METALLIZATION OF SILICON CARBIDE- AND SILICON OXIDE-BASED LAYER STACKS AS PASSIVATING CONTACTS FOR SILICON SOLAR CELLS

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Metallization schemes for temperature-stable passivating contacts

- Temperature-stable passivating contacts:
  - High surface passivation and charge carrier transport [1,2]
  - In principle compatible with industrial processes at high temperature

- Metallization schemes for passivating contacts:
  - High temperature process
    - Screen print and firing-through [3], [4]
      - Industrially compatible
      - Ag-frit etches through the poly-Si degrading passivation (, thickness poly-Si, Ag-paste optimization, …)
  - Low temperature process
    - PVD of Metals or TCO/metal stack [1,2,5-9]
      - Potential for industrialization for low-cost metals and In-free TCOs [6]
      - Sputtering damage not always fully recovered (soft-deposition techniques required e.g. LPCVD, evaporation, PECVD[6],…)

References:
[10]
Strategies for passivating contacts at PV-LAB

**Rear side upgrade**
Integration of passivating contact with treatment compatible with front side POCl₃

**Both side contacted**[^1-3] c-Si solar cells with passivating contacts

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**TCO still needed for:**
- Improving rear optic
- Improving lateral transport in case of bifacial cells (depending on the $R_{SH}$ of the in-diffused region)

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**TCO still needed for:**
- Improving front and rear optics
- Improving lateral conductivity (high $R_{SH}$ of the thin front passivating contact)

[^1]: F. Feldman et al., IEEE, Portland, (2016)
Both side contacted$^{[1,2]}$ c-Si solar cells with passivating contacts

Rear side upgrade
Integration of passivating contact with treatment compatible with front side POCl$_3$

Full area rear side passivating contact:
$\text{SiC}_x(p)$, $\mu$-c-SiO$_x$(p)

TCO still needed for:
- Improving front and rear optics
- Improving lateral conductivity (high $R_{SH}$ of the thin front passivating contact)
SiC<sub>x</sub>(p) passivating hole contacts

- Advantages of alloying a-Si:H with C:
  - Less prone to blistering
  - Better stability in standard wet chemistry
- a-Si(i) buffer layer displaces Boron and Carbon from the chem-SiO<sub>x</sub> layer

G. Nogay et al., SOLMAT 2017, doi: 10.1016/j.solmat.2017.06.039
SiC$_x$(p) passivating hole contacts

- i-V$_{OC}$ degrades for excessive annealing or doping

G. Nogay et al., SOLMAT 2017, doi: 10.1016/j.solmat.2017.06.039
SiC\(_x\)(p) passivating hole contacts

- i-V\(_{OC}\) degrades for excessive annealing or doping
- \(\rho\) decreases with annealing and doping
- Possibly explained with decomposition of chem-SiO\(_x\)
- Two optimum conditions:
  - 800°C, high 1.5 sccm
    \(iV_{OC}=717\text{mV}, \rho_c=16\text{mΩ cm}^2\)
  - 850°C, 0.5 sccm
    \(iV_{OC}=716\text{mV}, \rho_c=27\text{mΩ cm}^2\)

G. Nogay et al., SOLMAT 2017, doi: 10.1016/j.solmat.2017.06.039
Hybrid Cells with diffused rear side

- The effect of annealing $T$ for two different TMB flows

![Graphs showing $V_{oc}$, $J_{sc}$, and FF vs. annealing temperature for two TMB flows (1.5 sccm and 1.9 sccm).]

- $V_{oc}$ follows the $iV_{oc}$ trend
  - $V_{oc}$ up to 709 mV
  - $iV_{oc} - V_{oc} \geq 10$ mV (sputtering damage)

- Lower doping $\rightarrow$ higher $J_{sc}$
  - Less free carrier absorption

- Higher annealing $T$ $\rightarrow$ higher FF

- Higher doping $\rightarrow$ higher FF
  - FF up to 81%

G. Nogay et al., SOLMAT 2017, doi: 10.1016/j.solmat.2017.06.039
Full-area passivating hole rear contacts

- **SiC\textsubscript{x}-based layer stack**
  - 800°C
  - 850°C

- Tendency in literature: Thicker and denser SiO\textsubscript{x} beneficial for higher annealing temperature [1,2]

- **POCl\textsubscript{3} integration**
  - Attain higher thermal budgets with chem-SiO\textsubscript{x} grown in HNO\textsubscript{3} and PECVD?
  - µc-Si by PECVD, and introduce O in order to «support» the chem-SiO\textsubscript{x} (µc-SiO\textsubscript{x})

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µc-SiO$_x$(p) hole passivating contacts

Annealed at 900°C

| Voc (mV) | 707.7 |
| Jsc (mA/cm²) | 39.43 |
| FF (%) | 79.87 |
| Eff (%) | 22.29 |

FF: efficient carrier transport for the µc-SiOx(p) possibly still limited by the front i/n

J$\_SC$: Limited by the front contact

V$\_OC$: > 10 mV lower than i-V$\_OC$

η : > 22%

P. Wyss et al., manuscript in preparation

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Strategies for passivating contacts at PV-LAB

Rear side upgrade
Integrate contact formation with standard thermal processes
- Emitter diffusion

Both side contacted c-Si solar cells with passivating contacts

Full-area front side passivating contact
$\mu c-SiO_x(n)$
$SiC_x(n)$

Co-annealed

Full area rear side passivating contact:
$SiC_x(p), \mu c-SiO_x(p)$

Full area rear side passivating contact:
$SiC_x(p), \mu c-SiO_x(p)$
µc-SiO$_x$(n) for front side passivating contacts

- Parasitic absorption of Si layers on the front side can cause large $J_{SC}$ losses [1]

- Replace part of the Si layer by SiO$_x$

- Vertically oriented Si filaments within the SiO$_x$ matrix to ensure current transport

- Already present in the as-deposited state but also visible after annealing (850°C)

Patent pending (PCT filed in April 2017)

\( \mu c\text{-SiO}_x(n) \) for front side passivating contacts

\[ \rho_c \text{ strongly decreasing with increasing doping} \]

\( \rho_c \) for \( \mu c\text{-SiO}_x(n) \) metallized with evaporated Al lower than ITO/Ag sputtered

ITO sputtering damage for $\text{uc-SiO}_x(n)$

- Lowly doped samples
  => strong sputtering damage (curing does not help)
- Highly doped samples
  => Lower sputtering damage

- Surface passivation less sensitive to Auger recombination rather than induced sputtering damage

J. Stuckelberger et al., manuscript under review

andrea.ingenito@epfl.ch
Surface passivation of $\text{SiC}_x(n)$ for front textured side (PCD measurements)

- 800 °C; 8 min:
  - Auger-limited at low CH$_4$/SiH$_4$
  - Massive improvement after hydrogenation towards higher CH$_4$ flow

- SiH$_4$ flow constant
  - 735 mV
  - 7 fA/cm$^2$

Normalized CH$_4$/SiH$_4$ [-]
Surface passivation of $\text{SiC}_x(n)$ for front textured side (PCD measurements)

- **800 °C; 8 min:**
  - Auger-limited at low CH$_4$/SiH$_4$
  - Massive improvement after hydrogenation towards higher CH$_4$ flow

- **850 °C; 8 min:**
  - Auger-limited at low CH$_4$/SiH$_4$
  - Massive improvement after hydrogenation towards higher CH$_4$ flow
Surface passivation of $\text{SiC}_x(n)$ for front textured side (PCD measurements)

- **800 °C; 8 min:**
  - Auger-limited at low $\text{CH}_4/\text{SiH}_4$
  - Massive improvement after hydrogenation towards higher $\text{CH}_4$ flow

- **850 °C; 8 min:**
  - Auger-limited at low $\text{CH}_4/\text{SiH}_4$
  - Massive improvement after hydrogenation towards higher $\text{CH}_4$ flow

- **900 °C; 8 min:**
  - No variations with $\text{CH}_4$ and hydrogenation
  - Break-up of the oxide and/or high Auger recombination

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A. Ingenito et al., manuscript in preparation

- $\text{SiC}_x(n)$
- $\sim 13\text{ nm}$
- c-Si FZ (p-type)
Co-annealed SiC\textsubscript{x}-based solar cells

- \textbf{V}\textsubscript{oc}:
  - same trend as i-V\textsubscript{oc}
  - \(iV\textsubscript{oc}-V\textsubscript{oc} > 20\) mV

- \textbf{FF}:
  - decreases with increasing of the temperature (p-FF?)

- \textbf{J}\textsubscript{sc}:
  - peaks at 850 °C (poor transparency at 800 °C; high recombination at 900 °C)

- \textbf{\(\eta\)}:
  - highest at 800 °C

<table>
<thead>
<tr>
<th>V\textsubscript{oc} [mV]</th>
<th>FF [%]</th>
<th>J\textsubscript{sc} [mA/cm\textsuperscript{2}]</th>
<th>(\eta) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>708</td>
<td>80.2</td>
<td>37.8</td>
<td>21.5</td>
</tr>
</tbody>
</table>

V\textsubscript{oc}:
- [Image 726x460]

- VOC:
  - same trend as i-V\textsubscript{oc}
  - \(iV\textsubscript{oc}-V\textsubscript{oc} > 20\) mV

- FF:
  - decreases with increasing of the temperature (p-FF?)

- J\textsubscript{sc}:
  - peaks at 850 °C (poor transparency at 800 °C; high recombination at 900 °C)

- \(\eta\):
  - highest at 800 °C

Sputtered ITO/ screen printed Ag paste front side

Sputtered ITO/Ag rear side

SiC\textsubscript{x}(n) High CH\textsubscript{4}

SiC\textsubscript{x}(p)

c-Si(p)
Impact of the metallization process on $V_{OC}$ and FF

- $i-V_{OC}$ and $i$-FF almost untouched after ITO (no sputtering damage)
- Degradation at low injection after metallization ($p-\eta=22.2\%$)
- Dark diode losses $>7$ mV on $p-V_{OC}$ and $>1\%$ on the $p$-FF ($p-\eta=21.8\%$)

- $i-V_{OC}$ and $i$-FF untouched after ITO (no sputtering damage)
- Degradation at low injection after metallization ($p-\eta=21.9\%$)
- Dark diode losses $>6$ mV on $V_{OC}$ and $>2\%$ on the $p$-FF ($p-\eta=21.1\%$)
Both side SiC\textsubscript{x}-based solar cells (planar)

**Best Cell: J-V Curve**

- \(V_{oc} = 727.3\ \text{mV}\)
- \(J_{sc} = 33.5\ \text{mA.cm}^{-2}\)
- \(\text{FF} = 84.0\ %\)
- \(\eta = 20.5\ %\)

**Measured with ARF**

- \(V_{oc} = 729.6\ \text{mV}\)
- \(J_{sc} = 36.8\ \text{mA.cm}^{-2}\)
- \(\text{FF} = 83.5\ %\)
- \(\eta = 22.4\ %\)

<table>
<thead>
<tr>
<th>(iV_{oc}) before ITO [mV]</th>
<th>Total (J_0) [fA/cm(^2)]</th>
<th>(pV_{oc}) [mV]</th>
<th>(pFF) [%]</th>
<th>(p\eta) [%]</th>
<th>(R_s) [(\Omega\cdot\text{cm}^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>744</td>
<td>8.35</td>
<td>731</td>
<td>86.5</td>
<td>21.2</td>
<td>0.66</td>
</tr>
</tbody>
</table>

- 17 mV difference in \(iV_{oc}\) and \(V_{oc}\) after metalization due to sputtering damage
- ITO/low-T Ag-paste metallization is not FF-limiting!

*Microtextured anti-reflective foil (ARF) Ulbrich, et al. Prog. Photovoltaics 2013, 21, 1672–1681*
Summary

- Annealed rear side passivating contacts:
  - SiC<sub>x</sub>(p), \( iV_{OC} > 715 \text{ mV}, \rho_c < 20 \text{ m}\Omega \text{cm}^2 \)
  - μc-SiO<sub>x</sub>(p), \( iV_{OC} > 720 \text{ mV}, J_0 < 15 \text{ fA/cm}^2 \)

- Proof-of-principle cells with front side heterojunction:
  - Annealed SiC<sub>x</sub>(p), \( \eta = 21.9\% \)
  - Annealed SiO<sub>x</sub>(p), \( \eta = 22.3\% \)

- Annealed front side passivating contacts for better transparency
  - SiO<sub>x</sub>(n) \( \rightarrow \) \( iV_{OC} > 720 \text{ mV} \)
  - SiC<sub>x</sub>(n) \( \rightarrow \) \( iV_{OC} > 735 \text{ mV} \) (on textured)

- Co-annealed solar cells
  - SiO<sub>x</sub>(n)/SiO<sub>x</sub>(p), good \( J_{SC} \) and FF (planar)
  - SiC<sub>x</sub>(n)/SiC<sub>x</sub>(p), \( \eta = 21.5\% \), \( J_{SC} \) to be improved, good FF and \( V_{OC} \) (textured)
  - SiC<sub>x</sub>(n)/SiC<sub>x</sub>(p), reasonable \( J_{SC} \) excellent FF·\( V_{OC} \) (84.0·726) with low-T Ag paste
THANK YOU FOR YOUR ATTENTION!

ACKNOWLEDGEMENT

The authors gratefully acknowledge support by the Swiss National Science Foundation (SNF) under grant No. 200021_14588/1 and No. IZLIZ2_156641, by the Swiss Federal Office for Energy (SFOE) under grant No. SI/501253-01 and by the European Union’s Horizon 2020 research and innovation programme under Grant Agreements no. 727529 (project DISC)

We would like to thank all co-workers at PV-Lab & CSEM.
EQE co-annealed cells with front $\text{SiC}_x(n)$

- Blue response increases towards higher annealing temperature (higher crystallinity)

- At 900 °C, the high recombination rate and FCA limit the EQE in the IR region
Cell results: Co-diffused SiOx-based solar cells

- $V_{OC} = 686.1$ mV
- $J_{SC} = 34.8$ mA cm$^{-2}$
- FF = 79.6 %
- η = 19.0 %

**FF**: efficient carrier transport through SiOx layer  
**$J_{SC}$**: promising high for **planar** cell  
**$V_{OC}$**: improvable, compared to $iV_{OC}$  
**η**: proof of concept for SiOx(n)/Si(n) passivating contact

J. Stuckelberger et al., manuscript under review
March 18-22, on the Swiss EPFL campus in Lausanne in the amazing ROLEX Learning Center

Conference chaired by EPFL (IMT/PV-lab)
nPV-Workshop chaired by CSEM
Optical losses

- Alloying with C helps to widen the bandgap
- Increasing C-content shifts crystallization towards higher temperature
- Layers annealed at 900 °C are more transparent than a-Si(n)

To decrease $J_A$ below 1 mA/cm², thickness of 5 nm
Testing of different TCOs on SiCₓ(p)

- **ITO**
  - Minority Carrier Lifetime (seconds)
  - Minority Carrier Density (cm⁻³)

- **ZTO**
  - Minority Carrier Lifetime (seconds)
  - Minority Carrier Density (cm⁻³)

- **IZO**
  - Minority Carrier Lifetime (seconds)
  - Minority Carrier Density (cm⁻³)

Sputtering damage not fully recovered

<table>
<thead>
<tr>
<th>Conductivity [1/Ωcm]</th>
<th>ITO</th>
<th>ZTO</th>
<th>IZO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4x10³</td>
<td>2.5x10²</td>
<td>2.6x10³</td>
<td></td>
</tr>
</tbody>
</table>

| Mobility [cm²V⁻¹s⁻¹] | 30 | 17 | 50 |

Contact Resistivity (mΩ·cm²)

ITO IO:H ZTO IZO
Process flow of co-annealed front and rear contacted SiC\textsubscript{x}-based c-Si solar cells (patterning free)

**Single side texturing**

«Chem-SiO\textsubscript{x}» grown in HNO\textsubscript{3}

PECVD SiC\textsubscript{x}(n) front

PECVD SiC\textsubscript{x}(p) rear

Co-Annealing

Hydrogenation

Metallization*

*Sputtered ITO/Ag rear side

*Sputtered ITO/ screen printed Ag paste front side

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current [fA/cm\textsuperscript{2}]</th>
<th>Voltage [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C; 8 min</td>
<td>5-7</td>
<td>727</td>
</tr>
<tr>
<td>850 °C; 8 min</td>
<td>10-12</td>
<td>723</td>
</tr>
<tr>
<td>900 °C; 8 min</td>
<td>20</td>
<td>670</td>
</tr>
</tbody>
</table>

*Optimized by G.Nogay*
Surface passivation of SiC$_x$(n) on planar and textured surfaces (PCD measurements)

All samples after hydrogenation with a SiNx as donor layer

- **800 °C; 8 min:** Small losses when moving from planar to textured (5-10 mV)
- **850 °C; 8 min:** Moderate losses when moving from planar to textured (>10 mV)
- **900 °C; 8 min:** Strong losses when moving from planar to textured (>50 mV)