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The study of defect removal etching of black silicon for solar cells

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ABSTRACT

To enhance the absorption of incident light of solar cells, multicrystalline black silicon has been successfully fabricated by plasma immersion ion implantation using SF_6 and O_2. After that a defect removal etching (DRE) process under different conditions has been performed to slow down the surface recombination by decreasing surface area and plasma etching damage. The surface microstructures, reflectance and internal quantum efficiency have been investigated by a field emission scanning electron microscope, a spectrophotometer and a quantum efficiency measurement system, respectively. It is found that the height and density of nanohills on the surface of black silicon decreases with increase in time of DRE, and the surface reflectance decreases with increase in height and density of nanohills. The internal quantum efficiency(IQE) of solar cells with a DRE process shows a large improvement than that without a DRE process, so as the performance of conversion efficiency. The best performance of the solar cells with a DRE process shows the conversion efficiency, open circuit voltage and short circuit current density as high as 17.46%, 623 mV and 35.99 mA/cm^2, showing an improvement of conversion efficiency of 0.72% than that of conventional acid textured cells.

1. Introduction

Reducing surface reflectance is a very important way to improve the efficiency of solar cells by enhancing light absorption. Generally, surface reflectance can be reduced by depositing an anti-reflection coating (ARC), such as SiN_x [1]. However, surface texturing is a more effective way because it forms some permanent structures on the surface. For monocrystalline silicon, anisotropic etching in alkaline solution is widely used in experiments and industry to reduce surface reflectance by shaping randomly “pyramids” [2]. For multicrystalline silicon, isotropic etching in acid solution is an effective way and widely used technique [3]. The reflectance of monocrystalline silicon can be decreased as low as 11% after surface texturing, but it is still as high as 25% of multicrystalline silicon.

To reduce surface reflectance furthermore, especially for multicrystalline silicon, nanostructures have been produced on the surface through all kinds of ways, which make black silicon wafer and so called “black silicon” [4]. There are several ways to fabricate black silicon. Kontermann et al. made a monocrystalline black silicon solar cell prototype through a femtosecond laser pulse process and obtained the highest efficiency of 4.5% without any emitter diffusion step [5]. Dimitrov and Du formed nanostructures through an electroless treatment in an acidic aqueous

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solution of $Na_2S_2O_8$ and $AgNO_3$ onto the random pyramids, and obtained the best solar cell with efficiency of 17.5% [6]. Reactive ion etching (RIE) and plasma immersion ion implantation (PIII) are other ways to form nanostructures widely used [7], but Kumaravelu et al. found that ion etching would bring defects in nanostructures, and nanostructures on the surface could enlarge the surface area obviously, which may decrease the minority carriers lifetime seriously [8]. This means that a defect removal etching (DRE) process is needed to improve the performance of black silicon solar cells. Lee et al. made black multicrystalline silicon solar cells by RIE progress with a DRE step, of which the efficiency can reach as high as 16.32% compared to 15.62% of conventional acid textured solar cells [9]. This proved that a DRE process could greatly improve the performance of black silicon solar cells [10].

In this paper, black silicon wafers have been made by plasma immersion ion implantation. To study the DRE process, different conditions of DRE have been established. All the wafers have been made for solar cells and the influence of different DRE processes will be investigated at length.

2. Experimental

Commercially available p-type doped multicrystalline silicon wafers with thickness of 180–220 μm and area of 156 mm × 156 mm were used. Fig. 1 shows the procedure of fabricating multicrystalline black silicon solar cells. First, the saw damage removal (SDR) process was performed in 10% NaOH solution at 80 °C. Then, black silicon was fabricated by a plasma immersion ion implantation process of all the wafers with the following conditions. The SF_6/O_2 gas ratio was 3:1, the radio frequency was 13.56 MHz of which the power was 900 W, the etching time was 4 min and no DC bias voltage was used. After that, a DRE process with different conditions shown in Table 1 was performed to remove the surface defect at 23 °C (the mass fractions of HNO_3 and HF used are 70% and 40%, respectively). All the wafers were then phosphorus doped through a thermal diffusion process with $POCl_3$ as the dopant source at a temperature of 825 °C. Afterward, the edge etching process was performed in the environment of CF_4 and O_2 plasma for 40 min, and a phosphosilicate glass (PSG) layer removal was realized by using HF solution with volume fraction of 10%. Silicon–nitride layer (SiN_x) with thickness of 80 nm was then grown by plasma enhanced chemical vapor deposition (PECVD). Finally, back surface field (BSF) as well as front and back metallization was processed by a screen-printing technique, and then all the wafers were dealt with a co-firing process in a conveyer belt furnace.

Fig. 1. The procedure of fabricating multicrystalline black silicon solar cell with nine steps.

The microstructures of black silicon were investigated by a field emission scanning electron microscope (SEM). Surface reflectance in wavelength from 300 nm to 1100 nm was examined by a ultraviolet–visible–near infrared (UV–vis–NIR) spectrophotometer with an integrating sphere detector. The internal quantum efficiency (IQE) was measured by a Solar Cell Scan 100 quantum efficiency measurement system.

3. Results and discussion

The microstructures of black silicon after the DRE process with different conditions are shown in Fig. 2. The surface of each wafer from C2 to C6 is covered by nanohills of different height and density. C1 has no nanohill because it is not dealt with a PIII process to make black silicon and just an acid textured wafer. C6 shows the original microstructures of black silicon with no DRE process, covered with nanohills having a very high density and height, which are formed by the competition of ion etching, passivation and bombardment [11]. It can be seen that the height and density of nanohills of black silicon wafers etched from C5 to C2 decrease while using different DRE conditions. The DRE process can be explained using two steps. First, the surface of silicon wafer can be oxidized by HNO_3 or $NaNO_2$ so that a film of oxide fabricates onto the surface. Then, the oxide film will be etched by HF, leading to reduction of density and height of the nanohills. The nanohills of black silicon wafers etched by C2 and C3 have a much lower density and height than that of wafers etched by C4 and C5. It can be explained that the oxidizability of HNO_3 is much stronger than that of $NaNO_2$. In addition, it is obvious that the more time the DRE process lasts, the lower the density and height of nanohills, no matter what kind of solutions is used.

Surface reflectance of all the wafers after the DRE process has been measured by a UV–vis–NIR spectrophotometer with an integrating sphere detector over the wavelength ranging from 300 nm to 1100 nm, as shown in Fig. 3. The average reflectance is defined as [12]

$$R_a = \frac{\int_{300}^{1100} R(\lambda)N(\lambda)dy}{\int_{300}^{1100} N(\lambda)dy}$$

where $R(\lambda)$ is the total reflectance, and $N(\lambda)$ is the solar flux under AM1.5 standard conditions. It is found that black