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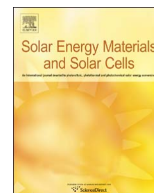

The influence of nitrogen on laser doping from phosphorous doped a-SiNx layers

Bernd Steinhauser [a,*], Ulrich Jäger [a], Jan Benick [a], Ellen Chong [b], Jenny Lam [b], Rob Steeman [b,1], Hannes Rostan [b], Jan Nekarda [a], Martin Hermle [a], Ralf Preu [a], Stefan W. Glunz [a]

[a] Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, D-79110 Freiburg, Germany
[b] REC Solar Pte. Ltd., 20 Tuas South Avenue 14, Singapore 637312, Singapore

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ABSTRACT

Laser diffusion from PECVD layers can result in the incorporation of impurities like nitrogen into crystalline silicon. It is shown that the nitrogen can have a significant influence on the laser doping process. The incorporated nitrogen can affect the material properties resulting in misinterpretation of measurement results and accumulation of nitrogen at the surface can lead to negative effects such as improper contact formation. An approach reducing the amount of nitrogen content in the PECVD layer and the LBSF is presented. This new approach allows for a partial decoupling of the passivation and doping properties of the passivation layers. The doping efficiency of the laser doping process was significantly improved while keeping the recombination properties low. The higher doping efficiency was found to be of major importance for a reproducible level of LBSF/metal contact resistivity on the rear side. Using the adapted process with reduced nitrogen content, it is shown that the doping concentration is high enough to be contacted by screen printed silver pastes. Solar cells using the new approach are presented reaching efficiencies up to 20.9% on a cell area of 149 cm^2. The influence of the higher doping efficiency reflected into the new solar cells allowing fill factors of up to 80.1%.

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1. Introduction

For high-efficiency silicon solar cells it is a requirement to keep recombination at the surfaces as low as possible. Passivated emitter and rear locally diffused (PERL) silicon solar cells utilize a local high-low junction underneath the rear side contacts, a local back surface field (LBSF), to minimize the recombination at the c-Si/metal interface and therefore were able to achieve highest efficiencies [1,2]. However, defining the localized contact structure on the rear can require complex and expensive processes such as photolithography.

Laser diffusion or laser doping was originally presented by Fairfield et al. who used a ruby laser to generate a phosphorous doped emitter on *p*-type silicon [3]. Due to the low laser pulse duration (usually in the range of femto-seconds to micro-seconds), defect studies where an important topic for laser diffusion e.g. [4–8] during early investigations.

Not only intrinsic effects were studied, but the effect of impurity inclusion as well. For dopants, Stuck et al. performed a broad investigation on the solubility of dopants in silicon after laser doping for which they found concentrations exceeding the equilibrium solubility limit [9]. A model of laser diffusion for dopants was presented by Wood et al. who predicted a segregation coefficient higher than the equilibrium segregation coefficient [10–12]. Not only the inclusion of dopant impurities was discussed, but the inclusion of impurities like oxygen [13] as well as nitrogen [14]. Hameiri et al. found that applying a laser doping process to a SiN_x (or SiO_x/SiN_x) coated surface can result in a high amount of nitrogen being included into the silicon, above equilibrium solubility [14]. They suggested that nitrogen can result in stress and therefore crystal defects in silicon. In addition, they proposed that remnants of the SiN_x layer as well as the high amount of nitrogen at the surface could lead to a lower conductivity at the surface as well as reduced contact ability. Geisler et al. found that (continuous-wave) laser doping on a SiN_x coated surface can result in

* Corresponding author.
E-mail addresses: bernd.steinhauser@ise.fraunhofer.de (B. Steinhauser), ulrich.jaeger@ise.fraunhofer.de (U. Jäger), jan.benick@ise.fraunhofer.de (J. Benick), shu-yunn.chong@recgroup.com (E. Chong), jenny.lam@recgroup.com (J. Lam), robert.steeman@gmail.com (R. Steeman), hannes.rostan@recgroup.com (H. Rostan), jan.nekarda@ise.fraunhofer.de (J. Nekarda), martin.hermle@ise.fraunhofer.de (M. Hermle), ralf.preu@ise.fraunhofer.de (R. Preu), Stefan.glunz@ise.fraunhofer.de (S.W. Glunz).
[1] Now with 1366 Technologies Inc., 6–8 Preston Court, Bedford, MA 01730, USA.

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voids created by nitrogen bubbles forming especially at the ablation edge [15].

After the initial experiments by Fairfield et al., it did not take long, until laser doping was proposed for the fabrication of solar cells, by laser doping of previously implanted [16,17] or evaporated dopant source layers [18]. While for these early applications of laser doping for solar cells, the focus was on generating a homogeneous junction, using a laser has the advantage of enabling localized processing of silicon wafers defining contact and/or selective emitter structures as well as a LBSF. In addition, as reported by Fogarassy et al. [18], the dopant source might require removal after the laser process for these early evaluations. This would especially be the case for local laser processing of a non-locally deposited dopant source.

This highlights one of the advantages of the laser fired contact (LFC) concept presented by Schneiderlöchner et al. [19]. The LFC concept used aluminum deposited on the rear as a dopant source to create a LBSF for *p*-type silicon solar cells. As the aluminum at the same time was used as the rear side metallization it was a part of the final cell structure and did not require removal after the laser process. However, as aluminum in silicon forms an acceptor state such an approach cannot be used for creating donor states, i.e. as (selective) emitter on *p*-type or as a LBSF on *n*-type silicon.

As an alternative solution, Wenham et al. proposed the use of dielectric passivation layers as a dopant source to create selective emitter structures [20]. The *PassDop* approach (Fig. 1) introduced by Suwito et al. demonstrated an industrially feasible realization based on SiC_x:P of such a concept with the focus on the rear side passivation of *n*-type silicon and using phosphorous as the LBSF dopant [21]. Similar to LFC, the dopant source—the rear side passivation layer—is an integrated part of the final solar cell and does not have to be removed after laser doping. The concept of using passivation layers as dopant sources for laser doping was since investigated by various groups. Laser doping from SiN_x:P and SiN_x:B was demonstrated by Paviet-Salomon et al. as well as Hameiri et al. for the application as emitter passivation/selective emitters formation or rear side passivation/LBSF formation [14,22,23]. Steinhauser et al. presented a similar approach called *fPassDop* based on SiN_x:P for the application as a rear side passivation of *n*-type silicon solar cells [24]. In contrast to the original *PassDop* layer based on SiC_x:P, the new stacks were stable under typical firing conditions. As an alternative to LFC on *p*-type silicon, Ortega et al. showed laser doping of aluminum from Al_2O_3/SiC_x:H stacks [25]. Laser doping of aluminum and boron for *p*-type silicon from Al_2O_3/SiC_x:B stacks was demonstrated by Steinhauser et al. [26].

In this article, an update to the *fPassDop*—the firing-stable variant for *n*-type surfaces—is discussed. Previously, three *fPassDop* variants were presented: a single layer and two layer stacks the latter two being called “Gen1” and “Gen2” [24]. For the single layer, the doping efficiency was not found to be high enough to result in a reproducible ohmic contact while retaining a good passivation level after firing. The Gen1 stack consisted of an N-rich SiN_x:P passivation layer ($n \approx 2.15$ at 632.8 nm) and a Si-rich SiN_x:P doping layer ($n \approx 2.5$ at 632.8 nm). The passivation layer is first deposited onto the silicon to electrically passivate the silicon surface. The doping layer is deposited in sequence on top of the passivation layer to increase the doping concentration within the local back surface field (LBSF) after applying the laser process. These terms “passivation layer” and “doping layer” are used throughout this work and always refer to a layout like described above. With Gen2, the hydrogen content in both layers was reduced to allow for the use of higher-refractive index layers for both passivation as well as doping layer and therefore slightly improve the doping efficiency while maintaining a low S_{Pass} after firing. However, the Gen1 and Gen2 concepts involved layers that were both at the edge of ineffectiveness (regarding passivation and doping properties) to ease the compromise necessary to combine a good doping efficiency with a good passivation quality. This compromise resulted in vulnerability to fluctuations of the deposition process. Especially the presence and role of nitrogen (originating from the a-SiN_x:P layers) during and after the laser process was unclear. For a “Gen3” of the *fPassDop* layer, the important aspect was to significantly improve the doping efficiency and—if possible—to decouple the passivation from the doping properties as well as to reduce the total amount of nitrogen in the layers as shown by an analysis of the Gen2 process below. Therefore the Gen3 stack is similar to Gen2, but uses a doping layer as close as possible to amorphous silicon (a-Si:P) to reduce the nitrogen content. The passivation layer was adapted to prevent blistering and achieve a low S_{Pass} after firing when used in conjunction with the new doping layer.

2. Experimental

2.1. fPassDop layers

The deposition of the layers was done in a Roth & Rau AK800 reactor by the plasma-enhanced chemical vapor deposition (PECVD) technique. While being a laboratory batch type reactor, plasma excitation is done by the pulsed microwave technique similar to common inline reactors. A radio-frequency plasma source is available but not used in these processes. As precursor gases, we used silane, argon, molecular nitrogen and phosphine diluted in hydrogen.

To characterize the passivation quality, shiny-etched 1 Ω cm *n*-type FZ Si wafers were coated symmetrically by our passivation layers. The wafer thickness was 200 μm. The measurements of the effective minority carrier lifetime were performed using a Sinton WCT-120 quasi-steady state photoconductance (QSSPC) measurement tool before and after the temperature treatment [27]. The latter was carried out in a single wafer rapid thermal processing reactor calibrated for this sample structure. Therefore, the samples were processed with a well-defined temperature profile. The peak temperature was applied for 3 s. Unless stated explicitly, the given temperatures represent the actual wafer temperature. For the lifetime measurement, the transient decay method was used [27]. The surface recombination velocity was extracted using the approximation of Sproul for symmetrical samples and low surface

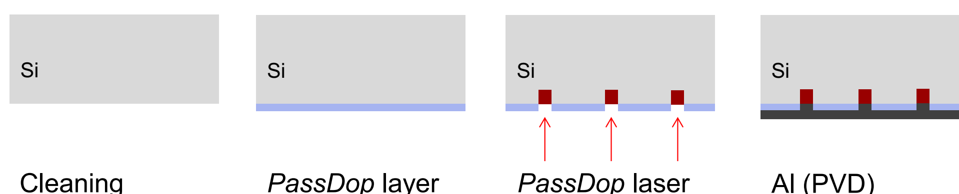

Fig. 1. *PassDop* process sequence: 1. Cleaning of the wafer. 2. Deposition of the PassDop layer. 3. Local opening of the *PassDop* layer and simultaneous diffusion of the dopants into the silicon to form a LBSF. 4. Metal deposition to create the actual contact.

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