THERMAL OXIDATION AS A KEY TECHNOLOGY FOR HIGH EFFICIENCY SCREEN PRINTED INDUSTRIAL SILICON SOLAR CELLS

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ABSTRACT

In this paper various options to integrate thermal oxidation into industrial cell production are presented, maintaining large parts of the standard cell fabrication process. Both the use of thin (15 nm) and thick (200 nm) wet thermally grown oxides are successfully implemented into pilot production at the Fraunhofer production research platform PV-TEC [1]. Solar cells are fabricated with both type of processes. On large area (149mm²) Cz-Si substrates 18% efficiency have been achieved. Furthermore a cost calculation including process and equipment improvements is carried out for the thermal oxidation process and it is shown that the cost for such a process can be well below 10€ct per wafer for thick and below 5 €ct per wafer for a thin oxide, thus meeting industrial requirements for cost effective production.

INTRODUCTION

In 1989 Blakers et al. presented the PERC (Passivated Emitter and Rear Cell) solar cell reaching solar cell efficiencies of 22.8% [2] and even exceeding 23% in later work [3]. This concept is based on fundamental device structure improvements by introducing a dielectrically passivated rear surface with local point contacts. Due to reduced surface recombination velocity and improved optical performance cell parameters were improved compared to cells which do not feature dielectrically passivated surfaces. To further reduce the recombination of the point contacts and to allow for the use of high-resistivity material the PERL (Passivated Emitter Rear Locally-diffused) solar cell structure was introduced by Zhao et al. [4] in 1990. With this concept cell efficiencies exceeding 24% have been achieved. These concepts relate to the passivation and contacting concept used for point contacted back contact solar cells introduced by Sinton et al. [5, 6].

Though these results for PERC and PERL were all achieved on high quality FZ silicon wafers, excellent results have been achieved on mc substrates [7, 8] and on Cz Silicon [9, 10] using such structures. Remarkable reduction in the complexity and cost of the process is achieved using the laser fired contact (LFC) approach in which the point contacts are punched through the passivation layer using a laser while the aluminum layer is already present [11]. Alternatively the so called i-PERC process [12], in which the dielectric layer is opened before screen printed Aluminum deposition with subsequent firing can be applied.

All the above mentioned high efficiency cells have in common that the passivation of the rear surface is carried out using thermally grown silicon oxide. It serves as a passivation layer and in combination with highly reflective Aluminum coating excellent optical properties can be achieved [13].

Other layers for passivation are also under investigation as summarized in [14-16]. Various workers have used silicon nitride to passivate the rear surface and excellent low surface recombination velocities have been achieved [17]. Different attempts to integrate silicon nitride as passivation layer for industrial solar cells have shown that in general the relatively high density of fixed positive charge in these layers can create a shunt like behavior leading to fill-factor and current loss imposing a challenge on the integration of this layer type [18, 19]. Furthermore layers combining silicon nitride and silicon oxide are also under investigation of various workers [16, 20, 21].

Various groups suggest the use of aluminum oxide as a passivation layer since it carries negative charge and allows to avoid shunting behavior. Excellent results have been achieved on high efficiency solar cell structures [22-25].

Currently most silicon solar cells are fabricated using screen printed pastes for the creation of front and rear contacts. From these pastes the contacts are formed during a fast firing process. In general the integration of the passivation layer can be carried out before or after the fast firing step. If integrated before fast firing, the layer must be capable of maintaining the desired properties during this process. If integrated after fast firing the surface conditioning has to be carried out with the front contact already in place and the rear contact cannot be formed using screen printing. Thus in both approaches challenges have to be met.

Integrating thermal oxides into a solar cell fabrication process the growth rate dependencies with respect to substrate doping [26] and orientation [27] have to be taken into account. Furthermore various options for thermal oxidation exist applying different oxygen sources [28]. Especially the high growth rates at moderate temperatures for wet (water steam based) thermal oxidations are very
promising with respect to industrial implementation at high
throughput and low cost [29, 30].

In this paper we want to illustrate why thermal oxides can help to meet process integration challenges and we
intend to show that an industrial implementation of the
aforementioned very successful rear surface passivation
concepts in combination with screen printing seems to be
within reach.

**PROCESS SEQUENCE OPTIONS**

A strong asymmetry of the properties of the solar cell
front and rear is created due to the passivated back
surface. In the following Figure 1 the general difference is
shown between an industrial standard solar cell and the
desired solar cell with passivated rear surface. The
asymmetry imposes the need for processes, which are
side selective either by process principle or by using
existing layers as masks.

With respect to the standard process S various
variations exist, which e.g. can incorporate wet chemical
ech back of the rear emitter replacing the laser isolation
step. Such a process sequence is very interesting in order
to create asymmetric structures as described above. Most
industrial processes are based on the firing through silicon
nitride approach, which is therefore used here as
reference process. One important boundary condition for
the process design is to create efficient processes which
are very close to this standard process in order to reduce
the need for new developments and allow for low market
entry barriers.

Process sequence A (later referred to as FEDIO)
shows an example of the integration of a thick thermal
oxide. In comparison to process S we introduce a
thermally grown thick oxide after damage removal and
cleaning (SC1;HF;SC2;HF) in subsequence A1. After
removing the front oxide the standard sequence S is
entered again. Since the thermally grown oxide is not
stable in the presence of screen printed aluminum at the
firing process, we have chosen a PVD metallization for the
rear contact together with an LFC process and a final
annealing step in subsequence A2. Please note, that the
laser edge isolation is not needed in this process.

Process sequence B (later referred to as SiNTO)
shows an example of the integration of a thin thermal
oxide. Within this process we can keep the front end of
process S unchanged. We introduce the subsequence B1
to create the passivated rear surface (cleaning like in A).
The nitride on the front serves as a mask thus avoiding
parasitic (even enhanced by highly doped and textured
surface) oxide growth on the front surface. Depending on
the desired backend process the passivating oxide is now
enforced by an additional e.g PECVD deposited layer. The
process shown here features a layer which allows a
subsequent cofiring process which is part of process S.
Finally LFC and annealing is added. Please note, that the
laser edge isolation is not needed in this process. The
process is fortunately very close to the standard cell
fabrication process thus quick transfer to industry seems
to be feasible.

Various other variants of the two processes are
possible but in general it is believed that the thick oxide is
efficiently applied as one of the first steps, whereas the
position of the thin oxide can be preferably located after
the front surface ARC deposition. However, an interesting
sequence could be to combine the frontend of B with a
PVD backend as described in A by growing a sufficiently
thick thermal oxide and omitting the rear capping layer.

**PROCESS DEVELOPMENT**

For process development various processing steps
have to be developed and integrated, please see [32-34]
for further details on the development for thin and for thick
oxides and solar cell results. Regarding the stability of the
passivation layer symmetric lifetime test samples
(featuring solar cell rear surface passivation on both sides)
have been processed along with the actual solar cells in

![Figure 1: The creation of a passivated solar cell requires a
change in the process sequence leading to a different
intermediate product at the front end with respect to the
standard fabrication process. Here the passivation is
implemented out before fast firing.](image1)

In the following Figure 2 we demonstrate two options (A
and B) to create the frontend process intermediate result
as shown in Figure 1 using thermal oxide formation. As
reference the standard fabrication process S is also
shown. Since the thermal oxide passivation process
involves high temperatures and we envisage a process
which is in principle compatible with screen printed rear
contacts the formation of the passivation layer is carried
out before fast firing.

![Figure 2: Process sequences for the standard Al-BSF
fabrication (S) and for the fabrication of rear surface
passivated solar cells (A and B).](image2)
order to allow the extraction of the surface recombination velocity changes along the cell process.

First, the results related to thick oxides are discussed. The change of the lifetime during the cell process is rather pronounced with a very high lifetime after the final annealing step. The achieved lifetimes for process A are displayed in the following graph.

Please note, that the final annealing step is very important for the recovery of the high interface quality. Even though this lifetime samples have been fabricated on Cz-Si, the conclusion can be drawn, that a high interfacial quality can be reached after Alneal, the high lifetime drop during processing could be related to Cz-Si specific behavior, however it is also observed on FZ-Si samples not shown here. Assuming an infinite lifetime the effective surface recombination velocity (including contact recombination) is below 200 cm/s. This is a good but not an excellent value, but it is has to be considered, that this value corresponds to an effective surface recombination velocity achievable at the end of an industrial cell fabrication process and is likely to be a very conservative upper bound since infinite bulk lifetime was assumed on Cz wafers.

Similar to the preceding process sequence also for process B lifetime samples have been fabricated. In this case FZ material was used. The corresponding carrier lifetimes are displayed in the following graph (Figure 4).

As in the previous case the final annealing step leads to a very strong recovery of the lifetime, which is reduced throughout the fabrication process. In this case no LFC process was carried out, but the high final lifetime of the samples shows that high efficiency processing should be possible here as well. The achieved lifetimes allow the expectation that the fabrication process also in this case will lead to very efficient solar cells. Please note, that in this case the al-neal process was carried out with evaporated aluminum, which was removed subsequently to access the wafer lifetime.

SOLAR CELL RESULTS

Solar cells have been fabricated with both process sequences using thick (FEDIO) and the thin (SiNTO) thermal oxides. The following Table 1 shows that with both cell process sequences solar cells exceeding with efficiencies 18% can be fabricated on large area substrates.

Table 1 Solar cell efficiencies for the various cell fabrication processes. Cell area is 149 cm² (Cz-Si). Base resistivity between 1.5-2 Ωcm. *denotes stabilized measurement by ISE Callab. **reduced area by 2mm masking of wafer edge.

<table>
<thead>
<tr>
<th>process</th>
<th>area [cm²]</th>
<th>wafer</th>
<th>V_{OC} [mV]</th>
<th>I_{SC} [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEDIO</td>
<td>149</td>
<td>180</td>
<td>632</td>
<td>37.4</td>
<td>76.4</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td></td>
<td>624</td>
<td>37.0</td>
<td>75.9</td>
<td>17.5*</td>
</tr>
<tr>
<td>Al-BSF</td>
<td>149</td>
<td>180</td>
<td>616</td>
<td>35.4</td>
<td>78.0</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
<td>638</td>
<td>37.3</td>
<td>76.8</td>
<td>18.2</td>
</tr>
<tr>
<td>SiNTO</td>
<td></td>
<td></td>
<td>635</td>
<td>37.3</td>
<td>76.0</td>
<td>18.0*</td>
</tr>
</tbody>
</table>

In case of the FEDIO cells a comparable Al-BSF reference solar cell is available. The passivated rear
surface is visible in both an increased short circuit density \( j_{sc} \) and a considerably higher open circuit voltage \( V_{oc} \). Fill Factor FF is somewhat reduced compared to the reference cells. Part of this reduction is attributed to the series resistance caused by the point contacts. Another important contribution to the reduction of the FF is caused by a non optimum rear side metallization with respect to the wafer edge. Measuring the IV-curve with masked wafer edge (2mm) leads to an increased FF of up to 77.3 % (stabilized) with final efficiency of 17.9 % (independently confirmed by ISE CalLab).

In case of the 120 µm thin SiNTO wafers no high quality reference cells exist. Due to the strong bowing of the Al-BSF cells the printed amount of Aluminum was reduced to a thickness where the Aluminum induced BSF quality is reduced.

In the following two graphs Figure 5 and Figure 6 the quality of the presented process sequences is clearly visible in the high red response of the solar cells.

Solar cells featuring Al-BSF have also been processed, but due to very high bow the deposited Al-paste amount was reduced considerably reducing the quality of the Al-BSF, thus results are not shown here because of limited comparability. Please see more details on the SiNTO process in the papers [32-33].

**COST CALCULATION FOR THERMAL OXIDES**

In this section we want to discuss the cost related to thermal oxidations which is commonly considered to be a rather expensive process. We want to show that significant cost reduction is feasible by tailored equipment.

Since the formation of thick and thin oxides is very different with respect to processing time they are considered separately in the following cost calculation. For thin oxide even an inline oxidation process seems to be possible at very low cost. Three different furnaces have been considered to be used for the oxidation (Table 2). First (B200) a furnace design corresponding to the development stage of roughly 2004 is taken into account featuring 200 wafers per quartz boat using the same slot distance as for diffusion (4.76 mm). Next a larger quartz boat with the double density of wafers is assumed corresponding to modern furnace architecture (B500). Finally an inline system with five track walking string transport [31] is assumed featuring a hot temperature plateau zone of 3.5 m length. In the following calculation a depreciation of 5 years is assumed. Further cost like labour, materials and electrical energy are taken into account.

Table 2 System description for cost evaluation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>B200</td>
<td>Automated 5 tube furnace</td>
<td>1.20 Mio€</td>
</tr>
<tr>
<td>B500</td>
<td>Automated 5 tube furnace</td>
<td>1.35 Mio€</td>
</tr>
<tr>
<td>Inline</td>
<td>Automated 5 track inline furnace (length of hot zone: 3.5 m)</td>
<td>0.73 Mio€</td>
</tr>
</tbody>
</table>

Dry and wet thermal oxidation has been considered with the wet thermal oxide subdivided into “hydrox” (creating water steam by burning of hydrogen with oxygen) and “purified” in which Di-water is directly purified and converted into steam. The latter process is substantially cost effective since it does not involve costly gases. Further it allows reducing safety measures and a somewhat increased oxidation rate, due to the fact that no excess oxygen is needed allowing a higher steam concentration in the process chamber. However, for the calculation this throughput advantage is not taken into account yet because no data is available comparing the rates in identical furnace systems.

The throughput extrapolated from PV-TEC data is shown in the following Table 3. It is based on measurements and expected optimization possibilities, if equipment and process are optimized. For the batch systems a DCE clean is included after every second shift for 2 hours.
Table 3 System throughput and related cost. The processes labeled with “O” are optimized processes with respect to process time (stabilization and ramps reduced).

<table>
<thead>
<tr>
<th>Process label</th>
<th>System type</th>
<th>Oxide type</th>
<th>Throughput wafers/h</th>
<th>Cost €/wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>200/200/D</td>
<td>B200</td>
<td>Dry</td>
<td>140</td>
<td>0.66</td>
</tr>
<tr>
<td>200/200/H</td>
<td>B200</td>
<td>Hydrox</td>
<td>350</td>
<td>0.22</td>
</tr>
<tr>
<td>200/200/P</td>
<td>B200</td>
<td>Purified</td>
<td>350</td>
<td>0.17</td>
</tr>
<tr>
<td>200/200/PO</td>
<td>B200</td>
<td>Purified</td>
<td>430</td>
<td>0.14</td>
</tr>
<tr>
<td>200/500/PO</td>
<td>B500</td>
<td>Purified</td>
<td>990</td>
<td>0.07</td>
</tr>
<tr>
<td>15/200/D</td>
<td>B200</td>
<td>Dry</td>
<td>450</td>
<td>0.16</td>
</tr>
<tr>
<td>15/200/H</td>
<td>B200</td>
<td>Hydrox</td>
<td>840</td>
<td>0.09</td>
</tr>
<tr>
<td>15/200/P</td>
<td>B200</td>
<td>Purified</td>
<td>840</td>
<td>0.07</td>
</tr>
<tr>
<td>15/200/PO</td>
<td>B200</td>
<td>Purified</td>
<td>980</td>
<td>0.06</td>
</tr>
<tr>
<td>15/500/PO</td>
<td>B500</td>
<td>Purified</td>
<td>2200</td>
<td>0.03</td>
</tr>
<tr>
<td>15/inline/P</td>
<td>Inline</td>
<td>Purified</td>
<td>1020</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Figure 7 Strong cost reduction is expected by specially tailored equipment (based on existing technology) and optimized processes for the creation of a thick (200nm) thermal oxide.

Figure 8 Possible options to create thin (15nm) thermal oxides with batch and inline production equipment.

In the figures 7 and 8 the corresponding data is graphically displayed. The conversion into €/Wp was carried out based on the assumption of 156x156 mm² wafers with an efficiency of 18% leading to 4.4 WattPeak/wafer.

The cost for thermal oxidation processes is especially for the thick oxides where the initial cost is above 60 €ct per wafer for a dry oxidation process (200/200D) reducible to values below 10 €ct per wafer (corresponding to 2.3 ct€ per Wp). This is mainly driven by the wet oxidation related throughput enhancement and the increased density of wafers. For the thin oxide formation the final process cost is expected to be below 5 €ct per wafer corresponding to approx. 1.2 ct€ per Wp. This shows that thermal oxidation can become an highly cost effective processing step even though it is a high temperature process and rather high processing times are needed.

EQUIPMENT

Fortunately most technology components needed to fabricate solar cells with passivated surfaces are already available on the market. In various studies it has been observed that annealing using forming gas (e.g. N₂/H₂; 97/3) can enhance both the passivation quality of the rear surface and the front side contact. To our knowledge annealing mostly has been carried out in tube furnaces, in spite of the process simplicity and the low process temperatures. To allow inline annealing under forming gas ambient we have designed with Centrotherm, Blaubeuren, Germany an inline annealing furnace based on the walking string principle [31]. This furnace does feature gas separation areas thus it is expected that the forming gas amount needed for such a process can be kept very low compared to a tube furnace, which has to be rinsed after each individual process run. Oxygen can be banned from the process atmosphere. The corresponding inline annealing system well be available at PV-TEC by Q3/2009. As this system does feature a metal free belt it can also be used to anneal various other types of lifetime samples and also annealing of metals like Nickel in Oxygen free atmosphere is expected to be possible.

CONCLUSION

We have demonstrated, that both thin and thick thermally grown oxides can be incorporated efficiently into screen printing based fabrication processes in order to create solar cells with passivated surfaces in an industrial environment. High passivation qualities can be achieved for both presented processing sequences. Especially an final annealing step is very important for realizing high passivation quality. Solar cells with efficiencies exceeding 18% for large area Cz-Si substrates have been fabricated. If thermal systems are adopted to the thermal oxidation process it is expected that the cost for thermal oxidation can be reduced drastically, thus allowing advanced cell concepts as already introduced more than two decades ago to find their way into mass production.

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