Solar Cell Fabrication Using Two-step Textured Quasi-single Crystalline Silicon by Alkaline and RIE Texturing Processes

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ABSTRACT

After alkaline chemical texturing process, SF₆/O₂ reactive ion etching (RIE) was used for maskless textured Si surface independently from crystal orientation. Additional RIE texturing on alkaline textured Si surface increased the light receiving areas and decreased the surface reflectance by random pyramidal structures with a width of hundreds of nanometers. The weighted average reflectance (WAR) of the textured Si surface by two-step texturing processes was achieved as low as 9.6% in the 300-1200

nm wavelength range. Compared to the alkaline texturing, the alkaline and RIE texturing of front Si surfaces decreased the WAR by 6%. By means of two-step texturing processes for quasi-single crystalline silicon (QSC-Si) surfaces, performance parameters of the solar cell such as conversion efficiency, short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) were examined in 18.2%, 36.6 mA/cm², 624 mV and 79.7%, respectively.

Keywords: Light Trapping, Quasi-single Crystalline Silicon, Reactive Ion Etching, Surface Reflectance, Conversion Efficiency

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Photovoltaic cells are one of the most promising devices which directly convert sunlight into electricity. The crystalline silicon (c-Si) solar cells are the most extensively commercialized solar cells and have increased over 90% global solar cell market share in photovoltaic industry [1-4]. The two main types of c-Si used in solar cell fabrication are monocrystalline (mono-Si) and multicrystalline silicon (mc-Si). The mono-Si is manufactured by the process technologies such as Czochralski (CZ), Float Zone (FZ) and Bridgeman method [5-9]. Also, mc-Si is grown by the casting and heat exchange methods [10, 11]. The mc-Si has high levels of contamination by the reaction with various contaminants during manufacturing processes using high temperature and high crystal defect content such as sub-grain boundaries, grain boundaries and dislocations [12-14]. Therefore, the mc-Si solar cell efficiency shows much lower than that made of mono-Si due to take effect in impurities and crystal defects [15, 16]. Nevertheless, the casting methods for growing mc-Si are widely used for solar cell fabrication due to the strength of higher throughputs, lower manufacturing costs and simpler processes in comparison to the CZ technique [17]. The crystal defects and impurities of mc-Si materials which are manufactured by relatively uncomplicated and cost-effective techniques can be solved by combination of the high purity levels connected with mono-Si processing. Quasi-single crystalline silicon (QSC-Si) known as quasi-mono or

mono-like Si is a relatively new PV technology that has met these requirements and has received much interest in the PV industry recently [18]. This material is positioned between mono-Si and mc-Si in respect of crystalline quality, production cost and solar cell efficiency. The crystallographic orientation of QSC-Si was formed from both $\langle 111 \rangle$ and $\langle 100 \rangle$ orientations. In addition, QSC-Si has good structural and electrical properties by improving the crystal quality and controlling the defects. Therefore, this material is very effective in reducing the cost of solar cell fabrication due to its ability to form thinner wafers and its better mechanical strength, resulting in faster processing [19-25]. In this work, we observed the QSC-Si surface morphology by two-step texturing processes using alkaline chemical and reactive ion etching (RIE) to achieve higher efficiency of solar cells by reducing the surface reflectance for optimization of light-trapping effects within the cell.

The boron-doped p-type QSC-Si wafers were used with an average thickness of 200 μm , a resistivity of 1-3 $\Omega\cdot\text{cm}$ and a size of 156 $\times$ 156 mm^2 (243.3 cm^2) for solar cell fabrication. To remove the contamination of Si surface, the wafer was cleaned by the solution containing deionized water (DIW) and KOH (1 wt%) in an ultrasonic environment of 40-50 kHz for 8 min at 25 $^\circ\text{C}$. Also, alkaline texturing process on the wafer surfaces was carried out by mixed solutions KOH (1.2 wt%), IPA (6-8 wt%) and

DIW at 80°C for 13 min. After alkaline texturing, the Si wafers were placed on power electrode of water-cooled type below 20°C in parallel-plate reactor with RF (13.56 MHz) generator at a base pressure of 0.075 Pa. The SF₆ and O₂ gases were mixed and fed into the Process chamber. In this work, RIE surface texturing was performed at a working pressure of 1.13 Pa, SF₆:O₂ gas ratio of 6:5 and a RF power of 4 kW for 6 min. The n⁺ emitter was formed by phosphorus diffusion using Phosphorus oxychloride (POCl₃) source in a furnace with the temperature at 840°C to obtain the sheet resistance ranged from 60 to 65 Ω/square. As an antireflection coating, the hydrogenated silicon nitride (SiN_x:H) layers were prepared by plasma enhanced chemical vapor deposition (PECVD) method at a temperature of 400°C. The reflective index and the film thickness of SiN_x:H layers were about 2.1 and from 80 to 82 nm, respectively. The metallic contact of the front and back Si surfaces was formed by Silver (Ag) and aluminum (Al) paste screen printing. After the drying process for these pastes at 150°C for 5 min, the Si wafers were subjected to co-firing cycle in IR-lamp-heated belt furnace for high-temperature sintering. Finally, the edge isolation process by laser technique was used for preventing any possibility of short-circuiting the p-n junction through the edges of the Si wafers.

Morphologies and compositions of the Si surface were examined by field emission

scanning electron microscopy (FESEM, Hitachi S4700, Japan at 10 kV), and energy dispersive spectroscopy (EDS, EDAX Genesis apex, acceleration voltage: 30 kV, collection time: 100 s with standardless method), respectively. The textured Si surface reflectance was investigated by UV-VIS spectrophotometer (UV-vis, Shimadzu Japan, UV-VIS-NIR 3101) with an integrating sphere in the 300-1200 nm wavelength range. The electrical sheet resistance (R_s) of the n^+ emitter layer was analyzed by a four-point probe (MCP-T610, Mitsubishi Chemical, Japan). The minority carrier lifetime measurements were carried out with a μ -PCD system from Semilab (WT-1000), which measured the lifetime to a precision of $\pm 0.01 \mu s$. External quantum efficiency (EQE) was investigated by using an IPCE (incident photon conversion efficiency) measurement unit (PV Measurements, Inc., USA). The Illuminated current-voltage (I-V) curve of Si solar cells was characterized by a solar simulator (94082A, Newport, USA) at $25^\circ C$ under 100 mWcm^{-2} illumination (AM 1.5 G).

Due to a $\langle 100 \rangle$ -oriented seed crystals, the grown QSC-Si ingot is formed mostly from $\langle 100 \rangle$ -oriented single crystals. But mc-Si is unavoidably generated at part of the QSC-Si ingots in mass production line by reason of the shape defects of the solidification interface and free nucleation on the crucible walls during the solidification process [26]. Fig. 1 shows the optical image of as-cut wafer with a size of 156×156

mm² (243.3 cm²) for solar cell fabrication and the SEM images of QSC-Si surface morphologies. As shown in Fig. 1(a), the wafer consists of the <100> -oriented single crystal and mc-Si areas. QSC-Si surface of Fig. 1(b) with the <100> -oriented single crystal has the same surface structure as that of conventional CZ-Si wafer. The increase in single crystals ratio of QSC-Si wafer has an effect on the improvement of solar cell efficiency [26]. Therefore, the QSC-Si wafers with a single crystal ratio of more than 90% were used for application of high-efficiency solar cell fabrication in this work. To improve the light-trapping effect for solar cells, the <100> -oriented single CZ-Si is usually textured by the anisotropic alkaline texturing technique, while the surface structure for reducing reflectance can be achieved in mc-Si wafers by using isotropic acidic or RIE texturing due to their random orientation of crystal grains [27-29].

After Saw damage removal (SDR) process, alkaline texturing was carried out for formation of uniform pyramid structures in the <100> -oriented single crystal surface with a single crystal ratio of more than 90%. RIE process using SF₆/O₂ as etch gases was also used for mask-less surface texturing of mc-Si areas which was polished by alkaline texturing. SEM images of surface morphology for the <100> -oriented single crystal and mc-Si areas textured by alkaline and RIE process are shown in Fig. 2. Fig. 2(a) shows a homogenous pyramidal structures of the <100> -oriented single crystal by

alkaline texturing technology. After the wet chemical alkaline texturing, RIE method forms the regular and dense surface structures on alkaline textured single crystal areas as shown in Fig. 2(b). The mc-Si areas polished by alkaline texturing are shown in Fig. 2(c). RIE-textured mc-Si surface is covered in random pyramidal structures with the RMS roughness of 115 nm as shown in Fig. 2(d). As a result, the RIE texturing technique has an effect on improving the trapping of incident light due to the formation of pyramidal structures with a width of hundreds of nanometers on alkaline textured single crystal and mc-Si areas. The atomic percent of silicon and oxygen is investigated by EDS analysis of QSC-Si surface. Based on the etch mechanism of strong sidewall passivation by adsorbed $\text{Si}_x\text{O}_y\text{F}_z$ layers, the oxygen atomic percent of 5.8% in RIE-textured QSC-Si surface has an influence on the morphological properties of the random pyramidal structure during the RIE process. In plasma chemistry and reaction mechanism during a SF_6/O_2 RIE process, SF_6 produces F^* radicals to use a chemical etching process of c-Si by forming volatile silicon tetrafluoride (SiF_4). Oxygen forms O^* radicals for the passivation of Si sidewall surfaces with $\text{Si}_x\text{O}_y\text{F}_z$ which has an effect on the control of etch profiles. The walls of the random pyramidal structures are covered with adsorbed $\text{Si}_x\text{O}_y\text{F}_z$ and are somewhat protected against etching. [30-35].

Reflectance spectra of QSC-Si surface with various kinds of surface conditions by

alkaline and RIE texturing processes are shown in Fig. 3. Prior to alkaline texturing process, the bare QSC-Si wafer was cleaned by SDR process which was performed by the solution containing DIW and KOH (1 wt%). The average reflectance of 30.6 and 15.6% measured in the wavelength range of 300 to 1200 nm was examined for bare and alkaline-textured QSC-Si surface, respectively. Compared to these measured values, the minimum average reflectance of 9.5% was investigated for RIE-textured QSC-Si surface on alkaline-textured wafer. As mentioned above, the oxygen atomic percent is related to the random pyramidal structure by the observed $\text{Si}_x\text{O}_y\text{F}_z$ layers which are covered with QSC-Si sidewall surface. These masking layers are just enough to be kept as a randomly perforated mask during RIE texturing. As a result of the pyramidal structure formed by two-step texturing processes, the optical reflectance decreased dramatically for enhancing the light-trapping effect by the increased surface area involved in the light absorption.

The comparison of minority carrier lifetimes in alkaline textured and alkaline and RIE textured QSC-Si by each sequential step in solar cell fabrication processes is shown in Fig. 4. As individual solar cell fabrication steps progress, the minority carrier lifetimes which was measured in the same values for two types of bare QSC-Si wafers increased. After solar cell manufacturing processes such as texturing, diffusion and

hydrogenated silicon nitride (SiN_x:H) deposition processes, the minority carrier lifetimes of alkaline and RIE textured wafers were improved more than those of alkaline textured wafers. These values of 0.8 μ s for bare QSC-Si wafers increased about 16.1 μ s and 19.8 μ s respectively for alkaline textured and alkaline and RIE textured QSC-Si after the SiN_x:H deposition by using PECVD systems. The minority carrier lifetimes by additional RIE texturing increased as solar cell fabrication steps from 0.3 μ s to 3.77 μ s. Due to the reduction in surface recombination velocity, the major effect on improving the minority carrier lifetime of QSC-Si is involved in increasing solar cell efficiency.

External quantum efficiencies (EQE) spectra and illuminated current-voltage (LIV) curves for QSC-Si solar cell are shown in Fig. 5. Fig. 5(a) shows the EQE spectra in 300-1200 nm wavelength range for alkaline textured and alkaline and RIE textured QSC-Si solar cells. According to the decrease in the surface recombination for the improvement of optical and electrical properties, the EQE analysis of the alkaline textured QSC-Si solar cell has a poor response for all wavelengths compared to that of alkaline and RIE textured QSC-Si solar cell. Therefore, additional RIE texturing on alkaline textured wafer has an effect on enhanced light-trapping in solar cells by the fine and dense pyramidal surface structures with a width of hundreds of nanometers.

Illuminated current-voltage (LIV) curves for QSC-Si solar cell fabricated by sequential process of alkaline and RIE surface texturing are shown in Fig. 5(b). After RIE texturing process on alkaline textured wafer, the open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) of solar cell increased about 1 mV, 1.4 mA/cm² and 1.1% compared to that of alkaline textured solar cell. The solar cell conversion efficiency of 18.2% was obtained by the increase in these electrical performance parameters.

In summary, due to high-rate crystal growth by enhanced productivity, mechanical stability and lower impurities, the QSC-Si is very promising material in manufacturing cost reduction for silicon solar cell. In this work, we performed the surface texturing processes for the formation of pyramidal structures in the <100> -oriented single crystal and mc-Si areas of QSC-Si wafer. To satisfy the surface morphology of these two areas, RIE texturing process was used as following process of conventional alkaline texturing. Additional RIE texturing on alkaline textured QSC-Si wafer decreased in optical reflectance and improved the minority carrier lifetimes by random pyramidal structure for increasing solar cell efficiency. The best 156 × 156 mm² (243.3 cm²) QSC-Si solar cell fabricated by two-step texturing processes showed J_{sc} =36.6 mA/cm², V_{oc} =624 mV, FF=79.7% and conversion efficiency=18.2%.

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Figure 1

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Figure 2

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