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Preparation of nano-patterned Si structures for hetero-junction solar cells

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ABSTRACT

The 220 nm and 300 nm periodically nano-patterned Si structures with low aspect ratio were fabricated by nano-sphere lithography technique. A good anti-reflection properties in a broadband spectral range (300–1200 nm) was exhibited due to the gradually changing refractive index of the formed Si nanostructures. After deposition of the intrinsic and phosphorous-doped (P-doped) amorphous Si (a-Si) film, the weighted mean reflection of the 220 nm and 300 nm periodic nanostructures was further reduced to 3.30% and 2.96%, respectively. Due to the enhanced light absorption, both the IQE and EQE of the nano-patterned cells were improved in a wide spectral range. For the 300 nm periodically nano-patterned prototype hetero-junction solar cell, the short circuit current density was increased to 34.5 mA/cm^2, which was obviously improved compared with 26.8 mA/cm^2 for the flat cell.

1. Introduction

Since the first solar cell was invented at Bell Laboratories in 1954, it has been developing rapidly and reached an efficiency of 24.7% for a single crystal Si solar cell in the laboratory [1,2]. Due to the high reflection at the interface between air and the Si material, light-trapping techniques are critical in improving the performance of the solar cells [3–5]. In order to further develop the Si-based solar cells with high power conversion efficiency and low cost, it is necessary to combine the advanced thin film technology with the nanostructures to enhance the optical absorption based on photon management.

Up to now, many kinds of Si nanostructures, such as Si nano-pillars, Si nano-holes, and Si nano-wires, were fabricated to realize the broadband anti-reflection properties [6–10]. For example, Kelzenburg et al. fabricated nano-wires on Si wafers and reached the peak absorption up to 96% due to the good anti-reflection properties of the Si nanostructures. Jin et al. fabricated the mixed Si nanostructures with nano-pores and nano-pillars by means of deep ion-reactive etching (DRIE) process. In the visible wavelength range (300–800 nm), the diffusion reflection can be as low as 2.2%. Usually, the prepared Si nanostructures have a high aspect ratio, and it will result in a large surface recombination velocity and the difficulty in conformal deposition of the ultrathin films [11]. Recently, it has been reported theoretically that the nanostructures with low aspect ratio can also show good light trapping characteristics, and the ultimate efficiency is about 35.7% with the optimized parameters [12].

In our previous work, we utilized the nano-sphere lithography technique to get periodically nano-patterned Si nanostructures [13]. It was found that the parameters of the Si nanostructures can be well controlled by changing the size of the nano-spheres as well as the etching conditions [14,15]. By varying sizes of the nano-spheres, different periodicities of the Si nanostructures can be formed and the light reflecting spectra are different from each other. The etching depth is growing with the radio frequency (r. f.) etching power increasing, which is leading to enhanced light trapping properties. With the optimized fabrication conditions, the reflectance can be lower than 5% in a broad wavelength range. This demonstrated that the good anti-reflection properties can be achieved even though the nanostructures have the quite low aspect ratio. By using the formed Si nanostructures, the nano-patterned Si quantum dots-based luminescent device and solar cells can be fabricated and the improved device performance was observed compared to the flat devices [15–18].

In the present work, the nano-patterned Si structures with two kinds of periodicity (220 and 300 nm) were fabricated. The anti-reflection behaviors were studied and compared. Furthermore, we tried to prepare the hetero-junction solar cells by using the Si nanostructures. It was found that after deposition, the nanostructures with the larger periodicity exhibited the better anti-reflection characteristics and the weighted mean reflection can be as low

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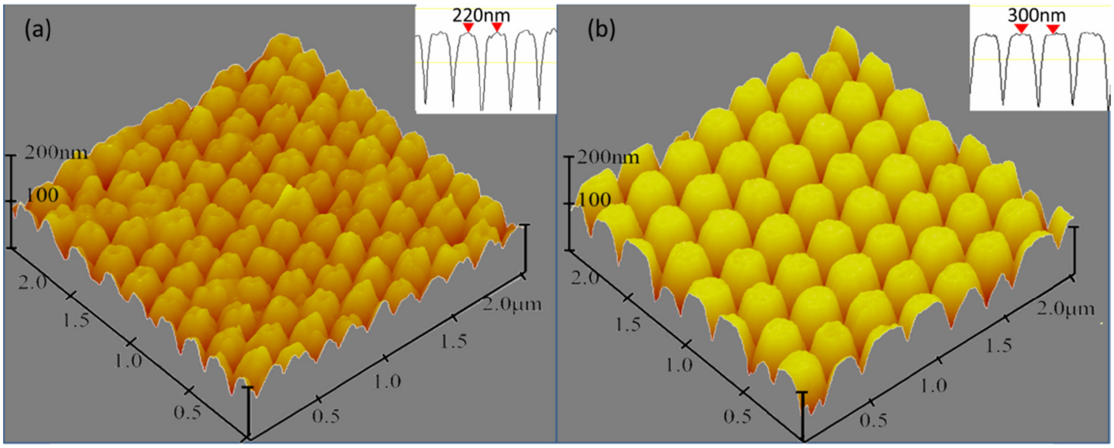

Fig. 1. (a and b) AFM 3D images of 220 nm and 300 nm periodic Si nanostructures, respectively. The insets are the cross sectional AFM images of the corresponding Si nanostructures.

Table 1
The experimental parameters of the RIE and PECVD experiments.

Parameters	RIE	PECVD
Power (W)	50	50
Reaction Gas	CF_4	SiH_4/PH_3 mixtures
Flowmeter (sccm)	30	5 and 5/30
Reaction time (min)	15	1 and 2

as 2.96%. Moreover, the nano-patterned solar cells exhibited the improved device performance, for which the short circuit current density and the corresponding power conversion efficiency were increased simultaneously.

2. Experimental

The periodic Si nanostructures were prepared on the (1 0 0) p-type Si wafer with the resistance of 1.5–3 Ω cm by using nano-sphere lithography technique. A monolayer of polystyrene (PS) nano-spheres was coated on the Si wafer by self-assembly technique. The blend solution of PS nano-spheres is prepared by mixing the PS solution and the ethanol with the volume ratio 1:4. The monolayer of PS nano-spheres was formed after a blob of the solution was dropped onto the transfer wafer. Then the thin film of PS was transferred to the water surface and a monolayer of PS nano-spheres was self-assembled on the water surface. After that we can put the Si wafer into water and taking up with the PS monolayer. The diameters of the nano-spheres were selected as 220 and 300 nm to form different periodicities. With the monolayer of nano-spheres as a mask, the Si wafer was etched in the conventional reactive ion etching (RIE) system for 15 min. The flow rate of CF_4 gas was 30sccm and the r. f. power was kept at 50 W during the etching process. Then the remaining PS nano-spheres were removed in the tetrahydrofuran (THF) solution. The hetero-junction solar cell was prepared by depositing the ultrathin intrinsic and n-type a-Si film on the nano-patterned Si substrate in the conventional plasma enhanced chemical vapor deposition (PECVD) system. The intrinsic a-Si film was deposited by using SiH_4 gas highly diluted by H_2 and the n-type a-Si film was deposited by using the SiH_4/PH_3 gas mixtures diluted by H_2. The radio frequency of the PECVD system was set at 13.56 MHz and the substrate temperature was 250 °C. Subsequently, transparent indium tin oxide (ITO) was sputtered on the front surface and Al electrode was evaporated as the back contact. The area of the solar cell was about 4 cm^2 (2 cm × 2 cm). The detailed experimental parameters are shown in Table 1.

The surface morphology was characterized by the atomic force microscopy (AFM) and the scanning electron microscopy (SEM). The reflection and transmission spectra were measured by the Shimadzu UV-3600 spectrometer in the range of 300–1200 nm. Based on the measured reflection and the transmission, we obtained the absorption spectra with the equation following:

$$A(\lambda) = 1 - T(\lambda) - R(\lambda),$$

where $A(\lambda)$, $T(\lambda)$ and $R(\lambda)$ are the absorption, transmission and reflection at the wavelength λ, respectively. The illuminated current–voltage (*I–V*) characteristics of the cell devices were measured under an AM1.5 (100 mW/cm^2) illumination by using a Keithley 610C electrometer. The external quantum efficiency (EQE) spectra were collected by the spectral response measurement system in the wavelength range of 300–1200 nm.

3. Results and discussion

Fig. 1(a and b) shows the AFM 3-dimension (3D) images of the formed 220 and 300 nm periodic Si nanostructures after removal of PS nano-spheres. The insets are the cross sectional AFM images of two kinds of Si nanostructures. The ordered and hexagonal-close-packed Si nano-cone-shaped structures can be clearly identified in the scanning area (2 μm × 2 μm), and the periodicity of the formed Si nanostructures is consistent with the size of nano-spheres. It has been demonstrated in our previous work that the Si nanostructures can be greatly influenced by the etching parameters [14]. Both the etching depth and the aspect ratio are increased with increasing the etching time, which can affect the optical properties of the formed Si nano-structures.

Fig. 2 shows the weighted mean reflection (R_w) as a function of etching time both for 220 nm and 300 nm periodic Si nanostructures. The R_w of the Si nanostructures was calculated by weighting the AM1.5 solar spectrum in the measurement range (300–1200 nm) according to the following equation:

$$R_w = \frac{\int_{\lambda_1}^{\lambda_2} F(\lambda) \cdot R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} F(\lambda) d\lambda}$$

where $F(\lambda)$ and $R(\lambda)$ is the flux of incident light and reflection at the wavelength of λ.

As seen in Fig. 2, the different anti-reflection behaviors of the Si nanostructures can be identified with changing the etching time.