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Influence of IR laser doping method on surface emitter with phosphosilicate glass for solar cells

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Abstract

Laser-assisted diffusion of phosphorus dopants has been investigated to realize selective emitters on mc-Si wafers. In this paper, we studied, in the presence of PSG, the effect of laser speed and power doping parameters on the sheet resistance \(R_{Sq}\) variation as a function of selective emitter formation. Four point-probe (FPP) measurements showed that 5.5–10 W with speed 100–1500 mm s\(^{-1}\) are, respectively, the best power values to form a selective emitter with 20–40 \(\Omega/\square\) typical values. Electrochemical Capacitance-Voltage (ECV) results showed that dopant concentration and junction depth increased with decreasing scan speed, resulting in lower sheet resistances. Thus, the greater the difference between the concentration of starting phosphorus and that created by laser treatment, the smaller the square \(R_{Sq}\) will be. Scanning Electron Microscopy (SEM) images demonstrated more pronounced patterns of laser ablation when the power is high and/or the scanning speed is low.

1. Introduction

Multicrystalline silicon (mc-Si) wafers are widely used in mass production of solar cells due to their lower cost, compared with monocrystalline silicon wafers [1, 2]. Mono-Si growth is 5 times more energy consuming than mc-Si [3]. Hence, improving the cell efficiency on mc-Si is still a major concern.

Currently, in the photovoltaic industry based on mc-Si, great efforts are devoted to implement cost-effective solutions to improve their performance.

Laser doping technique is one of the most promising alternatives to classical doping techniques because of its proven advantages [4, 5]. In particular, laser-assisted diffusion of dopants is an interesting method to produce advanced solar cells at low cost with high efficiency and a minimum number of processing steps [6, 7].

Laser doping from phosphosilicate glass (PSG) [8, 9] offers the possibility to implement a selective emitter solar cell in a fast and cost effective way [10]. PSG is a residual layer obtained consequently to thermal diffusion. It can be used as secondary source of phosphorous to produce highly doped selective emitters. Indeed, the residual PSG layer is rich in phosphorus.

Laser doping process is characterized by the redistribution of phosphorus in a diffusion process comprising two different mechanisms: (i) the first uses a limited source from the P contained in the emitter obtained after thermal diffusion. In this case the source is said to be limited as given in equation (1) and (ii) the second uses the source of P contained in the PSG layer, in this case we can consider the quasi unlimited source.

Finally, the obtained profile after a specific laser treatment exhibited a behavior of an unlimited source diffusion with an erfc shape more than a limited source with Gaussian profile.

From PSG doping source, leading to ERFC (complementary error function) doping profiles after phosphorus redistribution. The impurity concentration \(C\) after a time \(t\) in the depth \(Z\) is given by [11]:

\[ C(t,Z) = \frac{2}{\sqrt{\pi t}} \int_{Z}^{\infty} e^{-u^2} du \]
Where \( Q \) is the total amount of impurities and \( D \) the diffusion constant.

The complementary error function \((\text{erfc})\) can be written as:

\[
\text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} \, dt = e^{-x^2} \text{erfcx}(x)
\]  

(2)

In this paper, we demonstrate the selective emitter formation on a mc-Si wafer with the induced variation of phosphorus concentration \((C)\) on the surface. Phosphorous concentration is a function of the sheet resistance \(R_{sq}\). In this study, the \(R_{sq}\) parameter was measured with four point probe (FPP), while junction depth and surface concentration are obtained from electrochemical capacitance-voltage profiling (ECV).

We presented in [12, 13] some results where the cell performance is enhanced with 1064 nm laser treatment.

2. Experimental details

The substrate materials are 10 × 10 cm², p-type mc-Si wafers with a resistivity of 1-3 Ω·cm and 330 μm thick as-cut from ingots grown by HEM (Heat Exchanger Method) [14]. The samples were processed according to the flowchart shown in figure 1.

During the thermal diffusion step, a PSG layer is formed on the surface. Figure 2, illustrates the sheet resistance mapping undertaken on 10 × 10 cm² wafer with automatic FPP CMT-SR2000N after diffusion. The sheet resistance \((R_{sq})\) of the emitter is measured with a full automatic system of four point probe Resistivity Measurement and mapping CMT-SR2000N. We plotted the map of the sheet resistance variation on the 81 selected points of the mc-Si wafer. We obtain a mean value of 60 Ω/□, which is typical for industrial standard cells.
After diffusion, the wafers were processed using an Ytterbium fiber YLia M20 laser with a wavelength of 1064 nm and a pulse duration of 100 ns. The influence of laser parameters is studied to understand the laser induced doping process. The treated area has a square shape of 1 cm² as shown in figures 3 and 4.

In this work, the variation of both, laser speed between 2 and 20 mm s⁻¹ and power between 0.5 and 20 W are studied in order to understand their effect on the selective emitter formation. Laser treatment was used to decrease locally the sheet resistance. After laser doping, each square is then characterized by ECV to measure the concentration profile $C$, and by FPP to measure the sheet resistance $R_{sq}$. Scanning electron microscopy (SEM) images were also taken for each square.

Figure 2. Data Map (Outside) of the wafer surface by using the sheet resistance technique. Sample Size: 100 × 100 (mm²), Probe Space (mm): 1, TMeasure (ºC): 23, MMode: 81 pts, Analysis [ohm/sq]: 3.5 Sigma = Max : 59.78774 Min : 57.37856.

Figure 3. Schematic image of laser doping system.
3. Results and discussion

3.1. Sheet resistance measurements

Figure 5 represents the evolution of the sheet resistance as a function of the laser speed and the laser power.

Figure 5(a) shows the measured sheet resistance obtained using different power values applied to the square sample (5.5–6–10 and 20 W) for various scan speeds, from 40 to 1500 mm s⁻¹. Generally, typical sheet resistance values should turn around 30 Ω/□ in order to facilitate the formation of good ohmic contacts [15]. The laser treatment on the surface of mc-Si wafers with PSG reduced the sheet resistance from 60 Ω/□ to 20–30 Ω/□ compared to power values ranging from 5.5 to 10 W. The obtained Rsq profile was a plateau of quasi-constant values for those power values mainly for speed values beyond 100 mm s⁻¹. Beyond this power range, the plateau Rsq profile is deteriorated.

Figure 5(b) shows sheet resistance values obtainable using different scan speeds ranging from 40 to 1500 mm s⁻¹ for various powers (5.5–6–10 and 20 Watt). Compared to the scanning speed of the laser, the dispersion of the square Rsq values, with power variation, is consistent with speed variation case (figure 5(a)) which proves that the same effect is induced by laser treatment on silicon with PSG, on a power range of 5.5 to 10 W. One can see that non-uniform dispersion of Rsq values over the remaining power range is observed.
In its paper, Lauermann et al [16] showed that selective emitter cell performances were the best when $n^{++}$ emitter doping was 40 $\Omega/\square$, while no significant performance gain can be expected from the front surface if the sheet resistance of the emitter is increased beyond 100 $\Omega/\square$. Thus, we first investigated the evolution of the sheet resistance ($R_{sq}$) as a function of the laser speed for $P = 6$ W using a FPP sensor. The obtained results are presented in figure 6.

When increasing laser speeds, $n^{++}$ emitter sheet resistance rapidly starts decreasing down to 20 $\Omega/\square$. Sheet resistance decreases due to two phenomena: diffusion of phosphorus atoms from the PSG in molten silicon and activation of already incorporated but inactive atoms [17].

At low speed (region a), the sheet resistance dropped from 60 $\Omega/\square$ to values closed to ~ 28 $\Omega/\square$. When increasing laser speed (close view of region a), the sheet resistance decreased further as a result of longer and deeper melting of the silicon substrate and reaches finally the value of $R_{sq} = 20 \Omega/\square$, the laser irradiation melts the surface and phosphorus atoms diffuse from the PSG layer into the liquid silicon [18]. At very high laser speed, ablation starts and the sheet resistance increased again leveling off at $R_{sq} \approx 35–45 \Omega/\square$ (region b).

The speed range of 2 to 70 mm s$^{-1}$ seems to be very interesting in the we use a power of 6W.

Figure 7 shows the typical evolution of the sheet resistance ($R_{sq}$) with laser power variation measured at a speed of 20 mm s$^{-1}$ on mc-Si wafer with 60 $\Omega/\square$ initial emitters for samples with PSG layer. After that, different laser powers have been employed for diffusion within initial emitters with PSG layer, the sheet resistance evolution can be divided into two regions (A and B). At low fluence (below 7 W, region A), the sheet resistance, after a very slight enhancement, decreased from 70 to 20 $\Omega/\square$ due to laser-induced thermal effects which activate the interstitial dopants existing in the emitter (PSG layer). At high fluence (above 10W, region B), the
sheet resistance increased sharply indicating an ablation of the emitter; this high sheet resistance becomes representative of the bulk properties.

We can retain that a power ranging from 0.5 to 7W is adequate to obtain a redistributed emitter with a sheet resistance around 20 to 30 $\Omega/\square$.

3.2. Doping profile and sheet resistance

The dopant concentration and the junction depth depend on two primary parameters: (i) the scan speed of the focused laser beam over the silicon material and (ii) the laser power (the incident optical intensity) applied on surface. From the doping profiles of the various samples, it was possible to measure the junction depth as well as the phosphorus concentration created by the laser treatment.

Figure 8 represents the shape of the junction depth and the phosphorus concentration of the selective emitter created by laser according to the laser speed with a power corresponding to 6 W.

As a result, it has been found that the difference between the phosphorus concentration of the starting emitter and that created by laser treatment has a direct influence on the square resistance of the wafers.

From figure 8, it can be seen that dopant concentration and junction depth increases with decreasing scan speed, resulting in lower sheet resistances.

Thus, the greater the difference between the concentration of starting phosphorus and that created by laser treatment, the smaller the square $R_{S1}$ will be. A similar behavior has been reported and explained in detail by Kenji Hirata et al [19].
At the final we obtain emitters with surface concentration as great as $4 \times 10^{19} \text{ cm}^{-3}$ (active phosphorus) and junction depth larger than 1.0 $\mu\text{m}$ that is a favorable value to contact the emitter by screen printing.

### 3.3. Surface morphology

SEM images indicating the laser-irradiated area for the formation of a selective emitter are shown on figure 9. It is noticed that a pattern can be observed on the laser ablated surface. This pattern is more pronounced when the power is high and/or the scanning speed is low. The morphology after treatment at $P = 5.5 \text{ W}$ and speed between 2 and 15 mm s$^{-1}$ shows a 20–30 $\mu\text{m}$ large channels on the surface parallel to the laser scan corresponding to large and dark lines. The outer line of the channel representing the melted and recrystallized area. The diffusion process takes place and redistributes phosphorous atoms from the PSG in the treated region, creating n$^{++}$ doping-grade silicon [20].

It is shown in the figure 9(e), the channels created on the surface treated at 7 W–10 mm s$^{-1}$. The power of 10 W is dramatically harmful to the surface. Figures 9(a)–(d) seem to be identical and don’t present any damage of their morphology; this is a good result of the applied treatment.
4. Conclusion

In this work, the formation of selective emitters on mc-Si with PSG layer is investigated.

An emitter with high phosphorus concentration on the surface with a sheet resistance in the range of 20–30 $\Omega/\square$ is developed by using laser doping technique.

The PSG layer served as phosphorus source for silicon n$^{++}$ doping. The laser treatment on the surface of the tested samples allowed to redistribute the inactive phosphorus present in the PSG layer. Laser treatment parameters used, high speed and low power, are adequate for a high throughput cell production.

The diffusion of the phosphorus atoms allowed to reduce the sheet resistance of the emitter. Results obtained from FPP and ECV characterizations demonstrated that laser treatment allowed the formation of selective emitters on the studied samples.

In the future, this work will be the basis for producing silicon solar cells with selective emitters according to the proposed processes.

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