A simplified and masking-free doping process for interdigitated back contact solar cells using an atmospheric pressure chemical vapor deposition borosilicate glass / phosphosilicate glass layer stack for laser doping followed by a high temperature step

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Abstract

In this paper a simplified approach for the generation of laterally p- and n-doped structures applicable for cost-effective production of interdigitated back contact (IBC) solar cells is presented. We use a stack of doping glasses deposited by atmospheric pressure chemical vapor deposition (APCVD), consisting of borosilicate glass (BSG) and phosphosilicate glass (PSG) on Czochralski-grown (Cz) silicon substrates. A laser process creates the p-doped regions by local liquid phase diffusion of boron from the BSG layer into the underlying molten Cz-Si substrate. Simultaneously, the BSG-PSG stack is removed by laser ablation. In a subsequent high-temperature step, phosphorus diffuses from the remaining PSG-BSG layer into the crystalline silicon substrate under inert gas atmosphere, creating complementary to laser doped areas n⁺-doped regions. By the use of APCVD, phosphorus and boron contents of the doping glasses can be adjusted freely to vary the resulting p- and n-doped profiles. A higher boron content in the BSG layer enhances the diffusion of phosphorus through the BSG, especially at lower diffusion temperatures. The resulting doping profiles are characterized using electrochemical capacitance-voltage measurements and the resulting sheet resistances using the four-point probe method. The amount of minority dopant contamination in n- and p-doped regions is investigated by secondary ion mass spectrometry. Furthermore, transfer length method (TLM)-measurements indicate contactability of the generated doped regions.

KEYWORDS
atmospheric pressure chemical vapour deposition (APCVD), boron, borosilicate glass (BSG), interdigitated back contact (IBC), laser doping, phosphorus, phosphorus silicate glass (PSG), silicon, solar cell

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INTRODUCTION

The concept of interdigitated back contact solar cells represents a significant improvement over conventional cell designs like passivated emitter and rear cell (PERC),1 passivated emitter, rear locally diffused (PERL)2–4 or Al back surface field (BSF)5 concepts. Optical shading losses on the front side are completely eliminated by contacting the cell entirely from the rear side on alternating n- and p-doped regions.6–8 However, the manufacturing processes is still cost-intensive and relatively complicated involving often several diffusion and masking steps.9 With CVD technologies the deposition of doping glasses can be separated entirely from the tube furnace diffusion, opening new possibilities for optimized co-diffusion processes for simultaneous front and rear side doping.10,11 Additionally, laser doping and structuring processes can be implemented prior to tube furnace diffusions avoiding the need of masking steps and allowing for annealing of laser-induced defects.12,13 The goal of this work is the development of a simplified and masking-free manufacturing process for IBC solar cells by use of a high throughput APCVD system14 and a laser process followed by a single high temperature step.

STATE OF THE ART IBC-PROCESSES

Conventional IBC diffusion processes often require two high temperature steps and additional masking and structuring processes, such as photolithography or laser ablation to create the alternating p- and n-doped regions on the rear side. Additional etching and cleaning steps are necessary to remove the deposited glasses and masking layers. Figure 1 (left) shows an exemplary process sequence of the pn-junction formation for IBC solar cells similar to those reported in.9,15 Some additional details in this conventional IBC diffusion process are assumed by the authors, like the silicon nitride (SiNx) masking on the front side. Prior wet-chemical surface preparations, such as saw damage etch, one-sided texturing and cleaning as well as the subsequent surface passivation and metallisation are not shown here. In this process flow the n⁺-doped front surface field (FSF) and the n⁻-doped BSF are formed simultaneously in a POCl₃ diffusion step16 (1a). Phosphorus diffuses into the entire wafer surface, also on the edges and in the areas that later will be p-doped with boron. The deposited PSG is then wet-chemically removed (2a) and a masking layer, for example, SiNx is deposited by plasma-enhanced CVD (3a). This masking layer serves as a diffusion barrier for the subsequent boron diffusion step and for some cell concepts also as an etching barrier. The masking layer is structured by laser ablation so that the emitter regions are exposed to the following boron diffusion (4a). Alternatively, a screen-printed masking layer can be applied covering the BSF regions only. Photolithographic masking processes are also possible,17 but these involve besides the photolithography steps themselves even more wet chemical process steps. The unwanted phosphorus doping in the emitter regions can be etched prior to boron diffusion (not shown in Figure 1). Without this additional etching step, the phosphorus doping in the emitter region must be overcompensated by boron in the subsequent BBr₃ diffusion (5a) potentially limiting passivation quality.18 Finally, the masking layer is then removed entirely (6a).

SIMPLIFIED DIFFUSION PROCESS

Our newly developed and simplified doping process (patent pending) consists of only three main process steps, see Figure 1 (right). First, a PSG glass layer is deposited on the front side using, for example, an APCVD tool (1). This layer later serves as a diffusion source for the formation of the FSF during the high temperature step. A double doping glass stack consisting of BSG and PSG is deposited on the rear side. The glass properties of the PSG and BSG layers can be adjusted individually and adapted to the following high temperature step allowing, for example, for a stronger doping on the BSF (back side) than on the FSF (front side). The APCVD step is followed by a laser doping and simultaneous ablation process (2) for the creation of the p⁺ emitter regions and for...
pre-structuring the phosphorus doping source for the subsequent high temperature step. This laser process is the key element of the process presented here since it eliminates the necessity of masking steps completely. The FSF and BSF are then formed simultaneously in the diffusion furnace (3) by phosphorus diffusion from the PSG doping glasses, on the backside through the BSG. Additionally, potential laser-induced defects can be annealed during the high temperature step. The CVD-PSG on the front side can serve as a multifunctional layer and can therefore remain on the front side and backside for surface passivation.20 However, the rear side emitter regions must be repassivated, for instance, by a thermal oxide that can also be formed during the high temperature step in the tube furnace and a SiNx layer for hydrogen supply21 and as anti-reflective coating. In the following, the laser process and the phosphorus diffusion are described in more detail.

3.1 Laser doped $p^+$ regions

The following detailed microscopic description of the dynamics during the laser process is based on several publications on laser doping22–24 and performed simulations using LCP-Sim.25 During the laser doping process, radiation with a wavelength of 532 nm is absorbed in crystalline silicon mainly close to the surface (absorption length of about 1 μm26). With sufficient energy density (laser fluence) the silicon substrate melts at around 1414 °C leading to a propagating melt front starting from the surface to the bottom reaching its maximum melt depth of 1–2 μm. The doping glasses (here BSG and PSG) transmit the light almost completely and are therefore only heated indirectly by contact with the light absorbing silicon substrate. Consequently, the dopant glasses also start to melt from the glass-silicon boundary towards the top. The dopant atoms (here boron and phosphorus) then diffuse from the liquefied dopant glasses into the silicon melt reaching a depth of about 1 μm after about 1 μs. This is only possible because diffusion coefficients of boron and phosphorus in liquid silicon are many orders of magnitude higher compared to the case in crystalline silicon.27,28 The molten silicon recrystallizes epitaxially,29,30 resulting in a highly doped monocrystalline layer, for example, for the function of an emitter or a BSF. Figure 2 (top) shows the structure of the doping glass stack and the state of initial exposure to laser radiation (0–5 ns). Due to light absorption in the silicon substrate, the BSG layer, directly in thermal contact with the silicon substrate, is heated and liquefied earlier than the PSG layer above, which is further away from the heat source. In addition, the diffusion path for the n-dopants from the PSG to the substrate is longer than for the p-dopants in the BSG. Depending on the used laser fluence, indirect ablation of the glass layers due to silicon evaporation and gas expansion can occur, which stops further diffusion of dopants from the glass layer into the silicon substrate Figure 2 (bottom). With suitable laser parameters and glass properties, the diffusion of boron prevails over that of phosphorus, resulting in p-doped regions. The undesired diffusion of phosphorus in this area can be minimized by an appropriate selection of the boron and phosphorus concentrations in the glasses.

![Figure 2](image-url)

**FIGURE 2** Structure of the borosilicate glass (BSG)-phosphosilicate glass (PSG) doping glass double layer consisting of atmospheric pressure chemical vapor deposition (APCVD) glasses with a SiOx protective capping layer. The BSG layer is in direct contact with the Cz substrate and is heated indirectly via the silicon substrate during the laser doping process (top). The crystalline silicon liquefies and mainly boron diffuses into the silicon melt. Shortly afterwards the doping glass stack is ablated due to partial silicon gas expansion (bottom). This intended effect prevents further diffusion of phosphorus into the p-doped regions during the laser process and pre-structures the doping source for the subsequent high temperature step.
and most important the BSG layer thickness. Optionally, an additional capping layer (here APCVD SiOx) can be applied to protect the doping glasses from external influences such as humidity or other forms of contamination.

3.2 Phosphorus diffusion in high temperature step

For the generation of n-doped regions, which are arranged complementary to the laser treated p-doped regions, a subsequent high temperature step in a diffusion furnace under nitrogen atmosphere is used. Phosphorus diffuses faster within crystalline silicon (c-Si) compared to boron especially at lower diffusion temperatures\(^{31,32}\) and can also diffuse through oxides into the silicon substrate. In contrast, much higher temperatures are required for an equivalent diffusion of boron within c-Si. In addition, BSG is much more permeable for phosphorus than pure SiOx, and the glass transition point is lowered significantly by the amount of boron in the glass.\(^{33,34}\) The different diffusivities of phosphorus and boron within c-Si and the high diffusivity of phosphorus in BSG are used in the described application to drive phosphorus through the BSG into the silicon substrate and thus create n-doped regions. With suitable process parameters, the undesired diffusion of boron can be kept within 100 nm from the surface while the diffusion of phosphorus is dominant therefore leading to an n-doped region. In combination with the previously created p-doped regions, lateral pn-junctions are created, which are required for IBC solar cells (see Figure 3). During this process step, the FSF is formed simultaneously, as mentioned before. A so-called ‘floating emitter’ on the front side is also possible if BSG is applied on the front instead of PSG.

**Figure 3** Illustration of the diffusion of phosphorus during the high temperature step from a borosilicate glass (BSG)-phosphosilicate glass (PSG) layer stack. Phosphorus diffuses through the BSG layer into the crystalline silicon. Low diffusion temperatures minimize the in-diffusion of boron into the silicon substrate. The previously p-doped areas created by laser doping are only slightly affected by the high temperature step if the doping glass layer has been ablated there completely. Potential laser-induced defects in the p-doped regions can be annealed at the same time.

4 EXPERIMENTAL

4.1 Sample Processing

For proof-of-principle we used 5 × 5 cm\(^2\) p-type Cz silicon wafers (1–2 lpcm) with (100) crystal orientation. At first, the saw damage was etched and the surface was chemically polished and cleaned. The smooth surface of the samples is not a prerequisite for the function of the process, but allows for more exact measurement of the layer thicknesses by ellipsometry, as well as a more precise glass analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES).\(^{35}\) The doping glasses including a SiOx capping layer were deposited using a SCHMID APCVD tool.\(^{36}\) The nominal boron and phosphorus content in the glasses was varied for the different process groups. Subsequently, a part of the sample surface of each sample was laser-treated to create a p-doped region and simultaneously ablate the glass layers above. The laser process was carried out with a 532 nm laser with FWHM pulse duration of about 40 ns. To produce the n-doped regions, the samples were then subjected to a high-temperature step with two different plateau temperatures (850°C and 925°C) in a Centrotherm quartz tube furnace using an N\(_2\) inert gas atmosphere. Note that the used p-type doping differs from the introduced process flow (Figure 1) and was chosen to enable sheet resistance measurements of the n-doped areas (phosphorus diffusion). Additionally, alkaline textured and planar M2 n-type Cz samples were used for contact resistivity measurements using transfer length method (TLM). In this case, the n- and p-doping was generated on the entire wafer area according to the described process. After removal of remaining glasses, the surface has been thermally oxidized in a quartz tube furnace. The samples received a layer stack commonly used for solar cell fabrication, by depositing 60 nm SiN_xH via plasma-enhanced chemical vapor deposition (PECVD) onto the thermal oxide. The TLM structures were screen-printed onto the n-doped and p-doped samples using commercially available Ag and AgAl paste, respectively. The contacts were sintered at variable peak temperatures in a Centrotherm belt furnace while the temperature profiles were tracked on reference samples.

4.2 Sample characterization

After the laser treatment and high-temperature step, the sheet resistances \(R_{\text{sheet}}\) were determined in the n-doped areas by four-point probe (4PP) measurements. However, the sheet resistance measurement alone cannot determine the polarity type of doping. After HF cleaning, doping profiles (electrochemical capacitance-voltage [ECV]/secondary ion mass spectrometry [SIMS]) were recorded, which provide further information about the shape and polarity of the electrically active dopants. The net doping \(n_{\text{net}}\) is a measure of the difference between electrically active p- and n-doping. For these measurements, the remaining doping glasses were previously removed with diluted HF. The dopant concentrations of the glasses given in the following were estimated theoretically on the basis of the gas flows
used in the APCVD tool and may deviate significantly from the actual mass percentage of the deposited glasses. Nevertheless, they are in good approximation proportional to the real mass percentage and atomic density and therefore allow for a qualitative comparison between the individual glass recipes. This has been investigated in additional ICP-OES glass measurements for comparable glass recipes.37

5 RESULTS AND DISCUSSION

5.1 Sheet resistance (n+-doping)

Figure 4 shows the measured sheet resistances of the n+-doped regions plotted versus four different nominal phosphorus concentrations in the PSG for two different diffusion temperatures and for two different boron contents in the BSG. As expected, the measured sheet resistance of the n+-doped regions decreases with an increasing phosphorus content in the PSG and higher diffusion temperature. The dependence of the n+-doping on the boron content of the BSG may appear less intuitive at first. Here, a higher boron content also leads to a reduced sheet resistance, although additional boron atoms as p-dopants partially compensate the dominant n-doping. However, an increased boron content also leads to an increased phosphorus diffusion through the BSG as described by Gloger et al.38 The comparison with pure SiO₂ instead of BSG makes clear that SiO₂ even represents an effective diffusion barrier for phosphorus and only the boron content in the glass makes the oxide more permeable for phosphorus (see data points at the top right in Figure 4). The reason for this behaviour is a significantly reduced melting or glass transition point of borosilicate glasses compared to pure quartz glasses (SiO₂).34 With increasing softening of the BSG glass, the diffusivity of impurity atoms such as boron or phosphorus increases. The more boron is present in the glass layer, the softer and more permeable the glass becomes for phosphorus at a given temperature.39,40

5.2 n+ ECV profiles (furnace diffusion)

The n-type doping profiles generated in the high temperature step generally show a kink-tail shape typical for solid state phosphorus diffusion in diffusion furnaces.

For a diffusion temperature of 925°C, profile depths of more than 700 nm are achieved with resulting low sheet resistances of 30–50 Ω/□ (see Figure 5). The profile depth is defined here as the depth where the doping concentration drops below 1 x 10¹⁷ cm⁻². At a temperature of 850°C and low BSG boron content, phosphorus diffusion is strongly inhibited, resulting in very flat profiles with low surface concentration. This can be explained by the previously described dependency of phosphorus diffusivity in BSG from its boron content. Relatively high sheet resistances of about 125–2000 Ω/□ are derived from the net dopant concentrations and the profile shape deviates more from the typical profile shape. If the nominal boron content in the BSG is increased to 6%, pronounced kink-tail profiles with sheet resistances of about 30 Ω/□ (925°C) and about 62–132 Ω/□ (850°C) are created even at lower diffusion temperature (see Figure 6). This confirms the hypothesis that the diffusion of phosphorus through BSG increases with the boron content of the BSG.

5.3 n+ SIMS profiles (furnace diffusion)

In addition to ECV profiling, simultaneous P and B SIMS measurements have been performed for selected samples. Figure 7 shows the SIMS and ECV results of two selected n+ doping profiles produced from a BSG 6% and PSG 6% doping glass stack with two different diffusion temperatures.

Overall, the phosphorus profiles measured by SIMS are in good agreement with the n+ ECV profiles although they are not identical. Near the surface the actual phosphorus concentration measured by SIMS can be higher than the net n-dopant concentration measured by ECV because of inactive phosphorus atoms especially for high
concentrations (>10^{20} \text{ cm}^{-3}). Another reason can be partial compensation of n-doping due to underlying electrically active boron atoms (p-dopants), see orange curves in Figure 7. For greater depths (>50 \text{ nm}), the ECV curves are mostly slightly above the SIMS curves, which can be explained by measurement uncertainties, for example, due to surface roughness and therefore limited measurement calibration or sample in-homogeneities. With our multi-glass-layer approach unwanted boron doping during the high temperature step is inevitable to some extent. A possible solution would be an additional etch-back (EB) step (as described in 41) after the high temperature step, that would remove the recombination-active first 120 \text{ nm} with significant boron contamination and high (in-active) phosphorus concentration (see dashed line in Figure 7). For the higher diffusion temperature (925 \text{ C}), the resulting n\textsuperscript{−} profile would still be potentially well contactable with a remaining surface concentration of more than 4 \times 10^{19} \text{ cm}^{-3}.

5.4 | p\textsuperscript{+} ECV profiles (laser doping)

Figure 8 shows the ECV doping profiles of the laser doped p\textsuperscript{+} regions in linear representation. Characteristic for laser doping, the profiles are rather box-shaped with a maximum depth of about 1.4 \text{ \mu m}. Net surface doping concentrations of up to 3 \times 10^{19} \text{ cm}^{-3} are reached.

With increasing phosphorus content, the doping concentration decreases significantly, especially near the surface. This can be explained by the increasing compensation of the p-doping by in-diffusion of phosphorus atoms. Apparently, phosphorus diffuses through the 20-nm-thick BSG layer in significant amounts already during the short time frame available during the laser doping process. At a high phosphorus content (12\%) a reduction of the doping concentration near the surface is clearly visible due to the partial compensation by phosphorus. In addition, the net dopant dose (net dopants per cm\textsuperscript{2}) is indicated, which was determined directly by the ECV measured profiles. Accordingly, with PSG 12\% compared to PSG 6\% an additional 2/3 of the active boron dopants are compensated by phosphorus.

5.5 | p\textsuperscript{+} SIMS profiles (laser doping)

Figure 9 shows the p\textsuperscript{+} ECV doping profile as well as the atomic concentrations of phosphorus and boron measured by SIMS. The doping profile was produced by our laser process with a BSG 6\% and PSG 6\% stack.
The SIMS measurement reveals a significant phosphorus background, which represents about 16% of the boron concentration for a depth between 50 and 200 nm and about 4% for a depth greater than 1 μm. Closer to the surface, the phosphorus concentration exceeds the concentration of boron. Still, the ECV measurement results in a net p-doped profile. This means that the majority of incorporated phosphorus atoms near the surface (<30 nm) remained inactive. One can conclude, that the diffusion of phosphorus during the laser process was fast enough to penetrate the BSG layer of about 20 nm in a significant amount. Even with this unwanted phosphorus doping, the ECV measurement still results in a p⁺-doping profile. With a closer look at the boron concentration measured with SIMS, it is evident that there must be a huge amount of electrically inactive boron, since the difference between the p⁺- ECV doping profile and the SIMS boron profile cannot be explained by the compensating phosphorus only. The dashed line in Figure 9 indicates the calculated difference of boron concentration minus phosphorus concentration that is almost identical with boron concentration in a logarithmic scale for depths greater than 30 nm. An etch-back step until 120 nm as suggested for the n⁺-doped profiles would also be beneficial for the p⁺- profiles, as the spike of phosphorus contamination at the surface could be removed and the boron profiles are very flat in the range of about 30–400 nm. Additionally, a thicker BSG layer could help to lower the amount of unwanted phosphorus doping in the p⁺- profile, as the laser ablation effect might interrupt the diffusion before phosphorus diffuses through the thicker BSG in significant amounts. However, further investigations are necessary to test this approach.

5.6 | Combination of feasible p⁺ and n⁺ profiles for the IBC rear side

Figure 10 finally shows two selected pairs of p⁺- and n⁺-doped profiles, which were generated on M2 flat and textured Cz substrates by the described process, removal of dopant glasses and a subsequent thermal oxidation. The tube furnace diffusion and the additional thermal oxidation only leads to a redistribution of dopants within the laser doped profiles. The ECV measurements take the surface enlargement factors A, for different sample surfaces into account, which were determined by atomic force microscopy (AFM). The n⁺-doped textured substrates have a surface enlargement factor of A₁.45, while the flat n⁺-doped area is in good approximation equal to the projected area (A₁). Laser processing on the textured substrates leads to planarization resulting in A₁.08, while the initially flat substrates remain mostly flat after laser processing with A₁.03.

Both laser-doped and thermally diffused doping profiles exhibit higher depth on the textured substrate. However, the reasons are different. In case of laser doping (p⁺), the textured surface results in a greater absorption of the laser radiation and thus a higher melting and doping depth. However, for the furnace diffused samples (n⁺), the increased surface roughness results in a thinner BSG layer compared to the smooth surface. This in turn ensures that the phosphorus passes through the BSG layer more quickly and, in addition, less phosphorus remains in the BSG during intermixing of the glasses. Nevertheless, all resulting profiles have a sufficient surface concentration, that should allow contacting with commercial screen-printing pastes. This will be discussed in more detail in the next section.

5.7 | Contact resistivity

Samples with the doping profiles shown in Figure 10 were used to demonstrate the contactability in the case of compensated doping.

Figure 11 shows the contact resistivities obtained on p⁺ surface versus the peak firing temperatures for the flat and textured initial
substrates. Contact resistivities mostly in the range of about 4–10 mΩcm² are obtained for the flat samples, whereas those for the textured samples are mostly in the range of about 2–7 mΩcm². No obvious trend can be found over the temperatures considered. Since the laser process strongly changes the surface structure, ‘flat’ and ‘textured’ refer to the condition before laser doping. In fact, both sample types show a rather similar surface structure after the laser step. Therefore, it is assumed that the differences in contact resistivities are mainly caused by the differences in doping levels. In contrast, the surface structures remain unchanged during thermal diffusion, which is why differences in the contact resistivities of the non-lasered n⁺-samples can also be attributed to the different topology.

As shown in Figure 12, lower contact resistances on the n⁺ surface are obtained on textured surfaces. Comparable contact resistances can also be achieved on smooth surfaces, but often with deviations exceeding 15 mΩcm². Significantly lower, but still non-optimal resistivities in the range of 5 mΩcm² and smaller can be obtained at the lowest temperature shown of 767 °C. Although there is still room for improvement, a general problem with contacting is not apparent.

6 | SUMMARY

With the available results, a first proof-of-principle of a new and simplified doping process was demonstrated which is suitable for creating both p-type and n-type doping areas required for the IBC solar cell rear side within only three steps: In the first step, a doping glass stack consisting of BSG and PSG is deposited by a fast APCVD process. In the second step, a laser doping process creates the dominantly p-doped emitter regions and simultaneously structures the glass layer stack for the subsequent furnace diffusion step by laser ablation. For the p-type emitter, higher surface concentrations are achieved for a higher boron concentration in the BSG (6%) and a lower phosphorus concentration (6%) in the PSG as expected. In the third step, an n-doped BSF is created by tube furnace diffusion where the diffusion of phosphorus from the PSG layer through the BSG dominates over the diffusion of boron from the BSG. The approach allows to tune the n⁺-doped BSF regions independently from the laser doped p⁺-regions by adjusting the diffusion temperature.

ECV measurements of the n-doped regions reveal, that a higher boron concentration in the BSG enhances the diffusion of phosphorus through the BSG. This effect is more significant for lower diffusion temperatures. With a higher boron concentration (6%) and lower phosphorus concentration (6%) we achieved a p-type emitter with an active surface doping concentration of about 3 10¹⁹ cm⁻³.

For higher boron content, all n-type BSF doping profiles show a kink-tail profile shape with high active surface doping concentration above 10²⁰ cm⁻³. This allows for additional etch-back steps to remove unwanted boron doping near the surface. The resulting lower dopant concentration at the surface should still allow good contactability. As shown in the last section, even without an etch-back step, slightly lower doping profiles can in principle enable low contact resistivities and a general problem regarding contacting cannot be identified.

However, more research is necessary to further reduce the amount of unwanted phosphorus doping within the laser doped boron profile. One attempt could be the use of a thicker BSG layer to minimize phosphorus diffusion during the laser doping process.

By adjusting the laser parameters, the depth and shape of the p⁺-doping profile can be varied to create a selective emitter structure. The shape of the profiles can be further optimized with the choice of glass parameters.

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