Effect of forming gas annealing on screen-printed Ag metallization of silicon solar cells

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Outline

● Motivation & Objectives
  ▪ Mechanism of screen-printed Ag contact formation

● Experimental procedure
  ▪ FGA of cells optimally fired at 800°C and over-fired at 850°C

● Results
  ▪ Specific contact resistance measurement
  ▪ Contact microstructures before and after FGA
  ▪ FGA of Ag-containing glass on Si wafer

● Conclusions
Proposed Ag contact formation mechanism

After drying & burning

(a) Ag powder

Glass frit

(100) Si wafer

SiN_x layer

Heating

(b) 4Ag (s) + O_2(g) → 4Ag^+ (glass) + 2O^-2 (glass)

(c) N-rich layer

4Ag^+ + 2O^-2 + SiN_x → 4Ag + SiO_2 (glass) + x/2 N_2 (g)

Cooling stage

(d) 4Ag^+ + 2O^-2 + Si(s) → 4Ag(glass) + SiO_2(glass)

(e) Ag particle

(f) Ag crystallite

Hong et al., Met. Mater. Int. (2009)
**Motivation & Objectives**

- Over-fired contact has more Ag crystallites and a thicker glass than optimally fired one.

- Current transport at the over-fired contact is limited by the thick glass layer.

- It has been postulated that the beneficial effect of FGA is attributed to the reduction of metal oxide in glass.

- **To clarify the mechanism of the beneficial effect of FGA on the contact resistance of the screen-printed Ag front contacts of Si solar cells.**

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<th>Rs (Ω·cm²)</th>
<th>FF</th>
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<tbody>
<tr>
<td>As-fired</td>
<td>11.02</td>
<td>0.585</td>
</tr>
<tr>
<td>After FGA</td>
<td>0.749</td>
<td>0.766</td>
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*In over-firing condition*

Ebong A et al., *Proc. 21st EU PVSEC*, 2006

G. Schubert et al., *Proc. 21st EU-PVSEC*, 2006
Experimental procedures

- $\rho_c$ and contact microstructures before and after annealing

- Analyses
  - Microstructure: UHR-SEM (Hitachi S-5500)
  - Contact resistance: transfer length method

**Screen-printing & drying**

**Spike-firing at 800°C & 850°C**

**TLM measurement ($\rho_c$)**

**Annealing at 400°C for 30 min in N$_2$(NA) and N$_2$+10%H$_2$(FGA)**

**TLM measurement ($\rho_c$)**
Effects of FGA and NA on contact resistance

- Before post-annealing, contacts fired at 850°C exhibited higher $\rho_c$ than those fired at 800°C.

- NA had no beneficial effect on $\rho_c$.

- FGA resulted in an improvement in the contact resistance especially in over-fired case.
After spike-firing at 850°C

- Contact interface contained Ag crystallites grown into the Si emitter, a glass layer, and large pores.
- Ag crystallites were separated from the porously sintered Ag bulk by a glass layer.
- Ag crystallites grown onto the emitter surface underneath the large pores were covered by a thin glass layer: no contribution to the current conduction from the emitter Si to the bulk Ag.
Contact interfaces after annealing at 400°C

- After NA, no noticeable changes observed on pore surface and similar with as-fired state.

- After FGA, interfacial region away from the pores were little influenced by FGA.

- Dense layer of Ag particles were formed on the surfaces of interfacial pores.
Effect of FGA on surface of glass layer

Sample preparation

- Thick screen-printing
- Firing: 800 °C for 5 min

After NA, no changes were observed.

FGA had minor influence on glass/Si interface.

After FGA, dense layer of Ag particles were precipitated on the surface of glass.
Effect of FGA on surface of glass layer

- Measuring conductance between Pt pads

- $1.12 \times 10^{-3}$ S in as-fired case and $3.67 \times 10^{-3}$ S in after FGA.

- The formation of Ag particles on glass surface contributed to the difference between two value.

- High density of Ag particles on glass provide an extra path for current transport.
At the as-fired state, the current conduction occurs only through path A away from the pores.

After FGA, the pore surface decorated with dense layer of Ag particles provides another path for the current conduction (path B).

The Ag particles were formed by out-diffusion of Ag$^+$ ions contained in the glass layer and then by reduction by H$_2$ in the forming gas to precipitate as Ag particles.
Conclusions

- The glass layer at the as-fired contact interface already contains amount of Ag\(^+\) ions that can be reduced to form fine Ag particles during FGA.

- During FGA, the permeation rate of H\(_2\) molecules into the glass layer is negligible, compared to the out-diffusion rate of Ag\(^+\) ions toward the pore surface that is in contact with the forming gas.

- The beneficial effect of FGA on the over-fired Ag contacts of Si solar cells is attributed to the pore surfaces decorated by Ag particles, acting as an additional conduction path for the current flow.
Thank you for your attention!