

Approaches for reducing metallization-induced losses in industrial TOPCon solar cells

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Received: 16 August 2024 / Accepted: 5 December 2024

Abstract. Minimizing carrier recombination in silicon solar cells is key to increase the conversion efficiency, as recombination affects both the fill factor and the open circuit voltage. Recombination at metal-semiconductor interfaces plays a crucial part in this, however, processing conditions which lead to low recombination, such as e.g., a low firing set temperature or the use of thick dielectrics, typically result in increased contact resistivities. Also, a too low firing set temperature leads to an incomplete hydrogenation of the interfaces. Recently, laser-enhanced contact optimization has been introduced to decouple recombination and contact properties to some extent, which allows for high fill factors and high open circuit voltages, and which explains the growing interest from manufacturers in that technology. We elucidate on the need for improved hydrogenation of interfaces, which contradicts the wish to decrease firing temperatures for reduced carrier recombination at metal-semiconductor interfaces. The implementation of an additional annealing step, e.g. in a tube furnace, after dielectric surface passivation is shown to lead to improved passivation properties so that the thermal budget during contact firing can be optimized to minimize contact resistivities. Overall, contact optimization allows for solar cell efficiencies of 24.1%, measured at an industrial cell tester, for a traditional approach without additional annealing step, and applying an AgAl front side metallization paste. A comparison of Ag and AgAl front side metallization pastes reveals a higher open circuit voltage for the Ag paste, at the drawback of an increased contact resistivity.

Keywords: TOPCon / passivating contacts / recombination / solar cells

1 Introduction

The tunnel oxide passivating contact (TOPCon) structure has been widely accepted in industrial manufacturing. Such solar cells are made from *n*-type silicon wafers and feature a tunnel oxide in combination with a *n*-doped polysilicon layer on the rear side. The combination of passivation by the interfacial oxide layer and very shallow dopant profile beyond the oxide in the silicon wafer leads to a very low recombination current density. Furthermore, the carrier recombination after metallization (metal-induced recombination) is reduced significantly by such a contact stack. Overall, the implementation of passivating contacts in industrial solar cells (*i*TOPCon) led to solar cell efficiencies well over 25% [1–3].

To increase solar cell efficiency even further, a reduction of other loss mechanisms in *i*TOPCon solar cells is key. Overall carrier recombination is dominated by recombina-

tion at the front side of the sample, which includes the dielectrically passivated areas, and the contacted regions, whereas carrier recombination in the wafer itself becomes less important, due to the improvements in ingot pulling over the last years. For non-contacted areas, recombination is affected mainly by the dopant profile of the emitter, which often gets summarized by the emitter sheet resistance, and the passivation layer, here, in general a stack of Al₂O₃ and SiN_x. Usually, the recombination of the diffused emitter area is summarized by the term emitter dark saturation current density j_{0e} . Front side recombination at the metal contacts $j_{0e,met}$ is affected again by the emitter dopant profile, but also by the kind of metallization approach used. In case of flatbed screen-printing technology, which currently is the industry standard, this includes the composition of the metallization paste, the contact firing profile, and the metallization fraction, i.e., finger widths and pitch.

This paper addresses several approaches to reduce carrier recombination in *i*TOPCon solar cells. We first describe the impact of an Ag and an AgAl metallization

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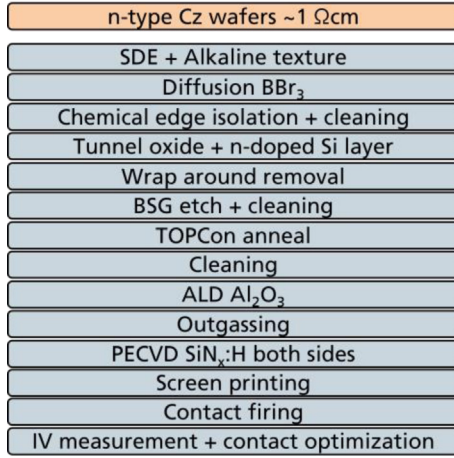


Fig. 1. Process sequence for fabrication of *i*TOPCon solar cells.

paste for the front side on solar cell parameters, and how those get affected by laser-enhanced contact optimization (LECO) treatment, which reduces the series resistance R_s by intense illumination under reverse voltage. In the following, we elaborate on the implementation of an anneal process, which is being performed after deposition of the passivation layers on both front and rear, in order to reduce overall recombination. The focus on solar cells in this study ensures the industrial compatibility and a possible fast transfer.

2 Process sequence for *i*TOPCon solar cells

The process sequence for *i*TOPCon solar cells, which is shown in [Figure 1](#), makes use of commercial *n*-type silicon wafers. The size of the wafer itself is of less importance at this stage, and our laboratory is capable of processing wafers of both 156.75 mm (M2) and 182 mm (M10) edge length. After saw-damage removal in KOH solution, etching in another KOH/additive solution bath leads to upright random pyramids. Gas-phase diffusion in an atmospheric tube furnace using boron tribromide (BBr₃) forms the emitter, followed by the combination of inline glass etching with HF/HCl and batch alkaline etching in KOH/additive solution to remove the parasitic emitter on the rear side. After growing an interfacial oxide of 1 to 2 nm thickness in oxygen containing ambient by thermal oxidation in a tube furnace, the phosphorous doped silicon layer is deposited on the rear side by a chemical vapor deposition process, either under low pressure (LPCVD) or plasma-enhanced (PECVD). Another inline etching step removes the wrap around on the front side as well as the borosilicate glass (BSG) stack grown during the diffusion process. Next to a cleaning step, a thermal annealing process leads to some drive-in of phosphorous into the silicon wafer and increases the crystallinity of the deposited silicon layer. The passivation sequence includes another cleaning step, the deposition of an Al₂O₃ layer by means of atomic layer deposition (ALD), an outgassing step in a tube furnace to prevent blistering and allow for low carrier recombination, and the deposition of SiN_x layers on both

front and rear by PECVD. For metallization, we rely on established flat-bed screen-printing technology of silver containing pastes, followed by contact firing in an inline conveyor belt furnace with a belt speed of 6 m/min. Optionally, a LECO unit [\[4\]](#) included in our cell tester is used to reduce contact resistivity ρ_c .

Sample characterization at different stages of processing includes photo-conductance decay (PCD) at a Sinton WCT-120 lifetime tester, spectroscopic ellipsometry at a M-2000 by J.A. Woollam, current-voltage (I - V) measurements of solar cells at a class AAA cell tester from halm elektronik GmbH with a Xenon flash unit, and determination of contact resistivity ρ_c by the transfer length method (TLM-SCAN from pv tools GmbH).

3 Results

3.1 Balance of passivation and contacting

For highly efficient TOPCon solar cells, both the passivation quality and the fill factor FF need to be on a high level. To address this topic, in a first step, we fabricate asymmetric lifetime samples, i.e. solar cells without metallization with LPCVD polysilicon layer and Al₂O₃/SiN_x antireflection coating (ARC), to determine the upper limit of the open circuit voltage implied V_{oc} (iV_{oc}) by means of PCD measurements, in dependence of the firing set temperature. In general, typical firing set temperatures for solar cell metallization are chosen, as will be visible further below in the paper. The results, which are shown in [Figure 2](#) (left), indicate a dependence of the overall passivation quality of our samples and thus the voltage potential on the firing set temperatures. Depending on the firing set temperature, mean iV_{oc} ranges between 723 mV and 730 mV, with higher values achieved for the highest investigated firing set temperature of 820 °C. This indicates an incomplete hydrogenation of the interfaces and thus an incomplete activation of the passivation layers at 780 and 800 °C. As a consequence, solar cells should be fired at a set temperature of 820 °C to exploit that potential.

In the same experiment, we also fabricate solar cells on sister wafers as described in [Figure 1](#), using an AgAl paste on the front side and an Ag paste on the rear side. Importantly, no LECO treatment is performed here on the solar cells. Looking at the I - V results in [Figure 2](#) (right), another strong dependency on the firing set temperatures is visible. The increase from 780 °C to 820 °C leads to a considerable increase of fill factor FF , a result from improved contact formation, but also a strong decrease of open circuit voltage V_{oc} by 14 mV due to increasing recombination at the AgAl front contact $j_{0e,met}$, or 2% relative, which leads to a maximum conversion efficiency η at 800 °C firing as a trade-off between FF and V_{oc} . The results indicate that the maximum iV_{oc} potential cannot be exploited, and quite contrary, metallization induced losses, here in brevity described by $iV_{oc} - V_{oc}$ strongly increase from 11 mV at 780 °C firing to 32 mV at 820 °C. In the solar cells, this is a result from j_{01} , which increases from 35 fA/cm² at 780 °C firing to 60 fA/cm² at 820 °C firing, and likewise from j_{02} , which increases from 2.3 nA/cm² to 3.5 nA/cm², respectively. Both j_0 values have been determined by a

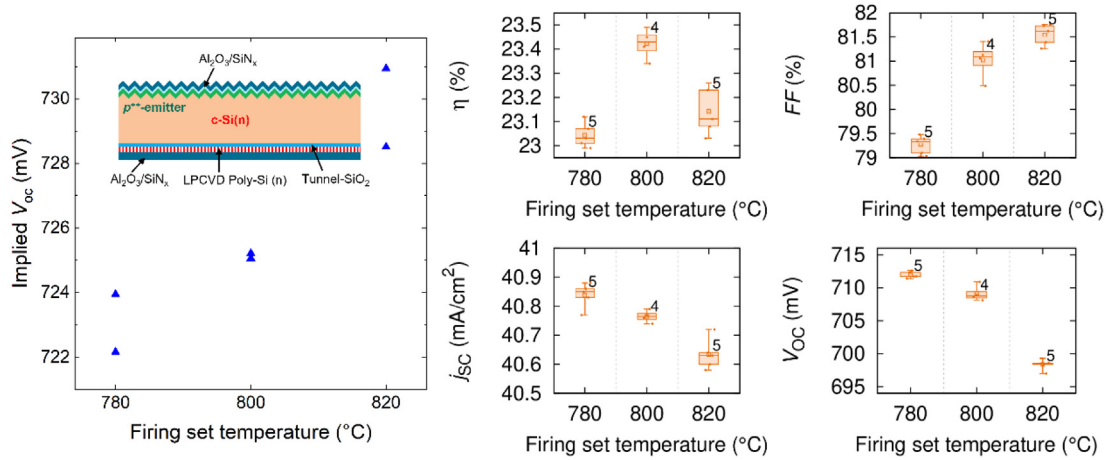


Fig. 2. (left) Implied V_{oc} for asymmetric lifetime samples with LPCVD polysilicon layer and $\text{Al}_2\text{O}_3/\text{SiN}_x$ ARC, measured after contact firing without any metallization for different firing set temperatures. The inset shows a schematic cross section of the samples. (right) I - V results of solar cells with AgAl front side metallization, fabricated in the same experiment and without any LECO treatment. The number next to the box plots refers to the group size.

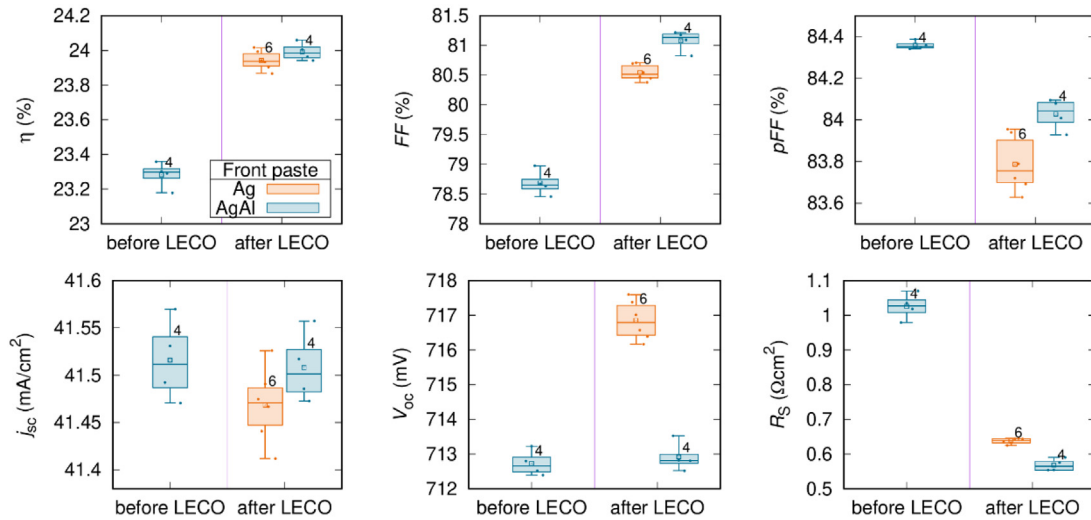


Fig. 3. I - V results of i TOPCon solar cells with PECVD polysilicon layer and $\text{Al}_2\text{O}_3/\text{SiN}_x/\text{SiO}_x\text{N}_y$ ARC fired at 790 °C set temperature and measured at an industrial cell tester, before and after LECO treatment for two different front side pastes. The number next to the box plots refers to the group size.

least-squares fit of the two-diode-model to the dark I - V curve. Thus, the task is to solve this tradeoff between ideal metallization and passivation conditions, i.e. to find processing conditions for ideal contact formation while minimizing metallization induced losses at the same time.

3.2 Impact of front metallization paste

For contacting of the boron emitter on the front side of the solar cell, a silver-based metallization paste is used. The actual composition of the metallization paste has a strong impact on overall cell efficiency, but also on the underlying I - V parameters. We compared the impact of two different metallization pastes in a single experiment, an Ag based paste and another paste to which Al was added by the

manufacturer (both commercial products, other components unknown). For both metallization pastes, the same screen layout with 24 μm wide openings (cell side) has been used. The results are shown in Figure 3. Differing from the process sequence described above, the solar cells in this experiment feature a polysilicon layer formed by PECVD on the rear side, a $\text{SiN}_x/\text{SiO}_x\text{N}_y$ double antireflection coating on the front side and all samples have been fired at the same firing set temperature of 790 °C. Typically, PECVD and LPCVD polysilicon layers give similar results, which makes this variation acceptable.

Before LECO, the AgAl paste yields a median solar cell efficiency $\eta = 23.3\%$, whereas the tested Ag paste does not form a low-ohmic contact and shows $FF < 30\%$ and $\eta < 1\%$. LECO processing leads to dramatic changes in the contact

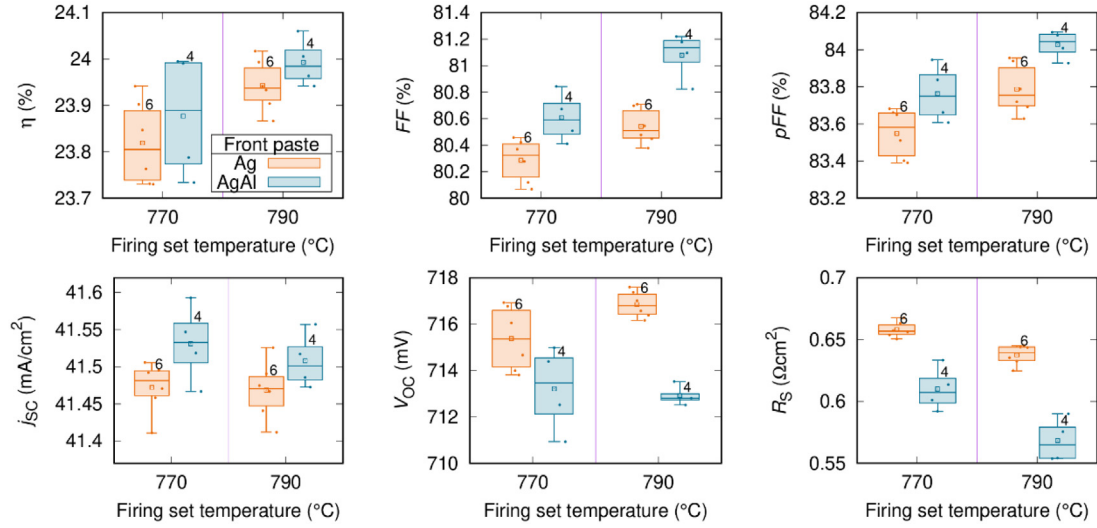


Fig. 4. I - V results of i TOPCon solar cells with PECVD polysilicon layer and $\text{Al}_2\text{O}_3/\text{SiN}_x/\text{SiO}_x\text{N}_y$ ARC, measured at an industrial cell tester, for two firing set temperatures and two different metallization pastes, after LECO treatment. The number next to the box plots refers to the group size.

properties of the metallization pastes, leading to an efficiency increase of 0.7% absolute for the AgAl paste by lowering the R_s of the cells (on both front and rear as was shown earlier [5]) and thus increasing FF . Nevertheless, there is a drop in pFF due to LECO for the AgAl paste, indicating changes at the metal-semiconductor interface, whereas short-circuit current density j_{sc} and V_{oc} are not affected. Keep in mind, that in general, pFF is viewed as an upper limit of the fill factor under maximum power point mpp conditions without R_s contribution, and while this view is correct, pFF and changes in it also provide information about contact recombination under mpp conditions.

After LECO, both metallization pastes allow for a solar cell efficiency $\eta = 24\%$, with a slight advantage for the AgAl paste. Both metallization pastes yield a similar high $j_{sc} = 41.5 \text{ mA/cm}^2$. However, completely different behaviors are found for fill factor FF and open circuit voltage V_{oc} . The AgAl paste leads to a 0.6%_{abs} higher FF , at the drawback of a 4 mV lower V_{oc} . The reason for this lies in the contacting behavior. The addition of Al leads to deeper contacts, as was shown earlier [6], and penetration depths approaching the emitter junction depth result in a strongly increasing recombination current density $j_{0e,met}$. On the other hand, the (compared to an Ag paste) larger metallized area fraction due to deeper spikes [6] (i.e. the actual 3D contact area, which is larger than the 2D projection) and the Al doping by the paste itself lead to a lower R_s ($\rho_{cAgAl} = 1 \text{ m}\Omega\text{cm}^2$, $\rho_{cAg} = 3 \text{ m}\Omega\text{cm}^2$). The improved self-passivation of the contact by alloying is visible in a higher pseudo fill factor pFF for the AgAl paste.

Apart from the results shown above for a firing set temperature of 790 °C, also 770 °C firing has been tested in parallel. The results for both temperatures, for the Ag as well as the AgAl paste after LECO are shown in Figure 4, thus including the data from Figure 3. Overall, η is found to be higher for 790 °C firing, culminating in a maximum $\eta = 24.1\%$ in case of the AgAl paste, with the Ag paste trailing by around 0.1%. The higher firing set temperature

also has a benefit with respect to the V_{oc} distribution, which is considerably shallower, which might be linked to local temperature differences over the wafer during contact firing, and higher set temperatures leading to a more effective hydrogenation of the interfaces. As can be seen, irrespective of the applied paste, in particular FF and pFF are higher at 790 °C firing set temperature. This again indicates an incomplete hydrogenation at 770 °C firing under mpp conditions. The results indicate that this is linked to a j_{02} effect, as the ideal fill factor FF_0 - pFF difference increases by 0.2%_{abs} for both pastes when increasing the firing set temperature from 770 °C to 790 °C, with a drop in j_{02} by 0.4 nA/cm² in case of the Ag paste and 0.7 nA/cm² for the AgAl paste. Here, the lower $j_{0e,met}$ in case of the Ag paste also explains why V_{oc} stays more or less constant or even slightly increases, in combination with an increase in iV_{oc} , when increasing the firing set temperature, whereas for the AgAl paste and the inherently higher $j_{0e,met}$, V_{oc} decreases, in accordance with Figure 2.

The trend in industrial manufacturing goes towards implementation of LECO [7] to reduce $j_{0e,met}$ and also metallization related recombination at the rear side. This gets combined with metallization pastes, that have been specially designed for being post-treated by LECO. To compensate for the otherwise lower pFF that might occur at lower firing set temperatures, other approaches have to be undertaken, and this will be the content of the following sub-section.

3.3 Tube furnace passivation anneal

As we have seen in the previous sub-section, the surface passivation layers might not have been fully activated at the lower firing set temperature of 770 °C. A desired solution would be to first find a solution for full hydrogenation of the interfaces at lower firing set temperatures to allow for a high V_{oc} and pFF , and later apply a

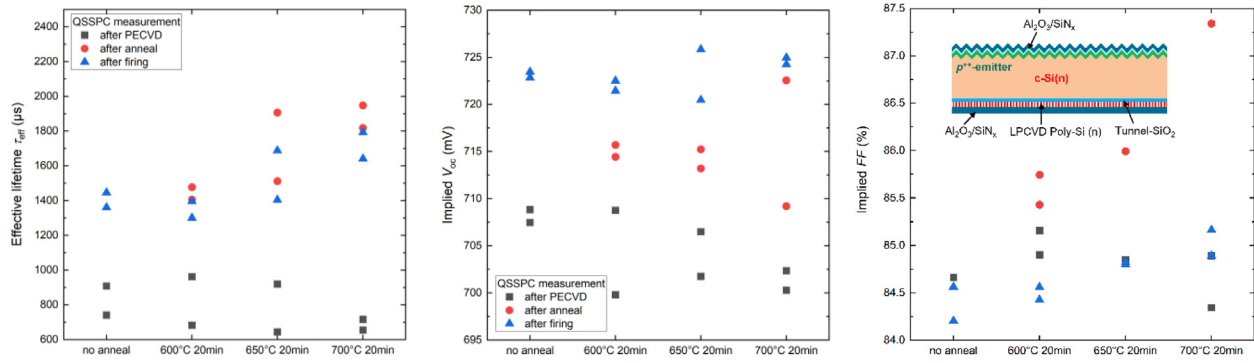


Fig. 5. Impact of passivation anneal on asymmetric lifetime precursors with LPCVD polysilicon layer and $\text{Al}_2\text{O}_3/\text{SiN}_x$ antireflection coating (ARC). The passivation quality has been determined after PECVD surface passivation, after an additional tube furnace anneal, as well as after firing. The inset shows a schematic cross section of the samples.

LECO step for low R_s . To increase pFF , the effect of a tube furnace anneal in nitrogen is tested, which is introduced after PECVD of SiN_x and before screen-printing of the metallization pattern. Asymmetric cell precursors with a polysilicon layer formed by LPCVD are used. The results are shown in Figure 5. The achieved level of passivation has been determined before (black symbols) and after tube anneal (red) in the center of the samples. For simplicity, a plateau time of 20 min is chosen, with the process being done in nitrogen, and plateau temperatures of 600 °C, 650 °C, and 700 °C, are compared to a reference group without tube anneal. All samples of one group have been subject to only one tube anneal after PECVD (or no anneal at all). Additionally, all samples were submitted to a firing process without prior metallization (800 °C set temperature), to yield the final passivation quality (blue).

In terms of effective lifetime τ_{eff} , which is determined at an injection density $\Delta n = 10^{15} \text{ cm}^{-3}$, annealing in a tube furnace leads to an increase in passivation quality. Compared to the values determined directly after PECVD (black squares), tube annealing leads to improved hydrogenation of the interfaces (red circles) by releasing hydrogen from the Al_2O_3 and the SiN_x layers, which results in a higher τ_{eff} . Higher thermal budgets seem to be more efficient. What is important for the implementation in solar cells, is that this trend is persistent even after a firing step (blue triangles), so the focus should be the discussion of the achieved passivation level after firing. On iV_{oc} level, which is determined at a higher Δn than τ_{eff} and iFF , only a small increase of around 2 mV is found due to annealing after firing, comparing the 700 °C group (725 mV) to the reference group without tube anneal (723 mV). At lower injection Δn , the implied fill factor iFF shows again a strong increase by tube annealing, which is again persistent after firing, and in a range of up to 0.7% absolute (blue triangles at 700 °C process compared to the reference group to the left without tube anneal). Based on these results (strong increase of iFF , moderate increase of iV_{oc}) an application of pre-firing annealing should be visible mainly in pFF and FF parameters at solar cell level.

To fabricate solar cells, the lifetime samples from Figure 5 have been taken and subjected to additional screen-printing of Ag pastes on front and rear and firing, combined with LECO treatment. This procedure implicates that all samples have been subject to in sum two firing steps. While keeping that in mind, the group “no anneal” serves as a reference group without any passivation anneal. The I - V results in Figure 6 show an increase in pFF and FF , but only up to 0.2% absolute due to other existing loss paths in the solar cell, and only for the 650 °C process, while other annealing temperatures did not show an increase of pFF . On the other hand, there is significant decrease on V_{oc} , with a drop of up to 8 mV between the different groups, which increases with increasing thermal budget of the passivation anneal. We also find an impact on the series resistance R_s (determined by comparing the maximum power point of the one-sun I - V curve with the dark I - V curve), again decreasing with thermal budget. Overall, the passivation anneal leads to a decrease of η for the 600 °C and 700 °C process, and possibly a slight η increase for the 650 °C process. The effect of V_{oc} and R_s is not yet understood at this point. The I - V measurements further reveal that j_{02} (determined from the dark I - V curve) decreases for 650 °C and 700 °C annealing by up to 20%, and j_{01} increases if an annealing process is performed. Moreover, in the investigated temperature range, j_{01} increases monotonically with increasing annealing temperature by up to 35%, leading to the observed decrease in V_{oc} . The combination of j_{01} and j_{02} then explains the maximum of pFF at 650 °C annealing, which is affected by both.

Ellipsometry measurements performed before and after the 650 °C annealing process do not indicate a compression of the dielectric layers due to annealing. Quite contrary, they reveal a decrease in refractive index n by 0.02 to 0.03, and changes in the layer thickness were not detected. The lowered refractive index might be due to the release of hydrogen during annealing, which would explain the increase in passivation quality in lifetime samples (red circles in Fig. 5). We speculate that annealing leads to certain changes in the morphology or composition of the SiN_x layer, which facilitates etching of the layer by the screen-printed metallization pastes during contact firing,

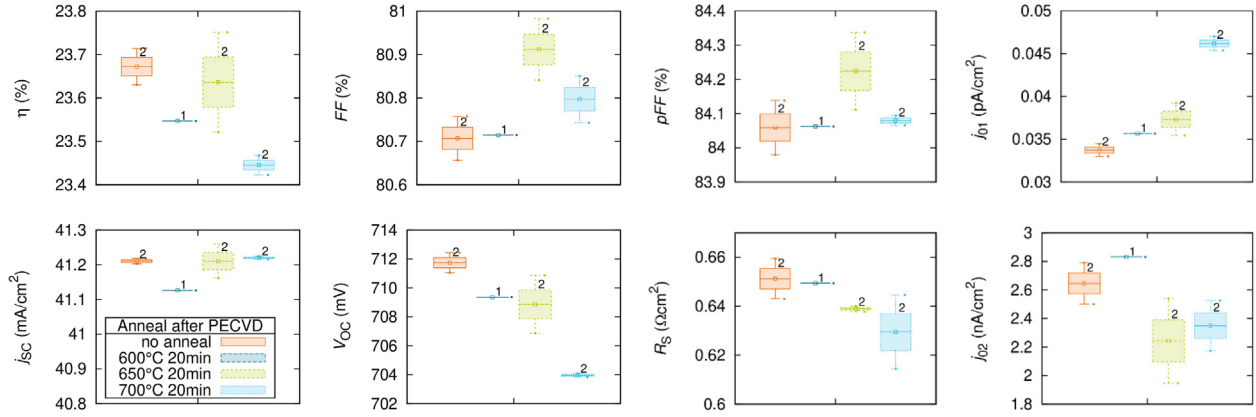


Fig. 6. Impact of passivation anneal on samples from Figure 5 with $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack on the polysilicon layer that have been fabricated to solar cells using an Ag paste and LECO treatment after firing. The number next to the box plots refers to the group size.

leading to a lower series resistance and also an increased recombination current density at the rear side (lower V_{oc} in Fig. 6).

We have also conducted the same experiment as that shown in Figure 6 with a $\text{SiO}_x\text{N}_y/\text{SiN}_x$ stack instead of a SiN_x layer on the rear side of our samples with practically the same results and the same trends. Future work should focus on exploiting the pFF potential, while at the same time reducing the negative impact on V_{oc} .

4 Discussion

The parameter pFF includes the loss paths of j_{01} , j_{02} and shunt resistance R_{shunt} . Typically, R_{shunt} is high enough in the order of several hundred $\text{k}\Omega\text{cm}^2$, which means, it can be neglected, leaving j_{01} and j_{02} . Included in j_{01} are the recombination current densities of wafer, passivated emitter and rear side, but also at metal-semiconductor interfaces. A standard approach for process optimization is reducing recombination at passivated interfaces, for example by lowering the total dopant dose in the emitter [8], or alternatively by lowering the recombination at passivated surfaces through optimization of dielectric passivation. As we have shown in Figure 6, also non-standard approaches like the implementation of an additional tube furnace annealing step before screen-printing can lead to an increased pFF in solar cells. The increase in pFF is a result of a decreasing j_{02} , in combination with an increasing j_{01} . The lower j_{02} indicates changes at transition regions between high and low doping. Still, statistics are not very large at this point, and this should not be the root source for the observed decrease in R_s . Further experiments have to be undertaken to understand the impact of tube annealing after passivation on pFF and R_s in more detail.

Often, the question arises, if an Ag or an AgAl paste should be used for front side metallization of n -type solar cells. From a solar cell point of view, the answer is rather simple. Both pastes should be compared on solar cell level, and the one with better results (in terms of e.g. cell efficiency, efficiency distribution, reliability, or reverse current density) should be used. Based on our experience,

Ag pastes without any Al addition tend to yield a higher V_{oc} , but a lower FF , and require some sort of post treatment after contact firing, e.g. by LECO, but also other methods have been proposed [9]. On solar module level, the negative effect of corrosion of Al containing pastes during damp-heat treatment has been mentioned recently [7], which is yet another reason to look into Al-free pastes or pastes with low Al content from a cell manufacturer's point of view. Even after LECO treatment, currently, ρ_c is higher for Ag pastes. Contact resistivity can be decreased by increasing the emitter dopant concentration at the surface, but typically, this goes along with an increase in surface recombination, and thus lower V_{oc} and lower j_{sc} . The impact of contact resistivity ρ_c can be decreased in solar modules by using half cells, which is industry standard already, so effort must be made to exploit the higher V_{oc} potential of Ag pastes. Keeping in mind, that LECO is still a rather new method to modify contact properties of screen-printed metallization pastes to doped surfaces, it is expected that by changes on the paste composition side as well as changes to the LECO process parameters, lower ρ_c will be achieved in the near future.

Finally, one can conclude that without the constant optimizations being realized on the metallization paste side and lately by the introduction of LECO, many possible optimizations during frontend processing, such as emitter dopant profiles with increased sheet resistance and thus reduced Auger recombination, would not have qualified for solar cell fabrication due to otherwise high contact resistivities, leaving the efficiency potential of TOPCon solar cells unexploited.

5 Conclusion

We have studied the effect of different processes on the pseudo-fill factor pFF and fill factor of $i\text{TOPCon}$ solar cells with maximum efficiencies up to 24.1%. Our results show a huge impact of LECO treatment on final solar cell parameters. LECO leads to an efficiency increase of 0.7%_{abs} for a reference paste containing Al, due to changes at the metal-semiconductor interface, but no drop in V_{oc} . Additionally, LECO enables the use of Ag pastes with low

or even no Al content on the front side, which boosts V_{oc} of solar cells compared to their AgAl counterparts. LECO also represents a way to reduce the required firing temperature to achieve high FF and high V_{oc} in i TOPCon solar cells, a benefit that can be fully exploited in solar modules. Nevertheless, our results also show that further work has to be done to minimize the negative impact of Ag front side pastes on pFF , most probably by modifications on the paste side. Also, contact resistivity in case of Ag front side pastes needs to be reduced, either by modifications to the paste itself or by changes in the LECO parameters. The implementation of tube furnace annealing after PECVD has been shown to increase iFF in asymmetric lifetime samples, and one of those processes has also led to a higher pFF in solar cells. The I – V results show a significant reduction in j_{02} due to tube furnace passivation annealing, while j_{01} increases. Given the current trend in industry towards lower firing set temperatures, which lead to an incomplete hydrogenation of the interfaces as has been shown in the paper, such an additional annealing process could represent a solution for higher efficient solar cells.

Acknowledgments

The authors would like to thank our lab staff for excellent processing.

Funding

The authors acknowledge the financial support by the German Federal Ministry for Economic Affairs and Climate Action in the projects “StroKoTOP” (Fkz 03EE1178A) and “WamTec” (Fkz 03EE1193, Funding via the Clean Energy Transition Partnership CETP).

Conflicts of interest

The authors have nothing to disclose.

Data availability statement

Data associated with this article cannot be provided.

Author contribution statement

Conceptualization, S. Mack, J.D. Huyeng and A. Wolf; Methodology, S. Mack; Validation, S. Mack.; Formal Analysis, S. Mack; Investigation, S. Mack, C. Tessmann, K. Krieg, M. Messmer, and D. Ourinson; Data Curation, S. Mack; Writing –

Original Draft Preparation, S. Mack; Writing – Review & Editing, S. Mack, J. Benick, J.D. Huyeng; Visualization, S. Mack; Supervision, A. Wolf; Project Administration, J.D. Huyeng, and A. Wolf; Funding Acquisition, J.D. Huyeng, and A. Wolf.

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Cite this article as: Sebastian Mack, Daniel Ourinson, Marius Meßmer, Christopher Teßmann, Katrin Krieg, Jan Benick, Jonas D. Huyeng, Johannes Greulich, Andreas Wolf, Approaches for reducing metallization-induced losses in industrial TOPCon solar cells, EPJ Photovoltaics **16**, 5 (2025)