Laser doping of boron-doped Si paste for high-efficiency silicon solar cells

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1. Introduction

Recent research on silicon solar cells has focused on improving the cell efficiency.1–8 To increase the cell efficiency by suppressing rear-side carrier recombination, passivated emitter and rear contact (PERC) cells and passivated emitter and rear locally diffused (PERL) cells were developed.9–11 PERC and PERL cells have local back surface field (BSF) on the rear side of the cell. The rear-side local BSF is important for improving the rear-side carrier recombination and the contact with Al electrodes. It was reported that the rear-side carrier recombination was controlled better when boron was used than when Al was used for the local BSF.12

Laser doping (LD) has advantages in terms of atmospheric room-temperature processing, easy control of doping depth and concentration, and patternability of doping area without lithography.13,14 Solar cells have various cell types. LD has been used to develop high-efficiency solar cells with a relatively complicated structure, selective emitters, and PERC and PERL based on p-type/n-type wafers.15–20 A high-efficiency solar cell can be fabricated with simple steps by using the LD process. As an application of the LD process, a PassDop proposed in which a local phosphorus layer and perform diffusion of dopant by LD simultaneously so that the solar-cell properties are not influenced.

2. Experimental methods

2.1 Fabrication of silicon nanoparticles and NanoGram® Si paste/ink

We used silicon nanoparticles (SiNPs) fabricated by NanoGram corporation using the laser pyrolysis method.20 This method can be used to control the particle size to less than 10 nm and the dopant concentration up to the order of 10^{21} atoms/cm^3. Two types of phosphorus- or boron-doped SiNPs can be produced by using a mixture of silane gas and phosphine or diborane. The laser pyrolysis method has a high yield in comparison with other methods. Figure 1 shows the transmission electron microscope (TEM) image of the SiNPs, in which the crystal lattice can be observed clearly. The image indicates that the SiNPs were highly crystalline. The average diameter of SiNPs was approximately 20 nm. NanoGram® Si paste/ink (Fig. 2) was prepared by dispersing the SiNPs in an organic solvent and regulating the viscosity in the range of 1 to 1000 cP by using a suitable mixture of solvents. NanoGram® Si paste/ink can be applied using conventional printing methods. The NanoGram® Si ink had a low viscosity of approximately 10 cP, which is suitable for spin coating, spraying, and ink-jet printing. The viscosity of the NanoGram® Si paste was greater than 1000 cP, which is suitable for screen printing. The metal impurity concentration in NanoGram® Si paste/ink is controlled to less than 10 ppb so that the solar-cell properties are not influenced.

2.2 Printing of the NanoGram® Si paste in a fine line and the LD process

NanoGram® Si paste is screen-printable on textured and SiN-passivated Si wafers. Figure 3 shows the line pattern obtained with the screen printing of NanoGram® Si paste on 6-in. textured Si wafer, and a homogeneous printing was obtained on a textured Si wafer. The textured Si wafer can be...
uniformly covered with NanoGram® Si paste. There was no exposure of the Si-wafer surface (Fig. 4).

The line width of the LD pattern is required to be less than 50 µm to widen the area of passivation layer and suppress rear side carrier recombination. The printing of fine lines is needed when the NanoGram® Si paste/ink is applied to the rear side of the solar cell, such as PERL cells, so that the stray paste remaining after laser irradiation can be minimized. Figure 5 shows optical microscope images of a screen-printed line of NanoGram® Si paste and LD on the Si-paste line. The screen mask had a line pattern that was 80 µm wide, and the line width of the printed Si-paste line was approximately 80 µm [Fig. 5(a)]. The laser doping area can be observed on Si-paste line obviously [Fig. 5(b)]. Therefore, the NanoGram® Si paste can be applied for fine line printing and LD with controlled alignment.

2.3 Fabrication of solar cells

The test structures of the solar cells are shown in Fig. 6. The NanoGram® BSF cell that has local boron BSF on the rear side was fabricated using NanoGram® Si paste and LD. The PERC cell with local Al BSF was used as the reference cell.

The fabrication process of the NanoGram® BSF cell is shown in Fig. 7. Cells of size 50 × 50 mm² were processed on p-type Czochralski-grown Si wafers of thickness 200 ± 30 µm. Alkali texturing was performed following a POCl₃ diffusion process. The sheet resistance after POCl₃ diffusion was 80 ± 5 Ω/□. Prior to the front- and rear-side layer passivation, the phosphorus-silicate glass was removed, and the rear side of solar cell was etched. Boron local diffusion into the rear side was performed using LD with NanoGram®
boron-doped Si paste/ink. The Si paste/ink was printed on Al$_2$O$_3$/SiN$_x$ layers and dried at 200 °C for 10 min. The thickness of the layer of dried Si nanoparticles was approximately 800 nm. A 532 nm Q-switched pulsed laser was used for LD. The frequency of the laser was 150 kHz, and the pulse width was 20 ns. The laser was irradiated along a pattern with 40-µm line width and 1-mm line pitch. Laser doping area was 3.48% on the rear side. The cells were contacted by screen-printing Al paste on the rear side and Ag paste on the front side, followed by co-firing in a furnace.

3. Results and discussion

3.1 Solar cells

Boron LD through the passivation layer was achieved using NanoGram® boron-doped Si paste/ink. The sheet resistance most suitable for local BSF was investigated. The solar cell with a sheet resistance of 35 Ω/□ yielded the highest efficiency. The laser fluence was 3.5 J/cm$^2$.

The solar cell characteristics are shown in Fig. 8. The NanoGram® BSF cell had increased efficiency in comparison with a reference cell. The cell efficiency was improved by more than 1%. All of the cell characteristics ($V_{oc}$, $J_{sc}$, FF) of the NanoGram® BSF cell were improved; in particular, an efficiency of up to 19.7% was obtained with open circuit voltages above 655 mV (see Table I). In contrast, the efficiency of the reference cell was only 18.5%. The efficiency of NanoGram® BSF cell measured using the Suns–$V_{oc}$ was 20.6%. The solar cell with local boron BSF formed using NanoGram® Si paste/ink has the potential for achieving >20% efficiency in solar cells.

3.2 Secondary-ion mass spectrometry analysis

Secondary-ion mass spectrometry (SIMS) was performed for the sample that was made opening for fabricating passivation layer and diffused the dopant at the same time. The sample was irradiated at a fluence of 3.5 J/cm$^2$, and the sheet resistance was 35 Ω/□. Figure 9 shows the depth profile.
of the boron dopant, which indicates that the surface boron concentration was $1 \times 10^{19}$ atoms/cm$^3$ and the doping depth was $>5 \mu$m. The boron dopant can be fully diffused into the Si wafer through laser irradiation in boron SiNPs printed on a passivation layer.

3.3 Measurement of internal quantum efficiency

To investigate the influence of recombination on the device performance, the internal quantum efficiency (IQE) of the solar cells was measured (Fig. 10). The value of the IQE increased in the long-wavelength region from 800 to 1100 nm. The improvement in the long-wavelength region indicates a beneficial modification at the rear side of the solar cell. The improvement is thought to have occurred because of a change in the rear-side reflectance, an enhancement of the passivation layer, and a reduction of the rear-side carrier recombination.

In this experiment, there was no change in the reflectance of the cell when using the same Al paste. It is thought that IQE was not affected, because the composition (Al$_2$O$_3$/SiN) and the rear-side opening ratio (line width 40 µm, line pitch 1 mm) of passivation layer for the irradiated laser were similar. It is concluded that local boron BSF formed by the NanoGram® Si paste/ink reduced the carrier recombination at the rear side of the cell. The laser-doped area of NanoGram® Si paste/ink produced the BSF effect. Dong Lin et al. also investigated the influence of the rear-side local boron BSF on the value of IQE. They also discussed the suppressing effect of rear-side carrier recombination of the solar cell with local boron BSF.$^{31,32}$

3.4 Measurement of electroluminescence

Figure 11 shows electroluminescence images of the reference cell with the best performance and the NanoGram® BSF cell. The images were measured from the front side of the solar cells. No cracks or defects were observed in both cells. Laser irradiation on the Si wafer did not cause any damage that affected the cell efficiency. We conclude that the LD process improves the cell efficiency while keeping the damage to a minimum.

The color of the NanoGram® BSF cell was brighter than that of the reference cell because more current flowed in the NanoGram® BSF cell.

4. Conclusions

We developed a printable dopant, NanoGram® Si paste/ink, that can be applied for fine line printing and boron LD through a passivation layer. The local boron BSF formed through boron LD using the NanoGram® Si paste/ink reduced the carrier recombination on the rear side of the cell, improving its efficiency. We demonstrated an efficiency of 19.7% in a solar cell with local boron BSF.

We will achieve the >20% cell efficiency by optimization of the cell fabrication and promote development of n-type Si-wafer-based solar cells.

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