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High efficiency multi-crystalline silicon solar cell with inverted pyramid nanostructure

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ABSTRACT

In this paper, we report inverted pyramidal nanostructure based multi-crystalline silicon (mc-Si) solar cells with a high conversion efficiency of 18.62% in large size of 156 × 156 mm^2 wafers. The nanostructures were fabricated by metal assisted chemical etching process followed by a post nano structure rebuilding (NSR) solution treatment. With increasing NSR treatment time, the reflectance and the dimensions of micro oval pits were both influenced. Resulting from both the light trapping ability and passivation efficiency, 500 nm inverted pyramid structure exhibited an ideal solar cell performance. The best solar cell showed a low reflectivity of 3.29% and a 0.91 mA cm^{-2} increase of short-circuit current density, and its efficiency was 0.45% higher than the acid textured solar cell. This technique presented a great potential to be a standard process for producing highly efficient mc-Si solar cells in the future.

1. Introduction

The multi-crystalline silicon (mc-Si) solar cell has dominated the silicon solar cell market due to its low cost. Despite the fact, there is a wide gap between the conversion efficiencies of mc-Si solar cell and the single crystalline silicon (sc-Si) solar cell. Texturization technology might be a crucial factor to narrow the gap in conversion efficiency. With current technology, sc-Si with pyramid structure based on anisotropic alkali etching has a mean reflectance of 10–12%, and mc-Si with random pits or wormlike texture based on isotropic acidic etching has a mean reflectance around 25%. Through the anti-reflection layer silicon nitride (SiN_x) formed by PECVD, the final mean reflectance of mc-Si solar cell decreased to 9%, in contrast to 3% of the sc-Si solar cell. Therefore, mc-Si had a large promotion space in reducing the reflectance.

Black silicon technique has been investigated for decades since it was found by Mazur (Tsing et al., 1998). Three major techniques, which consisted of femtosecond laser technique (Crouch et al., 2004), metal-assisted chemical etching (MACE) and reactive ion etching (RIE), showed different nanostructure black silicon (Yoo et al., 2006; Zhong et al., 2015). MACE technique took the lowest cost for its wet chemical process. The excellent light absorbance of black silicon gives a great potential improvement in silicon solar cell conversion efficiency, while the enlarged and defective surface would increase the specific surface area and Auger recombination rate of photogenerated carriers (Oh et al., 2012).

Several efforts have been done to change the situation. Although, optimising the nanostructure or improving the passivation technologies seemed to be the effective methods (Liu et al., 2012; Ye et al., 2014; Yue et al., 2014; Lin et al., 2015). Alto university combining Atomic Layer Deposition (ALD) passivating black silicon technique and IBC solar cell structure together and finally reached the highest reported efficiency of 22.1% (Savin et al., 2015). The cost is still not appropriate with industrial requirements. On the other side, structure optimisation, especially through chemical method, seemed to be more appropriate. Inverted pyramid structure emerged from other nanostructures for its low specific surface area and good antireflective ability (Lu and Barron, 2014; Chen et al., 2015; Toor et al., 2015; Wang et al., 2015; Yang and Lee, 2014; Shi et al., 2013; Fan et al., 2013). The regular configuration of inverted pyramid structure could be accessed by masking film method (Yang and Lee, 2014; Sivasubramaniam and Alkaisi, 2014; Wang et al., 2013). Research on another method has been undergoing in the past years. For upright pyramid structure, anisotropic etching was the formation

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principle. Pseudo pyramid structure on mc-Si could be accessed by a low concentration of alkaline treatment, and finally a conversion efficiency of 18.45% was obtained (Ye et al., 2014). The anisotropy of alkaline etching needed relative high temperature, and the post rinse was important for cell efficiency. In our previous work, we fabricated a high-efficiency black silicon solar cell with a conversion efficiency of 18.02% by using MACE followed by NaOH post treatment (Yue et al., 2014).

In current work, we proposed an acid post treatment method by nanostructure rebuilding (NSR) solution to obtain regular inverted pyramid structure. Formation mechanism of the NSR process was researched. With proper dimension of inverted pyramid structure, high efficiency solar cell was presented. It is expected that Si surfaces with inverted pyramids had a potential for mass production with all chemical processes.

2. Experimental section

P-Type mc-Si ($200 \pm 10\ \mu m$ thick, $1–3\ \Omega\,cm$) with standard solar wafer size of $156 \times 156\ mm^2$ were used for this work. The acid texture was taken as a standard process to obtain an oval pit structure and to remove the mechanical damage layer. For two-step MACE method, the wafers were first immersed in the 0.4 M HF solution containing 0.002 M $AgNO_3$ for 50 s. Then, the silver coated wafers were etched in the mixed solution of 0.34 M H_2O_2 and 1.54 M HF for 180 s to form the nanoholes structure. The as-etched mc-Si wafers were immersed into the solution containing ammonia and H_2O_2 for 90 s to remove the remaining silver particles in the mc-Si. After rinsed in 5 wt.% HF and DI water, the structure was restructured in NSR solution (2.52 M H_2O_2 and 0.42 M NaF) for different time (30–600 s) at 50 °C. The standard process for producing inverted pyramid silicon mc-Si solar cells was: phosphorus diffusion to form p-n junction emitters, PECVD to deposit the SiNx antireflection/passivation layer, and screen printing to metallise top/bottom electrodes.

The morphology was observed by scanning electron microscopy (Hitachi S-4800). The optical reflectance measurement was carried out by UV–Vis-NIR spectrophotometer (Shimadzu, UV-3600, with an integrating sphere) in the wavelength range of 300–1100 nm. Micron structure size distribution was analysed by Zeta 3D metrology systems. The quantum efficiency and photovoltaic conversion efficiency of these solar cells were tested by Enlitech QE-R and PVIV-411V systems, respectively.

3. Inverted pyramid nanostructure formation

It is well-accepted that the chemical reactions occur near the noble metal when the Si substrate is etched with an etchant consisting of HF and H_2O_2. In the silicon nanowires fabrication process, the noble metal acts as the catalyst to etch the Si substrate fast in solution with certain oxidants. Since the electrochemical potential of H_2O_2 is much more positive than the valence band of Si, this is why a bare Si substrate could be etched very slowly in HF/H_2O_2 (Li and Bohn, 2000). We proposed a more controllable NSR solution to restructure the Si nanowires. It was interesting that strong electrolyte NaF showed better performance than HF during our optimising experiments, which might be due to the relatively high concentration of F^-. The whole NSR process could be summarised into to the two reactions that direct Si etching by H_2O_2 (anisotropic) Yamamoto et al., 1999, and the SiO_2 etching by NaF (isotropic):

$$Si + H_2O_2 \rightarrow SiO_2 + H_2 \uparrow \quad (1)$$

$$SiO_2 + 6F^- + 4H^+ \rightarrow SiF_6^{2-} + 2H_2O \quad (2)$$

Because H_2O_2 has weak acidity so we defined the NSR as an acid process which was different from the alkaline process as in literature (Ye et al., 2014; Yang and Lee, 2014; Shi et al., 2013; Fan et al., 2013). Fig. 1 showed the surface and cross-section SEM images of black silicon by different NSR treatment time. Acid textured mc-Si wafer was used as a substrate for the fabrication of black silicon nanostructure. It can be seen in Fig. 1a that nanoholes were intensively distributed on the micro oval pits with $\langle 1\,0\,0 \rangle$ orientation. The fabricated black silicon with diameters ranging from 50 nm to 100 nm with the depth of 400–500 nm can reduce the reflectivity to below 5%. Obviously, the high surface area of the nanostructure had rough surfaces. It was reported that SiN_x by PECVD could not reach the bottom of the nanoholes with high aspect ratio (Liu et al., 2012). With the increase of NSR treatment time, inverted pyramid structure formed step by step. After 100 s treatment, Fig. 1c showed that nanoholes were enlarged by interconnecting each other and the flatness of the surface turned out to be better. Furthermore, we found that the bottom of the nanoholes has shown the formation of {1 1 1} pyramidal orientation. Accompanied by the depth reduction of nanoholes, the side walls of inverted pyramids formed, as shown in Fig. 1e. Though the depths of nanoholes were different when the black silicon was fabricated, inverted pyramids would interconnect together and form larger ones during the NSR process. Fig. 1g showed regular inverted pyramid structures formed by NSR treatment for 300 s, which were in the range of 300 nm. It also showed uniform inverted triangle cross section morphology and smooth inverted pyramid surface. As shown in zone A of Fig. 1g, the interconnected structure would overlap and merge into a bigger one. When the NSR treatment time was further increased, larger inverted pyramid structure could be achieved. With longer NSR treatment time, Fig. 1i and k showed inverted pyramid in a range of 500 nm and 700 nm. The 500 nm inverted pyramid structure distributed more uniformly, and less overlapped structure could be seen. The inset image in Fig. 1j showed the 500 nm inverted pyramid structure with SiN_x passivation layer, which smoothly spread on the surface of inverted pyramid structure that could result in good passivation effect. When the inverted pyramid reaches the range of 700 nm, the flat area would emerge as shown in zone B of Fig. 1k. It was interesting to find that NSR wet chemical etching is based on the different etching rates for the (1 1 1) and (1 0 0) crystallographic planes, which was also in good agreement with the formula (1) and formula (2). The dihedral angels maintained at 54.7° (Fig. 1d, f, h, j, and l).

4. Antireflection of inverted pyramid nanostructure

Inverted pyramid structure shows better light trapping ability than upright pyramid structure. It was reported that around 37% of incident light experienced a triple bounce on the front surface of the inverted pyramids (Chen et al., 2015). Both the oval pits structure and the inverted pyramid structure would lead to light-harvesting effect due to the strong forward scattering based on Mie theory (Meyer-Arendt, 1995). The light wave diffracted into several beams and partly bounces between the micro/nano structure, preventing light from escaping back to air. For simplicity, we have approximated the change in refractive index as illustrated in Fig. 2a and b and fixed the refractivity of air and Si to be 1 and 3.4. Although the refractivity changed gradually, the antireflective effect might not be very effective because the feature sizes were much larger than the wavelengths of the light as shown in Fig. 2a. When considering the smaller inverted pyramid structure in Fig. 2b, the geometric dimensioning improved the impedance mismatch of the refractivity from air to silicon, leading to gradually increased effective refractivity (Liu, 2015). Three-dimensional finite difference time domain (FDTD) analysis was carried out to