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Si paste technology for high-efficiency solar cells

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ABSTRACT

This study demonstrates the successful implementation of industrially feasible local B doping as a local back surface field via the Si paste technology to fabricate high-efficiency solar cells. Si paste formed by 25 wt% p-type Si nanoparticles and 75 wt% organic solvent is used as the B source. Si paste is fully screen-printed on the preprocessed p-type Si rear surface, and then a homogenous Si cladding layer is formed by picosecond laser cladding. During this process, B diffuses into the Si substrate. The Si cladding layer itself is a heavily doped layer and forms a metallurgical bond between Si substrate. After co-firing with Al paste, cells obviously avoid Kirkendall void formation at contact regions. The heavily doped Si cladding layer and localized B doping can decrease the contact resistance and reduce the minority carrier recombination at the local metal contacts. This optimized rear surface design finally contributes to push the overall average cell efficiency over 20.3% on p-type CZ wafers.

1. Introduction

The passivated emitter and rear contact (PERC) structure based on rear surface passivation, local openings, and full-area metallization are becoming increasingly attractive at the production level for high-efficiency solar cells (Green et al., 1990; Wang et al., 2012). However, Kirkendall void formation, inadequate local back surface field (LBSF) thickness, and other issues affecting industrial applications (Hallam et al., 2011; Rauer et al., 2011) have not been solved.

Kirkendall voids, regions in which an air gap exists rather than solid Si–Al, are a major limiting factor (Lin et al., 2013; J. Chen et al., 2013; D. Chen et al., 2013; Tjahjono et al., 2013; Lauermann et al., 2015) that affects both electrical contact and contact recombination. The voids occur when Si diffuses too far into the Al-matrix layer and cannot travel back to the Al–Si interface before the temperature drops down to the eutectic temperature (Lauermann et al., 2015). Another potential issue is the inadequate LBSF thickness between the bulk Si and Al–Si eutectic layer (Hallam et al., 2011; Rauer et al., 2011). Without the protection from an adequate BSF, the minority carrier recombination velocity at local contact regions is expected to be high.

Several studies investigated the impact of processing on the formation of a good-quality LBSF to mitigate the issues mentioned above. These studies found that specially designed pastes that contain a percentage of Si nanoparticles (NPs) can be used to increase the thickness of the LBSF and reduce the number of Kirkendall voids (Hallam et al., 2011; Dong et al., 2014). However, only few types of these pastes have been successfully developed for industrial applications. In addition, using local B doping instead of Al can reduce the recombination losses and improve the contact resistance (Zhao et al., 1996). Most B sources are hazardous and require extra complex processes to allow diffusion. Hence, the preparation of a specific paste containing both B and Si particles can have a great potential for industrial applications.

We incorporate feasible fabrication and industrially applicable processes to develop high-efficiency PERC cells. In this study, we use Si paste and PS laser doping as a possible solution to overcome the issue of Kirkendall void formation and establish localized B doping at the Al–Si interface. In fact, the Si paste that uses screen printing on preprocessing wafers from China Sunergy has demonstrated favorable doping performance (Hong et al., 2015). In the present study, we demonstrate uniform doping on the back surface field and present further details on the efficacy of Si paste in the cell fabrication.

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2. Si paste technology background

2.1. Si paste preparation

Si paste formed by p-type Si NPs and an organic solvent is used as the B source. Si NPs with a diameter of approximately 30 nm are prepared using the pulsed electrical discharge method. The diffusing performance of NPs can be easily tuned by choosing dopant atoms, such as B (p-type) or P (n-type), and varying concentrations in the raw material. Doped films can be created from the Si paste. We used p-type preprocessing wafers from China Sunergy as the substrate. After analyzing the printing and diffusing performance of the Si paste with different percentages of Si NPs, we chose the Si paste formed by 25 wt% Si NPs for applications (Hong et al., 2015).

The favorable performance of dispersion is a key factor in reducing the melting temperature of NPs (Goldstein, 1996). The diameter of our Si NPs is approximately 30 nm, thereby facilitating easy dispersion. The dispersion is relatively difficult in previously described pastes with Si NPs approximately 2–10 nm in size. Compared with other pastes, our self-doped Si NPs are used as the dopant source; hence, extra doping elements are not needed. According to the principle of self-fluxing and congruent melting point (Mirzade et al., 2013), Si NPs can easily form metallurgical bonding by laser cladding when Si wafers are used as the substrate.

One advantage of using Si NPs is reduced melting temperature as compared with bulk silicon (Goldstein, 1996), which has been confirmed by Innovalight's Cougar Process using NPs to prepare Si ink (Alberi et al., 2010). This merit allows the NPs to be cheaply and easily sintered into dense films at low temperatures without affecting the quality of bulk wafer. Another prominent advantage of this paste is that the Si NPs can be used as the B source diffused into the silicon substrate. It can also be turned into a heavily doped layer after laser cladding. When combined with the Al screen print firing process, the doped Si cladding layer in the openings can avoid Kirkendall void formation. Cell fabrication at high firing temperatures is possible when LBSF is preformed prior to Al–Si alloying. As the temperatures properly increase, the adequate BSF can be obtained (Lauermann et al., 2015).

2.2. PS laser doping

Laser doping has been widely used for semiconductor processing with early demonstrations of laser doping dating back to 1970 (Fairfield and Schwuttke, 1968). In general, laser doping using liquid or solid B as the B source and nanosecond (NS) laser result in doped regions with junction depths at the order of 2 μm or less (Hallam et al., 2015; Bounaas et al., 2013; Kray et al., 2008; Kim et al., 2014a; Green, 2015). Traditional B sources require a high energy to melt the Si substrate and a long time to maintain B diffusion; hence, NS laser is the best choice. However, NS laser causes various crystallographic defects on the processed regions. Thus, it must be properly and carefully removed to maintain any performance gain that would otherwise be lost by the laser-induced damage (Kim et al., 2014b; Hwang et al., 2015; Sameshima et al., 1987; Bähr et al., 2010).

When the NPs are used as the B source, we only need to use a relatively low energy to melt the Si NPs and define the local openings through the dielectric layer. Therefore, the PS laser is used to control the heat-affected zone and thus improve the cell performance. Meanwhile, the PS laser recognizes the metallurgical bond between Si substrate and forms a shallow boron-diffused region.

Adopting the local B-BSF concept is the Si paste technology developed by Nanjing University of Aeronautics and Astronautics in collaboration with China Sunergy based on the PERC cell structure. This paper presents a new approach that uses p-type Si NPs as the B source to form B-BSF and provides an industrially feasible approach for B diffusion.

3. Experimental details

Cell fabrication was completed on a 35 MW production line by using commercially available Si wafers. The preparation of SP-PERC cells, as shown schematically in Fig. 1, has three more steps (screen-printed Si paste, PS laser cladding, and redundant Si paste removal) compared with that of normal PERC cells. In typical PERC processes, the PS laser was used to open the dielectric layer. The off-the-shelf PS laser equipment can also be used in this case. However, laser irradiation conditions such as laser energy, duration, and wavelength must be changed. The conditions for PS laser irradiation are listed in Table 1.

In Fig. 1, the preprocessed Si wafers (after front and rear passivation) were used as the substrate. The Si paste was fully screen printed above the rear surface and then dried at 350 °C. After PS laser irradiation, the localized B doping and heavily doped cladding layer were formed. We measured the printing property by laser microscopy and scanning electron microscopy (SEM) and the B concentration in the Si wafers by secondary ion mass spectroscopy (SIMS). An arrow continuous line pattern with a line width of 40 μm and a pitch of 1 mm was selected as the rear laser pattern. After the redundant Si paste was removed by ethanol, a special Al paste (DuPont PV36A) designed for LBSF formation was screen printed on the rear surface and co-fired with the Si cladding layer to demonstrate the impact of the Si paste further.

The samples were fabricated using the process flow shown in Fig. 2. The substrates used were 156 mm × 156 mm pseudo-square, 180 μm thick, and 1–3 Ω cm CZ p-type wafers with surfaces textured with standard upright random pyramids. After chemical cleaning, the emitter was formed using $POCl_3$ diffusion in a tube furnace. The emitter sheet resistance after this step was 100 ± 5 Ω/□. The phosphorous glass was removed in HF and rear Si was etched in KOH to produce a polished rear surface. Then, a 75–85 nm SiNx layer on the front side was deposited by PECVD. The rear surface was further passivated by a stack of 5–10 nm of AlOx and 80–120 nm SiNx deposited by ALD and PECVD. All of the steps described above were processed using China Sunergy's production line, which can ensure the experimental data more in the same batch.

The samples were separated into two types: SP-PERC and PERC cells. After the Al paste was screen printed on the cells, the samples were fired at different co-firing temperatures within the range of 750–900 °C with an interval of 50 °C. That is, each type was divided into four groups for comparison. Every group contained 100 cells. Then, ten cells whose efficiencies were near the average level were chosen in each group for testing.

To determine the voiding percentage, 50 local contact regions in a cell were observed by SEM as a batch. These 50 points were equally divided into 5 parts, and each part took 10 points from the same cell at an interval of about 25 lines. To ensure that the data were statistically meaningful, 500 points were observed, and the number of voids was counted and then calculated as a percentage.

In calculating the percentage of the voids, the typical microstructure of the PERC and SP-PERC cells on the rear surface can be obtained by SEM. The feature of the eutectic region was mainly studied. Meanwhile, the difference of the minor elements among the Al-matrix layer, Al–Si alloy layer, and the BSF layer were analyzed using energy dispersive spectrometry (EDS). Ten points with adequate LBSF in each cell were chosen for research. These 10 points were uniformly sampled from 50 observed points (2