Anodic Aluminum Oxide for Silicon Solar Cell Passivation and Metallisation

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Outline

- Introduction
  - Motivation
  - Anodic Aluminium Oxide
- Anodic Aluminium Oxide Passivation for Silicon Solar Cell
  - AAO Stack
  - Hydrogen incorporation during anodisation
- Anodic Aluminum Oxide for Metallisation Scheme
  - AAO Localised Contacts
  - Laser-doped through AAO
  - Selective Anodisation
- Conclusion
Introduction
Motivation

Multifunction layer:
- SiN$_x$ – Surface passivation & Anti-reflection coating
- Screen Printed Al Electrode – Back Surface Field & Rear Electrode

High Efficiency Solar Cell:
- Well Passivated Surface
- Localised Contact
Anodic Aluminium Oxide

- **Anodic Aluminium Oxide (AAO):**
  Formation of a porous layer of aluminium oxide on an aluminium surface through the application of an external applied voltage.

- **Characteristics of an AAO film are controlled by the electrochemical process:**
  - Pore diameter;
  - Barrier depth; and
  - Spacing between pores.
Anodisation

Anodisation Process

- Wafer connected to positive terminal of a D.C. supplier
- Ni plate connected to negative terminal

- Cathode
  \[ 2H^+ + 2e^- \rightarrow H_2 \]

- Anode
  \[ Al \rightarrow Al^{3+} + 3e^- \]
  \[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]
  \[ 2H^+ + 2e^- \rightarrow H_2 \]
  \[ Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \]
  \[ Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \]
AAO Passivation
AAO Passivation

Stored Charge with AAO film - Field Passivation

Hydrogen Concentration with AAO film - Chemical Passivation


Anodised Al directly on Si wafer

Anodised a layer of Al on Si wafer

If anodised for too long:

- $O^{2-}$ and OH$^{-}$ anions migrate through AAO and reacts with Si wafer which generates $O_2$ bubbles at the interface

If a layer of Al is not fully anodised:

- Al rich region formed at interface between AAO and Si

An intervening layer such as $SiO_2$, a-Si, $SiN_x$ & $SiON_x$ can solve this problem and allow a wider anodisation process window.
Anodise in 25V 0.5M H₂SO₄ – Different intervening dielectric layers (3-10 Ω cm planar wafers)
Anodise in 25V 0.5M $\text{H}_2\text{SO}_4$– Different intervening dielectric layers (1-3 $\Omega$ cm 5” texture wafers)
# Stability

<table>
<thead>
<tr>
<th>Intervening Layer</th>
<th>SiO$_2$</th>
<th>SiN$_x$</th>
<th>SiON$_x$</th>
<th>a-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase in implied $V_{oc}$ after anodisation (mV)</td>
<td>40</td>
<td>47</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Variation in implied $V_{oc}$ (mV) over 60 days</td>
<td>±5</td>
<td>±17</td>
<td>±5</td>
<td>±5</td>
</tr>
</tbody>
</table>

![Graph 1](image1.png)

![Graph 2](image2.png)
Summary of AAO Passivation

- **3-10 Ω cm Planar Wafer**

<table>
<thead>
<tr>
<th>Rear Passivation</th>
<th>( J_{oe} ) (fA cm(^{-2}))</th>
<th>Implied ( V_{oc} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 nm SiO(_2)</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>140 nm SiO(_2) + 650 nm AAO</td>
<td>32</td>
<td>+40</td>
</tr>
<tr>
<td>75 nm SiN(_x)</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>75 nm SiN(_x) + 650 nm AAO</td>
<td>8</td>
<td>+37</td>
</tr>
</tbody>
</table>

- **1-3 Ω cm Texture Wafer**

<table>
<thead>
<tr>
<th>Rear Passivation</th>
<th>Optimal Electrolyte Temperature (deg)</th>
<th>Implied ( V_{oc} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm SiO(_2) + 650 nm AAO</td>
<td></td>
<td>+30</td>
</tr>
<tr>
<td>Rear emitter +10 nm SiO(_2) + 650 nm AAO</td>
<td>25–30</td>
<td>±5</td>
</tr>
<tr>
<td>10 nm SiO(_2) + 75 nm SiN(_x) + 650 nm AAO</td>
<td>55–65</td>
<td>+10</td>
</tr>
<tr>
<td>Rear emitter +10 nm SiO(_2) + 75 nm SiN(_x) + 650 nm AAO</td>
<td></td>
<td>±10</td>
</tr>
</tbody>
</table>
# Passivation Mechanism

## Field Passivation - Stored Charge

<table>
<thead>
<tr>
<th>Electrolyte Concentration</th>
<th>Anodisation Voltage (V)</th>
<th>Fixed Charge Density of SiO$_2$/AAO stack (cm$^{-2}$)</th>
<th>Fixed Charge Density of SiNx/AAO stack (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M</td>
<td>20</td>
<td>$6.5 \pm 0.1 \times 10^{11}$</td>
<td>$2.1 \pm 0.1 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>$5.9 \pm 0.1 \times 10^{11}$</td>
<td>$2.0 \pm 0.2 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>$4.8 \pm 0.1 \times 10^{11}$</td>
<td>$2.0 \pm 0.3 \times 10^{12}$</td>
</tr>
<tr>
<td>2.3M</td>
<td>8</td>
<td>$5.2 \pm 0.1 \times 10^{11}$</td>
<td>$1.9 \pm 0.1 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$4.7 \pm 0.1 \times 10^{11}$</td>
<td>$1.8 \pm 0.1 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$4.0 \pm 0.1 \times 10^{11}$</td>
<td>$1.5 \pm 0.1 \times 10^{12}$</td>
</tr>
<tr>
<td>Reference sample</td>
<td></td>
<td>$2.4 \pm 0.1 \times 10^{11}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Hydrogen Incorporation

P-type Cz Polish wafer
200 nm P-type a-Si
600 nm AAO

SIMS

![Graphs showing hydrogen incorporation](image)
Hydrogen Incorporation

- Anodised in H₂O
- Anodised in H₂O + Anneal
- Anodised in D₂O
- Anodised in D₂O + Anneal

SIMS

Reference
Summary

- Hydrogen content in the underlying a-Si layers was increased by a factor of ~3 after anodisation.
- Hydrogen incorporated during anodisation can deactivate recombination-active defects at the crystalline Si interface.
- Annealing at 400 °C after anodisation can result in increased hydrogen and deuterium in the underlying amorphous Si.
- AAO can act as a hydrogen reservoir able to supply hydrogen to underlying substrates when subsequently annealed.
AAO Metallization Scheme
AAO Metallisation Scheme

- Whether an AAO layer can be used as a template to form small-area, closely spaced metal contacts for solar cells
- The high concentration of Al within the layer to be used as dopant for p\textsuperscript{+} regions which are subsequently metallised
- An AAO can be selectively anodised by pre patterning the Al layer before anodising.
AAO Localised Contact
AAO Localised Contact

AAO Localised Contact

- A thin layer of thermal SiO$_2$ and AAO stack can result in an implied $V_{oc}$ of average in 660 mV, however, the strong inversion layer created by the stored charge within AAO layer and 0.2 µm shallow p$^+$ contact region resulted in cell efficiency of 15.5%.

The importance of forming localised BSF regions is to have at least 2 µm thickness for any small-scale metal contacting scheme.
Laser-Doped Through AAO
Laser-doped Through AAO

- Silicon can be locally-doped with aluminium to form localised p+ surface regions by laser-doping AAO layers formed on the silicon surface.
Laser Induced Damage

- Laser damage induced by laser doping through AAO layers at 11 W can be recovered more easily than damage incurred using the higher laser powers.
- After annealing there was no significant difference in the final implied $V_{oc}$ with a line spacing of 1.5 mm and 1.25 mm when a laser power of 11 W was used.
- Laser damage can be minimised by laser doping point regions through AAO layers
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Laser-doped Through AAO

- Lowest sheet resistance was recorded using two scribing passes and a laser speed and power of 500 mm/s and 9 W, however, the number of scribing passes generates more laser damage.
- AAO can be doped with other impurities, such as boron and phosphorus, by anodising in electrolytes containing the extrinsic impurities in ionic form.
- During laser-doping, aluminium can impurities can be doped into silicon layer simultaneously. This co-doping process can be used to create very heavily-doped surface layers.

SIMS Profile of LD Region

0.5 M of H₂SO₄ + 0.5 M of H₃BO₃

0.5M H₃PO₄ at 37 V

Spin-on Boron Source
B enhance Al diffusion

Laser-doped Through Doped AAO

Spin-coated poly boron dopant source

AAO layer formed by anodising aluminium at 25 V in an electrolyte comprising 0.5 M of H₂SO₄ and 0.5 M of H₃BO₃
AAO PERL Cell

(a) Reference 20% AAO PERL 19.9%

(b) Escape, ARC Reflectance, Active Area, Non-perfect IQE, Metal Shading

<table>
<thead>
<tr>
<th>LD line spacing (mm)</th>
<th>( iV_{sc} ) after deposition (mV)</th>
<th>( iV_{sc} ) after anodisation (mV)</th>
<th>Efficiency (%)</th>
<th>( V_{oc} ) (mV)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>FF</th>
<th>( R_s ) (( \Omega )cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M H(_2)SO(_4)</td>
<td>1</td>
<td>624</td>
<td>629</td>
<td>19.5</td>
<td>636</td>
<td>40.3</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>620</td>
<td>627</td>
<td>19.4</td>
<td>651</td>
<td>40.5</td>
<td>74.0</td>
</tr>
<tr>
<td>0.5 M H(_2)SO(_4) + 0.5 M H(_3)BO(_3)</td>
<td>1</td>
<td>621</td>
<td>616</td>
<td>19.4</td>
<td>635</td>
<td>40.1</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>620</td>
<td>621</td>
<td>19.9</td>
<td>652</td>
<td>40.1</td>
<td>76.5</td>
</tr>
<tr>
<td>Ref</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
<td>649</td>
<td>40.2</td>
<td>76.7</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>-</td>
<td>-</td>
<td>19.7</td>
<td>647</td>
<td>40.2</td>
<td>75.7</td>
</tr>
</tbody>
</table>
Summary

- The formation of localised p+ surface regions can be achieved by laser-doping through AAO layers.
- Anodic Al oxide layers can be doped with B by anodising in electrolytes containing B and during laser doping the underlying Si can become doped with both Al and B.
- This co-doping process can create very heavily-doped local regions with electrically-active p-type dopant concentrations exceeding $10^{20}$ cm$^{-3}$ for ~ 4 µm from the laser-doped surface.
- Laser doping through AAO layers can be performed without introducing any voids in the Si which is advantageous for cells with LBSFs.
- This local doping method was used to fabricate PERL cells with efficiencies of up to 19.9%. However, although the heavily-doped local p+ regions could reduce the $R_s$ to values as low as 0.54 Ω cm$^2$.
Selective Anodisation

- Selective anodization is a process that can enable the formation of isolated conductive regions in a dielectric layer.
- The process flow involves two steps.

An Anodic Aluminium Oxide (AAO) film can both passivate silicon surfaces and provide a dopant source for silicon.
Methodology

- Patterning

Masking Method
Isolate Al from the electrolyte during anodisation.

Isolation Method
Isolate Al from the anodic potential during anodisation.


Masking Method

- The effectiveness of printing a layer of mask depends on the surface morphology and the duration of the anodization process.
- Print 50% w/w H3PO4 while the wafer is heated to 200 °C, H3PO4 dehydrates to P₂O₅ and oxidises a surface layer of Al.
- XPS shows that under the mask the Al is metallic.

![Graph showing atomic percent over etch time](image)

5 layers of the novolac resin on the sputtered Al surface

5 layers of the novolac resin on the evaporated Al surface

Hot Plate
Masking Method (cont)

<table>
<thead>
<tr>
<th>Printing Condition</th>
<th>1 pL 1 layer</th>
<th>1 pL 3 layers</th>
<th>10 pL 1 layer</th>
<th>10 pL 3 layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width of printed line (µm)</td>
<td>40 ± 8</td>
<td>70 ± 15</td>
<td>160 ± 20</td>
<td>170 ± 40</td>
</tr>
<tr>
<td>Resistivity (Ω cm)</td>
<td>-</td>
<td>2.5 × 10⁻⁵</td>
<td>7 × 10⁻⁵</td>
<td>4.8 × 10⁻⁵</td>
</tr>
</tbody>
</table>

1 pL 3 layers 50% H₃PO₄

10 pL 1 layer 50% H₃PO₄

10 pL 3 layers 50% H₃PO₄
Isolation Method

- Inkjet print 50% (w/w) H$_3$PO$_4$ (without heating) to etch isolation lines in the Al.

$$2\text{Al} + 6\text{H}_3\text{PO}_4 \rightarrow \text{Al}^{3+} + 6\text{H}_2\text{PO}_4^- + 3\text{H}_2(\text{g})$$

- Digital images showing:
  a) Etched lines in an evaporated Al layer;
  b) A wafer fragment during anodisation; and
  c) After anodisation.
Isolation Method (cont)

10 layers of 50% (w/w) of $\text{H}_3\text{PO}_4$ was inkjet-printed on an evaporated Al surface and anodized at 15 V in 0.5 M $\text{H}_2\text{SO}_4$.

<table>
<thead>
<tr>
<th>Resistivity ($\Omega \text{ cm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium at 25 °C</td>
</tr>
<tr>
<td>Isolation Method</td>
</tr>
</tbody>
</table>
Metal Contact Applications

Bifacial Cells

IBC Cells

Al contact for n⁺ finger

P⁺ semiconductor finger

Unit Cell
IBC Cell Structure

$$P_{fr,loss} = \frac{S_J J_{mp} \rho L_f^2}{3 h_f w_f V_{mp}},$$

Plate-up $\rho_{cu} = 1.71 \times 10^6 \, \Omega \text{cm}$

$p^+$ Semiconductor finger $\rho/h_f = 1.27$
Summary

- Selective anodization of Al can be used to form patterns of dielectric and metal regions.
- It can be achieved by using either a masking or an isolation method.
- A selectively-anodized layer of Al is a multifunctional layer providing:
  - Surface passivation;
  - A source of dopants; and
  - A metal contact scheme.
- Selective anodization may find applications in metallization of bifacial and IBC cells.
Conclusion
Conclusions

- Anodising a layer of Al on top of an intervening layer of SiO$_2$, SiN$_x$ and a-Si resulted in an improvement on surface passivation.
- The formation mechanisms of AAO layers on Si surfaces in a way that can achieve minority carrier lifetimes by proving hydrogen incorporated during anodisation can deactivate recombination-active defects at the crystalline Si interface.
- The ability to form p$^+$ layers by laser-doping through AAO layers with doping being achieved by the high concentration of Al within the AAO layer.
- AAO layer can be doped with other impurities by anodising a layer of Al in electrolyte incorporated extrinsic ions to dope the AAO layer.
- Two selectively anodises methods to form Al contact region and dielectric layer for passivation regions from a single metal deposition.
Thank you for your time!
Any Questions?