



Formation of nanostructured emitter for silicon solar cells using catalytic silver nanoparticles

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ABSTRACT

A simple process for nanotexturing on the emitter of silicon solar cells using catalyzed wet chemical etching by size-controlled silver nanoparticles was reported. A fine textured black surface was achieved to realize the low light reflectivity less than 5%. After screen printing and firing by the industrial standard fabrication protocol, we obtained the nanotextured Si solar cells with 15.7%-efficiency without any additional antireflection (AR) coating. This result suggests that the inexpensive metal-assisted wet chemical nanotexture method is prospective to be used in photovoltaic industry.

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1. Introduction

In order to maximize the amount of absorbed incident light which can be converted to electricity, minimization of surface reflection losses is required strongly for high efficiency silicon solar cells. Typically, the reflectance is normally reduced in crystalline silicon by applying pyramidal texturing [1,2] and antireflection (AR) layers deposition [3] on the surface. However, the average reflectance (>10%) in the wavelength range of 400–1100 nm after current pyramid texture process is still high, which prevents improving the conversion efficiency of solar cells further. Furthermore, the interference single-layer structure of AR coating works only in a narrow spectral range and a limited angular of incident photons and the fabrication is expensive due to using vacuum equipments compared to chemical methods.

The nanoporous structures provide a promising approach to minimize surface reflection and replace conventional AR interference layers in Si solar cells [4]. In generally, the nanoporous surface can be formed by chemical etching in HF/HNO₃ solutions or forward-biased electrochemical anodic etching [5–8]. In recent years, metal-assisted chemical etching has attracted increasing attention in the potential solar cell application for nanotexturing. Because it is a simple, fast and low cost process to reduce the reflectance of Si surface [9–13]. However, among the previous reports, the nanoporous layer was made on *p*-type silicon

surface directly or the emitter surface which the screen printing process had applied on [13–16]. In the former case, the complicated nanoporous structure would impede the formation of a *p*–*n* junction [13,17]. Furthermore, in the solar cell fabrication procedure (phosphorus diffusion and phosphorosilicate glass removing), the nanoporous structure would be damaged or even disappeared. In addition, residual noble metals would also be detrimental to minority carrier lifetime of silicon and then to the efficiency of solar cells. In the latter case, metal grid would be dissolved causing the degradation of the fill factor (FF) and then cell efficiency [14]. Therefore, development of new methods to realize the antireflection ability of nanoporous silicon on the solar cell device is required.

In this paper, we develop a novel procedure to fabricate the nanoporous structures on the emitters of 125 mm × 125 mm silicon solar cells based on a standard industry process. Since our process could preserve the nanoporous structure of solar cells to a large extent and avoid damaging the metal grid compared to the peer's work [15], measurements such as reflectance and current–voltage (*I*–*V*) have shown a significant improvement in nanotextured solar cell performance compared with reference solar cell. Our work suggests the nanoporous silicon solar cell is prospective for the practical application in photovoltaic industry.

2. Experimental details

2.1. Materials

The *p*-type solar grade CZ (100) Si wafers (1–3 Ω cm, 125 mm × 125 mm) were purchased from Shuqimeng Photovoltaic

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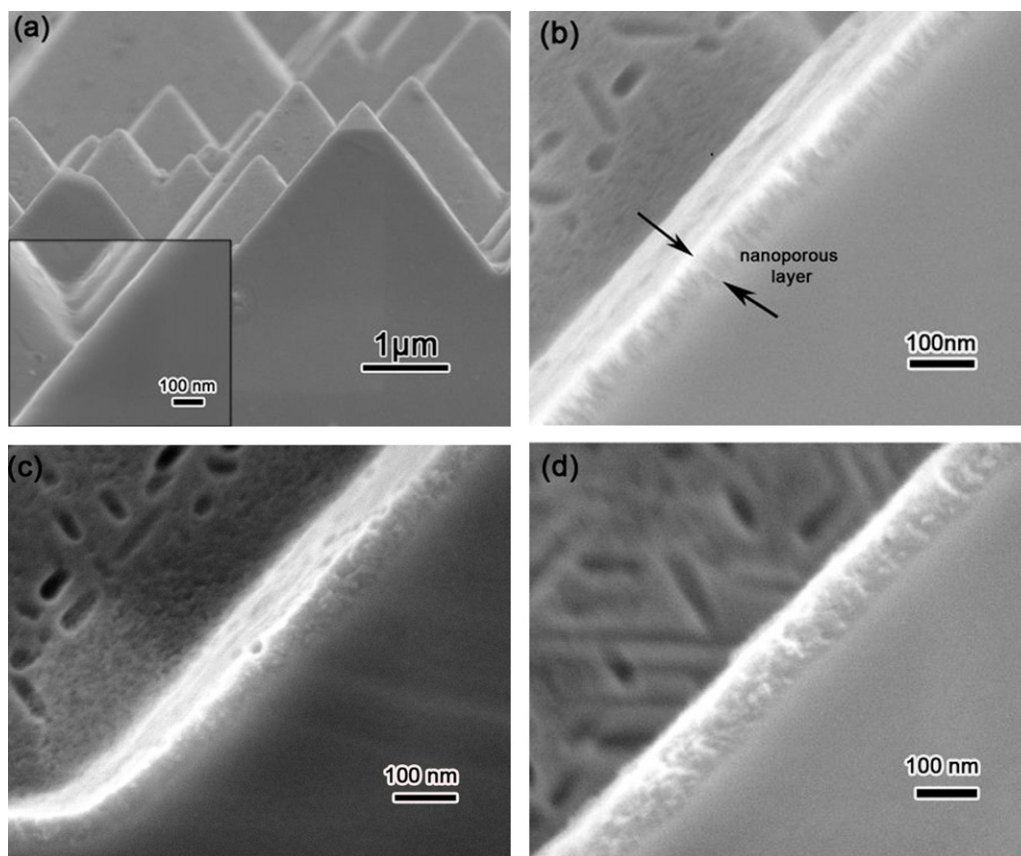


Fig. 1. Cross-sectional SEM micrographs of Si wafers etched by a size-controlled Ag catalyzed process for different times. (a) Before etching; (b) 2 min; (c) 3 min; (d) 5 min.

Technology Co., Ltd., Hangzhou, China. The HF (49%, AR), potassium hydroxide (KOH, AR), silver nitrate (AgNO_3 , AR), formaldehyde solution (CH_2O , AR), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28–30% NH_3 , AR), isopropyl alcohol (IPA, $(\text{CH}_3)_2\text{CHOH}$, AR) and the polyvinylpyrrolidone (PVP, K-30) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. The preparation of silver nanoparticles

The size-controlled colloidal Ag nanoparticles were synthesized by the method reported in the previous work from our group [18]. 37% CH_2O was added into AgNO_3 water solution using polyvinylpyrrolidone (PVP) as a surfactant, after that concentrated ammonia (28%) was injected to initiate the reaction. The reaction mixture was stirred for 30 min before centrifuging.

Fabrication of nanoporous silicon layers and nanoporous silicon solar cells. After removing the oxide layers on the surfaces by a 1% HF solution, pyramid structures were formed in a mixture of 3 wt% KOH and 7 vol% IPA solution at 80 °C for 60 min. After that the wafers were washed in an ultrasonic bath with deionized water for 5 min. Then, the emitters (*n*-type layers) were thermally generated using POCl_3 as the phosphorous-doped source. After removing the remaining phosphorous silicate glass, the wafers were immersed into the deionized water (DIW) containing Ag NPs while the rear surfaces were protected by the insulating tape from Ag NPs deposition. The solvent was evaporated in the atmosphere to make the Ag NPs firmly fixed on the Si wafer surfaces. Then, the wafers were etched in the $\text{HF}:\text{H}_2\text{O}_2:\text{DIW} = 1:5:10$ (vol.) solution in the dark at room temperature at different time durations (2–5 min) for Ag-catalyzed texturing. The residual Ag NPs on the nanotextured surfaces were removed by HNO_3 and the etched wafers were finally rinsed with DIW. Followed by a normal solar cell fabrication

process, after edge isolation, we fabricated the nanotextured cells with/without SiN_x coating separately while the reference cells were treated only through a standardized alkali texturing. The rear (Al/Ag) and front metal (Ag) for electrical contacts were printed by a conventional screen-printing method.

2.3. Characterization

The morphology of Ag nanoparticles (Ag NPs) was characterized by a transmission electron microscope (TEM, Philips CM200). The morphology and structures of the etched samples were characterized by a field emission scanning electron microscope (FESEM Hitachi U-70). Hemispherical reflectance spectra were measured on a spectrometer (Hitachi U-4100 Spectrophotometer) with an integrating sphere. Electrical characterization of the solar cells was carried out using an *I*-*V* and spectral response system (SEIKO NPC Co, Model: NCT-180AA-T14) under AM 1.5G spectral irradiance ($100 \text{ mW}/\text{cm}^2$ at 25 °C).

3. Results and discussion

3.1. Structure characterization and the reflectance characteristics

Fig. 1S(a) shows the TEM micrograph of the Ag NPs prepared in our experiment. Obviously, the Ag NPs are sphere-like. The size uniformly distributes in 60–70 nm range resulting from PVP regulating the Ag NPs growth process. Fig. 1S(b) shows the distribution of Ag NPs deposited on the pyramid structure. We can observe that the Ag NPs distribute uniformly on the silicon wafer surface.

Fig. 1(a) shows the cross-sectional microstructure of Si wafer before Ag-catalyzed texturing. The obtained average sheet resistance is about $20 \Omega/\text{sq}$, which is due to a heavily doped diffusion

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