Characterization and optimization of electroless nickel plating for front side silicon solar cells metallization

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Outline

- Motivations and issues
- Description of the technique
- Structural and electrical properties of the deposits
- Solar cell results
- Conclusions et perspectives
Motivations and issues

- Limitations of screen-printing technology
  - Requires high surface doping for contact formation
  - Requires patterning and alignment for selective emitter technology
  - Induces shadowing losses (fingers width > 80 µm)
  - Need to investigate an alternative technology
  - Development of Two-layer concept
  - NiP electroless seed layer + thickening with Ag


- Work focused on shunt formation

- Influential parameters
  - Characteristics of the NiP bath (pH, T°C, activation…)
  - Annealing conditions of the layer (T°C, duration, furnace…)
  - Ag layer deposition (deposition current density, thickness…)
Autocatalytic deposition of Nickel-Phosphorous (Ni-P) by immersion of a substrate in the plating bath

- oxidation of the sodium hypophosphite (NaH2PO2)
- reduction of the nickel ions (Ni2+)

\[ \text{Ni}^{2+} + 2 \text{H}_2 \text{PO}_2^- + 2 \text{H}_2 \text{O} \rightarrow \text{Ni}^0 + 2 \text{H}_2 \text{PO}_3^- + 2 \text{H}^+ + \text{H}_2 \]

- simultaneous P formation and incorporation in the metal film
  - inversely proportional to the pH
  - directly proportional to the operating temperature

Characteristics of the plating bath

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8-10</td>
</tr>
<tr>
<td>Temperature</td>
<td>95 °C</td>
</tr>
<tr>
<td>Agitation</td>
<td>Yes</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>~ 10 µm/h</td>
</tr>
</tbody>
</table>
Description of the technique

- Interest of the electroless NiP deposits
  - Low process temperature
  - Homogeneous coverage
  - Good adhesion (if < 5µm)
  - Selective deposition on Si
  - Barrier properties for copper diffusion
  - Low contact resistivity

**Best values of $\rho_c$ obtained on n-type POCl$_3$ emitter (40 $\Omega/\square$) by TLM after RTA annealing**

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_c$ ($\Omega$.cm$^2$)</td>
<td>$3.10^{-4}$</td>
<td>$9.10^{-5}$</td>
</tr>
</tbody>
</table>

→ Satisfying seed-layer for electrolytic deposition
Nickel silicides formation

- Ni = dominant diffusing specie
- 200 – 300 °C
  \[ \text{Ni/Si} \rightarrow \text{Ni/Ni}_2\text{Si/Si} \rightarrow \text{Ni}_2\text{Si/Si} \]
- 400 °C – 600 °C
  \[ \text{NiSi/Ni}_2\text{Si/Si} \rightarrow \text{NiSi/Si} \]
- 600 °C – 700 °C
  \[ \text{NiSi/NiSi}_2\text{Si} \rightarrow \text{NiSi}_2\text{Si} \]

Structural and electrical properties of the deposits

GIXRD spectra of NiP/Si pads after annealing under vacuum atmosphere from 300°C to 675°C

RBS Spectra of NiP/Si pads RTA annealed at different temperatures
Structural and electrical properties of the deposits

SEM views of a NiP layer on silicon annealed in RTA 30s

Increasing temperature

- Increase of the roughness
- Increase of the thickness

→ diffusion of Ni?
Structural and electrical properties of the deposits

Reduction of contact resistivity of NiP/Si pads versus annealing temperature in comparison with as-deposited TLM samples

- **200 °C - 400 °C = formation of Ni and Ni3P**
- **400 °C – 600 °C = formation of NiSi silicide**
- **700 °C = formation of NiSi₂**

Hypothesis:

- Highest purity of NiSi compared to Si
- "snowplow effect" = accumulation of P from Si near the NiSi-Si interface
- Rough aspect at the interface Si/NiSi₂
Solar cell results

Process 1

- Alkaline texturing
- POCl₃ 40 Ω/□ diffusion
- ARC SiNₓ:H PECVD deposition
- SP resist masking and etching
- Rear Al BSF + firing
- NiP deposition
  - bath at pH = 10
  - Width line ~ 130 µm
- Annealing in RTA
- Ag electrolytic deposition (7 µm)

Important decrease of the pFF measured by SunsVoc with annealing
Solar cell results

View with an infrared thermography camera

= Local shunt formation

- Two hypothesis
  - Activation mechanism at high pH = inhomogeneous thickness
  - Diffusion of Ni with annealing temperature

CONCLUSION OF PROCESS 1 for 300 °C < RTA T°C < 600°C

→ low contact resistance
→ BUT local shunt formation
Alternative: initiation by photoactivation

- **Principle**
  
  Generation of electron-hole pair by light application
  
  Electrons used to reduce Ni$^{2+}$

- **Advantages**

  - Very thin and homogeneous NiP layer (~50 – 70 nm)
  - Si not consumed
  - Short deposition duration (~2 – 5 s)
Process 2

Same process than process 1

BUT WITH

- NiP deposition photoactivated
  - bath at pH = 8
  - Width line ~ 130 µm
- Ag electrolytic deposition (7 µm)
- Annealing in RTA

Decrease of the pFF only until 500 °C
Solar cell results

- Best result ($S = 21.1 \text{ cm}^2$, annealing temperature of NiP = 200 °C)

<table>
<thead>
<tr>
<th></th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>pFF (%)</th>
<th>Rs (Ω.cm²)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Ag</td>
<td>35.4</td>
<td>617.3</td>
<td>76</td>
<td>80.1</td>
<td>0.82</td>
<td>16.6</td>
</tr>
<tr>
<td>SP ref</td>
<td>35.6</td>
<td>620.7</td>
<td>76.3</td>
<td>80.4</td>
<td>0.81</td>
<td>16.8</td>
</tr>
</tbody>
</table>

- Problem = contact resistance at the corners of the cells
- Hypothesis
  - inhomogeneous light application during NiP deposition
  - inhomogeneous annealing in RTA

SEM view of a NiP/Ag contact through a silicon nitride etched

Corescan of cells corners

Ni/Ag

SP ref
Conclusions

- Process 1 without photoactivation requires more investigations
  - define right parameters (annealing, Ni thickness…)

- Validation of process with photoactivation

- Achievement of efficiency similar to screen-printed solar cells with NiP annealed at low temperature

Perspectives

- Optimization of the deposits: annealing conditions, light homogeneity, electrochemical deposition, …

- Optimization of the cell parameters
  - Contacting shallow and lowly doped emitter
  - Reduction of fingers width (< 50 µm)
  - Thickening with Cu instead of Ag
Questions...