LASER CHEMICAL PROCESSING (LCP) DOPING FORMED THROUGH DIFFERENT DIELECTRIC LAYERS

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ABSTRACT: Laser chemical processing (LCP) has been proven to be an effective technology to form selective emitters and local back surface fields for high efficiency silicon solar cells. In this work, LCP n-type doping formed through different dielectric layers is presented, and is characterisaed by changes in the effective lifetime (τ_{eff}) and emitter saturation current density (J_{oe}). With the same LCP parameters, the sheet resistance of the n-type doping area could be made as low as 15-20 Ω/□ under various passivation layers. As the doping area fraction increases, we observe clear degradation in τ_{eff} and J_{oe} with different passivation layers. Under the same LCP parameters and doping fraction, SiO_2 passivated samples show a reduced τ_{eff} and J_{oe} degradation than those pssivated by SiN_x. The reason could be attributed to the different thermal properties of SiO_2 and SiN_x dielectric layers and the passivation effects of the H_3PO_4 doping solution on the Si-SiO_2 interface.
Keywords: Laser Chemical Processing, Silicon, Dielectric layers

1. INTRODUCTION

State-of-the-art high efficiency silicon solar cells (e.g. PERT and PERC) are achieved by reducing recombination losses through the use of locally structured passivation layers on the surfaces, and with local doping under the metal contacts, such as selective emitter (SE) and local back sueface field (LBSF) structures. A SE can reduce contact resistance by being heavily doped under the metal contacts, while ensuring low recombination elsewhere by being lightly doped in optically active regions, which results in a higher fill factor (FF) and a better blue response. A heavily doped LBSF can increase the fill factor due to a decreased series resistance, and increase voltage and current via reduced rear recombination. Laser processing has attracted considerable attention as a fast and cost-effective technique in forming SE and LBSF structures for solar cells. Laser-fired contacts (LFC), for example, form the LBSF by the diffusion of aluminium into the silicon.[1] A SE could similarly be formed by laser irradiation and melting of the silicon surface with a dopant-containing layer or precursor.[2-4] However, the laser processing still needs to be simplified to reduce cost and time during mass production.

Recently, a novel laser processing technology, laser chemical processing (LCP) has been developed at Fraunhofer ISE.[5] The coupling of a laser beam into a dopant-containing liquid jet enables the formation of local n-type or p-type doping to create SE and/or LBSF structures for either p- or n-type solar cells. The advantage of LCP over other laser processes is that the opening of dielectric layers, the SE or LBSF formation and damage etch are combined in one single step. Thus, the number of processing steps and the processing time can be reduced to achieve high efficiency solar cell structures. The formation of n-type SE with H_3PO_4 liquid jet and p-type boron-doped LBSF with alkaline aqueous boron solution by LCP have already shown good results on p-type solar cells.[6,7] Therefore, LCP has been proven to be a high efficiency and low cost technology to achieve high efficiency silicon solar cells with SE or/and LBSF.

Usually, LCP is used to form local doping through different passivation layers for p- or n-type solar cells. However, the doping functions under different dielectric layers has not been investigated in detail yet. In this work, n-type LCP doping formed with a H_3PO_4 liquid jet through different dielectric layers was investigated. LCP-induced degradations in the effective lifetime (τ_{eff}) and emitter saturation current density (J_{oe}) were also investigated, and the mechanism for these degradations is clarified.

2. EXPERIMENTAL PROCEDURES

P-type wafers with >100 Ω·cm base resistivity and (100) orientation were used, with different dielectric layers: 1) bare silicon; 2) thermal grown silicon oxide (SiO_2, ~70nm); 3) silicon nitride by PECVD (SiN_x, ~70nm); 4) silicon oxide and nitride stack (20nm SiO_2+ 50nm SiN_x). Diluted H_3PO_4 solution (50%) is used as the n-type dopant in the LCP system. LCP doping under different pulse energies is carried out on samples with different dielectric layers. The jet pressure, repetition rate and scanning speed are the same for all of the samples (532nm laser wavelength). LCP doping areas are formed by ~50% overlapping single laser grooves. A four point probe was used for sheet resistance measurement. The morphology of single laser grooves under different pulse energies and dielectric layers were observed by SEM. The phosphorus doping profiles were measured by SIMS.

In order to investigate changes in τ_{eff} and J_{oe} with different passivation layers, an experimental procedure was designed, as shown in Fig.1. High resistivity silicon wafers were damage etched and then cleaned with standard RCA cleaning. These samples were divided into two groups and then experienced $POCl_3$ diffusions to form symmetrical emitters with sheet resistances of ~60 and ~120Ω/□, respectively. The phosphosilicate glass on the surface was removed by HF dip. After emitter formation, the samples were passivated by thermal grown SiO_2 (1000℃, 60mins, ~70nm) and PECVD SiN_x (450℃, ~70nm), respectively. These samples were cleaved into

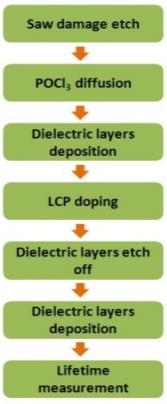

Figure1: Experimental procedure for investigating LCP induced τ_{eff} and J_{oe} degradation.

quarters, and τ_{eff} and J_{oe} are measured by the QSSPC technique before LCP doping, with one quarter left as a control sample without LCP doping for each group. LCP doping with the optimized parameters (yielding the lowest sheet resistance) were carried out on the front side of each quarter in a 30×30 mm^2 region, with different pitches, yielding different fractions of LCP doping area on each quarter. Then the dielectric layers on the samples (including the control sample) were removed by wet chemical etching. Finally, each quarter is passivated by the same dielectric layer before LCP doping, and the τ_{eff} and J_{oe} are measured by the QSSPC technique again.

3. RESULTS AND DISCUSSION

3.1 Influence of pulse energy on the sheet resistance

The sheet resistance results for increasing pulse energy with different passivation layers are shown in Fig.2. A clear dependence of the sheet resistance on pulse energy is visible. At a low pulse energy (<21 µJ), samples with different passivation layers show different sheet resistances under the same LCP parameters. The same can be observed at high pulse energies (>25 µJ). In the pulse energy range of 21-25 µJ, the sheet resistance reaches a minimum between 15-20 Ω/□ for all the samples, even with different passivation layers. The practical importance of this observation is that it is possible to use the same LCP parameters to achieve local doping with low sheet resistance through different passivation layers. It is not necessary to re-optimize the LCP parameters when changing the passivation layers. However, this is not the case when using a dry laser to form the local doping.[8]

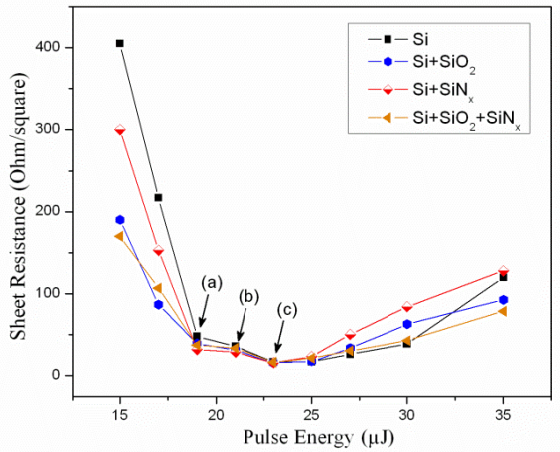

Figure 2: Sheet resisitance of LCP doping with 50% H_3PO_4 solution through different dielectric layers

Melting, evapration and dopant diffusion are the main mechanisms that occur during the laser-matter interaction. During the laser chemical processing, the laser radiation transmits through the dielectric layers and is absorbed by the underlying silicon. The laser pulse melts a thin layer of silicon which evaporates and build up pressure, and the dielectric layers are chipped off the surface with the help of the liquid jet, whilst dopant diffusion into the silicon occurs at the same time. Fig.3 shows the SEM images of the LCP grooves with different pulse energies and passivation layers. At a low pulse energy (19 µJ), no obvious silicon surface morphology change was observed.

The decrease of sheet resistance can be attributed to the significant increase of the phosphorus diffusion coefficient in the melt. However, the doped lines are not homogeneous, and are sometimes even interrupted by the dielectric layers. When the pulse energy increases (21 µJ), obvious silicon melting and melt movement driven by the liquid jet can be observed. The sheet resistance continues to decrease. At a higher pulse energy (23 µJ), the melt lifetime and depth are further increased, which leads to a lower sheet resistance. However, for even higher pulse energies (>25 µJ), the sheet resistance increases slightly in all the samples. One possible reason is the increasing evaporation of the molten silicon at a high pulse energy.[7,9]

With the optimized LCP parameters, the sheet resistance is almost the same under the different passivation layers (point c in Fig.1). The phosphorus doping profiles are measured by SIMS, as shown in Fig.4. The sample passivated by SiO_2 has the deepest phosphorus diffusion depth (2900nm), and the lowest surface concentration (3.6E19). In contrast, the sample passivated by SiN_x shows the shallowest phosphorus diffusion depth (2450nm) and the highest surface concentration (6.5E19). The results are not consistent with the sheet resistance measurement, which indicates that the doping profile should be similar to each other under different passivation layers. The reason may be attributed to the SIMS measurement inaccuracy. The surface roughness (as shown in Fig.3) may influence the dopant profile, because SIMS takes the mean value over a relative big area (~50 µm square) which leads to a spreading of the doping profile.

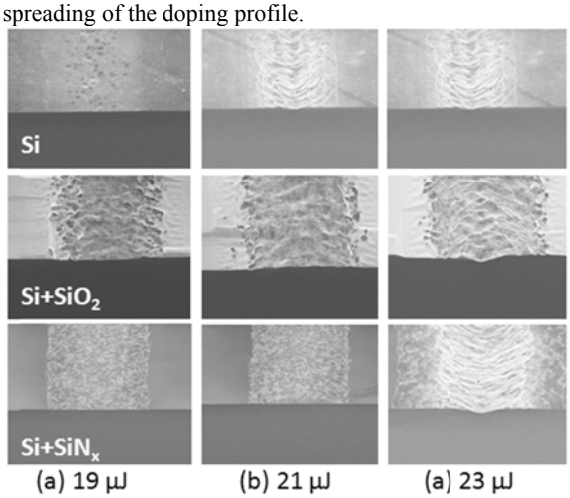

Figure 3: SEM images of the LCP processing surface with different energies and dielectric layers

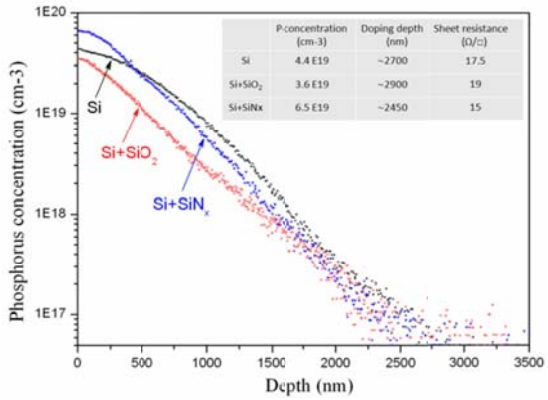

Figure 4: Phosphorus doping profile under different dielectric layers with the same LCP parameters (point c in Fig.1)

3.2 LCP induced effective lifetime and emitter saturation current density degradation

In the 30×30 mm^2 area on a quarter wafer, parallel single LCP grooves (~20μm) with different pitches are drawn on the front side with the same LCP parameters (23μJ). As the pitch increases, the LCP doping fraction decreases. QSSPC lifetime measurements were carried out before and after LCP doping and repassivation with SiO_2 or SiN_x. Fig.5 shows the LCP-induced effective lifetime measured by the QSSPC technique at a low carrier injection densities of 1E15 cm^{-3} as a function of LCP doping fraction, and the insert pictures are the LCP-induced J_{oe} (extracted at a higher carrier injection densities of 3E15 cm^{-3}). For all the samples with different passivation layers (SiO_2 and SiN_x) and emitter sheet resistances (60 and 120 Ω/□), obvious τ_{eff} and J_{oe} degradations are observed with increasing doping fraction. Table 1 shows the % changes in τ_{eff} and J_{oe} as the pitch decreases. Only the first three data points are listed. With the increasing LCP doping fraction, τ_{eff} decreases and J_{oe} increases. Under the same LCP doping fraction, the samples passivated by SiO_2 show slightly smaller τ_{eff} and J_{oe} degradation than the samples passivated by SiN_x. For the sample with higher emitter sheet resistance (120Ω/□), more obvious τ_{eff} and J_{oe} degradations are observed when compared with the sample with lower emitter sheet resistance, as expected due to the greater sensitivity of lighter diffusions to surface recombination. In a typical selective emitter finger pitch range (0.9-1.2mm), the LCP-induced τ_{eff} and J_{oe} degradations are about 10%, which is lower than dry laser induced τ_{eff} and J_{oe} degradations.[10,11]

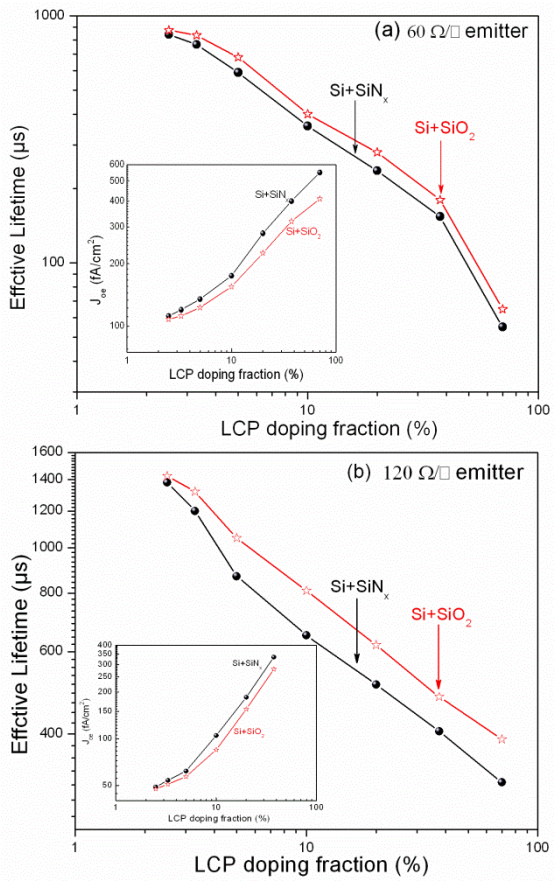

Figure 5: LCP-induced effective lifetime degradation (a) 60 Ω/□ emitter; (b) 120 Ω/□ emitter, the insert pictures are LCP-induced emitter saturation current density (J_{oe}) degradation.

Table 1 LCP-induced reduction in τ_{eff} and increases in J_{oe} as a function of LCP doping fraction with different passivation layers and emitter sheet resistances.

Dielectric Layer	Doping Fraction (pitch)	τ_{eff} ↓	J_{oe} ↑
SiN_x (60 Ω/□ emitter)	2.5% (1.2mm)	-6.5%	+7.0%
	3.3 % (0.9mm)	-15%	+14%
	5.0 % (0.6mm)	-35%	+29%
SiO_2 (60 Ω/□ emitter)	2.5 % (1.2mm)	-3.0%	+3.0%
	3.3 % (0.9mm)	-8.0%	+9.5%
	5.0 % (0.6mm)	-26%	+17%
SiO_2 (120 Ω/□ emitter)	2.5 % (1.2mm)	-5.0%	+5.5%
	3.3 % (0.9mm)	-12%	+12%
	5.0 % (0.6mm)	-30%	+26%
SiN_x (120 Ω/□ emitter)	2.5 % (1.2mm)	-8.0%	+9.0%
	3.3 % (0.9mm)	-20%	+20%
	5.0 % (0.6mm)	-42%	+38%

The τ_{eff} drop and J_{oe} degradation can be attributed to the laser induced defects (mostly dislocations) at the selectively doped area, which increase the Shockley-Read-Hall (SRH) recombination. For a typical industrial emitter (60 Ω/□), the lifetime is largely determined by the Auger recombination. In the case of the LCP selective doped emitter, there exits additional laser induced SRH recombination, and the resulting τ_{eff} is influenced by both Auger and SRH recombination. For the emitter with high sheet resistance (low doping concentrations), the effective lifetime is limited by the SRH recombination. Whereas emitter with low sheet resistance (high doping concentration), the influence of the SRH recombination on the effective lifetime is very small. Therefore, for a typical high efficiency emitter (120Ω/□) with LCP local doped selective emitter, the impact of LCP induced defect on τ_{eff} is more obvious, which is consistent to our experimental results. However, When the LCP is used for forming a selective emitter underneath contacted areas, the J_{oe} of the local doped areas will be dominated by the high surface recombination velocity due to the metal contacts. The effect of the LCP induced defects will, therefore, be even less important. This is especially so considering the relatively small impact of the LCP process on the total J_{oe} for small contact fractions (below 5%), which are typical for high efficiency solar cells.

Hameri et al. have investigated the dry laser induced defects under different passivation layers.[12] Fewer laser induced defects were observed when using a SiO_2/SiN_x stack compared to the standard single SiN_x and SiO_2 layer. It was suggested that induced stress due to thermal expansion mismatch between the different materials is the source of these defects.[13] During laser processing, the underlying silicon surface is placed under compression and tension when passivated by SiO_2 and SiN_x, respectively. Silicon is known to be weak and therefore easily defected under tension, but particularly strong under compression.[14] Therefore, less defects are generated during LCP processing when passivated by SiO_2, which leads to smaller τ_{eff} and J_{oe} degradation. Moreover, Zhang *et al.* reported that the immersion of oxidized silicon samples in H_3PO_4 solutions with elevated temperature could improve the passivation of Si-SiO_2 surface.[15,16] The atomic hydrogen in the H_3PO_4 solutions results in the passivation of a certain fraction of thermally stable interface defects, and a reduction of J_{oe}

could be observed. We also did the H_3PO_4 solution immersion experiment with the same oxidized silicon sample for LCP processing. A silicon sample with 60 Ω/□ diffused emitter and passivated by SiO_2 was immersed into 100℃, 50% H_3PO_4 solution for 5 minutes. The PL images of the sample before and after H_3PO_4 immersion are shown in Fig.6. It is observed that some black areas (low lifetime area, marked by red dashed circle in Fig.6a) were improved after the immersion, which indicated that the sample lifetime is increased. QSSPC lifetime measurement also indicated that the sample lifetime is improved by ~15% after H_3PO_4 immersion. We conclude that H_3PO_4 solutions used by LCP could also contribute to the smaller τ_{eff} and J_{oe} degradations of SiO_2 passivated samples. It could be another advantage of LCP over dry laser processing, although the stability of this increase would need to be confirmed.

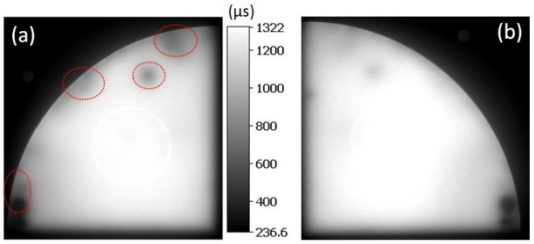

Figure 6: PL images of SiO_2 passivated sample (a) before H_3PO_4 immersion; (b) after immersion in 100℃ 50% H_3PO_4 solution for 5 minutes.

4. CONCLUSIONS

N-type LCP local doping with a H_3PO_4 solution through different dielectric layers is investigated. A low sheet resistance of the local doping area could be achieved with the same LCP parameters under different dielectric layers, which avoids the optimization process for selective emitter or LBSF formation with different passivation layers. Only small LCP-induced τ_{eff} and J_{oe} degradations are observed when the doping fraction is less than 3.3%, which is compatible with a selective emitter pitch between 0.9-1.2mm. Smaller τ_{eff} and J_{oe} degradations are observed in the samples passivated by SiO_2, which may partly attributed to the H_3PO_4 solution passivation effect on the Si-SiO_2 interface. Therefore, it could be a better choice to use SiO_2 passivation instead of SiN_x when LCP is applied to form n-type selective emitter or LBSF.

5. ACKNOWLEDGEMENTS

This work received funding from the Australian Solar Institute (ASI)/Australian Renewable Energy Agency (ARENA) under the ANU PV core project, Australia-Germany Collaborative Solar Research & Development project and Postdoctoral Fellowship project.

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