Diode Laser-Crystallization for the Formation of Passivating Contacts for Solar Cells

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A new method of diode laser treatment of passivating contacts for solar cells application based on electron beam evaporated highly doped amorphous silicon (a-Si) layers deposited on solar-grade Czochralski wafers with SiOx tunneling layers is investigated. In a first step, an interface oxide is grown and a highly doped n-type a-Si layer is deposited on both sides by electron beam evaporation. In a next step, the laser treatment is applied. Two different scanning speeds of 15 and 20 mm s\(^{-1}\) are used. Electron backscattering diffraction and quasi-steady-state photo conductance measurements indicate that the a-Si layer can be crystallized without breaking up the thin oxide layer. To determine the best parameters, the lifetime and the implied open-circuit voltage for each laser power are measured. The first results show a fitted lifetime of 4.06 ms and an implied open-circuit voltage up to 711 mV after a passivation step.

1. Introduction

Different approaches are being pursued to reduce the watt-peak price for solar cells and modules. The dominant loss mechanisms in highly efficient standard passivated emitter and rear cell and passivated emitter rear totally diffused crystalline silicon solar cells are recombination at the metal–semiconductor interfaces. There are promising achievements with a stack of a polycrystalline silicon layer and a thin interface oxide layer between the wafer and polycrystalline silicon.[1] These solar cells have achieved a high efficiency of 26.1%.[2] Recently laser crystallization and laser treatment to enhance the doping concentration in passivating polycrystalline contacts were investigated.[3] The advantages of the laser treatment are that the crystallization depth and the dopant activation of the poly-Si layer can be easily adjusted. Additionally, the laser crystallization technique could be faster, easier integrated into the production line, and improve productivity; therefore, is much more economic. Furthermore, a selective and local crystallization becomes possible, in contrast to furnace annealing. In this article, the laser crystallization of the a-Si layers of passivating contacts with a diode laser on electron-beam physical vapor deposition (EB-PVD) silicon layers on solar-grade Czochralski (Cz)-silicon wafers is introduced. Diode lasers are attractive options for the crystallization of silicon layers because they are cost-effective and the beam shape and wavelength can be adjusted.[4] These were used in the recent past of amorphous Si for the crystallization for thin-film solar cells on glass.[5–8]

2. Experimental Section

As initial substrates, 5 × 5 cm\(^{-2}\) n-doped planar Cz-Si wafers with a thickness of 160 μm and a resistivity of 7.1 Ω cm were used. A thin silicon oxide layer of about 1.6 nm was prepared on both sides by thermal oxidation. On both sides, a 75 nm thick amorphous silicon layer with a phosphorous doping level of around 2 × 10\(^{20}\) cm\(^{-3}\) and a rate of 12 nm s\(^{-1}\) was deposited by EB-PVD. The substrate temperature during the deposition was 250 °C. The laser treatment was applied with a diode laser (LIMO) with a wavelength of 808 nm. The diode laser has a top-hat beam profile with a rectangular line focus of 30 × 0.1 mm\(^2\). Due to a slightly flatter rise of the edges of the beam profile in the long dimension, the beam has a slightly elliptical shape on the last 200 μm on both sides. The diode laser was used in continuous wave mode as Figure 1 shows. Scanning speeds between 10 and 20 mm s\(^{-1}\) were used and laser powers between 50 and 400 W were applied. So, the power density is in the range of 1.5–13.3 kW cm\(^{-2}\). Four best-performing samples were further subjected to a hydrogenation step to saturate dangling bonds and further defects at the poly-Si/SiOx interface. For this purpose, a hydrogen-rich silicon nitride (SiNx), which is required as an anti-reflex coating in common solar cell concepts anyway, is deposited with an Oxford PlasmaLab 100 PECVD system on both sides. The hydrogenation step is completed by a fast
firing step in a conventional belt furnace optimized for metallization at a set temperature of 819 °C.

The crystallinity of the contact area was characterized by electron backscattering diffraction (EBSD). The microscope images were performed by a scanning electron microscope (SEM). For the quality of the passivated layers quasi-steady-state photo conductance (QSSPC) measurements with a Sinton WPT-120[9,10] were carried out.

3. Results and Discussion

The aim of the variation of the laser power and the scanning speed is to maintain the thin silicon oxide layer, so that it keeps the high passivation performance and serves as a tunneling contact. Since the absorption in the crystalline and amorphous Si for the 808 nm wavelength of the diode laser is quite low,[11] a high-power density for liquid-phase crystallization is required for very thin layers. As a first step, different laser powers with a scan speed of 10 mm s⁻¹ were adjusted, the results are analyzed with scanning electron microscopy at the cross-section of the cleaved wafers after the laser crystallization, and the SEM images are shown in Figure 2. In image 2a, the amorphous silicon layer was crystallized via liquid-phase crystallization with a laser power density of 13.3 kW cm⁻². The thin silicon oxide layer was completely destroyed and the silicon layer grew epitaxially. This was confirmed by EBSD measurements, where the silicon layer shows the identical crystal orientation (100) with the underlying substrate. A part of the transition region between microcrystalline and nanocrystalline can be seen in Figure 2b.

The transition area is located between the treated and untreated areas of the silicon layer. Parts of the thin silicon oxide layer seem to be preserved, but not as a continuous film as needed for a good passivation. The thin SiOₓ layer itself is not resolved here. Figure 2d shows an amorphous silicon layer on a wafer with an interfacial layer. The image implies that the visible interface should be the very thin thermally grown oxide layer. Nanocrystalline growth is achieved via solid-phase crystallization[12] at laser power densities between 3.3 and 6.7 kW cm⁻². Experiments in our and other groups with in situ reflectivity measurements suggest that solid-phase crystallization can be assumed.[13,14] In these publications, it was shown that the reflectivity during laser irradiation gives direct information about the physical state of silicon. Especially for molten silicon, an increase in the reflectivity can be observed. In ref. [14], laser irradiation at 12.5 kW cm⁻² for 3.5 s was performed for solid-phase epitaxy on wafers with different orientations. Due to the

![Figure 1. Schematic picture of the substrate during laser treatment (c-Si-crystallized silicon independent of grain size and growth structure).](image)

![Figure 2. Scanning electron microscope (SEM) images of the cross-section of: a) epitaxial crystallization (13.3 kW cm⁻²), b) transition area between microcrystalline and nanocrystalline range (10.8–6.7 kW cm⁻²), c) nanocrystalline area (3.3–6.7 kW cm⁻²), and d) amorphous silicon layer.](image)
comparatively lower power densities of max. 6.7 kW cm\(^{-2}\) and shorter irradiation times of 5–6.5 ms, the melting temperature of a-Si should not be reached. In Figure 2c, a continuous interface with a nanocrystalline area can be seen. Microcrystalline is defined as crystallites with a grain size in the micrometer range diameter. Smaller crystal structures are referred to here as nanocrystalline. Both are shown in Figure 3. Epitaxial growth is already evident in the micro-crystallized region as shown in Figure 4 (red in lower part). For confirmation, the transition area of the sample in Figure 3b was examined with EBSD. No epitaxial growth is shown in Figure 4b (colors in the upper part). The nanocrystalline region does not show a preferential growth direction, so it can be indicated that the thin silicon oxide layer is still present. Publications demonstrate that solid phase epitaxy is prevented by barrier layers\(^{[15,16]}\). Figure 4c shows an amorphous silicon area with no discernable pattern. The passivation and thus the quality of the existing SiO\(_x\) layer will be evaluated in the following.

For scanning speeds of 10 mm s\(^{-1}\) and below the laser must be operated in very low power ranges to remain in the nanocrystalline range. To work in a stable and higher range of laser power, the laser treatment was investigated at scanning speeds of 15 and 20 mm s\(^{-1}\). Only the front side was scanned with the laser. Due to a high thermal conductance of 150 W m\(^{-1}\) K\(^{-1}\) of silicon, a low absorption of 65% at 808 nm and a rather long irradiation time of up to 6.5 ms it can be assumed that the wafer is heated through the entire sample thickness.\(^{[16–18]}\) Preliminary tests indicated that the backside is also indirectly treated. Further analysis and experiments are ongoing and planned on this subject.

For the evaluation of the intact SiO\(_x\) layer, the lifetime of the minority carrier density and the implied open-circuit voltage (\(iV_{oc}\)) were determined for each sample.\(^{[9]}\) Figure 5a shows the fitted lifetime at a minor carrier density of 5 \(\times 10^{15}\) cm\(^{-3}\) versus power density for both scanning speeds. The curves show a relatively fast increase in which the lifetime improves significantly. Figure 5b indicates that both curves have a nearly equal energy input per unit area. For the 15 mm s\(^{-1}\), the curve has a slight shift toward higher fluences and thus leads to a slightly higher heat input. However, both curves show similar lifetime values above 1.1 ms and an implied open-circuit voltage of around 660 mV without further passivation of the surface. At much lower power densities, the samples still show lifetimes comparable with those as-deposited wafer with amorphous silicon. Here it seems that the laser treatment does not have any effect on the layer system yet. The improvement of the sample parameter with increasing laser densities can be attributed at this point to dopant activation and an increase in the crystalline fraction.\(^{[1,19]}\) At much higher power densities, the oxide layer seems to be already affected due to the higher heat input. Studies show that with increasing heat input, dopant diffusion is enhanced due to a higher hole density and the passivation effect is lowered, resulting in lower sample parameters.\(^{[20,21]}\) There, the thermal behavior of the interfacial oxide layer was investigated. Particularly in refs. \(^{[19,21]}\) the influence of the annealing temperature on the lifetime and implied open-circuit voltage values is shown. This corresponds generally with our measurements. The peak in the middle region presents the best values for the crystallized Si layer. The two best-performing samples of each scanning speed were further subjected to a hydrogen passivation step. The \(iV_{oc}\) values in Table 1 already seem to show a slight alteration of the passivation effect by the laser treatment. Presumably, the heat input of the laser has already broken up small parts of the oxide layer, and there is already dopant diffusion taking place here. However, the values show that it can be assumed that, in addition to the improved dopant activation and crystallization, the passivation effect is still largely present. For comparison, the best values are around 740 mV for furnace crystallized solar cells.\(^{[21]}\) Since the laser has a simultaneous influence on crystallization, dopant activation, and oxide layer quality, further experiments are planned to

![Figure 3](image_url)  
**Figure 3.** Microscope images of the transition area between: a) of a liquid phase crystallization and microcrystalline range and b) microcrystalline and nanocrystalline range.

![Figure 4](image_url)  
**Figure 4.** EBSD image of: a) the microcrystalline area, b) the region between micro- and nanocrystalline area crystallized by a diode laser, c) an amorphous silicon area and the color-coded map of the crystal orientation.
further investigate the individual processes, especially the optimization of the layer thickness of the oxide for diode laser treatment.

Additionally, we expect a gettering effect of the impurities from the substrate in the crystallized Si layer, however, the improvement of the performance might be expected for wafers with rather low quality.\textsuperscript{[22]}

Table 1 shows the measured parameters for a specific minority carrier density of $1\times10^{16}$ cm$^{-3}$. For the best sample, a fitted lifetime of above 4.06 ms and an implied open-circuit voltage of up to 711 mV has been reached. In a next step, solar cells will be prepared and the $J$–$V$ parameters, efficiencies, and EQE values will be determined.

### 4. Conclusion

A new method of crystallization and dopant activation for the fabrication of passivating contacts for solar-cells-based laser treatment using a diode laser was investigated. For the two different scanning speeds of 15 and 20 mm s$^{-1}$, approximately the same lifetime values could be achieved. The best results could be measured at the scanning speed of 15 mm s$^{-1}$ and laser power density between 4.8 and 5.0 kW cm$^{-2}$. There the silicon layers can be crystallized with minimal affecting the very thin tunneling oxide. An $iV_{OC}$ value of 711 mV and a $\tau_{fit}$ of 4.06 ms after hydrogen passivation could be achieved.

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### Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

crystalline silicon, laser treatment, lifetime, passivating contacts, solar cells

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