Solar Energy 169 (2018) 153–158

Contents lists available at ScienceDirect

Solar Energy

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

18.88%-efficient multi-crystalline silicon solar cells by combining Cu-catalyzed chemical etching and post-treatment process

Ping Wang[a], Shaoqing Xiao[a,*], Rui Jia[b,*], Hengchao Sun[b], Xiaowan Dai[b], Guoyu Su[b], Ke Tao[b]

[a] Engineering Research Center of IoT Technology Applications (Ministry of Education), Department of Electronic Engineering, Jiangnan University, Wuxi 214122, China
[b] Institute of Microelectronics, Chinese Academy of Sciences, 3# Bei-Tu-Cheng West Road, Beijing 100029, China

ARTICLE INFO

Keywords:
Cu-catalyzed chemical etching
mc-Si solar cell
Post-treatment
Polygonal chamfered cone structure

ABSTRACT

Mass production of diamond-wire-sawn (DWS) multi-crystalline silicon (mc-Si) solar cells reached a significant point of maturity through utilization of metal-catalyzed chemical etching (MCCE). However, the reported studies always focus on how to optimize the MCCE process but there are few studies concentrating on the post-treatment techniques to improve the cell efficiency. In this paper, we use a combination of Cu-MCCE method and a HF/HNO_3/H_3PO_4 post-processing treatment process to decorate the surface of Si textures for the first time. The submicron polygonal chamfered cone structure produced by the post-processing treatment is demonstrated to be helpful in reducing surface recombination and improving the cell performance in terms of surface morphology, reflectivity, internal quantum efficiency (IQE) and external quantum efficiency (EQE) measurements as well as Electroluminescence (EL) spectra characterizations. The highest efficiency of Cu-MCCE mc-Si solar cells subjected to such post-processing treatment process is 18.88% with short circuit current (Isc), open circuit voltage (Voc) and fill factor (FF) of 36.67 mA/cm^2, 638.6 mV and 80.64%, respectively, in great contrast to that (16.81%) of Cu-MCCE mc-Si solar cells without any post treatment. The post-treatment process is, therefore, of great potential for the Si photovoltaic industry, especially for the Cu-MCCE mc-Si solar cells.

1. Introduction

Low surface reflectance is the key to achieve high performance of Si-based solar cells, and it helps maximize the number of incident photons absorbed by the semiconductor and then converted into electrical energy (Yuan et al., 2009). Black silicon (BS) has drawn much attention in recent years because of its extremely low surface reflectance as well as great potential in high-efficiency Si solar cells (Cao et al., 2015a,b; Wang et al., 2015). BS could be an ideal material for Si photovoltaics due to its outstanding light management properties in the solar spectrum which benefit from a gradually changed reflective index at the silicon/air interface (Lu and Barron, 2014; Yuan et al., 2009). BS is usually fabricated by three major techniques, namely electrochemical etching, laser etching technique and reactive ion etching (Wang et al., 2017a,b; Tian et al., 2011; Levchenko et al. 2018). Among them, metal catalyzed chemical etching (MCCE) or metal assisted chemical etching (MACE) is one of the most popular methods to fabricate nanostructured black silicon due to its good controllability and low cost (Toor et al., 2016). Indeed, MCCE has also been employed as an effective way to texture diamond-wire-sawn (DWS) multi-crystalline silicon (mc-Si) wafers which can't be uniformly textured by conventional acid methods (Huang et al., 2011; Cao et al., 2015a,b).

Silver (Ag) has been investigated for the MCCE process because of its excellent catalytic activity and good controllability (Huang et al., 2010; Zheng et al., 2014; Ying et al., 2016). Also, the Ag-MCCE process has been proved to be an effective way to produce black silicon and promote the conversion efficiency of such black silicon solar cells (Jiang et al., 2017). However, the introduction of Ag contamination during the Ag-MCCE process may counteract the advantages of BS and thus limit its application in the cell process. In contrast, Cu impurities have been demonstrated to be less detrimental to the silicon solar cell performance than Ag (Davis et al., 1980). As such, Cu-MCCE process has raised a great attention in recent years and is believed to be a promising method for BS (Toor et al., 2015). In particular, Liu et al. studied the mechanism of forming nanostructured porous layer on silicon surface at low Cu^{2+} concentration region and calibrated the etching rate in the different etching dilutions (Cao et al., 2015a,b). Wang et al. developed a Cu assisted chemical etching method for maskless texturization of c-Si with so-called inverted pyramid arrays, and the inverted pyramidal structure not only has superior light trapping characteristic but also ensures low recombination rates (Wang et al., 2015). By using the Cu-MCCE process on an industrial production line, Su et al. achieved 19.06% efficient

* Corresponding authors.
E-mail addresses: larring0078@hotmail.com (S. Xiao), jiarui@ime.ac.cn (R. Jia).

https://doi.org/10.1016/j.solener.2018.04.049
Received 27 February 2018; Received in revised form 20 April 2018; Accepted 23 April 2018
0038-092X/

DWS mc-Si solar cells with submicron textures, which could suppress the visibility of saw marks and color differences in the DWS mc-Si cell, solar cells with their Cu-MCCE techniques lead to a higher Voc via improved surface passivation (Zha et al., 2017). Du et al. achieved an inverted pyramid structure and met the tradeoff between the light reflection minimization and carrier recombination by adjusting the one-step Cu-assisted texturization of silicon wafer. They also demonstrated the better performance and manufacturability of such inverted pyramid structured silicon solar cells (Yang et al., 2017). However, the reported studies always focus on how to optimize the Cu-MCCE process to achieve the tradeoff between the light reflection minimization and carrier recombination but there are few studies concentrating on the post-treatment techniques after the Cu-MCCE process to improve the cell efficiency.

In this work, two-step Cu-assisted MCCE method consisting of the deposition of Cu nanoparticles using Copper nitrate ($Cu(NO_3)_2$)/hydrofluoric acid (HF)/isopropanol (IPA) solution and the formation of Si nanostructures by HF/hydrogen peroxide (H_2O_2) solution etching is utilized for the texture of the mc-Si solar cells. We systematically investigate the effect of the different parameters of etching step on the surface morphology as well as reflectivity of Si nanostructures. On this basis, a HF/nitric acid (HNO_3)/phosphoric acid (H_3PO_4) post-processing treatment is adopted to decorate the surface of such Si nanostructures. The impact of such post-processing treatment is carefully studied in terms of surface morphology, reflectivity, cell performance, internal quantum efficiency (IQE) and external quantum efficiency (EQE) measurements as well as Electroluminescence (EL) spectrum. The submicron polygonal chamfered cone structures produced by the post-processing treatment is demonstrated to be very helpful in reducing surface recombination and improving the cell performance.

2. Experimental

Raw p-type DWS mc-Si wafers with a size of $156.75 \times 156.75\,mm^2$ and a thickness of 200 μm were used in this study. The wafers were first cleaned with acetone, ethanol, and deionized water in series for 10 min, and then were immersed in HF/HNO_3 aqueous solution to remove cutting damage layer and rinsed in deionized water and dried by nitrogen gas.

Two-step Cu-assisted chemical etching of silicon took place in a polytetrafluoroethylene containers. The mc-Si wafers were first immersed in the aqueous solution composed of $Cu(NO_3)_2$, HF, and IPA. In this process, the Cu particles were randomly deposited on the mc-Si substrates, and the function of IPA is to improve the surface activity so that the copper particles can be more easily deposited on the Si substrates. Subsequently, the wafers were etched in HF/H_2O_2 aqueous solution to form the nanostructure on the surface. Residual Cu nanoparticles were removed by using concentrated nitric acid for at least 20 min and alkali bath for 2 min. The silicon samples were thoroughly rinsed with deionized water and dried by flowing nitrogen gas. After this Cu-MCCE process, a HF/HNO_3/H_3PO_4 post-processing step was used to form the polygonal chamfered cone structures, where H_3PO_4 acts as a buffering agent in the reaction. The post-treated wafers were then immersed in Potassium hydroxide (KOH) solution to smooth the structure surface. After a standard RCA cleaning, the p-n junction with a sheet resistance of ~90 Ω/sq was formed by phosphorus diffusion using a Phosphorus oxychloride ($POCl_3$) source. The phosphosilicate glass that formed during phosphorus diffusion was removed by 5% HF for 120 s. An ~80 nm SiNx layer was then deposited on the surface by plasma enhanced chemical vapor deposition (PECVD) to passivate the surface as well as for the antireflection function. Screen-printed aluminum paste was used as back metal contacts and screen-printed Ag grid pattern front metal contacts.

The morphology and microstructure of Si nanostructures were characterized by scanning electronic microscopy (SEM) (HITACHI-S4800, Chiyoda-ku, Japan). The reflectance, internal quantum efficiency (IQE) and external quantum efficiency (EQE) were measured by Incident Photon to Charge Carrier Efficiency (IPCE) of solar cells measurement system (sofn, 7-SCSpecII, China). The sheet resistance was tested by 4D auto four point probe meter (MODEL 280) while I-V curves of cells were measured by IV measurement system (QuickSun, 120CA-HC, Finland). Electroluminescence image was measured by EL sorting machine (zhewei, SA-220, China).

3. Results and discussion

It is well known that metal particles could act as catalysts in MCCE etching process, that is the silicon beneath the metal particles can be more easily etched than the bare silicon and the driving force comes from the electrochemical reaction between Si and Cu^{2+}/Cu for the specific Cu-MCCE process. Like the well-known metal-assisted chemical etching method (Wang et al., 2015; Hsu et al., 2014), the Cu- assisted reaction can be described as two half-cell reactions namely cathode reaction (Eqs. (1) and (2)) and anode reaction (Eqs. (3) and (4)).

$$Cu^{2+} + 2e \rightarrow Cu \quad (1)$$

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+ \quad (2)$$

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e \quad (3)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (4)$$

Each Cu^{2+} ion in the HF/$Cu(NO_3)_2$/IPA dilution can capture two electrons (e) from Si atoms because of its higher electronegativity than Si (Peng et al., 2010). For the first step, the Cu particles were deposited on the silicon substrate and the real-time SEM image of Si surface with Cu particles is presented in Fig. 1 Form both the high resolution and low resolution SEM images, one can observe that the distribution of Cu particles is uniform and compact. Furthermore, the growth rate of Cu particles show a monotonous increase with the ratio of $Cu(NO_3)_2$ in the diluted $Cu(NO_3)_2$/HF/IPA concentration (Lee et al., 1997). For the second step, the oxidized Si was etched by HF under the catalysis of Cu particles. During the etching process, apart from the oxidation process where each Cu^{2+} ion captures two electrons from Si atoms, Cu particles can be also oxidized by H_2O_2 so that silicon atoms beneath Cu particles can be strongly oxidized finally leading to the larger pits than those obtained by Ag-MCCE method.

We now turn to investigate the effect of the different parameters of etching step on the surface morphology of Si nanostructures. Fig. 2

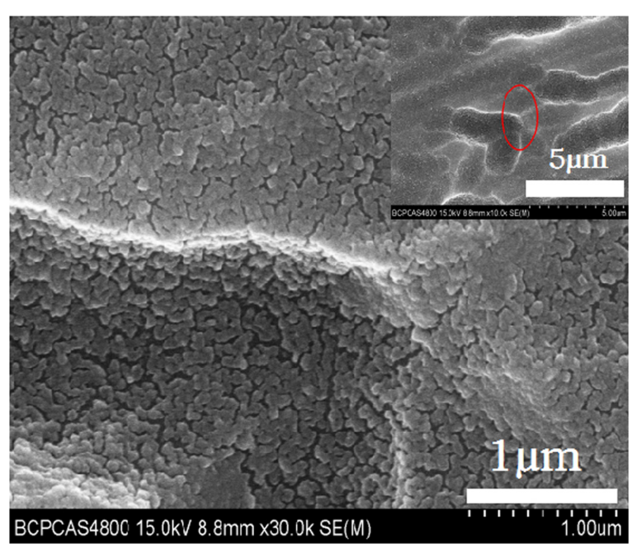

Fig. 1. A representative high resolution SEM image of the silicon substrate surface with deposited uniform and compact Cu particles. Inset is the corresponding low-resolution SEM image.