Solar Energy Materials & Solar Cells 100 (2012) 33–38

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Silver catalyzed nano-texturing of silicon surfaces for solar cell applications

Sanjay K. Srivastava*, Dinesh Kumar, Vandana, Mukul Sharma, Ravi Kumar, P.K. Singh

National Physical Laboratory, Council of Scientific and Industrial Research (CSIR), Dr. K.S. Krishnan Marg, New Delhi-110012, India

A R T I C L E I N F O

Available online 20 May 2011

Keywords:
Silicon solar cells
Wet etching
Nano-texturing
Antireflection coating
LBIC

A B S T R A C T

We report a relatively simple process for fast nano-texturing of p-type (1 0 0) silicon surface using silver catalyzed wet chemical etching in aqueous hydrofluoric acid and hydrogen peroxide solution at room temperature. In this approach, a fine textured black surface was achieved in about 15–30 s duration with reflectivity less than 4% in 400–1000 nm range. The reflectivity versus texturization time has been investigated and co-related with morphological characteristics of the nano-textured-silicon (nT-Si) surfaces. The nano-texturization process is also applicable in multi-crystalline silicon. Further, n^+–p–p^+ structured solar cells have been fabricated on such nT-Si substrates following the standard fabrication protocol. Significant improvement in short circuit current density (>20%) and efficiency (~1.25% absolute) has been achieved compared with planar control cell without deterioration of other performance parameters (such as open circuit voltage and fill factor). Light beam induced current measurements have also been carried out to show the spatial distribution of the light trapping and current in the planar and the nT-Si solar cells.

1. Introduction

Polished silicon surface has a high natural reflectivity (>35%) with a strong spectral dependence and therefore, minimization of reflection losses is extremely important for efficient silicon solar cells. Usually, transparent quarter wavelength layers of silicon oxide (SiO_x), silicon nitride (Si_xN_y) or titanium oxide (TiO_x) with intermediate or gradient refractive indices are used as antireflection coating (ARC) [1, pp. 345,2]. These coatings have resonant structures and work effectively only in a limited spectral range. A variety of other approaches have also been developed to minimize the reflection losses through modifying surface topography [3,4] wherein the losses are reduced by surface texturing using anisotropic etching generally done in aqueous alkaline solution. However, this process is limited to single crystalline silicon (c-Si) only [1,4] and not very effective in multi-crystalline silicon (mc-Si) due to different orientations of grains. Porous silicon, formed by electrochemical etching, is another such approach to reduce reflection loss in the range of 5–8% [5].

Another promising approach to minimize reflectivity utilizes a nano-textured (nT) surface, comprising features on the nanometer scale. Such surfaces are called sub-wavelength structures (SWSs) [6]. The SWSs are the surface relief structures with dimensions smaller than the wavelength of incident light. Hadobas et al. [7] have shown that surfaces based on SWSs can reduce surface reflection to minimum at 600 nm for SWSs layer depth (d) to wavelength (λ) ratio 0.4 and effectively to zero for the higher ratio ($\geqslant 0.4$) [7]. Moth-eye structures are typical example of SWS surfaces and a number of attempts have been made to achieve the low reflecting silicon surface [8,9] using this approach. To date, different dry etching methods based on reactive ion etching (RIE) [10], employing selective etching through alumina template, silicon dioxide (SiO_2) micro-masks, catalytic action of various metals and nano-imprint lithography have been developed for the fabrication of SWS surfaces to produce 'black silicon'[6–14]. However, the process complexity, low throughput and cost are big concerns for these methods and therefore, limit their applications such as for silicon solar cells in particular. Recently, Koynov et al. [15] reported gold (Au) catalyzed process for nano-texturing of silicon surface suppressing reflection loss below 5% wherein Au thin film (1–2 nm) was pre-deposited on polished silicon by the thermal evaporation technique. However, in our view Au-assisted process is deleterious to the solar cell device as it is a known lifetime killing metal impurity [16] and traces of which may kill the solar cell performance completely. Thus, development of a simple process to prepare low reflecting surface and integration of such surface into silicon solar cell fabrication needs to be explored. In our earlier study, we have found that silicon nanowire (SiNW) arrays prepared via wet chemical etching of silicon in aqueous hydrofluoric acid (HF) and silver nitrate ($AgNO_3$) solution can reduce reflection as low as ~2% [17]. However, SiNW arrays solar cells had technical problems associated with the inherent SiNW arrays

* Corresponding author. Tel.: +91 11 45608617; fax: +91 11 45609310.
E-mail addresses: srivassk@nplindia.org, sksrivastava78@gmail.com (S.K. Srivastava).

0927-0248/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2011.05.003

structural characteristics such as non-compact metal contact formation, enhanced surface area, etc. besides processing related issues [18]. Such problems could be minimized in the nano-textured-silicon (nT-Si) surfaces. Therefore, motivation for the present investigation was to develop a relatively simple process for the preparation of nT-Si surface with excellent antireflection property, which should be compatible with silicon solar cells fabrication protocol.

In this paper, we report a relatively simple and fast process for nano-texturing of p-Si surface using Ag-catalyzed wet chemical etching in aqueous HF and hydrogen peroxide (H_2O_2) solution at room temperature wherein wafer-scale black nT-Si surface can be obtained in a very short duration (about 15–30 s) with reflectivity (R_λ) below 4% in 400–1000 nm range. The reflectivity versus texturization time has been investigated and co-related with morphological features of the nT-Si surfaces. Further, we have demonstrated that the nT-Si process can easily be integrated in conventional silicon solar cells fabrication protocol. Measurements such as current–voltage (I–V), quantum efficiency and light beam induced current (LBIC) have shown a significant improvement in nT-Si solar cell performance compared with planar cell made on polished silicon.

2. Experimental details

2.1. Sample preparation

The nT-Si samples were prepared using (1 0 0) p-type ($1.2 \pm 0.05\ \Omega$ cm, boron doped), Czochralski (CZ) silicon wafers of $325 \pm 10\ \mu$m thickness. All the samples used in the present investigation have the same material specifications. In the very first step of the process, as-cut or lapped wafers were etched using HF and nitric acid (HNO_3) solution or concentrated potassium hydroxide (KOH) solution to remove surface damages ($\sim$15 μm from each side) caused by saw wires, etc. This step is essential in solar cells fabrication. After damage removal the chemical polishing or alkaline texturization (in 2% KOH+20% iso-propyl alcohol solution at 80 °C for 30 min) was carried out. In the case of Ag-catalyzed nano-texturization, both chemically polished (CP) and commercially available chemically mechanically polished (CMP) wafers were used. It was noticed that nano-texturization of silicon wafers was not affected by the initial wafer surface morphology (CP or CMP silicon).

The silicon wafers were sequentially cleaned with acetone, deionized (DI) water and boiled in piranha solution using sulfuric acid (H_2SO_4) and H_2O_2 in 3:1 (vol.) ratio for 60 min. The wafers were then rinsed thoroughly with DI water followed by 5% HF solution dip to remove native oxide. The nano-texturization process included two steps, and schematic of these are shown in the steps (i–iii) in Fig. 1. In step (i) a thin layer of Ag film ($\sim$5 nm) was deposited over the polished Si (CP or CMP) using the electro-less metal deposition (EMD) at room temperature in aqueous 4 M HF solution containing 0.008 M $AgNO_3$ for 10 s followed by DI water rinse. In this process no external electric current (or electrodes) is required. The EMD process, in an ionic metal containing HF solution, is based on micro-electrochemical redox reaction in which both cathodic and anodic reactions occur simultaneously at the metal/semiconductor interface. This resulted in a thin layer of Ag nano-islands uniformly distributed over the entire sample area. After deposition of the Ag nano-islands film, wafers were thoroughly rinsed in DI water and dried in nitrogen for the next processing step. In step (ii) Ag deposited silicon wafers were immersed in H_2O_2:HF:DI water::1:2:10 (vol.) solution at room temperature for different time durations (15–120 s) for Ag-catalyzed texturization. The polished Si surface

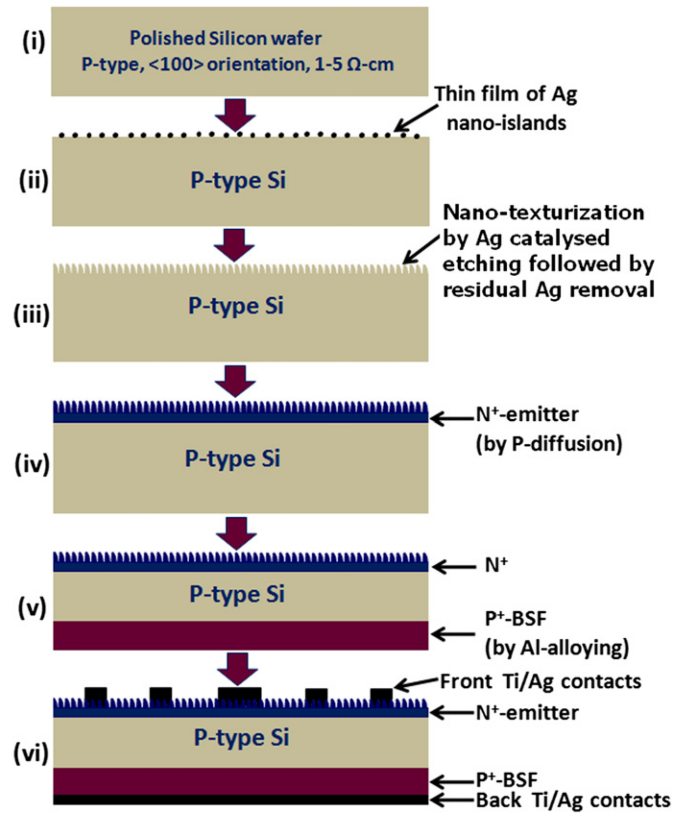

Fig. 1. Schematic of nT-silicon solar cells processing. Steps (i–iii) correspond to the nano-texturization process and steps (iv–vi) to fabrication of solar cells.

turned uniformly black within 15–30 s. The residual Ag nanoparticles from the nT-Si were removed completely by etching in ammonia (NH_3) and H_2O_2 solution in 3:1 (vol.) ratio at room temperature. Finally, the nT samples (as shown in step iii) were rinsed with DI water, blown dry in nitrogen and subjected to further investigations. Morphology of the samples was examined by scanning electron microscope (SEM; Model LEO 440 VP) and reflectivity measurements were carried out using spectrophotometer (Shimadzu; Model UV 3101PC with an integrating sphere) in 350–1200 nm wavelength range.

It is also important to mention that the present nano-texturization process is equally applicable to mc-Si wafers wherein lapped mc-Si wafers were subjected to nano-texturization after damage removal.

2.2. Solar cell fabrication

Solar cells were fabricated on CMP, CP, alkaline (KOH) textured (aT-Si) and nano-textured-silicon (nT-Si were prepared using both as-cut and commercially available CMP wafers) of identical electrical/electronic properties (resistivity, orientation, thickness, etc.) in the same batch. For the co-relation of the reflectivity data with nT-Si solar cells performance, only the results of nT-Si cells fabricated on CMP (as starting wafers) are reported. This is because no significant difference was observed in the CP and CMP based nT-cell performances. The cells made on CMP wafers were used as control in our process because of their known reflectivity as well as for comparison of the cells performance having different surface morphologies (anisotropically textured and nT surfaces). In true sense a comparison with anisotropically textured (aT) cell would be interesting but the reflectivity of aT-surface depends on several parameters such as temperature, time and etching solution concentration used to create random pyramids [4].