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
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- Anodic Aluminum Oxide for Metallisation Scheme
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  - Laser-doped through AAO
  - Selective Anodisaiton
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Introduction

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Motivation

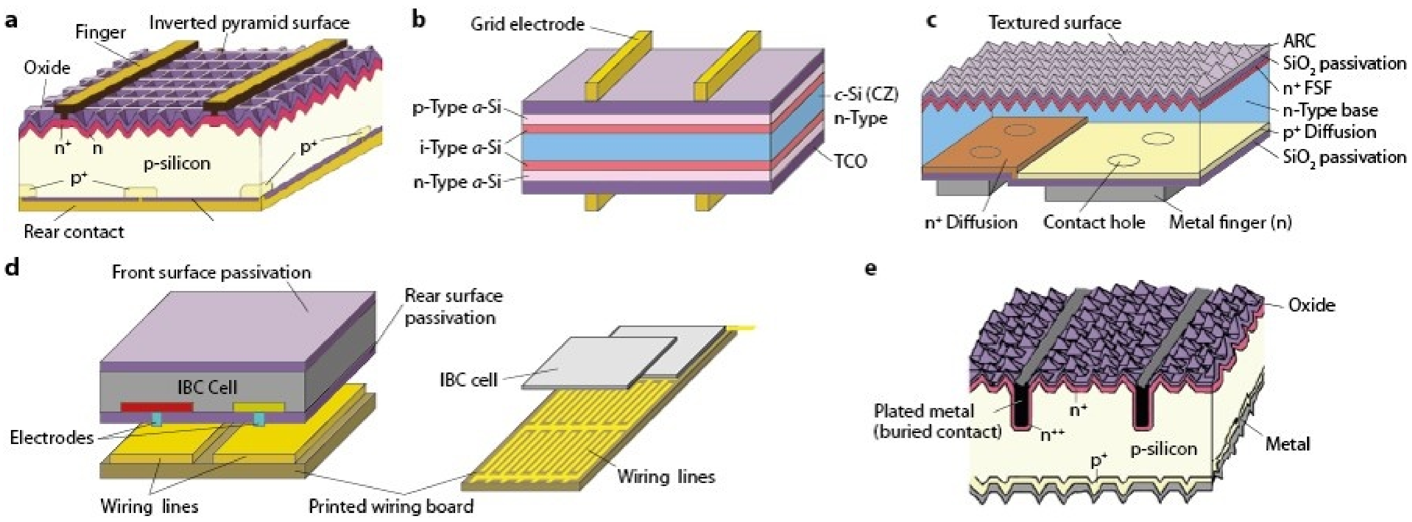
Multifunction layer:

- ❑ SiN_x – Surface passivation & Anti-reflection coating
- ❑ Screen Printed Al Electrode – Back Surface Field & Rear Electrode

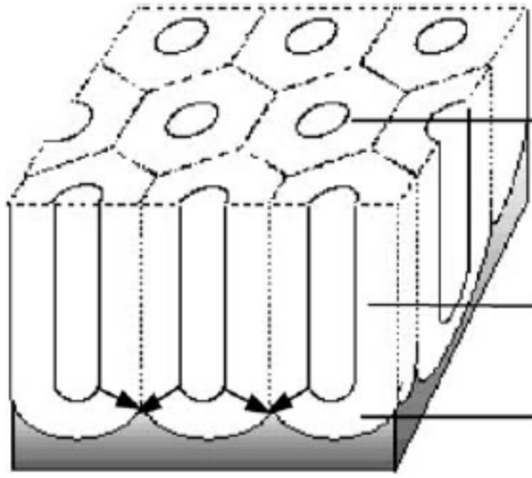
Passivation

High Efficiency Solar Cell:

- ❑ Well Passivated Surface
- ❑ Localised Contact



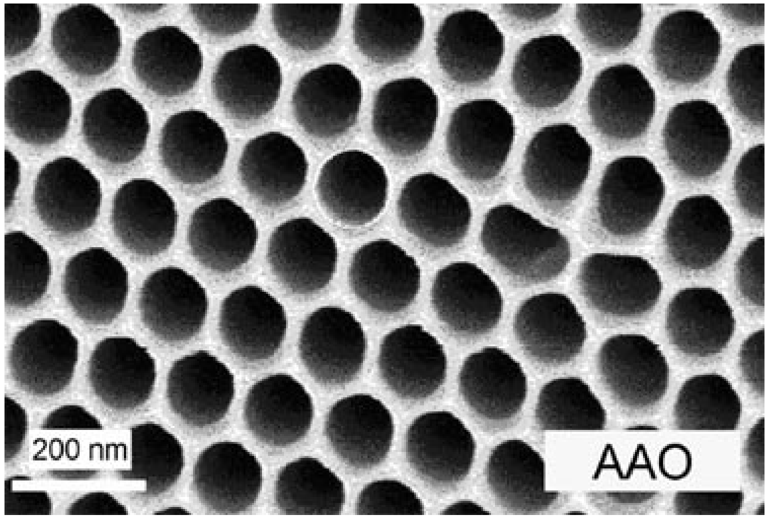
Anodic Aluminium Oxide



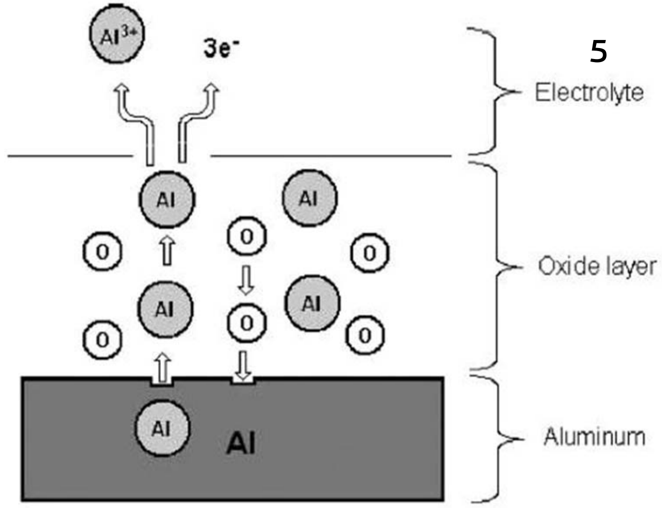
- ❑ Anodic Aluminium Oxide (AAO):

  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.

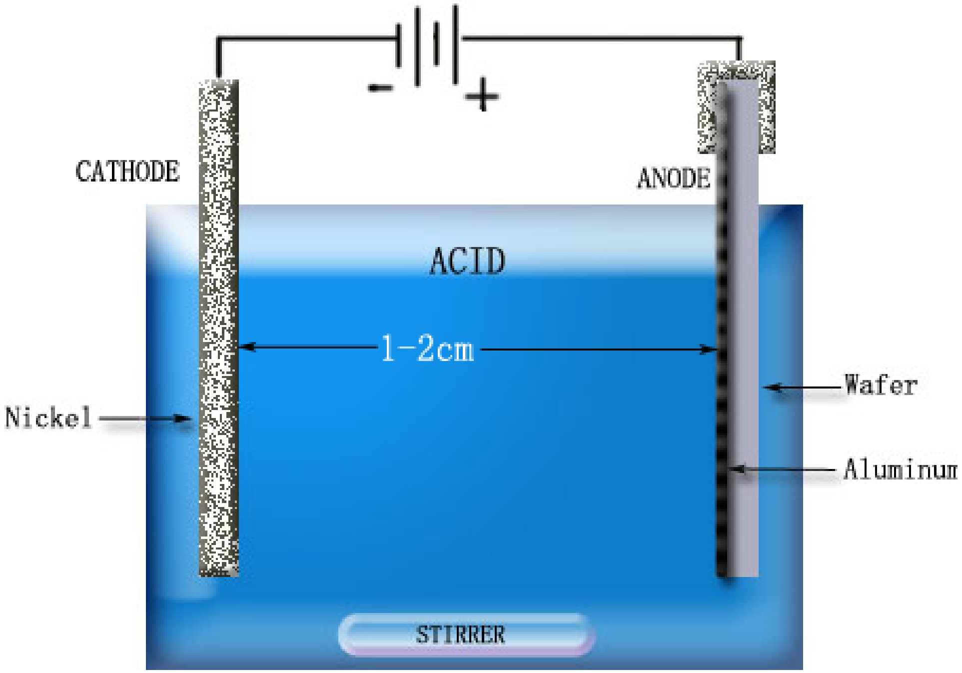


Anodisation



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

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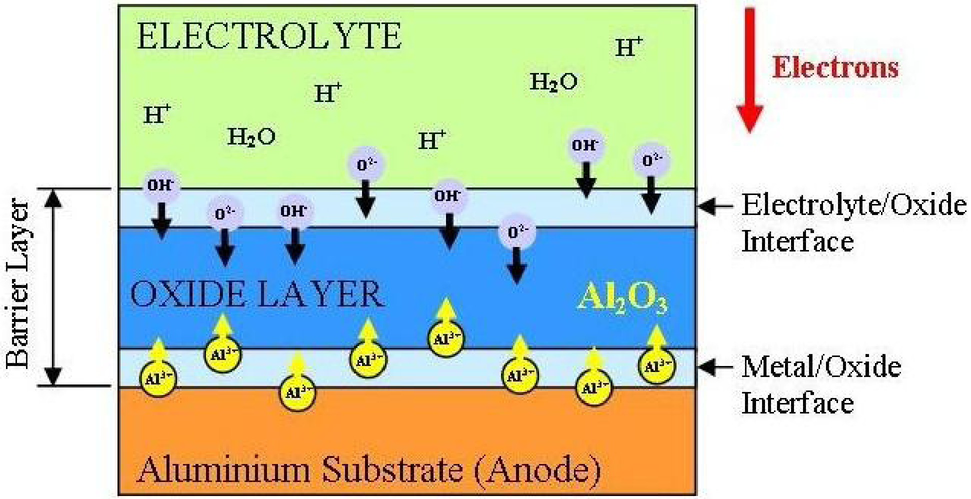
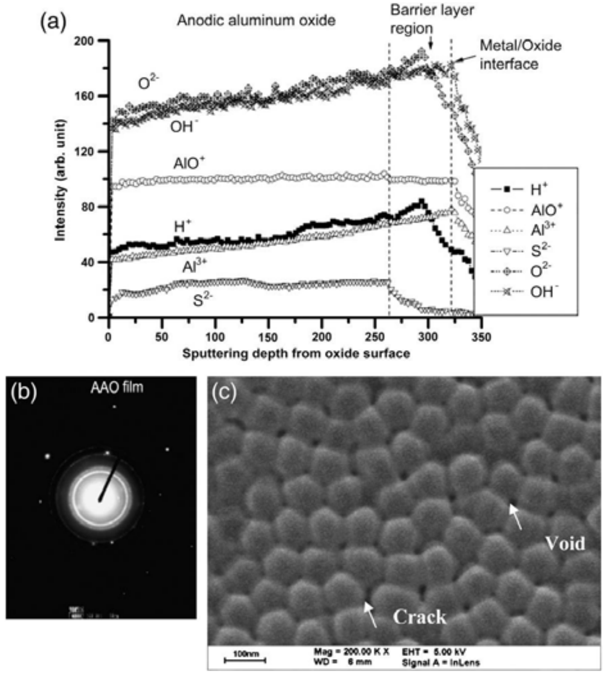
AAO Passivation

Stored Charge with AAO film
-Field Passivation



G. E. J. Poinern, N. Ali, and D. Fawcett, "Progress in Nano-Engineered Anodic Aluminum Oxide Membrane Development," *Materials,* vol. 4, pp. 487-526, 2011

Hydrogen Concentration with AAO film
- Chemical Passivation



T.-S. Shih, P.-C. Chen, and Y.-S. Huang, "Effects of the hydrogen content on the development of anodic aluminum oxide film on pure aluminum," *Thin Solid Films,* vol. 519, pp. 7817-7825, 2011

Anodised Al directly on Si wafer

Anodised a layer of Al on Si wafer

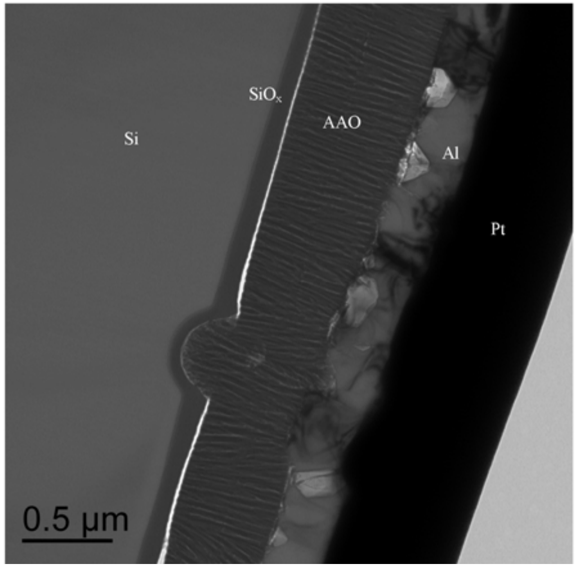
If anodised for too long:

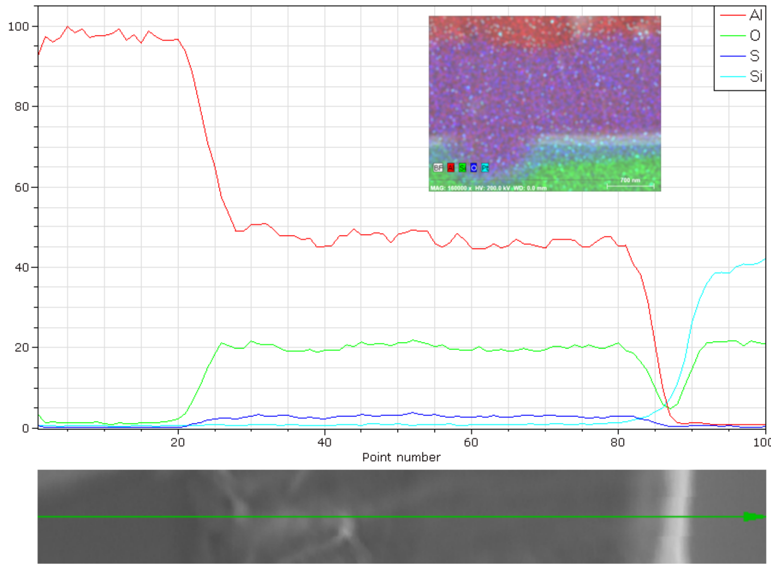
- O^{2-} and OH^{-} anions migrate through AAO and reacts with Si wafer which generates O_2 bubbles at the interface

If a layer of Al is not fully anodised:

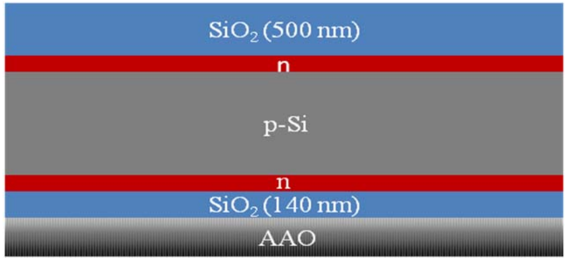
- Al rich region formed at interface between AAO and Si

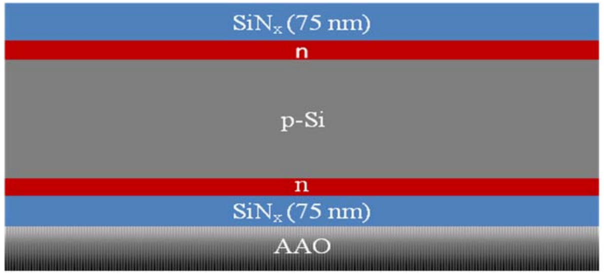
An intervening layer such as SiO_2, a-Si, SiN_x & $SiON_x$ can solve this problem and allow a wider anodisation process window.

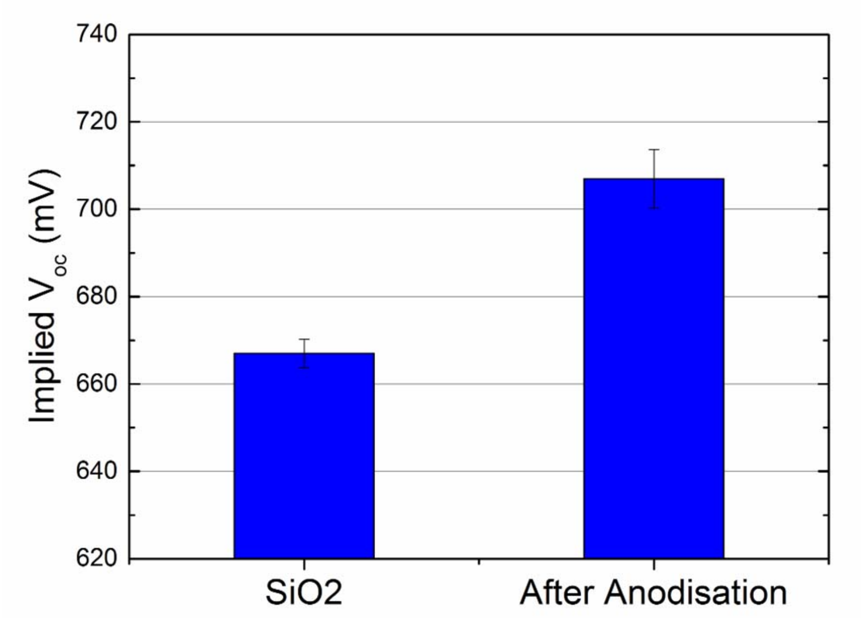


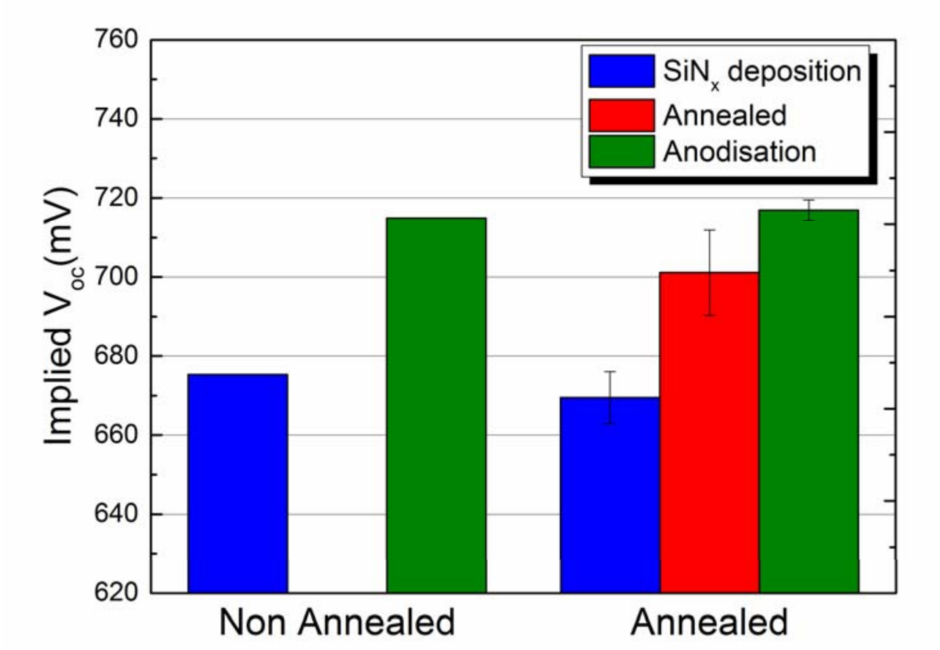


Anodise in 25V 0.5M H_2SO_4 – Different intervening dielectric layers (3-10 Ω cm planar wafers)

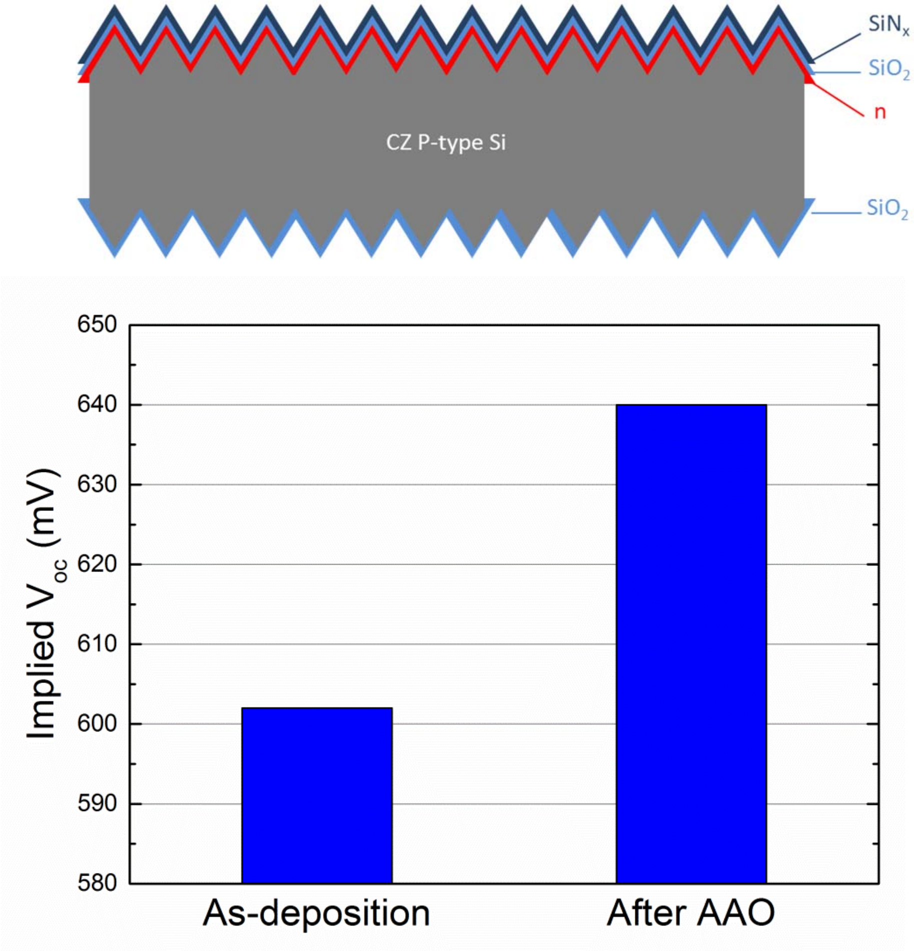


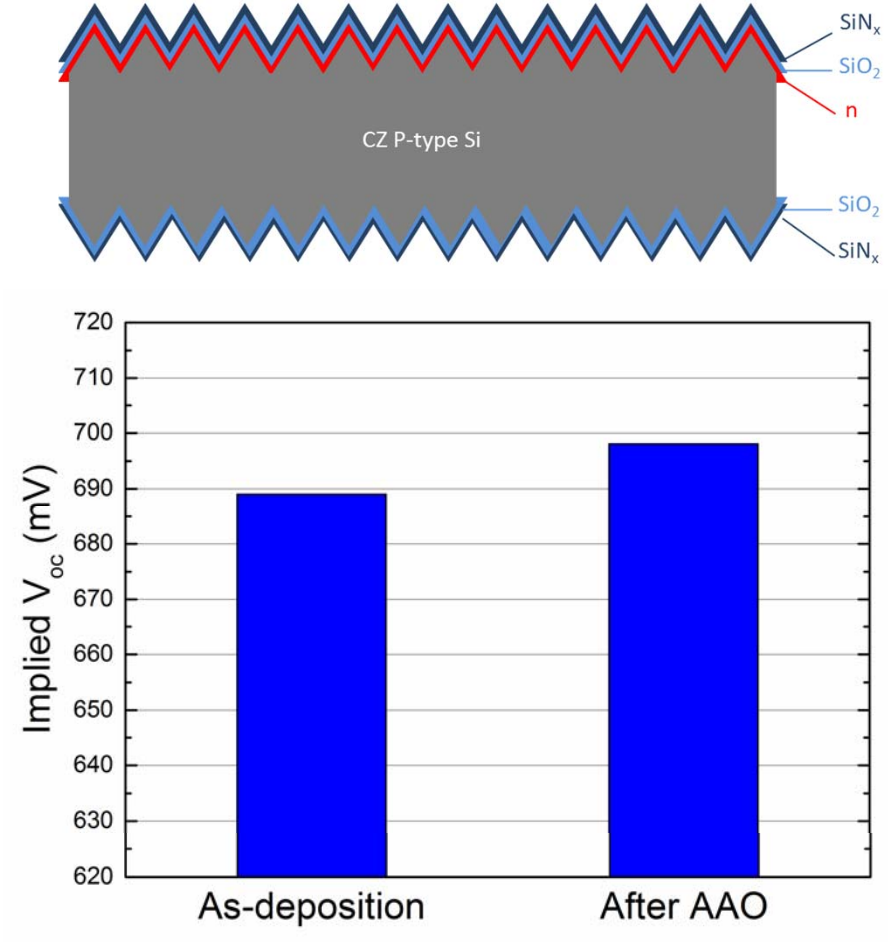


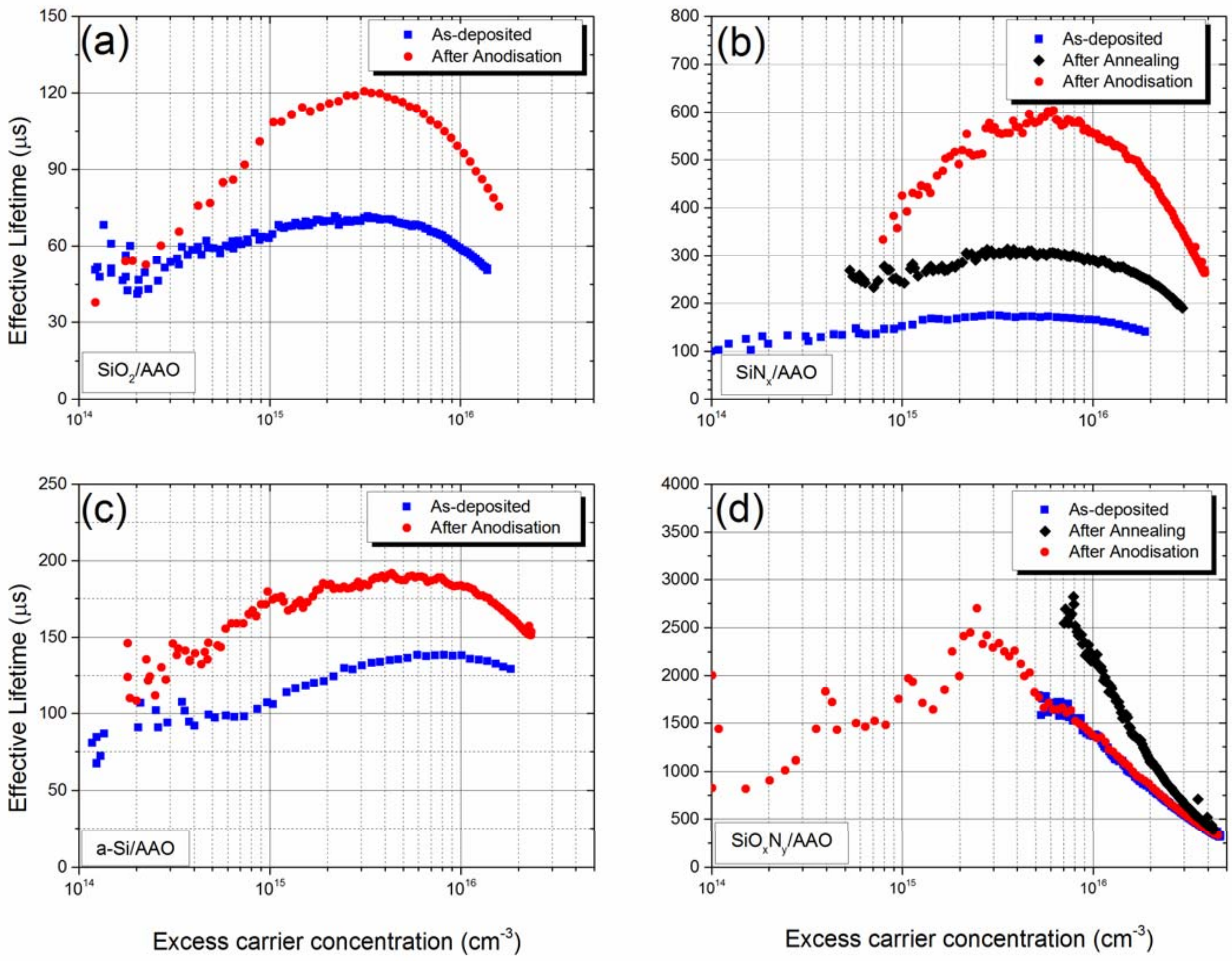




Anodise in 25V 0.5M H_2SO_4– Different intervening dielectric layers (1-3 Ω cm 5’’ texture wafers)



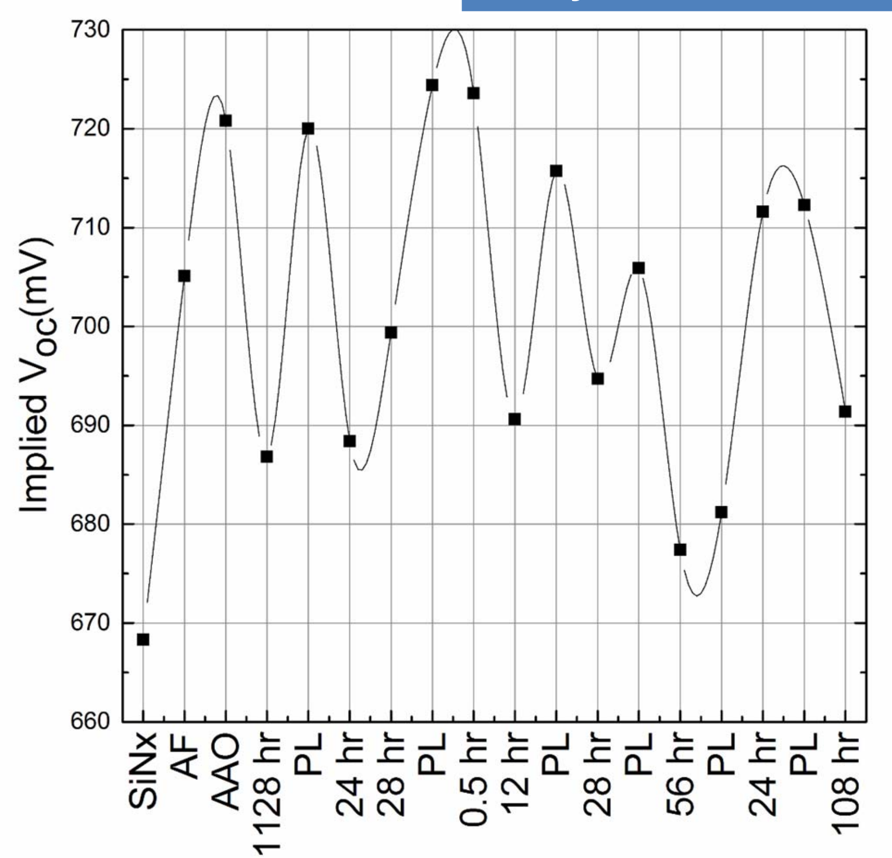


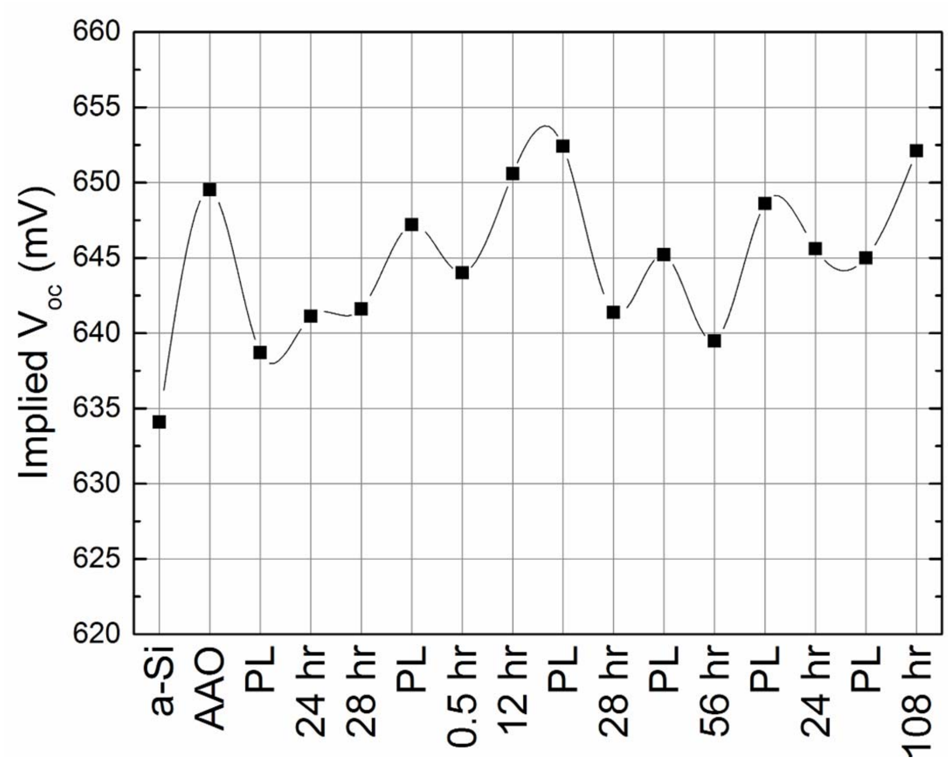


(a)
As-deposited
After Anodisation
SiO2/AAO
Effective Lifetime (µs)
(b)
As-deposited
After Annealing
After Anodisation
SiNx/AAO
(c)
As-deposited
After Anodisation
a-Si/AAO
Effective Lifetime (µs)
(d)
As-deposited
After Annealing
After Anodisation
SiOxNy/AAO
Excess carrier concentration (cm-3)
Excess carrier concentration (cm-3)

Stability

Intervening Layer	SiO_2	SiN_x	$SiON_x$	a-Si
Increase in implied V_{oc} after anodisation (mV)	40	47	0	5
Variation in implied V_{oc} (mV) over 60 days	±5	±17	±5	±5





Summary of AAO Passivation

- 3-10 Ω cm Planar Wafer

Rear Passivation	J_{0e} (fA cm^{-2})	Implied V_{oc} (mV)
140 nm SiO_2	92	
140 nm SiO_2 + 650 nm AAO	32	+40
75 nm SiN_x	22	
75 nm SiN_x + 650 nm AAO	8	+37

- 1-3 Ω cm Texture Wafer

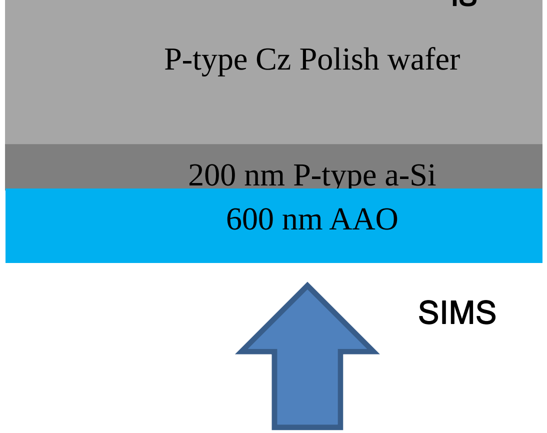
Rear Passivation	Optimal Electrolyte Temperature (deg)	Implied V_{oc} (mV)
10 nm SiO_2+ 650 nm AAO	25~30	+30
Rear emitter +10 nm SiO_2 + 650 nm AAO		±5
10 nm SiO_2 + 75 nm SiN_x+ 650 nm AAO	55~65	+10
Rear emitter +10 nm SiO_2 + 75 nm SiN_x+ 650 nm AAO		±10

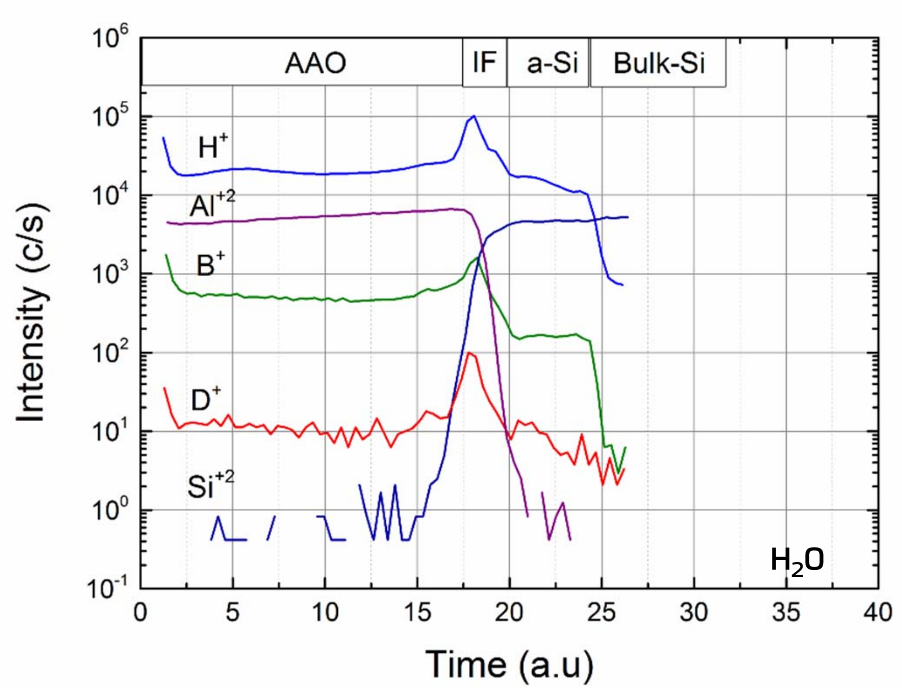
Passivation Mechanism

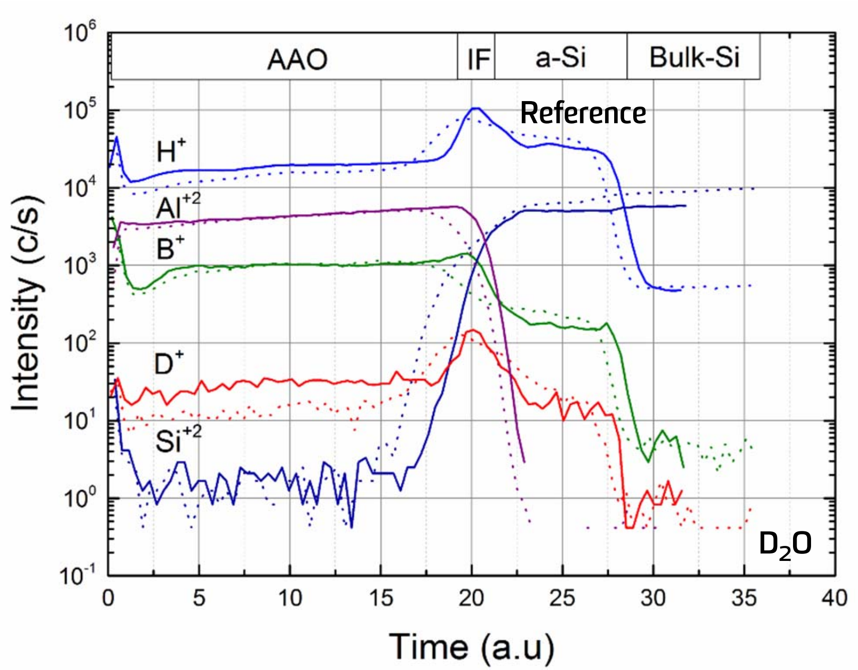
Field Passivation - Stored Charge

Electrolyte Concentration	Anodisation Voltage (V)	Fixed Charge Density of SiO_2/AAO stack (cm^{-2})	Fixed Charge Density of SiNx/AAO stack (cm^{-2})
0.5M	20	$6.5 \pm 0.1 \times 10^{11}$	$2.1 \pm 0.1 \times 10^{12}$
	22.5	$5.9 \pm 0.1 \times 10^{11}$	$2.0 \pm 0.2 \times 10^{12}$
	25	$4.8 \pm 0.1 \times 10^{11}$	$2.0 \pm 0.3 \times 10^{12}$
2.3M	8	$5.2 \pm 0.1 \times 10^{11}$	$1.9 \pm 0.1 \times 10^{12}$
	10	$4.7 \pm 0.1 \times 10^{11}$	$1.8 \pm 0.1 \times 10^{12}$
	12	$4.0 \pm 0.1 \times 10^{11}$	$1.5 \pm 0.1 \times 10^{12}$
Reference sample		$2.4 \pm 0.1 \times 10^{11}$	-

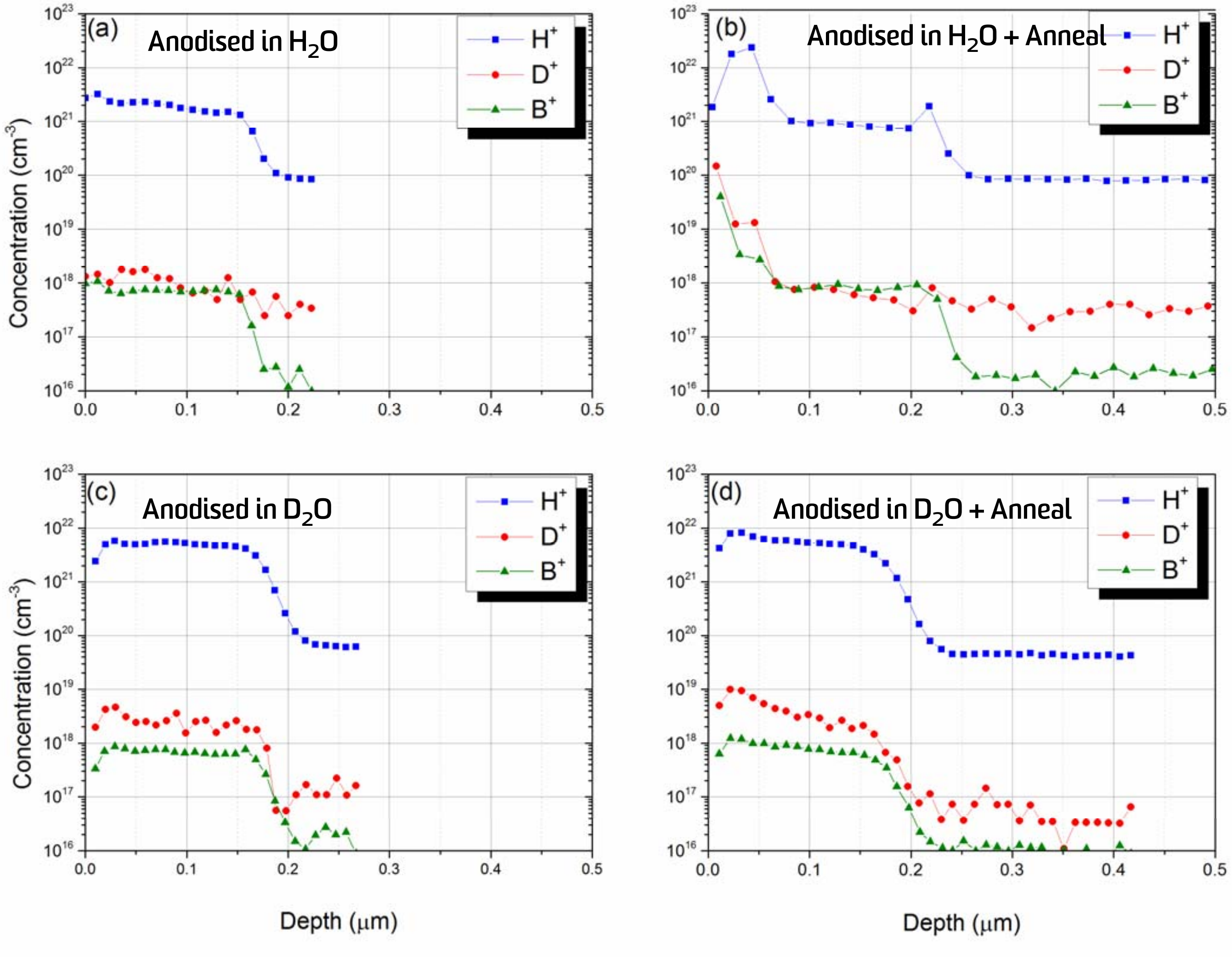
Hydrogen Incorporation

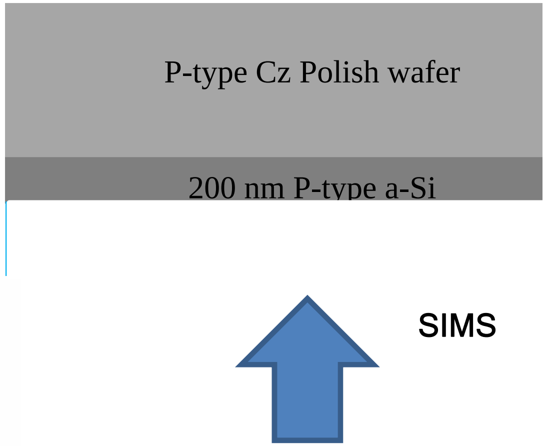


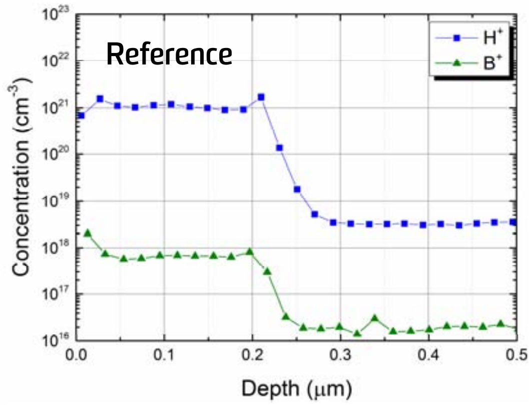




Hydrogen Incorporation





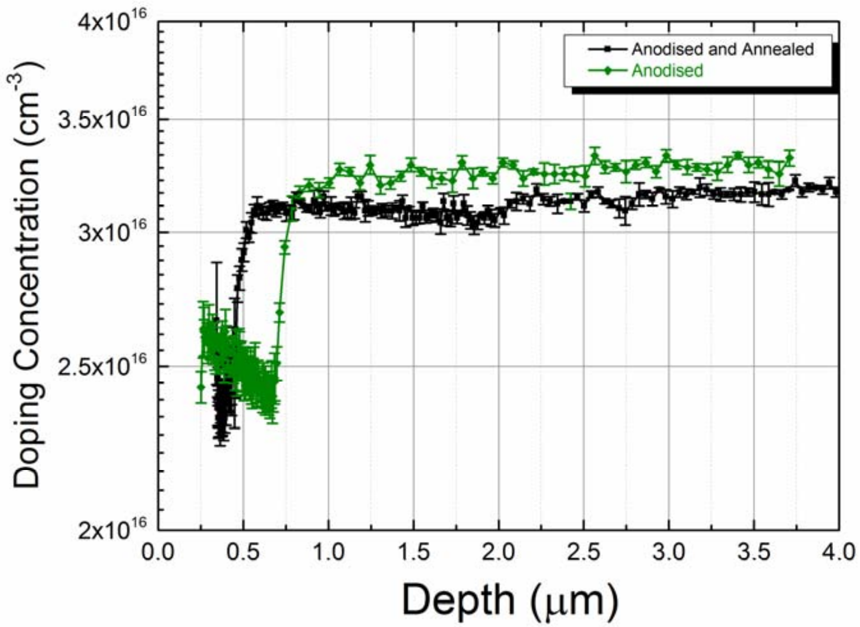


Summary

- 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

→ increased minority carrier lifetimes of wafers after anodisation of Al

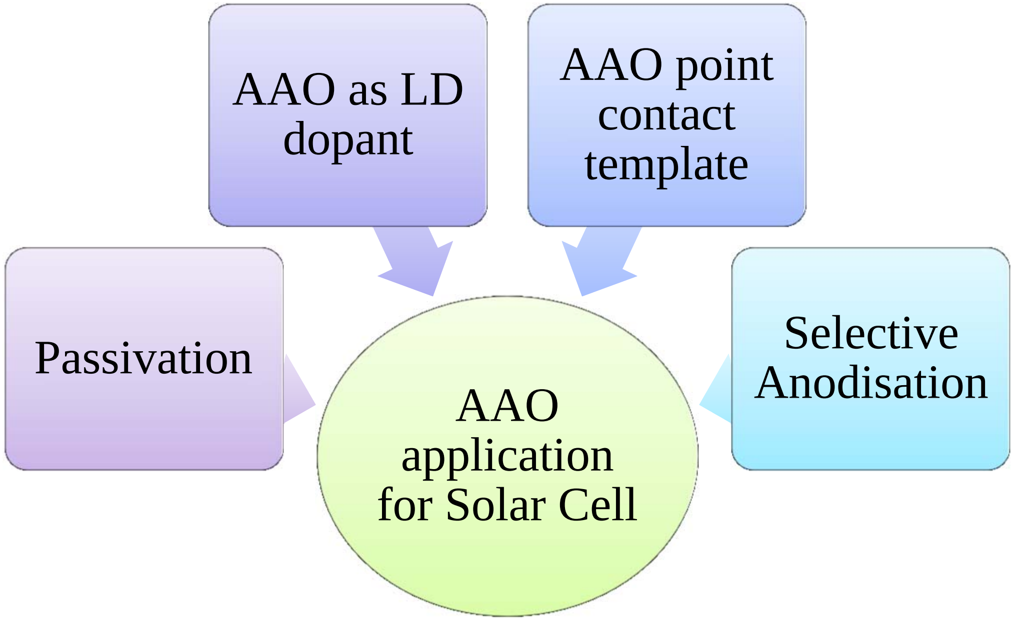
- Annealing at 400 °C after anodisation can result in increased hydrogen and deuterium in the underlying amorphous Si
- AAO can act as a hydrogen reservoir able to supply hydrogen to underlying substrates when subsequently annealed.

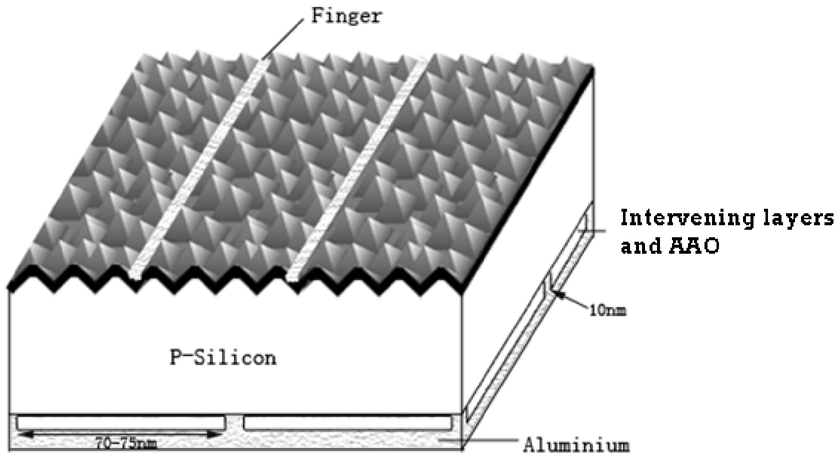


AAO Metallization Scheme

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^+ regions which are subsequently metallised
- An AAO can be selectively anodised by pre patterning the Al layer before anodising.





AAO Localised Contact

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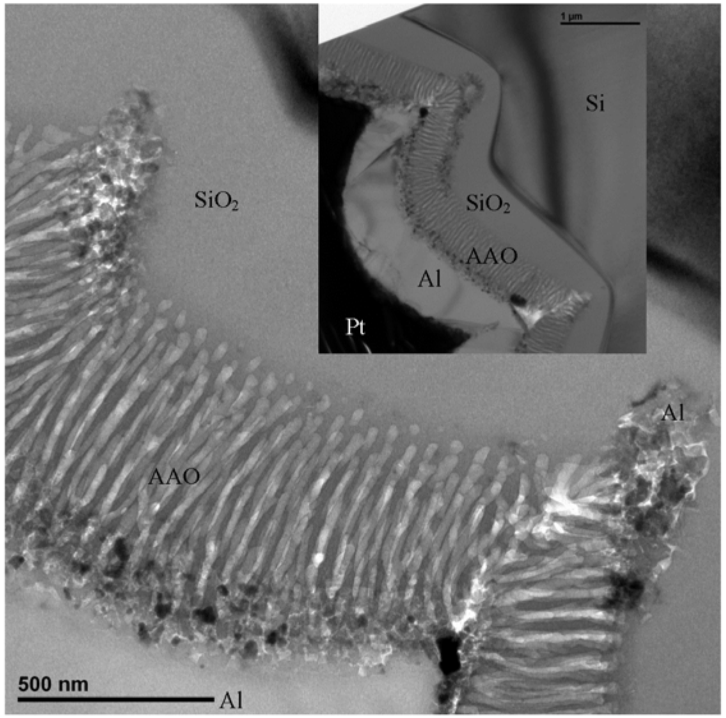
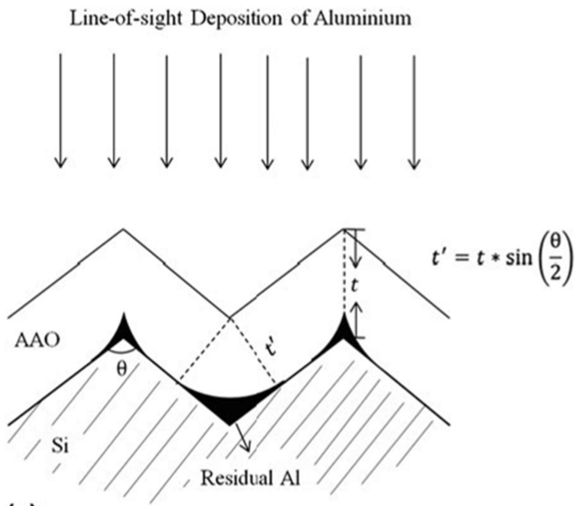
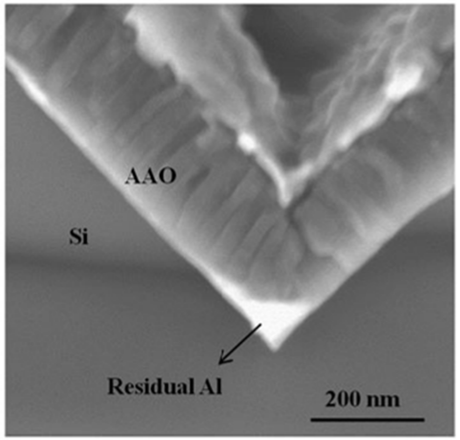
AAO Localised Contact





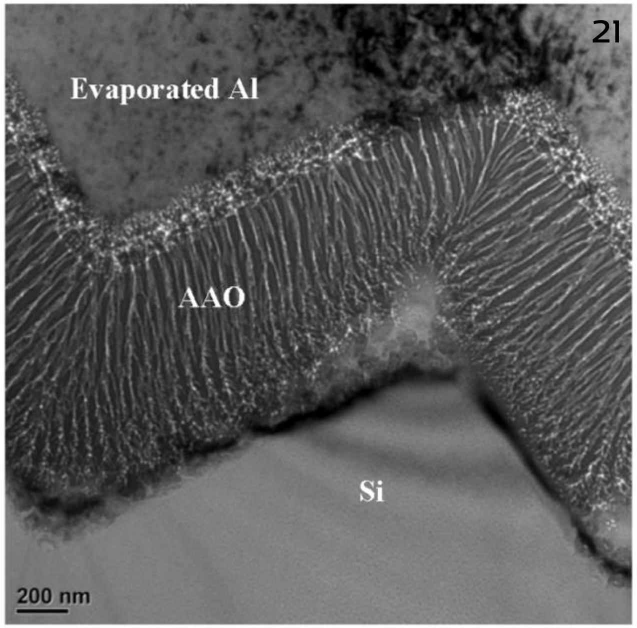
(a)



(b)

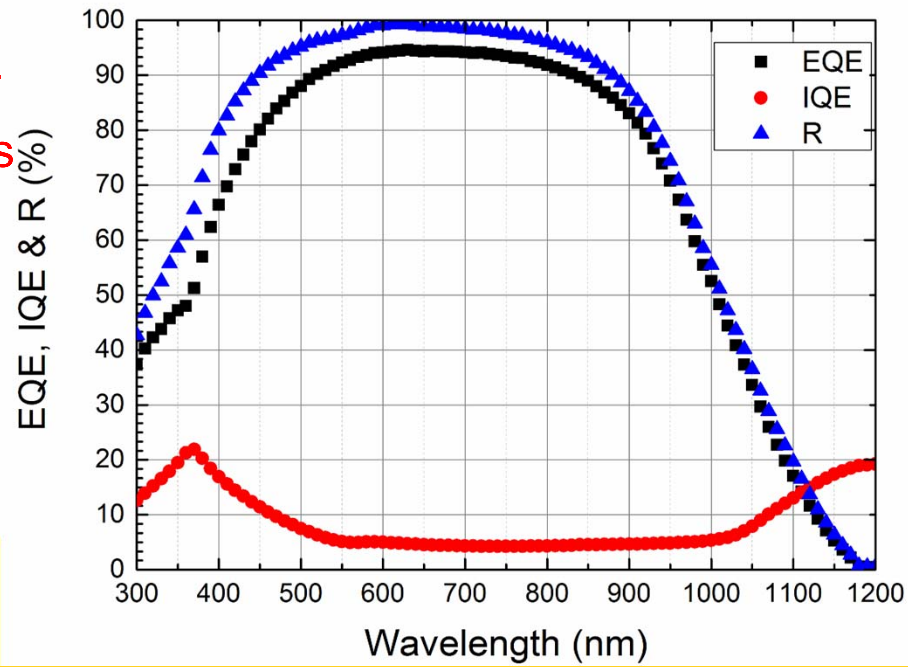
Z. Lu, P. H. Lu, J. Cui, K. Wang, and A. Lennon, "Self-patterned localized metal contacts for silicon solar cells," *Journal of Materials Research,* vol. 28, 2013

AAO Localised Contact



- A thin layer of thermal SiO_2 and AAO stack can result 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%.

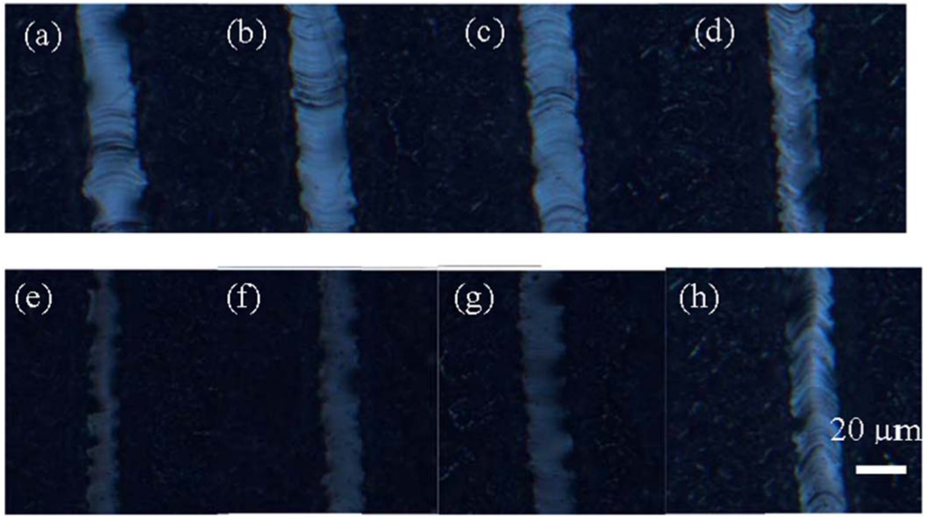
The importance of forming localised BSF regions is to have at least 2 μm thickness for any small-scale metal contacting scheme.

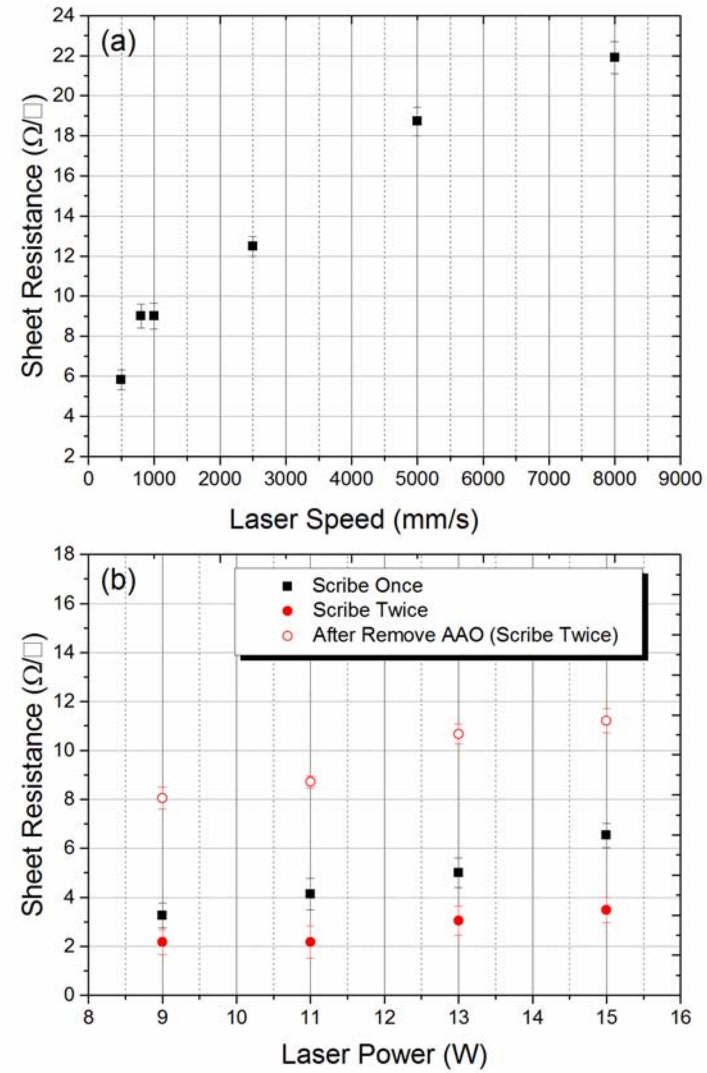


Laser-Doped Through AAO

Laser-doped Through AAO

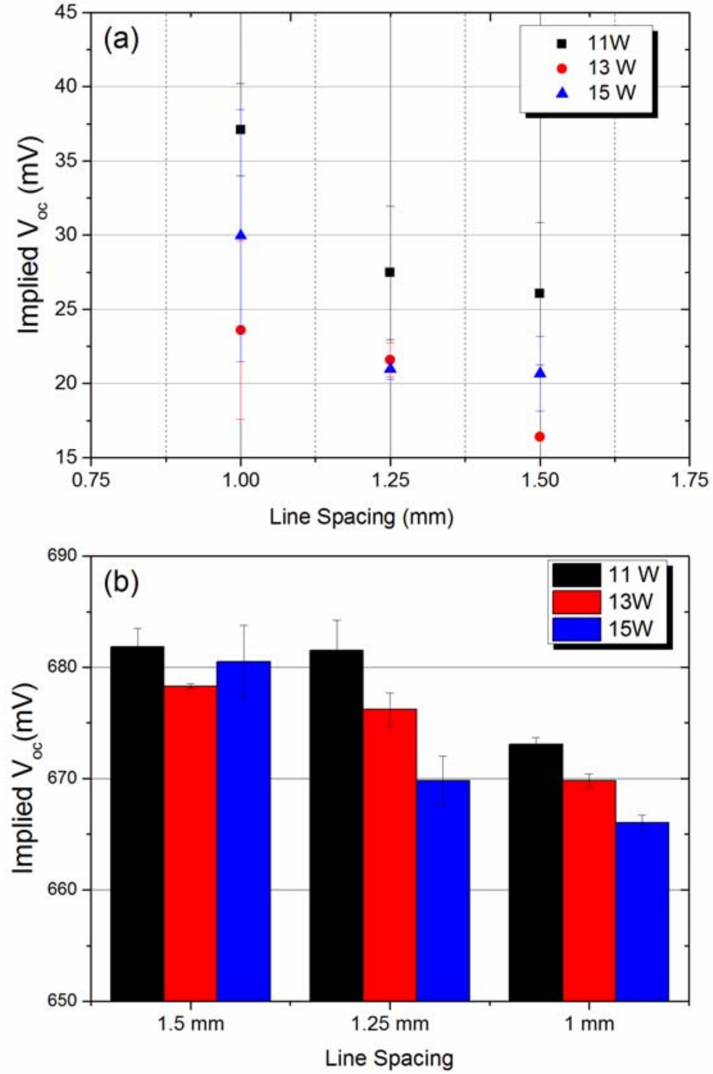
- ❑ Silicon can be locally-doped with aluminium to form localised p+ surface regions by laser-doping AAO layers formed on the silicon surface.





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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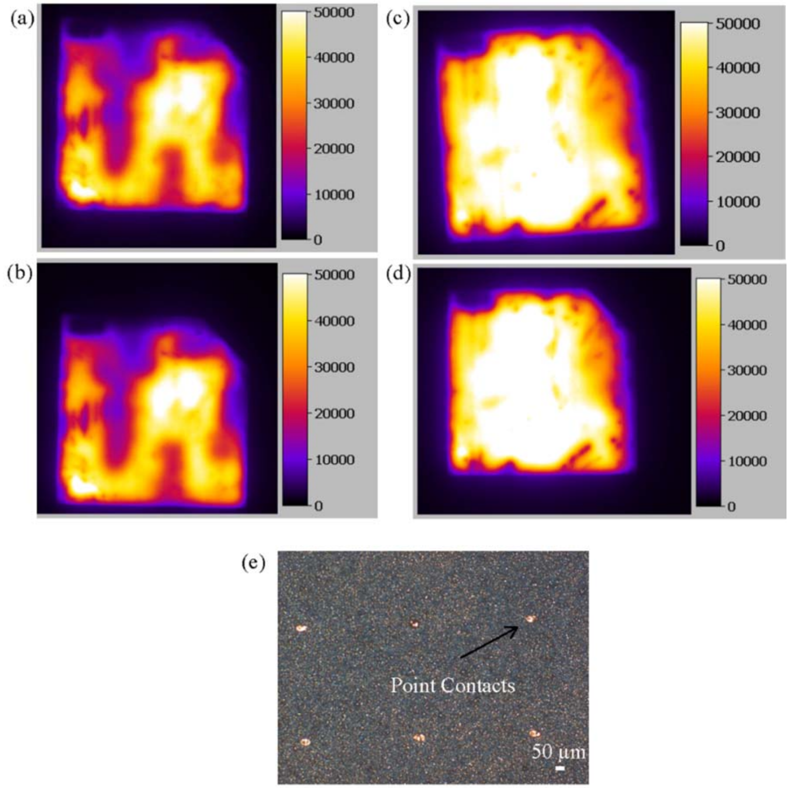
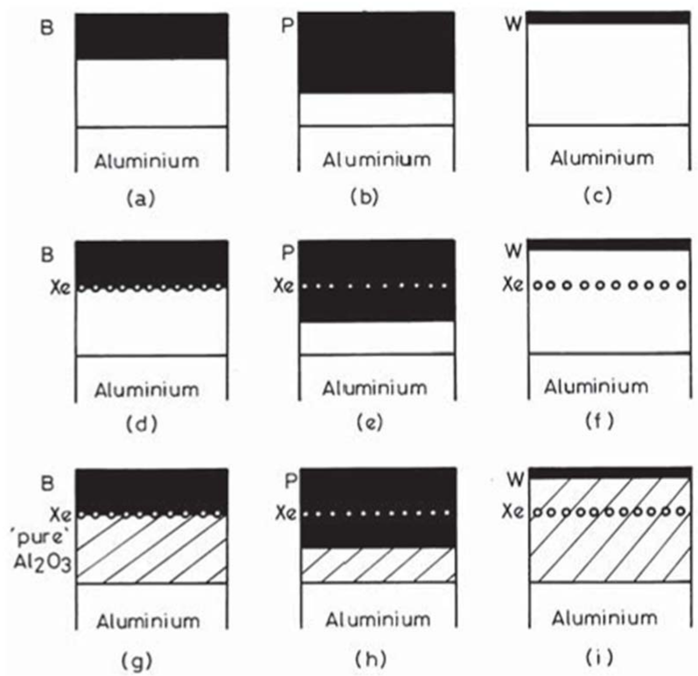


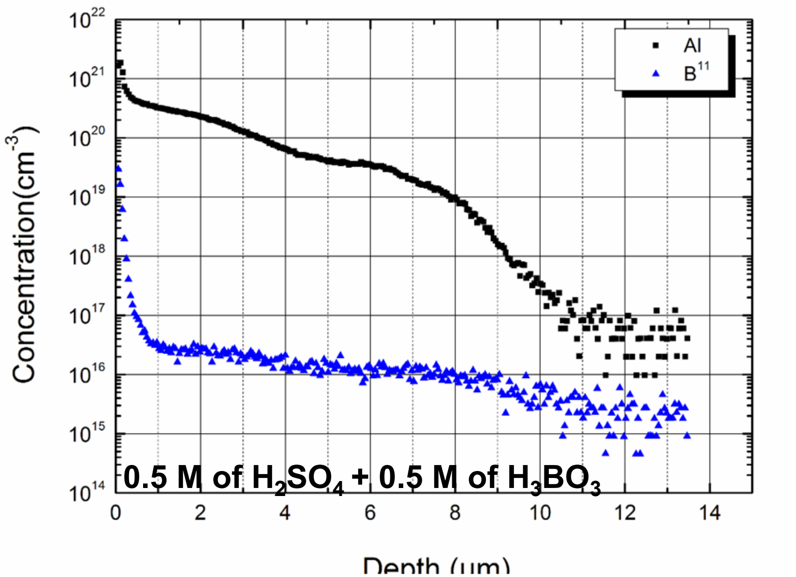
Laser-doped Through AAO

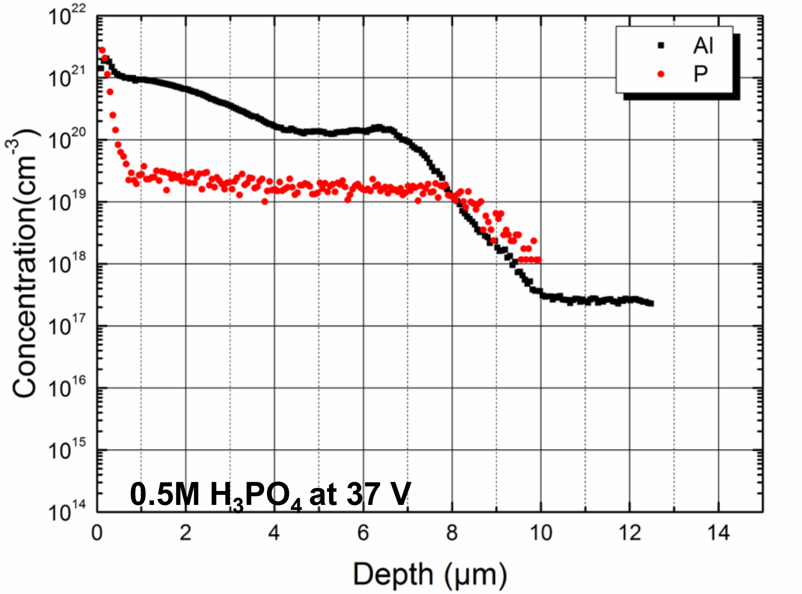
- Lowest sheet resistance was recorded using two scribing passes and a laser speed and power of 500 mm/s and 9 W, however, the number of scribing passes generates more laser damage.
- AAO can be doped with other impurities, such as boron and phosphorus, by anodising in electrolytes containing the extrinsic 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

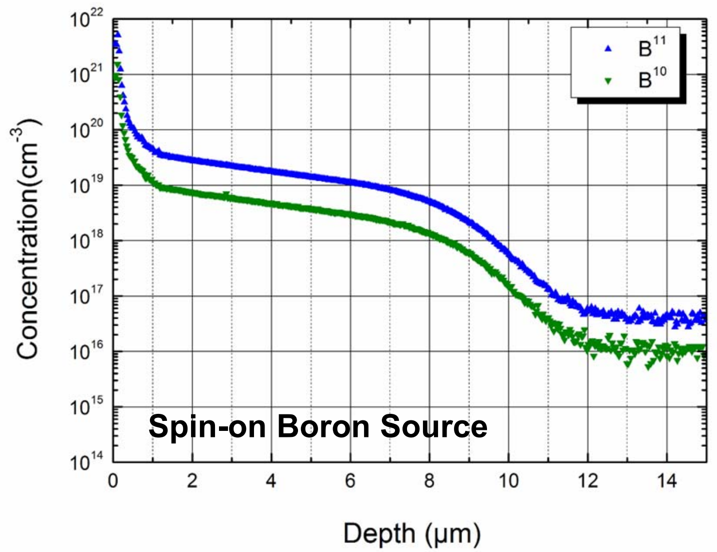


G. E. Thompson, "Porous anodic alumina: fabrication, characterization and applications," *Thin Solid Films,* vol. 297, pp. 192-201, 1997

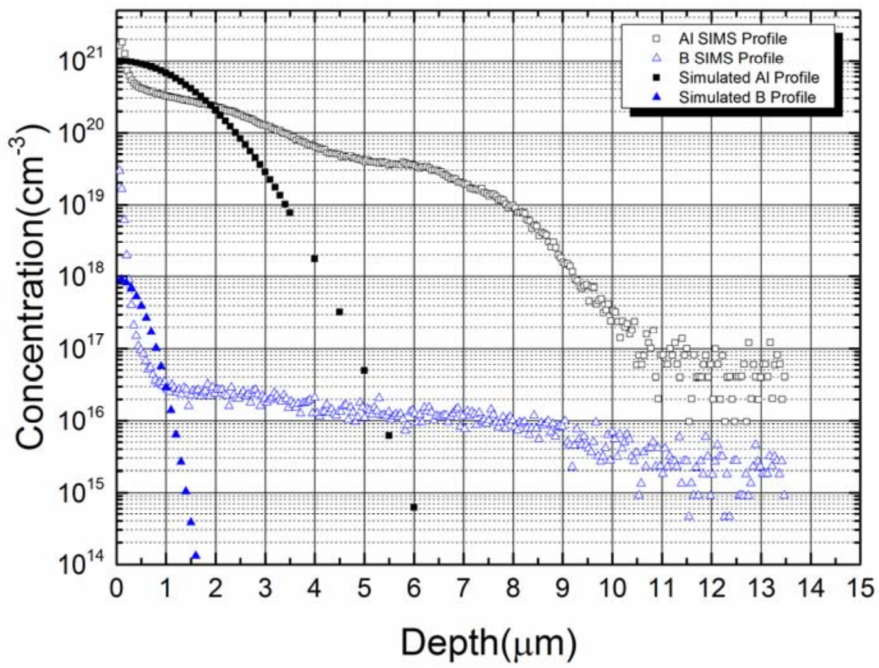
SIMS Profile of LD Region

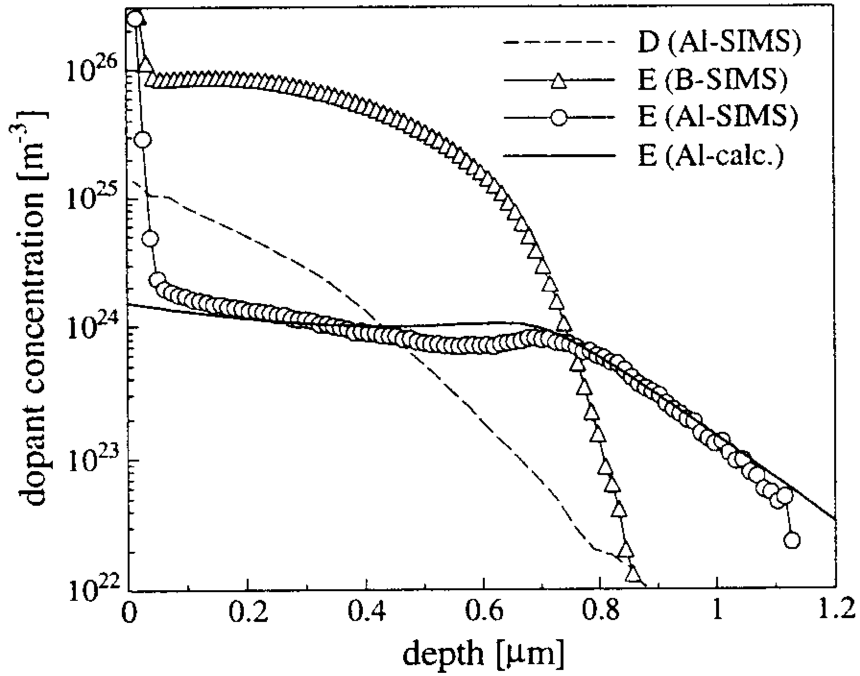






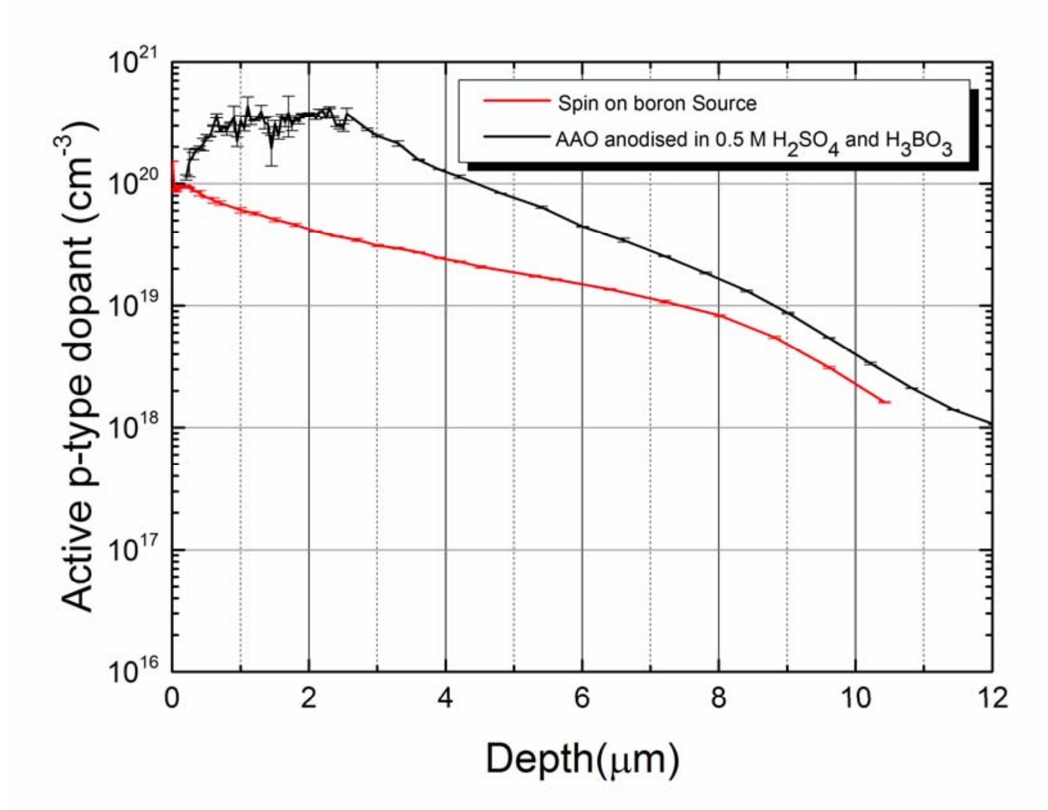
B enhance Al diffusion

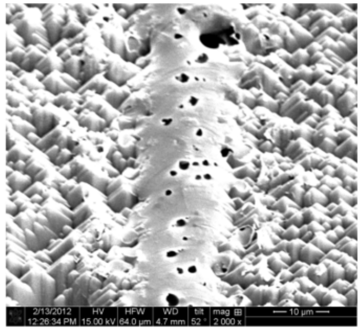




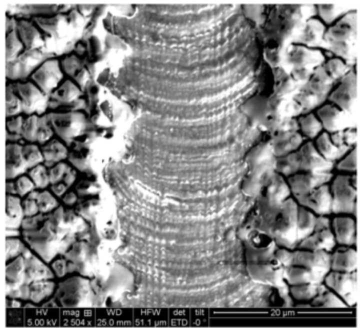
U. Kuhlmann, D. Nagel, and R.Sitting, "Short-Time Diffusion of Aluminium in Silicon and Co-Diffusion with Phosphorus and Boron " *Diffusion in Materials DIMAT 1996,* vol. 143-147, 1997.

Laser-doped Through Doped AAO



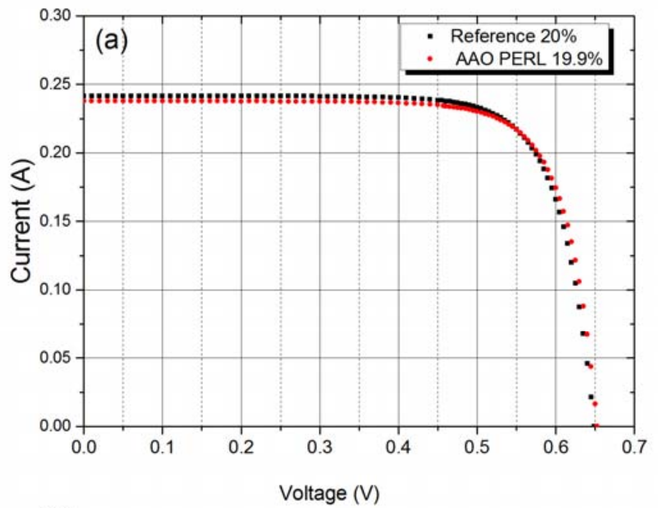


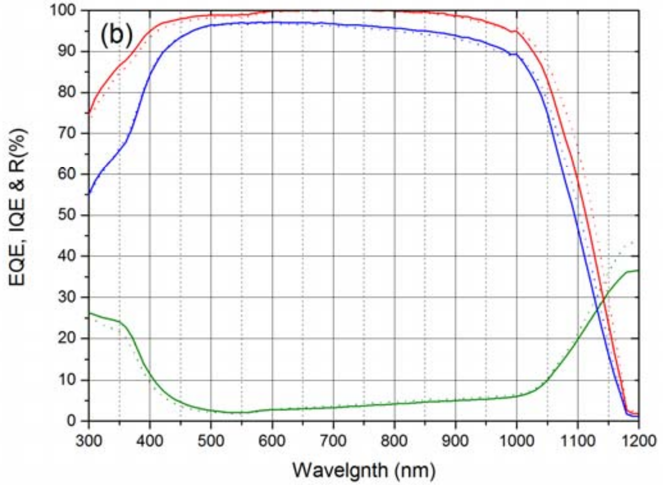
Spin-coated poly boron dopant source

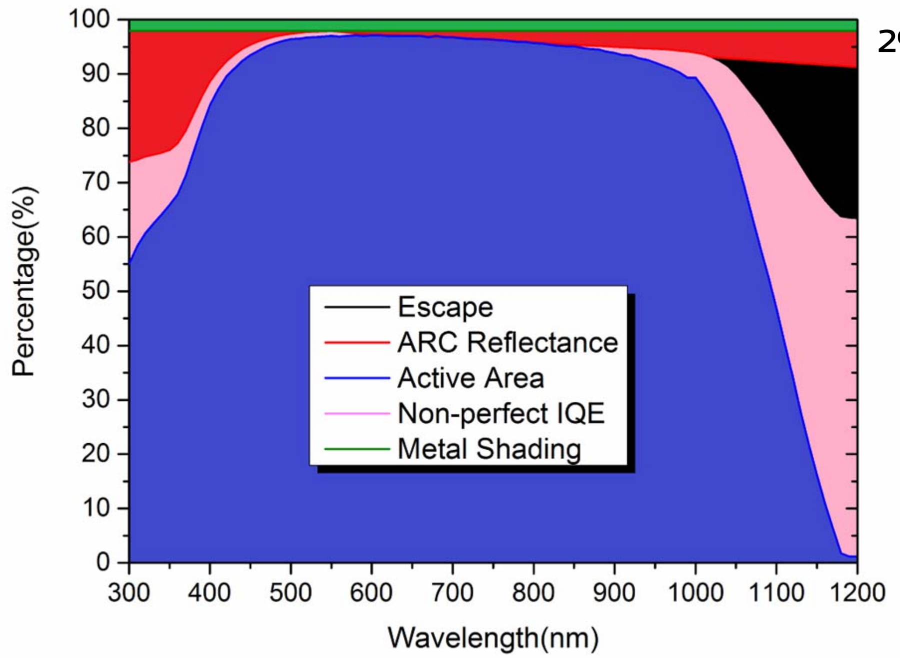


AAO layer formed by anodising aluminium at 25 V in an electrolyte comprising 0.5 M of H_2SO_4 and 0.5 M of H_3BO_3

AAO PERL Cell







	LD line Spacing (mm)	iV_{oc} after deposition (mV)	iV_{oc} after anodisation (mV)	Efficiency (%)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	R_s (Ωcm^2)
0.5 M H_2SO_4	1	624	629	19.5	636	40.3	76.0	0.9
	1.25	620	627	19.4	651	40.5	74.0	1.2
0.5 M H_2SO_4 + 0.5 M H_3BO_3	1	621	616	19.4	635	40.1	76.0	0.54
	1.25	620	621	19.9	652	40.1	76.5	0.66
		619	616	19.6	640	40.0	76.7	0.66
Ref	1	-	-	20.0	649	40.2	76.7	0.66
	1.25	-	-	19.7	647	40.2	75.7	0.84

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 Anodisaton

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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.

It can result in patterns of metal and dielectric regions and can potentially be used to form metal contacts to both polarities [e.g. in interdigitated back contact (IBC) cells].

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

Methodology

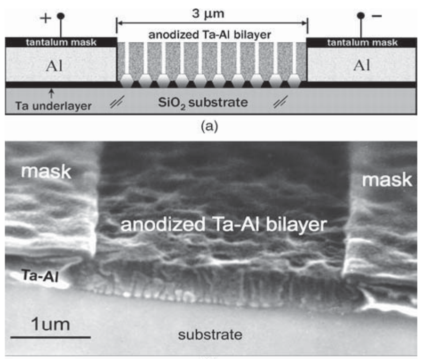
- **Patterning**

Masking Method

Isolate Al from the electrolyte during anodisation.

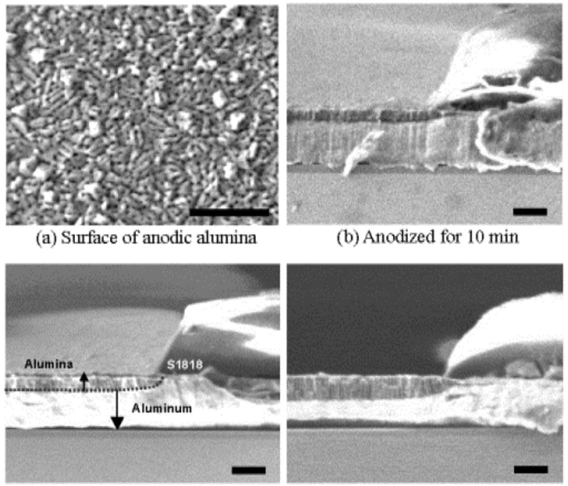
Isolation Method

Isolate Al from the anodic potential during anodisation.

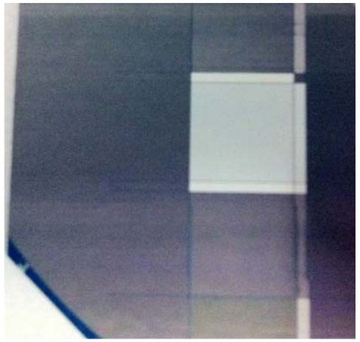


(a)

(b)



(a) Surface of anodic alumina (b) Anodized for 10 min (c) Anodized for 15 min (d) Anodized for 20 min

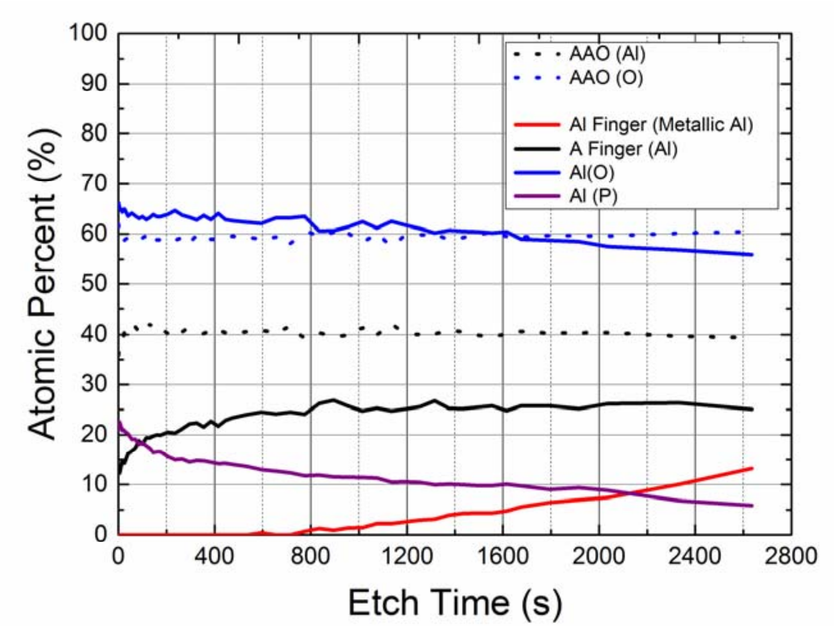


A. Mozalev, G. Gorokh, M. Sakairi, and H. Takahashi, "The growth and electrical transport properties of self-organized metal/oxide nanostructures formed by anodizing Ta-Al thin-film bilayers," *Journal of Materials Science,* vol. 40, pp. 6399-6407, 2005/12/01 2005

J. Park, J. Fattaccioli, N. Takama, H. Fujita, and B. Kim, "Localised Anodisation of Aluminum for the Formation of Aluminum.Alumina Patterns," presented at the Asian Symposium for Precision Engineering and Nanotechnology 2009, Kitakyushu, Japan, 2009

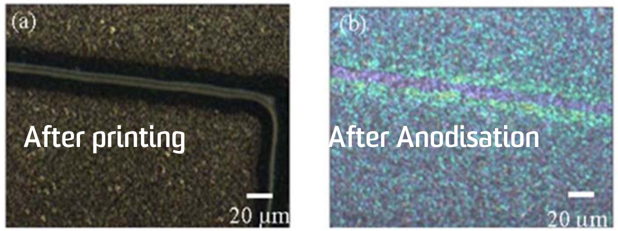
Masking Method

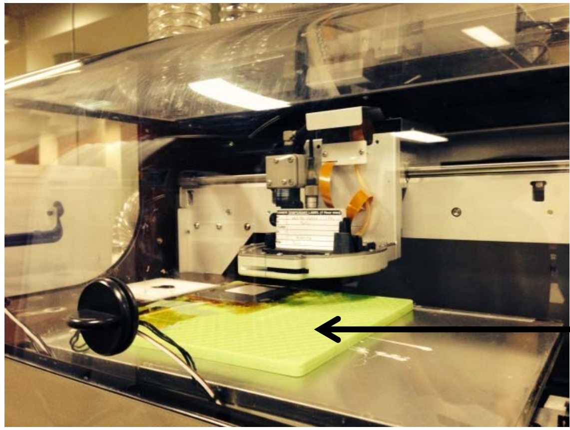
- The effectiveness of printing a layer of mask depends on the surface morphology and the duration of the anodization process.
- Print 50% w/w H3PO4 while the wafer is heated to 200 ºC, H3PO4 dehydrates to P_2O_5 and oxidises a surface layer of Al.
- XPS shows that under the mask the Al is metallic.



5 layers of the novolac resin on the sputtered Al surface

5 layers of the novolac resin on the evaporated Al surface





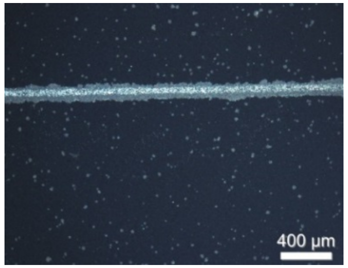
Hot Plate

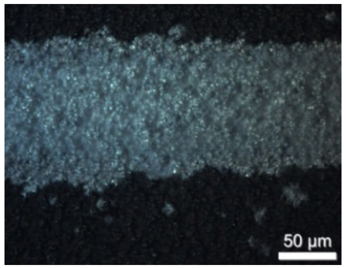
Masking Method (cont)

Printing Condition	1 pL 1 layer	1 pL 3 layers	10 pL1 layer	10 pL 3 layers
Width of printed line (μm)	40 ± 8	70 ± 15	160 ± 20	170 ± 40
Resistivity (Ω cm)	-	2.5×10^{-5}	7×10^{-5}	4.8×10^{-5}

1 pL 3 layers

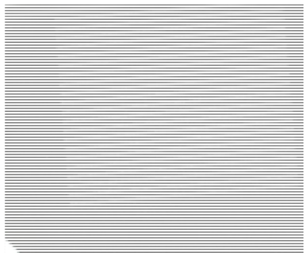
50% H_3PO_4

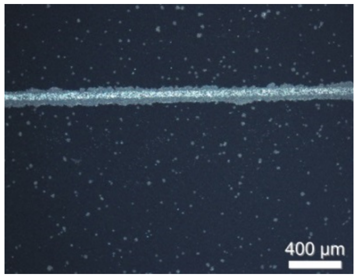


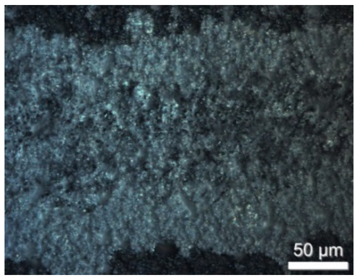


10 pL 1 layer

50% H_3PO_4

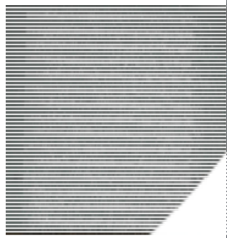


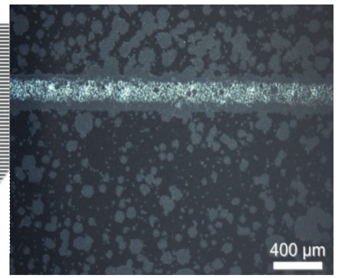




10 pL 3 layers

50% H_3PO_4



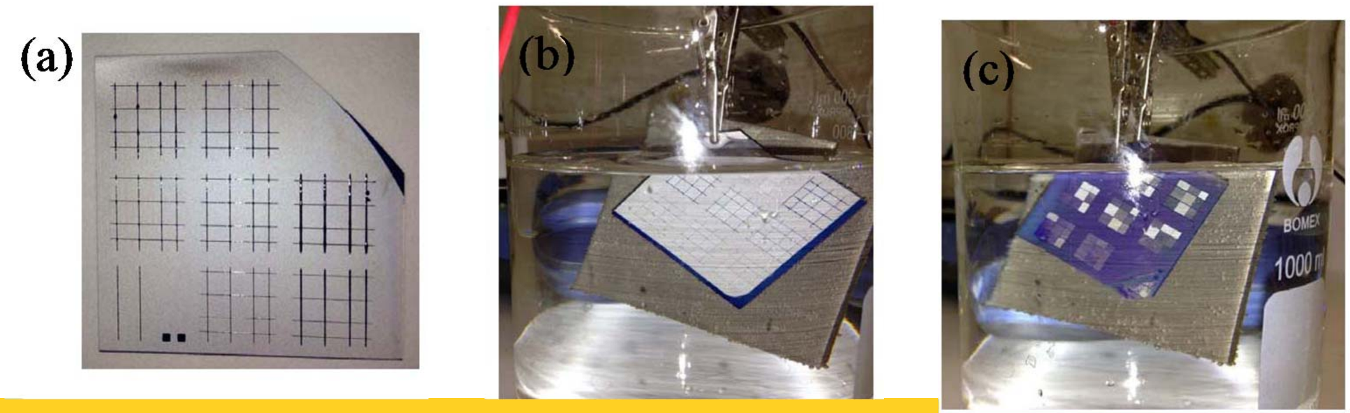


Isolation Method

- Inkjet print 50% (w/w) H_3PO_4 (without heating) to etch isolation lines in the Al.

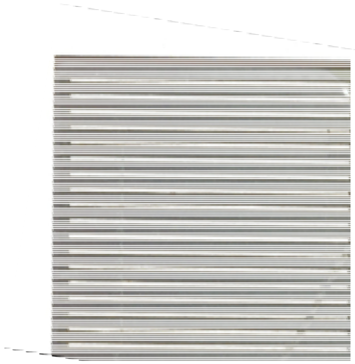
$$2Al + 6H_3PO_4 \rightarrow Al^{3+} + 6H_2PO_4^- + 3H_2(g)$$

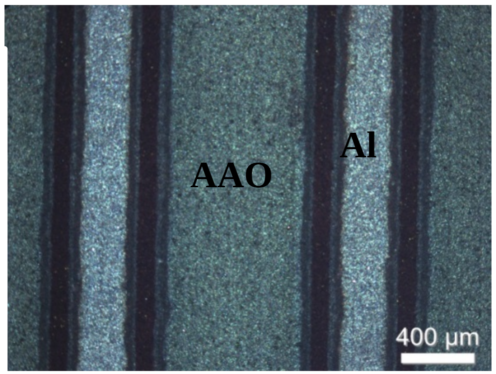
- Digital images showing:
  a) Etched lines in an evaporated Al layer;
  b) A wafer fragment during anodisation; and
  c) After anodisation.



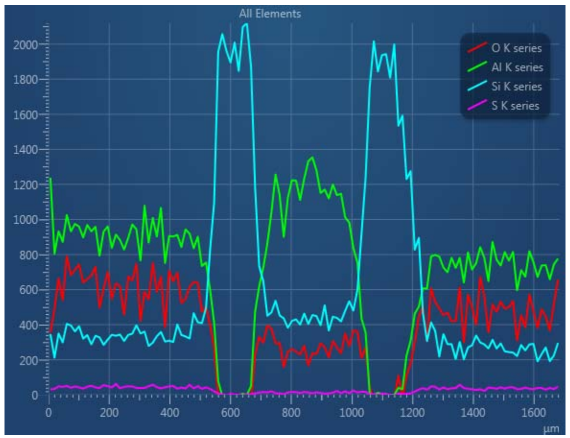
Isolation Method (cont)

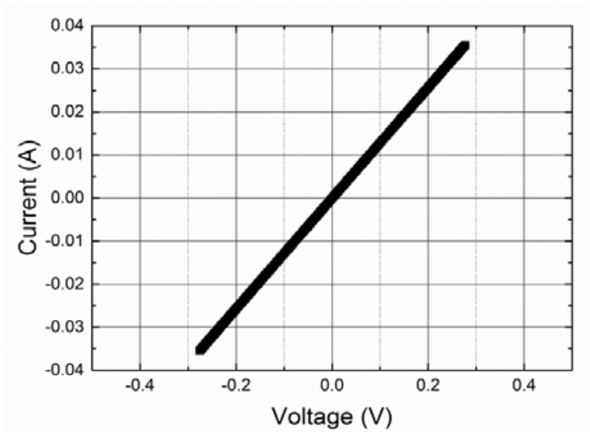
10 layers of 50% (w/w) of H_3PO_4 was inkjet-printed on an evaporated Al surface and anodized at 15 V in 0.5 M H_2SO_4.





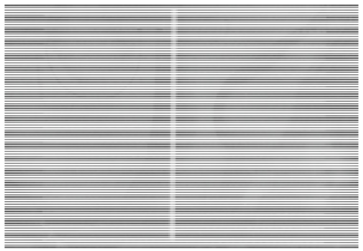
	Resistivity (Ω cm)
Aluminium at 25 ° C	2.71 × 10^{-6}
Isolation Method	1.6 × 10^{-5}

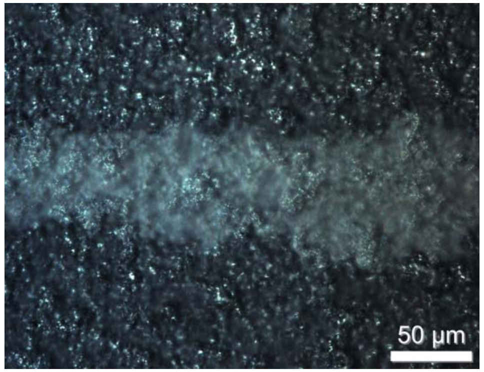


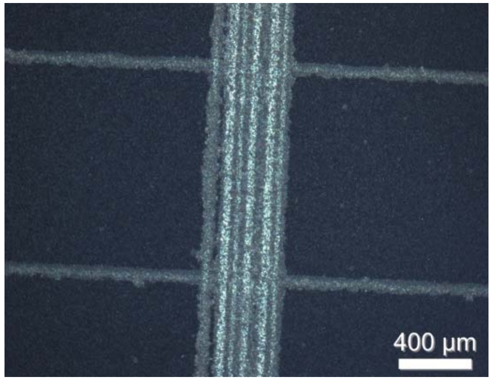


Metal Contact Applications

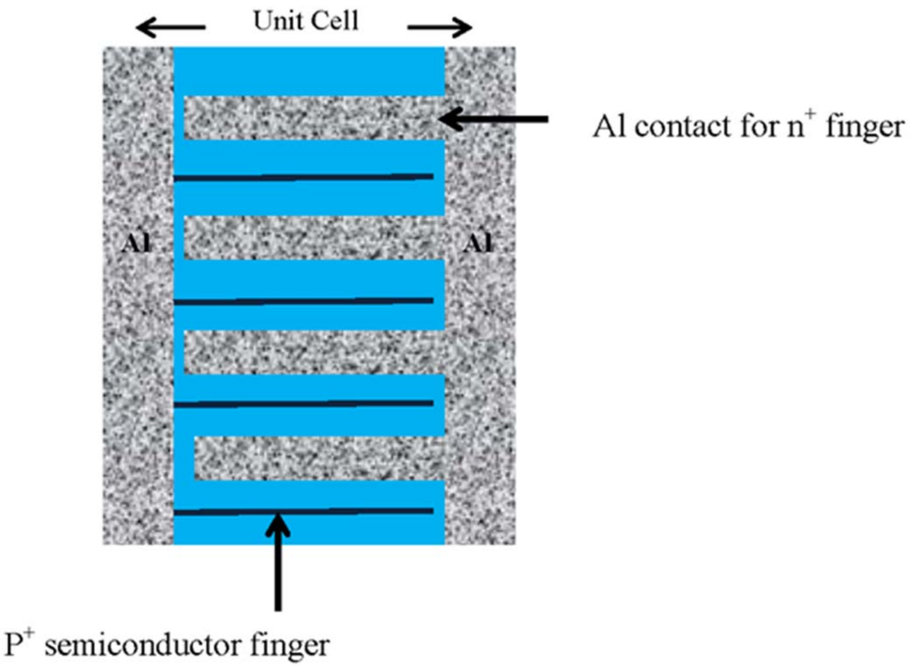
Bifacial Cells





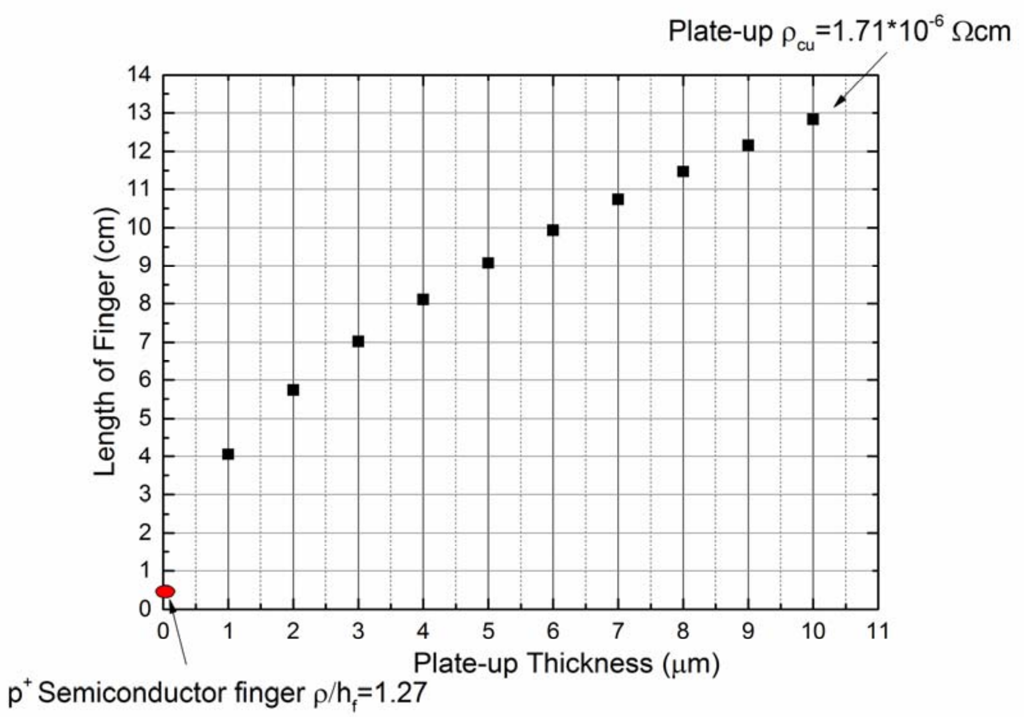


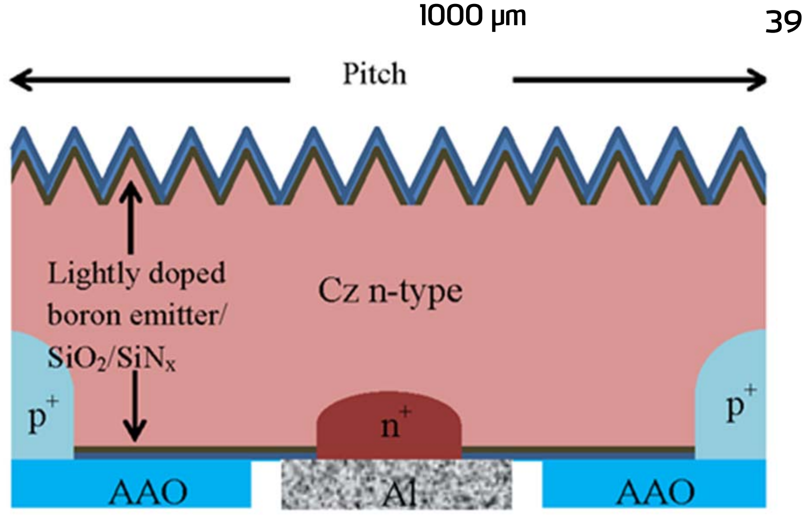
IBC Cells

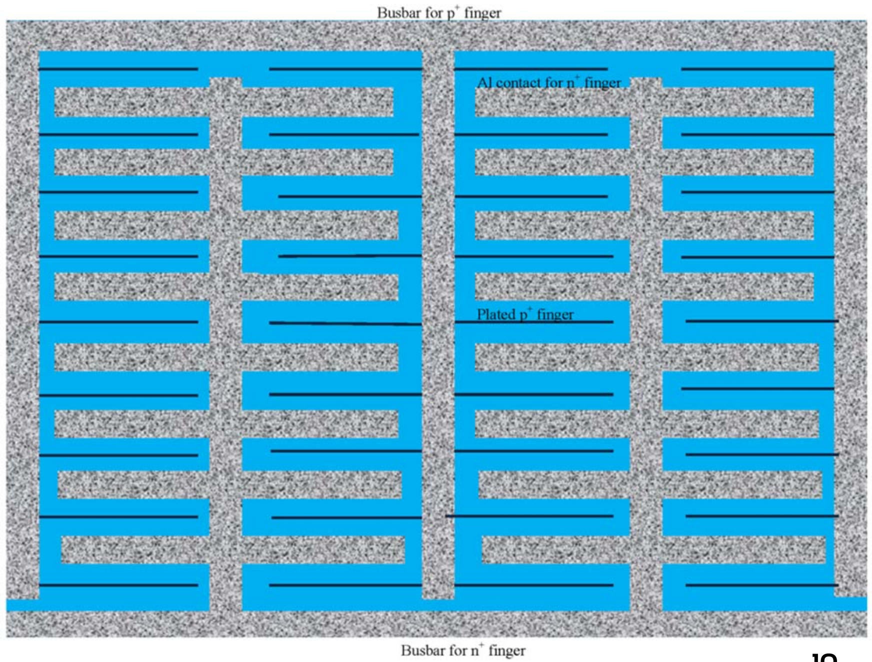


IBC Cell Structure

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







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.

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Conclusion

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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?

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