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Investigation of surface features for 17.2% efficiency multi-crystalline silicon solar cells

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ABSTRACT

Maskless reactive ion etching (RIE) texturing using a gas mixture of sulfur hexafluoride–oxygen (SF_6/O_2) and sulfur hexafluoride–oxygen–chlorine ($SF_6/O_2/Cl_2$) was investigated to reveal the proper shape in surface features for higher efficiency multi-crystalline silicon (mc-Si) solar cells; hence, needle-like and round-top cone (RT cone) shapes were formed by RIE texturing with SF_6/O_2 gas, and pyramid and inverted pyramid shapes by RIE texturing with $SF_6/O_2/Cl_2$ gas. RIE-textured mc-Si solar cells were fabricated on these surface features except for an inverted pyramid structure in the industrial production line. Performances of cells with RT cone and pyramid shapes were enhanced, whereas those with a needle-like cone were degraded, compared to the reference cells. Among these cells, those with RT cones represented the highest efficiency at 17.22%. By considering diode characteristics and electroluminescence images of fabricated solar cells, the proper shape for surface features was intimately related to control of the formation of a stable emitter layer as well as the reduction of surface reflectance.

1. Introduction

Multi-crystalline silicon (mc-Si) solar cells have around 50% of the market share in worldwide photovoltaic (PV) production, and that market share is steadily increasing due to lower cost compared to mono-crystalline silicon (mono-Si) solar cells, even though their conversion efficiency is 2 to 4% lower than mono-Si solar cells [1,2]. Hence, demand for higher efficiency at the mass production level has been increasing. To increase the efficiency of mc-Si solar cells, many studies have been conducted, including electrodes with lower resistance [3–5], anti-reflection coatings (ARC) [6–8], surface texturing [1,2,9–13], laser doping [14,15], an etch-back process [16,17] and so on. Surface texturing among them has attracted attention as one of the techniques to increase efficiency through increasing photo absorption, since the surface of mc-Si wafers fabricated as mc-Si solar cells usually reflects around 30% of the incoming light, with wavelengths ranging from 300 to 1200 nm [18]. Conventional wet texturing using an alkali solution with anisotropic etching characteristics, which is applied to mono-Si solar cells, is not suitable for texturing the mc-Si surface due to randomly orientated crystallites. Thus, an acidic solution of a hydrogen fluoride–nitric acid (HF/HNO_3) solution, which is independent of crystallographic orientation of grains, has been employed to carry out simultaneously texturing and saw damage removal (SDR) at the mass production level, but the mc-Si surface after texturing was still characterized by high surface reflectance. In order to reduce surface reflectance further, RIE texturing (among many techniques) has been intensively investigated to develop low-cost, large-area, and maskless texturing, since RIE has an anisotropic etching characteristic regardless of the various grain orientations and shorter process time than others [1,11–13,18–22]. Besides, it is easy to apply at the mass production level. Recent studies for RIE texturing have reported improved efficiency of RIE-textured cells since Inomata et al. reported on a special result of 17.1% efficiency for RIE-textured mc-Si solar cells using chlorine (Cl_2) gas plasma [23–25]. Although showing some feasibility for improving efficiency of the mc-Si cell, it has not yet been reported obviously and experimentally how surface features are formed by maskless RIE texturing and among them what shape is efficient to increase efficiency.

In this paper, we investigated forming various surface features by maskless and large-area RIE texturing with sulfur hexafluoride–oxygen (SF_6/O_2) and sulfur hexafluoride–oxygen–chlorine ($SF_6/O_2/Cl_2$) gas mixtures, and we have tried to reveal surface features to improve the efficiency of the RIE-textured mc-Si solar cell by comparing each surface feature. As a result, four shapes of surface

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features were formed. It is difficult to control the shape of surface features by only altering the RIE set-up parameters, and so both SF_6/O_2 and $SF_6/O_2/Cl_2$ gas mixtures are employed, even though Cl_2 gas is toxic. SF_6 and Cl_2 gas appear highly attractive for self-masking effects. Both the fluorine (F^*) and chlorine radicals (Cl^*) play a role as an active etchant species of silicon resulting in volatile silicon fluoride (SiF_x) and silicon chloride (SiCl) species, depositing passivation layers consisted of silicon oxyfluoride (SiO_xF_y) and silicon oxychloride (SiOCl), respectively, during the etching process. But it is well-known that Cl_2 gas, with an etching rate lower than SF_6 gas, can control the etch profile much better than SF_6 gas [21,22,26,27].

2. Experiment

2.1. RIE texturing

A gap of two parallel plate electrodes in an RIE system could be controlled from 7 to 16 cm, and the size of the bottom electrode, including an AC power supply for the bottom water-cooled cathode, was 8 in. One wafer could be loaded on the bottom electrode for each run through the load-lock chamber, and a pumping system for a main chamber was designed with a turbo molecular mechanical pump and a rotary pump, which made low vacuum and aided the turbo molecular mechanical pump. The specifications of solar-grade (SoG) mc-Si wafers for RIE texturing included sheet resistance of $1.4\sim1.6\ \Omega$ cm, minority carrier lifetime of $>1.5\ \mu s$, 200 μm thickness, B-doped, and a size of $15.6\times15.6\ cm^2$. A HF/HNO_3/de-ionized (D.I) water (HND) solution with an optimized volume ratio of $HF{:}HNO_3{:}D.I=1{:}2.7{:}3$ was applied to every wafer before RIE texturing in order to simultaneously accomplish SDR and wet texturing. After dipping in the HND solution, a standard cleaning process using potassium hydroxide (KOH), hydrogen chloride (HCl), and a diluted HF (DHF) solution, in that order, was carried out.

The RIE texturing process time was 5 min, to be compatible with the mass production level, except for inverted pyramid structures, and aimed basically to form homogeneous surface features over the $15.6\times15.6\ cm^2$ mc-Si surface. The main set-up parameters of RIE were gas flow rate, power, and working pressure (W.P). During RIE texturing with the SF_6/O_2 gas mixture, the optimized gas flow rates to design the homogeneous surface features were 1:1.2 and 1.2:1. The plasma power and W.P were applied below 100 W and 50 mTorr, respectively. The gas flow rate of the $SF_6/O_2/Cl_2$ gas mixtures was 1:1:0.6. Power and W.P varied from 70 to 600 W and from 50 to 150 mTorr, respectively. After RIE texturing, a damage removal etch (DRE) with the HND solution was conducted to compensate for the effect of plasma damage of the silicon surface and for the by-products made during RIE texturing. DRE for RIE texturing was completed with cleaning in an hydrogen chloride-hydrogen peroxide-de-ionized water ($HCl{:}H_2O_2{:}D.I$) solution followed by a D.I rinse and dry.

Surface reflectance was measured for wavelengths varying from 310 to 1100 nm using a diffuse/8° (D/8) integration sphere spectroscopic reflectometer with the light source based on an air mass (AM) of 1.5. Surface reflectance of the center position was represented, surface features were observed using a field emission scanning electron microscopy (FE-SEM), and the detailed size/aspect ratio of RIE-textured surface features was analyzed.

2.2. Fabrication of RIE-textured mc-Si solar cells

An emitter layer was formed with a conventional diffusion process based on a pre-deposition and drive-in method. A phosphoric acid-de-ionized water–ethanol ($H_3PO_4/D.I/C_2H_5OH$) diffusion source was deposited by using a spray coating method for pre-deposition, and then a diffusion process was carried out in a belt furnace with conveyor belt speed of 750 mm/min, a total process time of 18 min, and a gradual temperature change from 650 to 850 °C controlled by top and bottom infrared lamp. Phosphorus silicate glass formed during the drive-in was removed in a DHF solution. A hydrogenated silicon nitride layer (a-SiN_x:H) of around 85 nm thick, which acts as an ARC and surface passivation, simultaneously, was deposited on the front side through plasma-enhanced chemical vapor deposition (PECVD). The front and back electrodes were formed through a screen printing technique and then completed simultaneously in a co-firing process where the set temperature varied from 235 to 983 °C in the belt furnace with a belt speed of 605 mm/min. Edge isolation was carried out through a laser isolation method. Reference cells were fabricated using the same process as describe above only without the RIE texturing process.

The performance of the fabricated mc-Si solar cells was examined by measuring the illuminated current-bias (LIV) response under the standard test conditions of $100\ mW/cm^2$ and AM 1.5 at 25 °C. The dark J–V (DJV) was examined to reveal diode characteristics [28,29]. A commercially available electroluminescence (EL) system (Model K3300 ELX, McScience Inc.), which was developed for in-line application on the direct current (D.C) basis, was employed to reveal the effect of defects caused by raw material, the fabrication process, and RIE texturing [28,29].

3. Results and discussion

Fig. 1 shows the surface features formed by RIE texturing with SF_6/O_2 and $SF_6/O_2/Cl_2$ gas mixtures on the mc-Si surface following the SDR process. The formation of the surface features by RIE with SF_6/O_2 gas mixtures was dependent on the RIE set-up parameters, such as gas flow rate, amount of total gas flow, working pressure, power, and texturing time. When using SF_6/O_2 gas, the gas flow rate was the most important function to determine whether or not surface features were formed. Texturing time and other parameters were mainly related to the size of the features and the uniformity of the etching over a large area. Fluorine-rich processes tended to form a passivation layer with lesser area, since it reacted with the Si to produce SiF, making the etching profile more isotropic, whereas oxygen-rich processes formed a greater passivation layer that consisted of SiO_xF_y, so that the etching characteristics became less isotropic due to interruption for homogeneous etching. The more the oxygen content increased, the more the etching mechanism became anisotropic, and simultaneously, the etching rate decreased. Fig. 1(a and b) represent the surface features formed from SF_6/O_2 gas with gas ratios of 1:1.2 and 1.2:1, respectively. Unlike Moreno's paper [30], our RIE texturing with SF_6/O_2 gas could not form pyramid and inverted pyramid structures. At a gas ratio of 1:1.2, needle-like structures possessing a 130 ± 29.15 nm height and 35 ± 14.14 nm width were found, and RT cone structures at 265 ± 59.71 nm for height and 184 ± 64.86 nm for width were formed at a gas ratio of 1.2:1. This indicated that gas ratio determined the density of the micro-mask and the strength or thickness of the sidewall passivation altered the height and width of the surface features. In spite of such distinctive results, the SF_6/O_2 gas was not easy to control with regard to the surface features due to its high etching rate and volatile SiO_xF_y passivation layer. To try to form different shapes of surface features, Cl_2 was added into the SF_6/O_2 gas since it is well-known that Cl_2 gas with a lower etching rate can control the surface features better than SF_6 gas [21,26]. The angle of the sidewalls of the silicon features etched with Cl_2/O_2-based mixtures is directly determined by the thickness of the SiOCl passivation