Influence of pulse duration on the doping quality in laser chemical processing (LCP)—a simulative approach

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Abstract The laser chemical processing (LCP) technique for the local doping of crystalline silicon solar cells is investigated. Here, a liquid jet containing a dopant source acts as a waveguide for pulsed laser light, which results in the melting and subsequent doping of the silicon surface. Typical LCP pulse durations are in the 15 ns range, giving satisfactory results for specific parameter settings. While great potential is assumed to exist, optimization of the pulse duration has until now not been deeply investigated, because it is hard to change this parameter in laser systems. Therefore, this paper accesses the influence of the pulse duration by a simulative approach. The model includes optics, thermodynamics, and melt dynamics induced by the liquid jet and dopant diffusion into the silicon melt. It is solved by coupling our existing finite differences Matlab-code LCPSim with the commercial fluid flow solver Ansys Fluent. Simulations of axial symmetric single pulses were performed for pulse durations ranging from 15 ns to 500 ns. Detailed results are given, which show that for longer pulse durations lateral heat conduction significantly homogenizes the inhomogeneous dopant distribution caused by the speckled intensity profile within the liquid jet cross section. The melt expulsion by the liquid jet is low enough that a sufficiently doped layer remains after full resolidification for all pulse durations. Last, temperature

gradients are evaluated to give an indication on the amount of laser damage induced by thermal stress.

1 Introduction

In the field of silicon solar cells, laser doping processes are on their way to industrialization, providing an efficient method for producing selective emitters [1–3] and local back/front surface fields [4, 5]. This paper focuses on a special laser doping technique called laser chemical processing (LCP), in which a liquid jet is used to guide laser light together with a suitable dopant source to the wafer surface [6]. Here, promising results have been achieved for selective emitters [7, 8] and local boron dopings [9], using a 532 nm laser with a pulse duration in the range of 15 ns.

In regard to the laser parameters, it is in common agreement that the wavelength of 532 nm is well suited for laser doping applications, showing a high absorption in silicon and being provided by industrial standard frequency doubled Q-switched solid state lasers. Other parameters like the pulse energy and the pulse distances have been experimentally widely investigated. However, the pulse duration, which is assumed to have a major impact on the resulting quality of the processed surface, has not yet been investigated for LCP and has just recently started to be investigated for dry laser doping processes [10]; that this is so is due to the pulse duration being a hard-to-change parameter in available laser systems.

In LCP, one has to deal with an inhomogeneous intensity profile within the liquid jet, caused by its multimode waveguide properties [11, 12]. This results in lateral inhomogeneous dopant distribution, which can be disadvantageous due to the resulting probability of shunting between the metal contact and the base and in regard to shielding

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from surface recombination. It has to be mentioned that even for a flat top profile and also in dry laser processes, a strong inhomogeneous intensity distribution is caused by interference effects when processing on a textured surface [13]. For LCP, the doping is usually homogenized by using overlapping pulses with a small pulse distance, which strongly limits the achievable scanning speed for an industrial process.

Another possibility for homogenization of the dopant distribution is to use longer pulse durations to benefit from the increased lateral heat conduction, which smears out the molten region, and thus the dopant distribution. However, the resulting higher melt lifetime increases the melt expulsion by the liquid jet, which partly removes the molten layer, and thus reduces the doping depth.

Because the pulse duration of 15 ns is not assumed to be optimal, and experimental variation of pulse duration is, as previously mentioned, difficult, this paper investigates the influence of the pulse duration by a simulative approach. For this, the existing model for laser light reflection, absorption, heat conduction, phase changes, and dopant diffusion [14] is transiently coupled to the fluid flow solver Ansys Fluent for consideration of melt expulsion by the liquid jet. The dopant distribution, as well as thermal gradients during a single laser pulse impact are analyzed, which are assumed to be the most meaningful results for the overall process quality.

2 Model

A detailed description of the model and the used material properties is given in [12, 14, 15]. In this section, only a short overview is presented.

Basically, the enthalpy based heat transport equation is solved, including a convection term due to melt movement with velocity field $\mathbf{v}$ and a source term S_{heat} due to absorption of laser light.

$$\frac{dH}{dt} = \nabla \cdot K \nabla T(H) - \mathbf{v} \cdot \nabla H + S_{\text{heat}} \quad (1)$$

Here, H denotes the enthalpy in energy per volume units, K the heat conductivity, and T the temperature. The relation between enthalpy and temperature is given by the following stepwise integral, including the temperature dependent heat capacity c_p and density ρ , where the latent heat of melting is considered.

$$H(T) = \int_0^T \rho c_p dT \quad (2)$$

The absorption of the laser light intensity I , directed in z -axis only, is calculated with a spatially dependent absorption coefficient α .

$$S_{\text{heat}} = -\frac{dI}{dz} = \alpha I \quad (3)$$

Reflection at the surface is calculated by the complex temperature dependent refraction indices $n + ik$ of the silicon surface and the environment.

$$R = \frac{(n_{\text{env}} - n_{\text{Si}})^2 + k_{\text{Si}}^2}{(n_{\text{env}} + n_{\text{Si}})^2 + k_{\text{Si}}^2} \quad (4)$$

The diffusion of dopant atoms in silicon melt is considered by the transport equation of the dopant concentration C , including a diffusion coefficient D . Due to the diffusion coefficient being orders of magnitude higher in molten silicon compared to solid silicon, diffusion in solid silicon is neglected.

$$\frac{dC}{dt} = D \nabla^2 C - \mathbf{v} \cdot \nabla C \quad (5)$$

In LCP, a fast transport of the dopant source is provided by the high velocity liquid jet and, therefore, an infinite source boundary condition with constant surface concentration C_0 can be assumed.

$$C|_{\text{surf}} = C_0 \quad (6)$$

Fluid flow for the three immiscible phases air, liquid jet medium, and silicon is considered by a volume of fluid (VOF) model as implemented in Ansys Fluent. The properties of the mixture are defined by the volume fractions a and the properties of the individual phases, respectively. One momentum conservation equation (7) for the mixture is solved. For each but the primary phase, a mass conservation equation (8) is solved, while the primary phase volume fraction is determined by $\sum_{q=1}^3 a_q = 1$.

$$\begin{aligned} \frac{d}{dt}(\rho_{\text{mixture}} \mathbf{v}) + \nabla \cdot (\rho_{\text{mixture}} \mathbf{v} \mathbf{v}) \\ = -\nabla p + \nabla \cdot [\eta_{\text{mixture}} (\nabla \mathbf{v} + \nabla \mathbf{v}^T)] + \mathbf{S}_{\text{mom}} \end{aligned} \quad (7)$$

$$\frac{d}{dt}(\alpha_q \rho_q) + \nabla \cdot (\alpha_q \rho_q \mathbf{v}) = 0 \quad (8)$$

$$\rho_{\text{mixture}} / \eta_{\text{mixture}} = \sum_{q=1}^3 a_q \rho_q / \eta_q \quad (9)$$

$$\begin{aligned} \mathbf{S}_{\text{mom}} = (\sigma_{\text{Si}} - \sigma_{\text{env}}) \frac{\rho_{\text{mixture}} \chi_{\text{Si}} \nabla a_{\text{Si}}}{0.5(\rho_{\text{Si}} + \rho_{\text{env}})} \\ - \frac{(1 - \beta)}{(\beta^3 + 0.001)} 10^8 \frac{\text{kg}}{\text{m}^3 \text{s}} \mathbf{v} \end{aligned} \quad (10)$$

Here, p denotes the pressure, η the dynamic viscosity, $\mathbf{S}_{\text{mom}}$ the momentum sources (due to surface tension and melting/solidification), and χ the surface curvature. The continuum method published in [16] is used for modeling silicon surface tension effects as a momentum source. The viscosity and surface tension of liquid silicon σ_{Si} are set constant to their values at the melting temperature [17], which is justified by the fact that after the relatively short laser pulse the melt movement dominantly takes place at melting temperature. Note that the temperature dependent density of silicon

as given in [18] is used to account for thermal expansion effects within the incompressible fluid flow. To account for melting and solidification on the fluid flow side, a momentum sink is incorporated dependent on the fraction β of latent heat incorporated into each grid element [19], shown as the second term on the right-hand side of Eq. (10). The values of the constants presented in this term achieve the best overall numerical performance for the conditions used in this work; for the liquid jet medium and silicon separate temperature fields are solved, while the heat transfer at the interface J_{surf} is considered by the liquid jet side temperature gradient and heat conductivity.

$$J_{\text{surf}} = K_{\text{liquid}} \left. \frac{dT}{d\vec{n}} \right|_{\text{surf,liquid}} \quad (11)$$

Note that in the model no vapor phase between the liquid jet and the silicon melt is considered, which potentially changes viscous stresses and pressures exerted at the silicon melt surface as well as the interfacial heat transfer. However, it can be shown that the influence on the results presented in this paper is negligible. First, simulations with largely different viscosities of the liquid jet gave very similar results, showing that dominantly the pressure gradients rather than the viscous stresses induce the movement of the silicon melt. Secondly, in [15] (pp. 84–87), a virtual film thickness of <500 nm is derived from the temperature profile in the liquid jet. It can be shown by one-dimensional heat transport considerations that due to a lower thermal conductivity of the vapor film its real thickness is even smaller. Considering the high temperatures and pressure gradients induced by the laser heating and the liquid jet impingement, it can further be shown that evaporation and vapor flow dynamics happen considerably faster than heat transport, and in particular silicon melt flow. Thus, the vapor film can be assumed to be in quasi-steady state and thin, which validates the simplification that the pressure exerted on the silicon surface is equal to the pressure induced by the liquid jet flow. Lastly, simulation results and analytical estimations show that heat transfer to the liquid jet has significant influence for long pulse durations only and also on the hump formation in the regions outside the laser impact only, which is not the region analyzed in this work. Evidence for the still approximately correct amount of heat transfer as well as the model in general is given by the agreement with experimentally observed melt flow structures; see [15], pp. 109–111. Due to the complexity of the involved physics still some uncertainties of the model assumptions remain, so the results shown in this paper should be considered to be qualitative indications only.

The presented model equations are solved in a way that is 2d axially symmetric. The optical effects, including the heat sources as well as the diffusive parts of the transport equations (1) and (5) are solved by the finite differences code

LCPSim developed at Fraunhofer ISE [14, 15]. Ansys Fluent is used to calculate the multiphase flow including surface tension and density changes of silicon melt. It further solves heat transport in the liquid, heat transfer between silicon and liquid, and the convective parts of Eqs. (1) and (5) by user-defined scalars. The coupling is realized by user-defined functions in such a way that after every Fluent time step, the current silicon phase distribution, silicon enthalpy, and dopant concentration is exported to LCPSim, where the time integration occurs over several smaller time steps and the results are exported back to Fluent. This efficiently accounts for the different time scales in which laser heating and fluid flow occur. The data export and import is done within the overlapping region of the LCPSim and Fluent solution domain only and on an identical rectangular grid to prevent interpolation errors.

3 Simulation setup

The grid sizes used for the simulations in this work are 200 nm in radial (x) direction, and 100 nm in axial (z) direction within the data exchange region. These grid sizes admittedly state a rough discretization of the velocity and temperature fields, especially at the boundary layer of the liquid jet impinging on the silicon surface. However, it is shown in [15] pp. 87 and 90 that the resulting melt movement is sufficiently grid independent. This can be explained by the fact that both the viscous stress and the heat transfer to the liquid jet are not dominant for the overall process dynamics.

Process parameters similar to the standard LCP doping parameters are applied in the simulations. In detail, this is a 50 μm jet diameter with a velocity of 140 m/s, assuming water properties for the liquid. As mentioned before, using an increased viscosity to account for highly concentrated phosphoric acid does not change the melt flow dynamics and, therefore, the simulation results. The surface concentration of the dopant was experimentally derived to be $C_0 = 3 \times 10^{20} \text{ cm}^{-3}$ [12]. A plane silicon surface at $z = 0$ before the beginning of the laser pulse is assumed.

Special care has been given to the intensity profile, which is inhomogeneous within the liquid jet. For this, a measured profile was used and the intensity data along a line starting from the spot center was used as the axial symmetric intensity distribution $I(x)$, giving an representative exemplary case for LCP; see Fig. 1.

A variation in pulse duration is performed starting at 15 ns, being the standard value in current experiments, and additionally for 50 ns, 150 ns, and 500 ns. To have a fair comparison, the pulse energy has been adjusted in such a way that for every pulse duration, the maximum temperature reached is the boiling temperature of silicon, which is estimated to be roughly 3500 K considering the increased ambient pressure by the liquid jet impingement. This also ensures

Fig. 1 Intensity distribution as used in the axial symmetric simulations; values derived from a line scan within a measured intensity profile as shown in the upper right insertion

Fig. 2 Intensity (black) together with surface contour (green), absolute doping depth at 10^{16} cm^{-3} (red), and maximum melt depth (blue) for single laser pulses with different pulse durations after full resolidification; note that an equal axis scale is applied

that the used model is valid, because it neglects evaporation and a vapor phase.

The resulting computation time was between 1 day (15 ns) and 6 days (500 ns) on a single state-of-the-art processor.

4 Results and discussion

The pulse energies found to raise the temperature on the silicon surface to a maximum of 3500 K were 2.9 μJ for 15 ns, 5.3 μJ for 50 ns, 10.7 μJ for 150 ns, and 23.3 μJ for 500 ns. Note that experimental values are significantly higher (around 10–15 μJ for 15 ns), which is caused by the differences in the applied intensity profile. However, conclusions of the presented results are also valid for the actual intensity profile case.

In Fig. 2, the resulting melt depths, doping depths, and the surface contour after full resolidification are shown for

Fig. 3 Doping depth at 10^{16} cm^{-3} relative to the actual surface geometry

the different pulse durations. Here, the melt depth is the maximum occurring over the entire process time. The doping depth is the iso-line of the dopant concentration at 10^{16} cm^{-3} , which corresponds roughly to the location of the p-n junction if opposite doping to the silicon bulk is applied. First, it can be seen that with increasing pulse duration a bigger hump is created at the outer region of the spot, which is due to increased melt movement by increased melt lifetime and molten volume. However, the expulsion is not too strong and leaves a significant amount of doped melt within the spot for all pulse durations. Secondly, a homogenization of the melt and dopant distribution by increased lateral heat conduction is observed; while for 15 ns the doping depth is more or less a direct image of the intensity distribution, for 150 ns and more at least the 2 major peaks located away from the spot center are nearly fully united to one homogeneously doped region.

In Fig. 3, the doping depth relative to the actual surface geometry, which is the absolute doping depth less the surface contour, is shown as being the relevant value for assessment of the resulting electrical properties. It can be seen in detail that, as well the maximum doping depth, but more importantly also the homogeneity of the dopant distribution increases with increasing pulse duration. If one sets a suitable doping depth at 400 nm, for example, the maximum continuously doped length increases from $\sim 4 \mu\text{m}$ for 15 ns to $\sim 14 \mu\text{m}$ for 150 ns. At the same scale, the pulse distance for overlapping pulses can be increased, ensuring a continuously doped line. These effects are even more increased for 500 ns. However, a major part of the doped region then consists of expelled silicon lying on the original silicon surface, which is assumed to have high crystal defects and, therefore, poor electrical properties.

While it seems highly beneficial to use higher pulse durations by considering the dopant distribution, one also has to consider laser damage, which possibly results in higher crystal defects and recombination activity in the processed region for higher pulse durations.

Fig. 4 Temperature gradient [10^9 K/m] maximized over time and corrected by melt evolution plotted together with the doping depth (solid line) and maximum melt depth (dashed line) after full resolidification for 50 ns pulse duration

At present, only empirical data for the complex influence of laser parameters on the electronic properties of the processed region exist in regard to solar cell performance. No model or corresponding experimental data are known which could be used to predict the actual amount of laser damage introduced for the different pulse durations. However, in [20], it is mentioned that thermal stress could be a dominating mechanism to cause laser damage. Therefore, temperature gradients, which are the cause of thermal stress, were analyzed during the simulation to at least give an indication of the thermally induced damage. The region to be looked at is around and underneath the doping depth, being most sensitive to carrier recombination, and thus solar cell performance. Above the doping depth, the minority carriers are strongly reduced because of the high doping level, and in this way recombination stays relatively low even for poor crystal quality. The distribution of the thermal gradients is evaluated at every integration time step and the maximum values for each grid element are used for analysis. Once molten, the gradient is set to zero until resolidification to account for the melt releasing previously generated stress. It is observed that the maximum temperature gradients occur at the maximum melt depth, which is below the doping depth in any case; see Fig. 4.

To compare the different pulse durations, the maximum value of the maximum temperature gradient distribution like in Fig. 4 is evaluated for each pulse duration; see Fig. 5. Here, one can see an accurate exponential decrease for increasing pulse duration, which means thermal stress is also decreased. However, this value does not consider the different dynamics and time scales involved, resulting in different impacts on actual crystal damage. Also, any crystal defects caused by imperfect resolidification or by impurities are not considered. Nevertheless, the results indicate that laser damage may not be critical and may even be lower for increasing pulse durations.

Fig. 5 Maximum temperature gradient during single pulse impact below the doping depth for different pulse durations

5 Conclusions

In this paper, the impact of pulse durations greater than 15 ns, as used in standard LCP doping, are investigated by simulations. For this, an existing finite differences code coupled with Ansys Fluent was used to solve the equations of optics, thermodynamics, dopant transport, and multiphase flow in a transiently and fully coupled way. The 2d axial symmetric simulations of single laser pulses consider a typical inhomogeneous intensity profile as it occurs within the liquid jet cross section in LCP.

The results show an increased melt expulsion to the outer spot regions for higher pulse durations, which is expected due to increased melt lifetime and molten volume. The remaining doped layer is significantly homogenized for increasing pulse duration, because lateral heat conduction smears out the molten regions. In detail, the maximum size of a continuously doped region is increased from ~ 4 μm for 15 ns to ~ 14 μm for 150 ns pulse duration. Considering a line scan is the usual application for LCP doping, the distance between consecutive pulses can be set to approximately this value to achieve a continuously doped line. This scales directly the achievable scanning speed, which is of major interest for an industrial application.

In addition to the dopant distribution, temperature gradients were evaluated, which decrease exponentially with increasing pulse duration. Being the source for thermal stress, this is an indication that laser damage could even be lower for higher pulse durations. However, the actual process of laser damage formation and its impact on solar cell performance are far from being quantitatively understood, so this result is only an indication.

Note that all results are valid on flat surfaces and 2d axial symmetry only. On 3d textured surfaces, additional optical effects and a somewhat different melt dynamics occur. However, the concluded trends and scales of values should

be comparable, and thus give a high motivation for applying longer pulse durations in our future experiments.

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