasi-inverted pyramid

The quasi-inverted pyramid was fabricated by a well-known two-step Ag assisted chemical etching method followed by a post NSR process. Typically, the wafers were firstly dipped into an aqueous solution containing HF and AgNO$_3$ for 10 s at room temperature for electro-less Ag plating. Then, the silver coated wafers were immersed into an etching solution consisting of DI water, HF and H$_2$O$_2$ for 60 s to form the nanopore structures. In order to obtain QIP with different size, AgNO$_3$ concentration ([Ag$^+$]) was varied to deposit Ag particles onto the c-Si substrate. The [Ag$^+$] used here was 0.25 mM, 0.5 mM and 0.75 mM, respectively, and the detailed etching parameters were listed in Table 1. Finally, the as-etched wafers were immersed into a solution containing NH$_3$·H$_2$O and H$_2$O$_2$ for 90 s to remove the silver particles remaining in the c-Si. The reaction can be described by two half-cell reactions:

Table 1
Summary of etching solutions.

Ag deposition solution				Etching solution			
[Ag$^+$] (mM)	HF (ml)	H$_2$O (ml)	Deposition time (s)	H$_2$O$_2$ (ml)	HF (ml)	H$_2$O (ml)	Etching time (s)
0.25	32	218	10	31	39.2	29.8	60
0.50	32	218	10	31	39.2	29.8	60
0.75	32	218	10	31	39.2	29.8	60