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A laser induced forward transfer process for selective boron emitters

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A B S T R A C T

In this work, we present a novel technological approach to form highly boron-doped selective emitters. The selective emitters are formed by using a Laser Induced Forward Transfer Doping (DLIFT) process, which allows precise adjustment of the doping profile by tuning the laser parameters and choosing an appropriate doping source. Surface dopant concentrations of up to $N_s \approx 1 \times 10^{21}$ cm^{-3} were achieved by using DLIFT. Subsequent BBr$_3$ tube furnace diffusion was performed to form a low surface concentration ($N_s \approx 1 \times 10^{19}$ cm^{-3}) homogeneous emitter. In comparison to the conventionally applied BBr$_3$ tube diffusion, an increase in open circuit voltage of up to 6 mV is predicted based on the photoluminescence measurements performed after passivation, screen-printing and firing processes. Simulations suggest that this voltage gain is most possibly due to a lower emitter saturation current density (j_{0e}) of the highly doped DLIFT samples compared to the BBr$_3$ diffusion samples. Moreover, it is observed that the laser-induced defects are reduced successfully after a subsequent boron tribromide (BBr$_3$) tube diffusion, which is used to form the homogeneous emitter after the DLIFT process. The micro Raman spectroscopy results indicated that the compressive stress of −200 MPa in the silicon crystal lattice after DLIFT process is released by the subsequent BBr$_3$ tube diffusion. These results demonstrate that the DLIFT process in combination with the conventionally applied BBr$_3$ tube diffusion can be an effective approach to form selective boron emitters in high efficiency *n*-type crystalline silicon (c-Si) solar cells.

1. Introduction

Laser based approaches are widely applied in the photovoltaic industry for local [1] and large area doping [2], laser edge isolation [3], marking [4], via hole drilling [5], buried contacts [6] and laser fired contacts [7] and lately local contact opening [8]. The major reasons for this evolution are high process flexibility, throughput and positional accuracy [9]. Local doping is used in solar cells manufacturing to form selective emitter (SE) or Back Surface Field (BSF) in standard [10] and Interdigitated Back Contact (IBC) [11] solar cells. A SE is a two-sectioned emitter design featuring a lightly-doped emitter region between front metal fingers and a highly-doped emitter region underneath the metal fingers [12]. The high dopant concentration region under the metal contacts reduces the recombination at the silicon-metal interface and simultaneously lowers the metal-silicon contact resistivity. Thus, selective emitter is formed to optimize the energy conversion efficiency of high efficiency solar cells. Typically, boron emitters contacted by screen printing use silver aluminum (AgAl) metal pastes [13,14]. Although low contact resistances can be achieved [29], high recombination losses under metal and shunts due to metal spiking are present [15]. Another option is to use silver (Ag) paste. However, standard silver (Ag) pastes to contact phosphorous emitters result in

high specific contact resistance in the case of boron emitters [16], due to the high potential barrier for the silver-silicon Schottky contact [17]. One way to reduce the barrier height is by increasing the acceptor concentration [17]. The development of new Ag pastes has allowed to achieve specific contact resistances < 1 mΩ cm^2 [18]. Recently, an approach of electron injection during the firing processes allowed low specific contact resistivity (ρ_C) of 0.021 mΩ cm^2 in boron emitters contacted with Ag paste [19]. In spite of all the research and development effort, recombination loss in boron emitters remains a critical issue.

In *p*-type solar cells, the laser based SE uses the remaining phosphorous in phosphorous silicate glass (PSG) layer formed during state of the art POCl$_3$ diffusion process. The laser pulse drives the phosphorous (P) atoms in the Phosphosilicate glass (PSG) layer into Si by locally melting the silicon [20]. For selective boron emitters, one of the main challenges is the presence of low concentration of boron atoms in the borosilicate glass (BSG) layer that is formed during the BBr$_3$ based diffusion process [21,22]. Selective emitters are also structured by using either Laser Chemical Processing (LCP) [23] or laser processes combining dielectric ablation with laser doping, to form the self-aligned laser doped selective emitter [24]. In this paper, the selective emitter is formed by using a laser induced forward transfer

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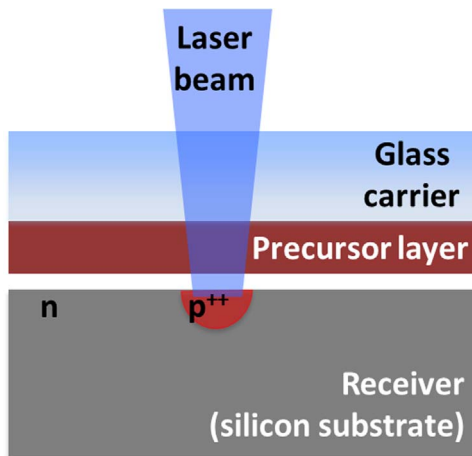 *E-mail address:* Susana.Fernandez.Robledo@ise.fraunhofer.de (S. Fernandez-Robledo).

Fig. 1. Schematic drawing of the DLIFT process showing laser beam irradiation of the precursor layer and the receiver through a glass carrier. Dopants from the precursor layer are transferred to the Si substrate.

(LIFT) approach. LIFT was reported for the first time by Bohandy 30 years ago [25]. In the following years, tremendous experience has been gathered, especially in regard to photovoltaic applications [26–29].

Laser Induced Forward Transfer Doping (DLIFT) combines the advantages of LIFT and laser doping methods. In DLIFT, the dopant is contained in a so-called precursor layer, which is deposited on a transparent carrier substrate. During the DLIFT process (see Fig. 1), the a-SiB:H precursor layers are brought into contact with a receiver. The laser pulses propagate through the glass and are absorbed mainly in the a-SiB:H layer, due to its low optical penetrations depths of 10 nm [30]. Thus, the precursor layer is locally removed from the substrate and is transferred to the silicon substrate receiver by means of laser beam irradiation. The receiver is locally melted and is diffused with the dopant from the transferred precursor layer. Due to the spatial overlapping of the laser pulses, the deposited precursor layer on the wafer is irradiated again by the subsequent laser pulse and melts together with the underlying silicon. The boron diffuses quickly through the complete volume of the molten silicon [31], resulting in a highly boron rich p^{++} silicon crystal remains after solidification.

As a doping technique, the DLIFT approach provides multiple benefits. The use of the precursor layer can be maximized, since the layer is only irradiated in the desired doping locations. Additionally, masks are not required to pattern the dopant design, as in the cases of photolithography and inkjet printing [32] techniques. Besides, DLIFT offers large process flexibility, since the precursor layer and the laser parameters can be adjusted over a large range to get the optimum profile for the particular application. Furthermore, the continuous developments in the laser technology is expected to improve the process throughputs by increasing repetition rates and the scanner velocity [33,34] of the laser.

During the dopant transfer in DLIFT process, it induces defects in the irradiated regions of the silicon wafer. Such DLIFT-induced defects can be reduced by using either a high temperature treatment in a furnace [35] or by laser annealing [36,37]. Our findings imply the potential of BBr_3 tube diffusion process to heal the DLIFT-induced defects in the SE regions. The main aim of this work is to show how the energy conversion efficiency of a standard n-type solar cell benefits from SE emitter, which is formed by forming DLIFT highly doped regions under metal contacts. In Section 3.1, we present the boron doping profiles obtained by DLIFT in combination with the BBr_3 diffusion of the homogeneous emitter. Additionally, the emitter properties for different precursor layer thicknesses and laser energy densities are discussed. Silicon defects after DLIFT and BBr_3 diffusion processes are analyzed in Section 3.2. Finally, in Section 3.3, we simulate the recombination in the emitter region for different doping profiles.

Besides, we discuss in detail the influences of the DLIFT doping profiles on the electrical performance of the solar cell.

2. Material and methods

Layers of hydrogenated amorphous silicon doped with boron (a-SiB: H) [38] were used as precursor layers and soda-lime-silica glasses of 1.0 mm thickness and 156.0×156.0 mm^2 were used as carriers. The precursor layers were deposited with thicknesses 50, 100 and 200 nm by plasma enhance chemical vapor deposition (PECVD), using an industrial-type inline microwave PECVD system (Roth & Rau SiNA L) [39]. The layers were grown by applying a microwave plasma frequency of 2.45 GHz to a flow of silane (SiH_4) and diborane (B_2H_6). The depositions were carried out with a gas flux ratio $[B_2H_6]/[SiH_4]=41.7$ under a pressure of 350 µbar and temperature of 300 ºC. The glass carriers were moved with a velocity of 30 cm/min during the deposition of layers. The receiver samples were shiny-etched float zone (FZ) silicon wafers of 125.0×125.0 mm^2 size, 250 µm thickness with base resistivity of 10 Ω cm (n-type) and < 100 > crystal orientation. The precursor layer and the silicon receiver were irradiated through the glass with a diode-pumped solid-state Nd: YVO$_4$ laser by using a frequency tripled to the UV wavelength of $\lambda=355$ nm and a pulse length of approximately $\tau_{Laser}=25$ ns (Coherent AVIA 355X). By overlapping laser pulses and lines, fully doped areas were formed. The doping fields were formed on one side of the wafer. The process parameter was repeated in two different positions at each wafer. As reference from the DLIFT doping processes, we took BBr_3 tube furnace diffusion (Diff) and the laser doping from BSG doping processes. The first reference had a low dopant concentration compared to DLIFT samples, but it had not DLIFT-induced defects. In the case of the second reference, the dopant concentration was lower than DLIFT samples whereas higher than BBr_3 tube diffusion samples. Besides, the second reference consisted of DLIFT-induced defects.

The characterization of different DLIFT samples was performed by using four point probe technique, electrochemical capacitance voltage (ECV), photoluminescence (PL) and micro-Raman-spectroscopy (µRS) measurements as summarized in Fig. 2.

DLIFT fields with 100 nm of a-SiB:H were carried out at laser pulse energy densities or fluence $E_{p,d}$ between 1.0 and 4.0 J/cm^2 for four point probe, ECV and PL measurements in silicon wafer 1 and 2. The same procedure was done for DLIFT of 50 and 200 nm of a-SiB:H in wafers 1 and 2. In another silicon wafer (wafer 3), DLIFT fields were carried out with 100 nm a-SiB:H at laser energy pulse densities $E_{p,d}=1.9$, 2.6, and 3.2 J/cm^2 for the µRS measurements (µRS sample). The laser doped fields formed for four point probe and ECV measurements were square with size of 15.0×15.0 mm^2, while the fields PL and µRS measurements were rectangular with size of 7.5×15.0 mm^2. After DLIFT and before BBr_3 diffusion, the remaining transferred material was removed by a borosilicate glass (BSG) etching process: 20% hydrofluoric acid (HF) bath during 5 min. Then a p^+ homogeneous emitter (Diff) of $R_{sheet}=112.4 \pm 3.5$ Ω/sq was formed by thermal BBr_3 tube furnace diffusion by means of an industrial tube furnace system TS81255 from Tempress Systems [40]. Laser doping from BSG was performed in the wafers 1 and 2. Afterwards, the BSG layer was removed by BSG etching. Then DLIFT fields of 100 nm a-SiB:H at laser energy pulse densities $E_{p,d}=1.9$, 2.6, and 3.2 J/cm^2 were carried out in wafer 3, and DLIFT fields of 50, 100 nm and 200 nm of a-SiB:H at $E_{p,d}$ between 1.0 and 4.0 J/cm^2 were performed in wafers 1 and 2. The sheet resistance (R_{sheet}) and the concentration of active boron were measured for the samples indicated in Fig. 2 by means of four point probe technique [41] and ECV [42] using the tool CVP21 from WEP, respectively. µRS measurements [43] were performed on wafer 3 with a spectral resolving WITeC confocal laser-scanning microscope by using a green excitation laser of 532 nm wavelength and spot size < 1 µm at laser power of 1 mW. Every point on the sample was measured 40 times for 1 s. The given values for stress were obtained by fitting the