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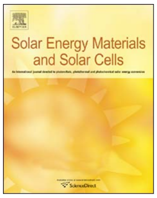

Ultrathin Si solar cell with nanostructured light trapping by metal assisted etching

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ABSTRACT

We report an 8 μm-thick silicon solar cell with an efficiency of 9.60%. Nanostructured silicon surface formed via metal assisted etching shows a broadband reflection below 10%. Despite the excellent optical performance, a moderate short-circuit current (J_{SC}) of 25.44 mA/cm^2 was collected. Relatively low external quantum efficiency (EQE) at short wavelengths was associated with carrier recombination at the enhanced surface and by the Auger process. Moreover, parasitic absorption at the back contact is the main factor resulting a relatively low EQE in long wavelength region of the spectrum. Our optical simulations show that planarization of the rear Si surface and insertion of a low refractive index dielectric spacer between Si and the rear metal can significantly reduce the parasitic absorption in the metal, resulting in J_{SC} values over 35 mA/cm^2.

1. Introduction

Recently, much attention has been given to reducing the cost of silicon (Si) solar cells, which are currently dominating the photovoltaics (PV) market with their over 90% share [1]. One of the most promising methods of reducing cost of Si solar cells is to fabricate them on thinner Si wafers. Several ways of obtaining a thin monocrystalline Si wafer have been well explored, some of which have reached a high level of maturity. These methods include porous Si based lift-off [2], thermo-mechanical thin Si exfoliation [3] and SMART-cut [4]. Aside from reduced cost, ultrathin (1–10 μm) Si solar cells also allow for flexible devices, which are attractive for niche applications.

In an ultrathin Si, the thickness is much smaller than the typical diffusion length of carriers. Therefore, it is possible to fabricate solar cells using lower quality Si wafers while maintaining a relatively high efficiency [5]. Moreover, higher open-circuit voltage (V_{oc}) can be achieved if the solar cell surface is well-passivated and if short-circuit current (J_{SC}) is maintained [6]. Despite these advantages, ultrathin Si solar cell performance is outweighed by incomplete light absorption due to its indirect bandgap. This has become the limiting factor for achieving high efficiency ultrathin Si solar cells. The conventional method to improve light absorption in Si solar cells is to form random upright pyramids whose size range in between 5–10 μm. However, this method is clearly not suitable for ultrathin Si with thicknesses less than 10 μm [7]. New methods of obtaining light trapping structures with minimized material loss are therefore deemed necessary. Several nanophotonic light trapping structures have been proposed, including inverted nanopyramids [8,9], nanocones [10], nanodomes [11] and nanoholes [12]. In addition to their small feature size, nanostructures are also advantageous because of minimal material removal from the surface. Some of these structures, however, require the use of lithography, which is not ideal for large-scale applications due to its relatively high cost.

Random nanostructures enabled by simple chemical etching processes can provide alternative methods for light trapping structures in ultrathin Si. One candidate for such simple chemical etching processes is metal assisted etching (MAE). MAE is a highly flexible technique for fabricating various structures on Si, ranging from nanometers to micrometers in size [13–16]. Weighted reflection of less than 3% over full commercial size of Si solar cells was previously achieved [17–19]. In spite of excellent optical performance, efficiency of a solar cell with nanostructure texturing is limited by enhanced surface recombinations due to increased surface area. Nevertheless, an efficiency of 22.1% has been realized for a thick Si solar cell with nanostructure texturing obtained via MAE with improved surface passivation [20].

In this contribution, we present an 8 μm-thick Si solar cell decorated with a nanostructured texture obtained via MAE, and having an efficiency of 9.60%. Optical simulations were performed to gain better

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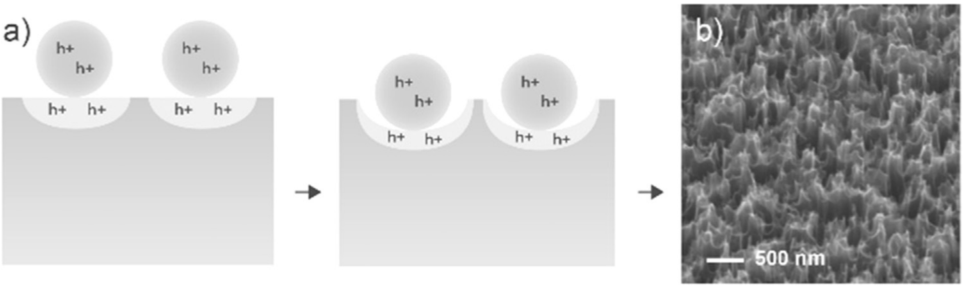

Fig. 1. (a) Schematics of metal assisted etching process. (b) Tilted (45°) SEM image of nanostructured surface of ultrathin Si.

insight into optical losses partially responsible for a reduced J_{SC} of 25.44 mA/cm^2

2. Experimental details

A 525 μm-thick monocrystalline p-type (100) Si wafer with a resistivity of 1–5 Ω cm was etched in 50 wt% potassium hydroxide (KOH) solution at 90 °C to obtain an ultrathin Si membrane. Metal assisted etching was performed to form nanostructures on the Si surface. Prior to MAE, the ultrathin Si was cleaned with RCA solution to remove any metallic contaminants. The details of the MAE process can be found elsewhere [13]. In brief, the MAE process can be explained as accelerated oxidation and etching of Si by hydrofluoric acid (HF) near metal nanoparticles formed on the surface by electroless deposition. A schematic of MAE process and an example of Si surface achieved by MAE are shown in Fig. 1. The mechanism of reactions is as follows.

In the cathode, reduction of Ag ions and HNO_3 at the surface occurs via the following reactions:

$$Ag^+ \rightarrow Ag(s) + h^+ \tag{1}$$

$$HNO_3 + 3H^+ \rightarrow NO + 2H_2O + 3h^+ \tag{2}$$

While at the anode, oxidation and etching of Si takes place via the following reactions:

$$2Si + 12HF + 6h^+ \rightarrow 2H_2SiF_6 + 6H^+ + H_2 \tag{3}$$

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^- \tag{4}$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{5}$$

Holes generated by reaction (1) and are transferred to the metal-Si interface through metal dendrites. Etching of Si occurs in hole-rich regions. The reaction repeats until all the chemical species are consumed. After the MAE process, the residual silver dendrites were removed with HNO_3 and subsequent RCA cleaning.

In this study, phosphorus doping was performed in a low vacuum furnace at 830 °C under $POCl_3$ and O_2 gas flows, resulting in a sheet resistance of 50–60 Ω/□. Phosphosilicate glass, grown during the diffusion process, was removed by diluted HF solution. Silicon dioxide (SiO_2) was thermally grown on the Si membrane to facilitate surface passivation [21]. The oxidation was performed at 800 °C for 30 min resulting in a SiO_2 of about 8 nm. Although the nanostructures exhibit good anti-reflection capability, an additional silicon nitride (SiN_x) layer was deposited using plasma enhanced chemical vapor deposition (PECVD) for further minimization of reflection and to take advantage of field effect passivation [22]. An aluminum (Al) layer was thermally evaporated onto the rear side of the ultrathin Si membrane, after removing the rear SiO_2 layer by diluted HF solution. An alloying of Al and Si to create a back surface field was performed at 800 °C under nitrogen environment for 40 min. Excess Al was removed by acidic HCl solution. Back contact was realized by thermally evaporating Al. The front contact was defined by standard photolithography. A titanium/silver stack was evaporated onto the predefined front contact through a shadow mask. Lastly, a forming gas annealing was performed at 400 °C for 30 min.

Current-voltage (I-V) measurement was performed in a calibrated QuickSun (WCT) under AM1.5 illumination to assess the performance of the fabricated ultrathin Si solar cell. External quantum efficiency, reflection and transmission measurements were carried out between 350 and 1100 nm with 10 nm steps in an optical setup equipped with an integrating sphere. Spectroscopic ellipsometry (Semilab) measurements were performed to obtain the optical constants of SiO_2 and SiN_x layers. The Cauchy model was used to fit the measured parameters. Surface morphology of the solar cell was imaged using a scanning electron microscopy (ZEISS EVO HD16).

Optical simulations were performed using a commercially available FDTD software to gain better insight into the parasitic absorption within the rear Al layer [23]. A 2D full-field electromagnetic wave simulation was performed. A built-in random function in MATLAB was used to form the 2D structure. The boundaries of the randomization were determined using the SEM images. A plane wave was directed normal to the surface. A perfectly matched layer boundary condition was implemented at the top and bottom of the solar cell. Meanwhile, Bloch periodic boundary condition was set along the film direction. At the front side, SiN_x with a thickness of 80 nm was placed. Meanwhile, a 100 nm of Al layer was placed at the rear side. The dimensions of the simulation domain were taken as 10 μm x 3 μm (height x width). The optical properties of Si, Al and Ag were obtained from reference [24]. Meanwhile, the refractive index of SiO_2 and SiN_x were experimentally obtained by spectroscopic ellipsometry.

3. Result and discussion

A cross sectional SEM image of the fabricated ultrathin Si solar cell with a total thickness of ~ 8 μm is shown in Fig. 2(a). Additionally, an SEM image of the nanostructure-textured surface after MAE process and prior to SiN_x deposition is shown in Fig. 2(b). The maximum height of the nanostructures was found to be around ~ 500 nm. Metal-coated front and rear surfaces of the Si solar cell are shown in Fig. 2(c) and (d), respectively.

Reflection measurement of the Si solar cell before the front side metal contact evaporation is shown Fig. 3. The reflection from the ultrathin Si solar cell with the nanostructured surface is well below 10% over the measured wavelength range. At relatively short wavelengths light is mainly absorbed in Si due to the excellent anti-reflection property of the nanostructured surface. However, at relatively long wavelengths, enhanced absorption is due to the presence of Al metal and light trapping provided by the nanostructured surface. Note that there is no transmission through the cell due to the presence of the Al layer at the rear side. The total absorption, calculated via $A = 1 - R$, is also shown in Fig. 3. The simulation result is in good agreement with the measured total absorption. Our simulations indicate that a significant amount of light is absorbed in the real Al layer.

The result of I-V measurement is presented in Fig. 4 together with an optical image of the ultrathin solar cell. The solar cell exhibits a very dark appearance thanks to its very low reflection over the whole wavelength region of interest. The nanostructure-textured ultrathin Si solar cell has $V_{oc} = 522$ mV, $J_{SC} = 25.44$ mA/cm^2, FF = 72.30%, and an overall efficiency of 9.60%.