## **ARTICLE IN PRESS**

Applied Surface Science xxx (2016) xxx-xxx



Contents lists available at ScienceDirect

### Applied Surface Science



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

# Light trapping of crystalline Si solar cells by use of nanocrystalline Si layer plus pyramidal texture

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#### ARTICLE INFO

Article history: Received 29 January 2016 Received in revised form 19 April 2016 Accepted 19 April 2016 Available online xxx

Keywords: Si solar cells Texture Light trapping Nanocrystalline Si layer Low reflectivity

#### ABSTRACT

The surface structure chemical transfer (SSCT) method has been applied to fabrication of single crystalline Si solar cells with 170 µm thickness. The SSCT method, which simply involves immersion of Si wafers in H<sub>2</sub>O<sub>2</sub> plus HF solutions and contact of Pt catalyst with Si taking only ~30 s for 6 in. wafers, can decrease the reflectivity to less than 3% by the formation of a nanocrystalline Si layer. However, the reflectivity of the nanocrystalline Si layer/flat Si surface/rear Ag electrode structure in the wavelength region longer than 1000 nm is high because of insufficient absorption of incident light. The reflectivity in the long wavelength region is greatly decreased by the formation of the nanocrystalline Si layer on pyramidal textured Si surfaces due to an increase in the optical path length. Deposition of phosphosilicate glass (PSG) on the nanocrystalline Si layer for formation of pn-junction does not change the ultralow reflectivity because the surface region of the nanocrystalline Si layer possesses a refractive index of 1.4 which is nearly the same as that of PSG of 1.4-1.5. The PSG layer is found to passivate the nanocrystalline Si layer, which is evident from an increase in the minority carrier lifetime from 12 to 44  $\mu$ s. Hydrogen treatment at 450 °C further increases the minority carrier lifetime approximately to a doubled value. The solar cells with the <front Ag electrode/nanocrystalline Si layer/pyramidal Si substrate/boron-diffused back surface field/Ag rear electrode> structure show a high conversion efficiency of 18.5% in spite of the simple cell structure without antireflection coating. In this case, the short circuit photocurrent density is 40.1 mA/cm<sup>2</sup> under AM1.5 100 mW/cm<sup>2</sup> irradiation.

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#### 1. Introduction

The reflectivity of flat Si surfaces is high in the range between  $\sim$ 30% (at 800 nm wavelength light) and  $\sim$ 50% (at 300 nm) because of the large difference in the refractive indexes between air (i.e., 1) and Si (3.7 at 800 nm and 5.6 at 400 nm). The conventional method to decrease the reflectivity of Si surfaces employs formation of pyramidal structure for single crystalline Si solar cells, which structure is formed by alkaline etching (e.g., KOH or NaOH plus alcohol such as isopropanol [1], butanol [2], etc.). Alkaline etching utilizes anisotropic etching, i.e., the etching rate of Si is much higher in the (100) direction than that in the (111) direction. In the case of poly-crystalline Si (poly-Si) solar cells, however, various surface orientations other than the (100) surface are present, and thus anisotropic alkaline etching cannot form uniform pyramidal structure. Therefore, for poly-Si solar cells, acid etching (i.e., HNO<sub>3</sub> plus HF solutions) [3,4] is employed to produce textured surfaces. These

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http://dx.doi.org/10.1016/j.apsusc.2016.04.132 0169-4332/© 2016 Elsevier B.V. All rights reserved. textured surfaces utilize multiple reflection to decrease the reflectivity, but light reflected twice at Si surfaces and reflected light with low incident angle go out. Consequently, the reflectivity cannot be made very low, i.e., above ~10% and ~20% for single crystalline and poly-Si wafers, respectively. Another method to produce textured Si surfaces employs, e.g., reactive ion etching [5], but the fabrication cost is much higher than those for wet-etching.

Insufficient light absorption is another problem arising from thin Si wafers for solar cell use (wafer thickness of commercial crystalline Si solar cells:  $180-130 \,\mu$ m). To avoid this problem, light should effectively be confined in Si. The conventional pyramidal structure possesses light trapping effect due to total reflection (i.e., light with incident angle larger than  $\sim 16^{\circ}$  is totally reflected at Si surfaces without going out of Si).

It has recently been shown that micro- plus nano-order structures on Si surfaces can achieve ultralow reflectivity. Nano-structures are produced on pyramidal textured Si surfaces by use of metal-catalyzed method [6,7], etching in HNO<sub>3</sub> plus HF solutions [8], electrochemical etching [9], etc. Deposition of needle-like Er-doped ZnO structure on silicon nitride film-covered pyramidal textured Si substrates can also achieve ultralow reflectivity [10].

Please cite this article in press as: K. Imamura, et al., Light trapping of crystalline Si solar cells by use of nanocrystalline Si layer plus pyramidal texture, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.04.132

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Fig. 1. Experimental set-up for fabrication of ultra-low reflectivity Si wafers.

We have recently developed a fabrication method for ultralow reflectivity crystalline Si wafers which method simply includes contact of platinum (Pt) catalyst with Si wafers immersed in a hydrogen peroxide ( $H_2O_2$ ) plus hydrofluoric acid (HF) solution called surface structure chemical transfer (SSCT) method [11–14]. In the present study, a nanocrystalline Si layer has been produced on a pyramidal Si surface by use of the SSCT method, and it is clearly shown that this structure possesses excellent light trapping effect. Using the nanocrystalline Si layer/pyramidal structure, high conversion efficiency of 18.5% and high short-circuit photocurrent density of 40.1 mA/cm<sup>2</sup> have been achieved in spite of simple solar cell structure without antireflection coating. The short-circuit photocurrent density of 40.1 mA/cm<sup>2</sup> is about 94% of the theoretical limit [15].

#### 2. Experiments

Crystalline Si wafers used in this study were (i) polished borondoped p-type Si wafers and (ii) pyramidal textured boron-doped ptype Si wafers. The polished Si wafers had a thickness of 725  $\mu$ m and a resistivity of 7–12  $\Omega$ cm. The pyramidal textured surface structure was produced by use of anisotropic alkaline etching after removal of a damaged layer introduced during slicing. The thickness and the resistivity of the pyramidal textured Si wafers were 170  $\mu$ m and 3–4  $\Omega$ cm, respectively. After the RCA cleaning, the Si wafers were immersed in 15 wt% H<sub>2</sub>O<sub>2</sub> plus 25 wt% HF solutions at room temperature, and Pt catalyst installed on a roller was contacted with the Si wafers. The period of contact of the Si wafer with the Pt catalyst was between 10 s and 30 s. After rinse with ultra-pure water, phosphosilicate glass (PSG) and borosilicate glass (BSG) were



**Fig. 2.** Reflectivity of the single crystalline Si wafers with a flat surface: (a) before the SSCT treatment, and after the SSCT treatment for the following periods: (b) 10 s, (c) 20 s, and (d) 30 s.

deposited on the front and rear Si surfaces, respectively, using a spin coating method, followed by heat treatment at 925 °C for 30 min in nitrogen. PSG and BSG were used for fabrication of pn-junction and back surface field (BSF), respectively. Front silver (Ag) electrodes were fabricated by use of an Ag paste, and rear Ag electrodes were formed using a vacuum deposition method after removal of the BSG layer. Then, the specimens were annealed in 5 vol% hydrogen plus 95 vol% nitrogen atmosphere at 400 °C for 10 min.

Reflectivity of Si surfaces was measured using a JASCO V-670 UV–vis spectrometer with an integrating sphere. Scanning electron microscopy (SEM) measurements were performed using a JEOL JSM-6335F field emission scanning electron microscope. Transmission electron microscopy (TEM) measurements were carried out with a JEOL EM-3000F transmission electron microscope with 300 keV incident electron energy. Effective carrier lifetime was measured at an injection level of  $1.5 \times 10^{14}$  cm<sup>-3</sup> using a Sinton Instruments WCT-120 apparatus. Photocurrent density vs. photovoltage (J<sub>ph</sub>-V<sub>ph</sub>) curves were observed under AM 1.5 100 mW/cm<sup>2</sup> irradiation using a YAMASHITA DENSO YSS-50A solar simulator. Quantum efficiency was measured by use of a Bunkoukeiki BQE-100 spectrometer.

#### 3. Results and discussion

Fig. 1 shows the experimental set-up for production of ultralow reflectivity Si surfaces. Si wafer with a size of  $5 \times 5 \text{ cm}^2$  (A) is placed



Fig. 3. Cross-sectional TEM micrographs of the single crystalline Si wafers with a flat surface after the SSCT treatment for the following periods: (a) 10 s, (b) 20 s, (c) 30 s.

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