Selective Laser Doping From Boron Silicate Glass

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Abstract

Laser-assisted diffusion of dopants is a promising way to produce selective doping structures such as selective emitters or localised BSF with a reduced number of technological steps. This paper discusses laser-induced selective diffusion of boron from two types of borosilicate glasses (BSG) produced either by low-pressure diffusion using a BCl\textsubscript{3} gas source or deposited by PECVD from a trimethylborate (TMB) liquid source. Laser parameters were optimised for efficient heat-assisted diffusion of boron atoms with reduced damage to the silicon substrate. Sheet resistance variation of about 60 ohm/sq was measured.

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1. Introduction

Laser processes are becoming more present in the Photovoltaic industry as they offer many opportunities. Lasers have been used successfully to achieve high efficiency p-type solar cells with selective phosphorus emitter and/or aluminium local back surface field \cite{1,2}. Laser-assisted diffusion of boron has not been so extensively studied. However, controlled boron doping is a key procedure to produce selective emitter in n-type silicon and back surface field in p-type silicon. In this paper, we present a preliminary study of selective laser doping from borosilicate glass. Borosilicate glass formation was either carried out at low pressure using BCl\textsubscript{3} gas source in LYDOP\textsuperscript{TM} furnace (Semco-Engineering)
or deposited by PECVD from trimethylborate, nitrous oxide and silane precursors [4]. Borosilicate glass obtained by thermal diffusion can be used to produce selective emitters on n-type cells in the same way as phosphosilicate glass (PSG) is used as doping source for selective emitters on p-type cells. On the other hand, BSG deposited by PECVD can be used to implement boron localized back surface field on p-type cells (Fig. 1). Laser treatment is particularly interesting as boron diffusion requires high temperature treatment, often above 960 °C in order to obtain high dopant concentration and sufficient diffusion depth [3]. This range of temperature maintained during 15 to 30 minutes might induce structural defects, particularly in multicrystalline silicon.

It is known that, exposed to air atmosphere, boron oxide slowly absorbs water and reverts to boric acid. In order to avoid deterioration of the BSG layer and facilitate initial tests, silicon nitride (SiNₓ) or silicon oxide (SiO₂) protective coatings deposited by PECVD were used. In the case of BSG obtained by thermal diffusion, samples without protecting coatings were also used to approach the final process. Various laser fluences were investigated. Laser doping process was characterised by means of sheet resistance and SIMS measurements. The laser used is a frequency tripled Nd:YAG laser with a Gaussian profile, a wavelength of 355 nm and a pulse duration of 10 ns.

2. Laser doping from borosilicate glass obtained during thermal diffusion

In the case of a borosilicate glass obtained by thermal diffusion (Lydop), the growth of the BSG layer was followed by a high temperature step (above 925 °C), leading to the formation of an initial boron emitter at the silicon surface. Laser treatment was used to decrease locally the sheet resistance.

![Fig. 1. Laser-induced diffusion processes with PECVD BSG and Lydop BSG](image1)

![Fig. 2. Sheet Resistance versus laser fluence on monocrystalline Si, textured or polished, with borosilicate glass formed during thermal diffusion (Lydop process). SiNₓ protective coatings were deposed by PECVD.](image2)
Fig. 2 shows the evolution of the sheet resistance with the laser fluence measured on polished and textured n-type monocrystalline Si wafers with a $75 \, \Omega$/sq initial boron emitter. Samples were covered by a BSG layer deposited during the thermal diffusion and in some cases by a subsequent PECVD SiNx protective layer with a thickness of 75 nm. The minimum sheet resistance was around $30 \, \Omega$/sq in all samples.

Surface texturation does not seem to have an important impact on the final sheet resistance. The PECVD SiNx protective layer alters the sheet resistance evolution with the incident laser fluence. For fluence lower than $0.3 \, \text{J.cm}^{-2}$, the decrease of the sheet resistance is faster with a borosilicate glass layer without protecting coating. Previous work on phosphorus diffusion from a phosphosilicate glass showed similar behaviours [5], which can be explained by the thermal properties of the different stacks (mostly the thermal conductivity) and by the different reflection coefficients of the surfaces. Moreover, SIMS profiles showed a more effective doping process with BSG layer without protective coating (Fig. 3).

![Fig. 3. SIMS profiles obtained with Lydop BSG](image)

SIMS profiles obtained on samples without silicon nitride show a Gaussian shape whereas profiles measured on samples with protective coatings show a shape closer to the reference profile. This difference can be explained by a greater laser interaction in the first case, leading to a redistribution of boron atoms in a deeper melted zone. The high doping level at the silicon surface (more than $5 \times 10^{21}$ atoms/cm$^3$) suggest the presence of SiB.

3. Laser doping from borosilicate glass deposited by PECVD

Laser-induced diffusion from a PECVD BSG layer capped with a 100 nm SiOx layer on n-type CZ monocrystalline silicon wafers showed sheet resistance variation around $100 \, \Omega$/sq and a lower limit of $60 \, \Omega$/sq with a fluence of $0.7 \, \text{J.cm}^2$. This very encouraging result makes possible the implementation of localized BSF on p-type cells, using PECVD BSG. The evolution of the sheet resistance with the incident laser fluence is very similar to that observed with Lydop BSG. The typical laser fluence needed for effective doping was also around $0.6 \, \text{J.cm}^2$, comparable to the one used for phosphorus diffusion. SIMS
measurements for the typical doping profiles obtained with laser-assisted diffusion (Fig. 4) show that the concentration of boron is however one order of magnitude lower than with the Lydop BSG. The higher the fluence is, the longer and deeper the melting of silicon, thus resulting in a deeper diffusion. These results are comparable to those obtained in recent literature [9] with other selective doping process like sputtered precursor [6], liquid source [7] or laser chemical processing [8]. Finally, preliminary tests without a protective coating over the BSG deposed by PECVD showed inconsistent results due to a rapid deterioration of the doping layer.

![Fig. 4. SIMS profiles obtained after laser treatment and before thermal treatment on a PECVD BSG / SiO₂ stack](image)

4. Conclusion

Borosilicate glass produced by low-pressure diffusion or deposited by PECVD appears to be an effective doping source for laser assisted diffusion. For both types of layer, the measured sheet resistances are compatible with considered processes. The results after Lydop thermal diffusion show the possibility of a selective emitter process for n-type solar cells very similar to that used for standard p-type cells. At the same time, BSG deposited by PECVD leads to doping level required for local back surface field. SIMS measurements show that profiles can be easily tailored by optimising the laser-assisted diffusion parameters. In the future, this work will be the basis for producing silicon solar cells according to the proposed processes.

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References