

Comparison of Laser-Doped Emitters from As-Deposited and Thermally Diffused APCVD Doping Glasses on Silicon Substrates

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Abstract. In this comparative study, atmospheric pressure chemical vapor deposited (APCVD) silicate glasses are used as a doping source for laser drive-in applied to mono-crystalline silicon under three conditions: First, laser drive-in from APCVD glasses after being heat treated in a tube furnace, *i.e.*, after forming a shallow emitter; second, laser drive-in from as-deposited APCVD glasses newly deposited after removing the one used to form a shallow emitter; and third, laser drive-in from as-deposited APCVD layers directly on the Si wafer with only a base doping below 10^{16} cm^{-3} . We analyze sheet resistances and doping profiles after laser-doping of all three approaches within a wide laser parameter space, using APCVD phosphosilicate glass (PSG) and borosilicate glass (BSG) as doping sources. We found that in general, laser doping from as-deposited APCVD doping glasses creates higher surface doping concentrations compared to laser doping from thermally treated APCVD glasses. The presence of shallow emitters ($170/146 \Omega/\square$) before laser-doping leads to about 100–200 nm deeper doping profiles compared to laser-doping from glasses on the base substrate. With as-deposited APCVD layers, surface concentrations above $5 \cdot 10^{19} \text{ cm}^{-3}$ (P) and about $2 \cdot 10^{19} \text{ cm}^{-3}$ (B) allow for low-ohmic silver contacts. Low sheet resistances of about $18 \Omega/\square$ (P) and $42 \Omega/\square$ (B) are opening wider parameter windows for laser fluence reduction in order to avoid laser-induced defects compared to the application of heat treated APCVD glasses for laser drive in.

INTRODUCTION

The approach of creating laser-doped selective emitters from gas phase diffused layers is by now a well-established topic within the photovoltaics community [1, 2]. In addition, new approaches of creating laser-doped selective emitters using CVD layers, such as BSG and PSG were investigated for solar cell applications [3]. The selective emitter approach represents a compromise between sufficiently high lateral conductivity and the lowest possible surface recombination of free charge carriers due to the dopant-related defects in the metal contact area. The highly doped area under the metal fingers ensures in addition a low contact resistances between the metallization and silicon substrate. Furthermore, a deeper emitter doping profile under the front side metallization is beneficial to avoid electrical shunts to the base substrate. This can be accomplished by laser doping from CVD doping glasses such as PSG or BSG. One advantage of CVD over gaseous diffusion sources is the separation of the layer deposition from the diffusion step, which allows performing the laser doping process *prior* to the following high temperature steps [4]. These high temperature steps, such as the creation of a shallow emitter, could then anneal simultaneously possible laser-induced defects. In addition to these advantages, APCVD systems allow for very high throughput of industrial solar cell production. Since laser doping from as-deposited APCVD layers has not yet been well investigated, the following questions arise:

- Are as-deposited doping glasses as effective for laser doping as thermally diffused doping glasses?
- What effect does the substrate doping have on the laser doping process?
- What are the differences for laser doping when PSG or BSG is used?

To clarify these questions, a detailed comparison of electrical properties from laser-doped emitters is presented.

EXPERIMENT

We use p-type and n-type Czochralski silicon (Cz-Si) material of 2-8 Ωcm base resistivity in $\langle 100 \rangle$ -orientation. The saw damage was removed and an alkaline surface texture was applied. The p-type samples then received a 60 nm APCVD PSG layer with about 8% phosphorus (groups P1–P3, see Fig. 1), while on n-type samples an APCVD BSG layer of 40 nm with about 6% boron was deposited (groups B1–B3). Additionally, all samples received a SiO_x layer of 10–20 nm thickness to seal the PSG/BSG. Part of the samples (groups P1/B1 and P2/B2) were then temperature treated in nitrogen atmosphere for 60 min in order to create a shallowly doped emitter by thermal diffusion in a tube furnace. The BSG samples received an additional thermal oxidation of 15 min. For reasons of comparison, group P2/B2 received a freshly deposited PSG/BSG layer after diffusion, respectively, similar to the initially deposited layer before diffusion. Groups P3/B3 received no diffusion and remained with the as-deposited APCVD layer on the base substrate. All samples were then laser-treated by a laser with a wavelength of 532 nm and a pulse width of around 40 ns to create the laser-doped areas.

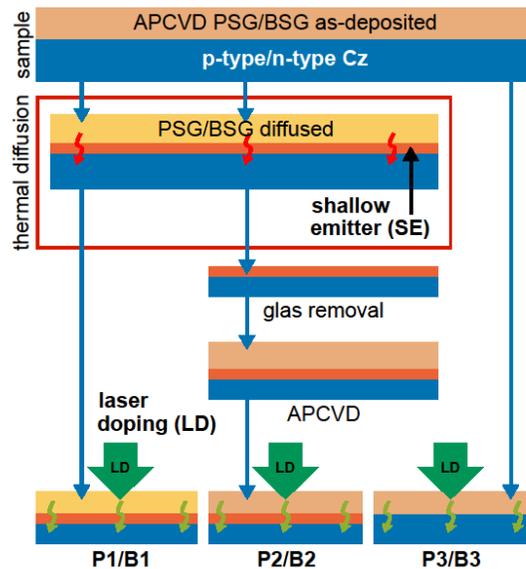


FIGURE 1. Process flow diagram of the steps performed to generate doped emitters by tube furnace diffusion and laser doping from the APCVD glasses PSG (group P1, P2, P3) and BSG (group B1, B2, B3).

Investigations of Sheet Resistances Using the New *ParamSearch*-Approach

To characterize the resulting sheet resistances in dependence of laser parameters, a matrix of 81×81 laser-treated areas each of about $1.6 \times 1.6 \text{ mm}^2$ with quasi-continuous laser parameter variations was applied on the $156 \times 156 \text{ mm}^2$ Cz-Si substrate samples. We investigate laser parameters in the range of 0–8 W (average power) and a distance of the sample to the beam focus of 0–6 mm (defocus). The spatial distance between the laser pulses was kept constant at $16 \mu\text{m}$. We use an automated four-point probe measurement setup to measure the sheet resistance R_{sheet} on 41×41 measurement positions and transform the coordinates into average power and defocus values. The resulting laser parameter-dependent overview of sheet resistances (hereinafter referred to as *ParamSearch* field) is shown in Fig. 2. Additional samples with $30 \times 30 \text{ mm}^2$ laser doped fields were prepared to measure the sheet resistance more precisely and investigate the doping profiles using electrochemical capacitance-voltage (ECV)-measurements.

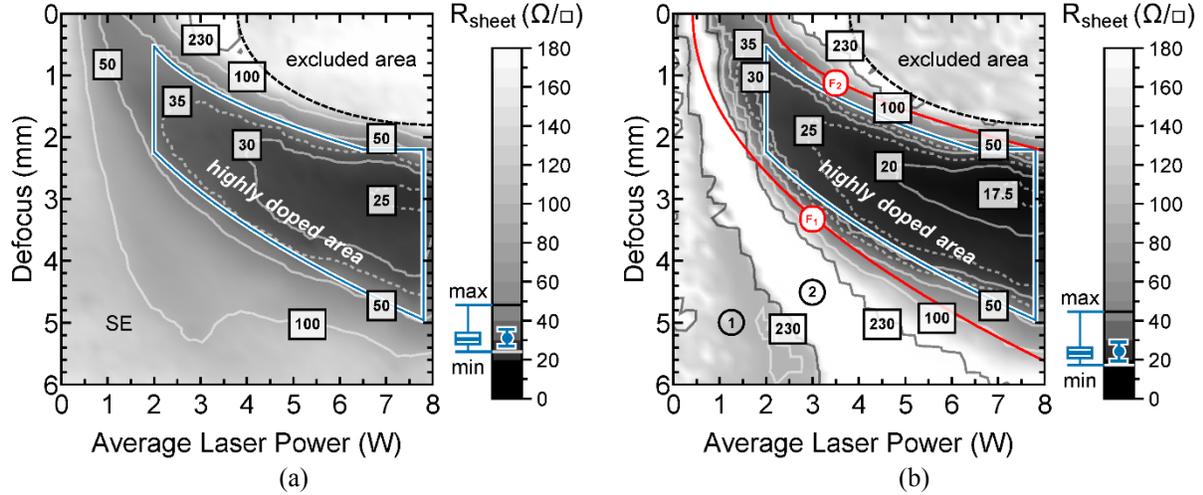


FIGURE 2. Comparison of the measured sheet resistances of laser-treated areas between group P1 (a) using tube furnace-diffused APCVD PSG on a shallow emitter (SE) and group P3 (b) using as-deposited APCVD PSG on base substrate. Sheet resistances are shown in grayscale and additional contour lines indicate areas of comparable R_{sheet} . Parameter combinations with very high fluencies have been excluded to avoid ablation. Box-whisker markings (min and max) refer only to data points within the *highly doped area*.

RESULTS AND DISCUSSION

The small step size between laser parameters within the *ParamSearch* field leads to a quasi-continuous variation of laser fluence. It is visible, that areas of comparable sheet resistance generally follow *equifluential lines* F_i (lines of same laser peak fluence, with $F_1 < F_2$), exemplarily shown in Fig. 2b. This means that the laser fluence is a crucial parameter for the resulting electrical properties of the laser-doped layers. It is known that certain physical effects such as melting of silicon, ablation of dielectric layers, formation of laser-induced defects or evaporation of silicon only occur above certain threshold fluencies [5]. This explains why different regions of sheet resistance are observed on the Si wafer. In the case of laser doping from as-deposited PSG on base substrate, one can see clearly several distinguishable regions of sheet resistance mainly separated by certain threshold fluences (see Fig. 2b). The peak fluences stated in the following were derived using standard Gaussian beam theory. Beam properties needed for fluence calculation such as beam waist, Rayleigh length and pulse energy were determined using subsequent beam profiling and thermal power measurement. The effective overlap of the molten areas varies within the *ParamSearch* field, as diameters of molten areas are dependent on defocus and average laser power.

Common Observations for PSG and BSG

The following observations describe general physical effects and differences in measured sheet resistances within the *ParamSearch* field using the example of PSG. However, they are also representative for results of BSG.

Peak fluences of below 0.6 J/cm^2 per laser pulse do not create a measureable emitter doping concentration. In this region (marked with (1) in Fig. 2b), the four-point-probe system only determines the effective sheet resistance of the base substrate. In case of laser doping of temperature treated APCVD PSG layers after tube furnace diffusion, the formed shallow emitter of $170 \text{ } \Omega/\square$ (P) remains unchanged from laser treatment in terms of sheet resistance. Similar sheet resistances are observed for the excluded area, where no laser treatment was applied. A possible explanation for this observation is that the laser fluence in this region is lower than the threshold fluence needed for melting of crystalline silicon. Melting of silicon is a prerequisite for successful laser doping with nanosecond laser pulses because liquid phase diffusion is necessary to reach sufficient dopant transportation within the treatment time. The diffusion coefficients for phosphorus and boron in liquid silicon are about 6 orders of magnitude higher compared to Si in solid state [6]. With slightly higher fluences, the sheet resistance of the previously generated shallow emitter is reduced (P1), while the measured sheet resistance for laser doping with as-deposited doping glasses on base substrate strongly increases (P3), even above the measurement range of the four point probe of $500 \text{ } \Omega/\square$ (see (2) in Fig 2). This can be understood as a measurement problem, because the threshold fluence for

laser doping is only partly reached within a narrow area in the center of the Gaussian laser spots. Therefore, no continuous emitter can be formed in this range of laser fluences with the selected lateral pulse distance of 16 μm . The tips of the four-point-probe measurement system would be partly connected to this isolated emitter regions which blocks the measurement current, since one pn-junction is always oriented in the reverse direction to the current. Even if continuous emitters can be created in that region closely above the threshold fluence, the resulting emitter would be very narrow and lowly doped with high resulting sheet resistance. In contrast, in case of group P1 these narrow emitter regions are embedded in the previously created shallow emitter and therefore contribute only to a higher conductivity and lower sheet resistance. However, further investigations of lateral doping profiles of single and partly overlapping laser pulses need to be carried out to prove this hypothesis.

With higher laser fluences a *highly doped area* with sheet resistances lower than 50 Ω/\square (P) and 90 Ω/\square (B) is observed for the used PSG/BSG layers. This represents the process window that is potentially suitable for laser doping for the generation of highly doped regions for selective emitters. In this area the surface of the originally textured samples is completely molten and very smoothly solidified with high reflectivity.

Above approximately 7 J/cm² (peak fluence), the sheet resistance starts to increase with a large gradient, which can be interpreted as an increasing crystal damage and removal of material due to laser ablation and evaporation (resp. sublimation) of silicon. This can be also observed as dust emission during laser processing visible by eye and very rough surface structures visible in scanning electron microscope (SEM) images (not shown here).

Beside the strong correlation of sheet resistances to laser fluences, lower sheet resistances are accomplished for higher defocus values especially within the mentioned *highly doped area*. This can be explained by multiple laser treatment due to higher grade of lateral overlap between the wider Gaussian laser pulses [7].

Phosphorus-Doped Emitters

For all three groups, phosphorus emitters show sheet resistances <50 Ω/\square within a defined *highly doped area* (see Fig. 2). With optimized laser parameters, the minimum sheet resistance value for group P1 was 26.1 Ω/\square and for group P3 19.2 Ω/\square , both measured within large homogeneously laser-doped areas. This shows that the APCVD PSG layer after diffusion is a less effective source for laser doping than as-deposited APCVD PSG. Group P2, also with a shallow emitter, but with a freshly deposited APCVD PSG layer, shows comparable results to group P3 with 17.5 Ω/\square . This means, that the previously diffused shallow emitter only gave a small contribution to sheet resistances after the laser-doping process. The ECV doping profiles from the samples considered above show higher surface doping concentrations for as-deposited APCVD PSG of about $n_{P2, P3} = 5.4 \cdot 10^{19} \text{ cm}^{-3}$ compared to $n_{P1} = 3.2 \cdot 10^{19} \text{ cm}^{-3}$ from furnace-diffused PSG (see Fig. 3, left). With a previously diffused shallow emitter, phosphorus doping profiles of P1 and P2 are about 100 nm deeper compared to laser doping on base substrate (P3).

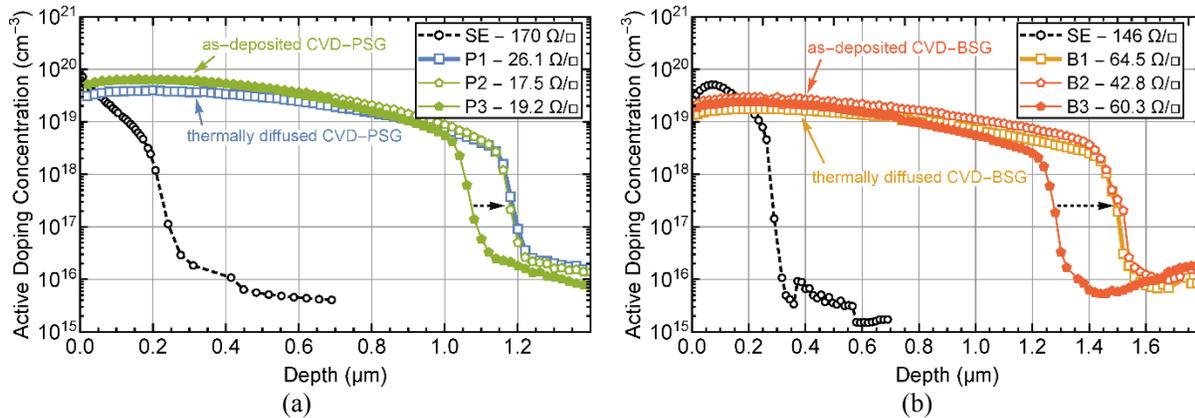


FIGURE 3. ECV-measured doping profiles of laser-doped layers using APCVD PSG (a) and APCVD BSG (b) as laser doping source. Thermally diffused APCVD layers P1/B1 create lower active doping concentrations than as-deposited layers (P2/B2 and P3/B3). Doping depth depends only on the previous substrate doping, meaning base doping (P3/B3) or shallow emitters (SE), for P1/B1 and P2/B2.

Boron-Doped Emitters

For APCVD BSG compared to APCVD PSG the *highly doped area*, i.e. laser parameter sets leading to sheet resistances lower than $90 \Omega/\square$, is narrower and shifted to higher fluences (see Fig. 4). For BSG, higher sheet resistances are observed compared to PSG. Since the diffusion coefficient of phosphorus in liquid silicon $D_{P,liquid} = (5.1 \pm 1.7) \cdot 10^{-4} \text{ cm}^2/\text{s}$ [5] is about a factor of two higher than the diffusion coefficient of boron in liquid silicon ($D_{B,liquid} = (2.4 \pm 0.7) \cdot 10^{-4} \text{ cm}^2/\text{s}$ [5]), liquid phase diffusion is therefore faster for phosphorus than for boron. Group B1, after tube furnace diffusion of an emitter ($136 \Omega/\square$), and B3, with as-deposited BSG, show comparable minimum sheet resistances of about $60 \Omega/\square$. With an APCVD BSG layer newly deposited after tube furnace diffusion (B2), *minimal* sheet resistances are 18-22 Ω/\square lower compared to B1 and B3. In addition, *average* sheet resistances within the *highly doped area* of B2 are about $23 \Omega/\square$ lower compared to the other groups. This means, that in contrast to APCVD PSG, the priorly diffused emitter from APCVD BSG contributes clearly to the resulting laser-doped emitter. ECV measurements reveal that the presence of this emitter doping leads to about 200 nm deeper doping profiles compared to laser doping on base substrate (see Fig. 3b). Both groups B1, with diffused BSG, and B2, with as-deposited BSG, have emitter depths of about $1.5 \mu\text{m}$. This means, that the reduction in sheet resistance comparing as-deposited BSG with diffused BSG originates only from higher doping concentrations.

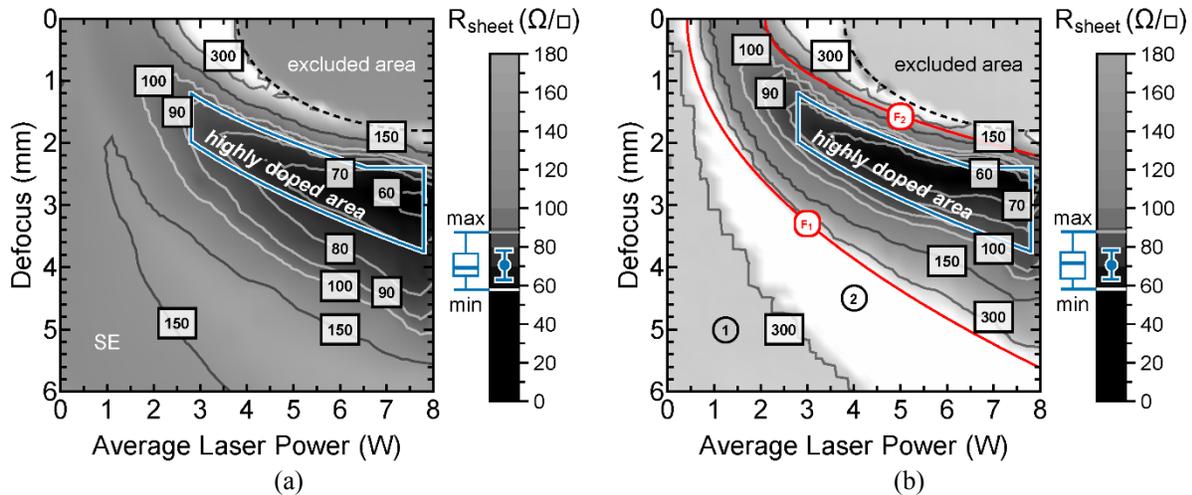


FIGURE 4. Comparison of measured sheet resistances after laser doping as a function of laser parameters between process group B1 (a) using temperature treated APCVD BSG for laser doping after formation of a shallow emitter and process group B3 (b) using as-deposited APCVD BSG on base substrate. Equifluential lines with $F_1 < F_2$ indicate similar laser pulse fluences.

CONCLUSIONS

The investigation of laser-doped emitters from as-deposited and thermally diffused APCVD doping glasses has shown that higher surface dopant concentrations can be achieved with as-deposited PSG and BSG layers compared to APCVD glasses after diffusion. This leads to lower possible sheet resistances for laser-doped emitters compared to high temperature treated APCVD doping glasses. One possible reason is that the dopant concentration within the glasses could be lower after diffusion due to emitter formation and possible diffusion of dopants into the SiO_x capping layer. Additionally chemical composition, density and optical properties can change during high temperature steps [8]. However, further investigations and simulations are needed to quantify the changes in BSG layer properties and their effect on liquid phase diffusion during the laser doping process.

The presence of shallow emitters diffused before laser doping can increase the depth of laser-doped emitters compared to laser doping on the base substrate. The used characterization method for sheet resistances depending on laser parameter power and defocus revealed clear correlations with certain threshold fluences. Above a peak laser fluence of about $2\text{-}3 \text{ J}/\text{cm}^2$ a highly doped area could be created. With higher peak fluences above $7 \text{ J}/\text{cm}^2$ sheet resistances increase again due to material removal. With the very low reachable sheet resistances of about

19 Ω/\square (P) and 60 Ω/\square (B) as well as sufficient surface doping concentrations for contacting, laser doping from as-deposited APCVD doping glasses can be a promising process for current silicon solar cell concepts.

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