Electron contacts to crystalline silicon

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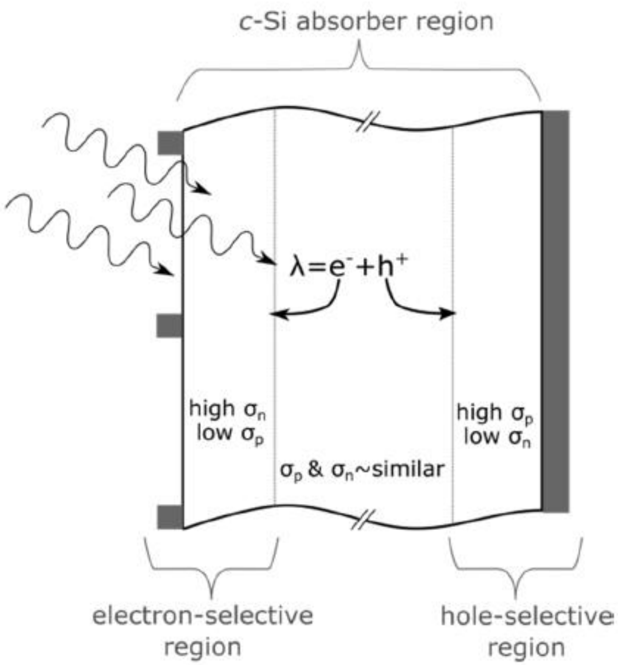
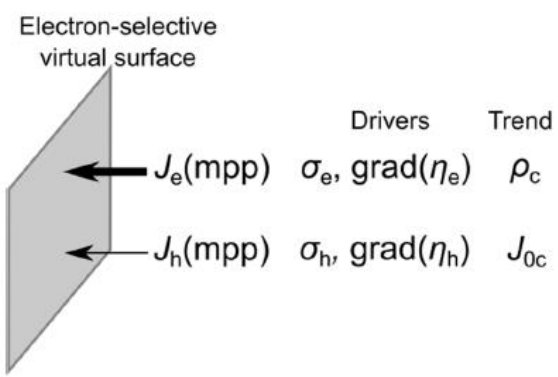
THE UNIVERSITY OF NEWCASTLE AUSTRALIA

What is a solar cell?





majority carrier flow causes a resistive loss

contact resistance ρ_c

minority carriers towards the "wrong" contact region will recombine

recombination current J_{0c}

$$J_{rec} = J_{0c} \exp\left(\frac{E_{Fn} - E_{Fp}}{kT}\right)$$

We need:

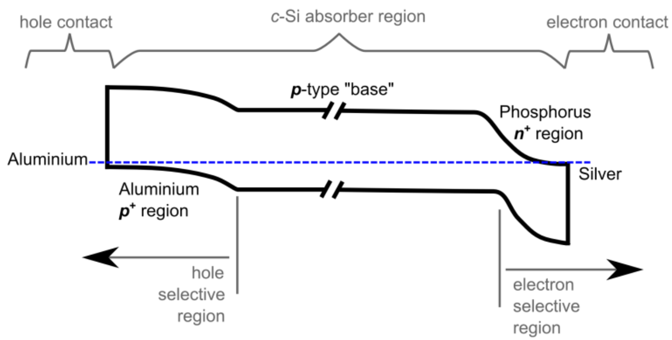
- ***sufficient*** conduction (low ρ_c)
- the ***best*** passivation possible (low J_{0c})

R. Brendel & R. Peibst, IEEE JPV, 2016

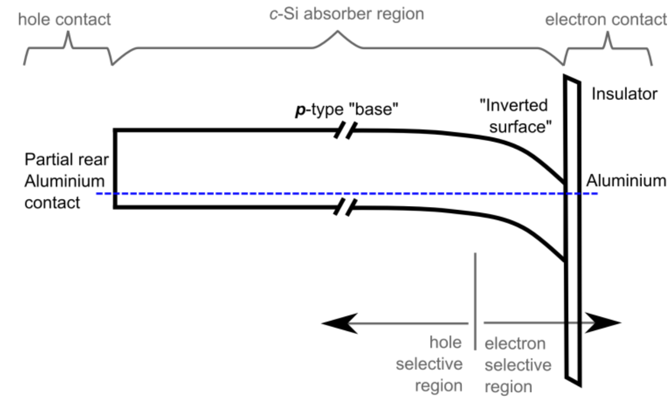
U. Wurfel et al., IEEE JPV, 2015

The c-Si family tree

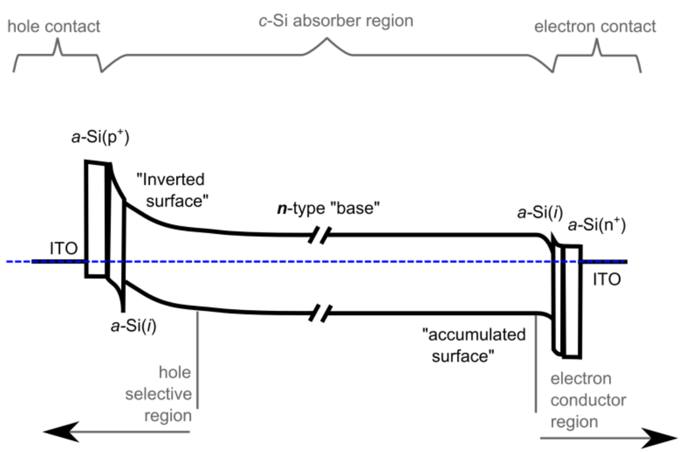
Homojunction solar cell



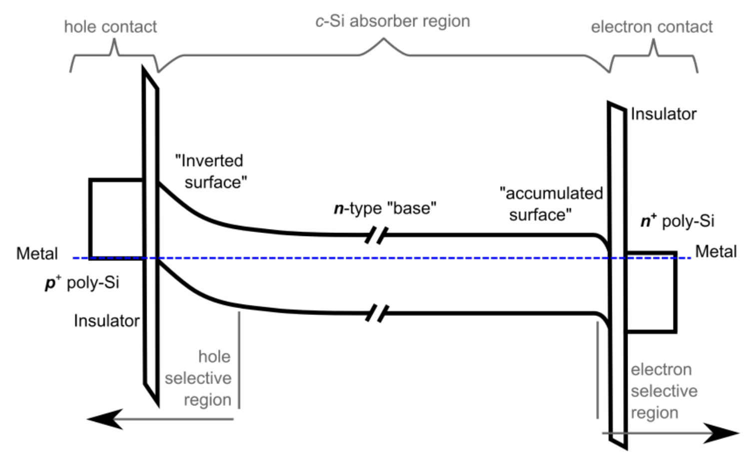
Inversion layer solar cell



Silicon heterojunction solar cell



Double polysilicon solar cell



Quantifying carrier selectivity

Contact resistivity ρ_c

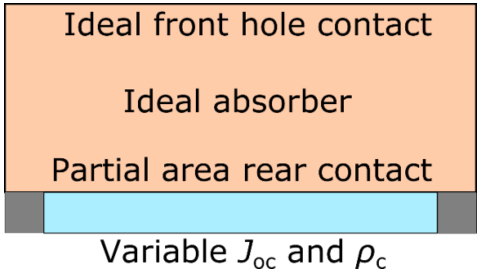
•Indicates the conductivity presented to the **collected** carrier

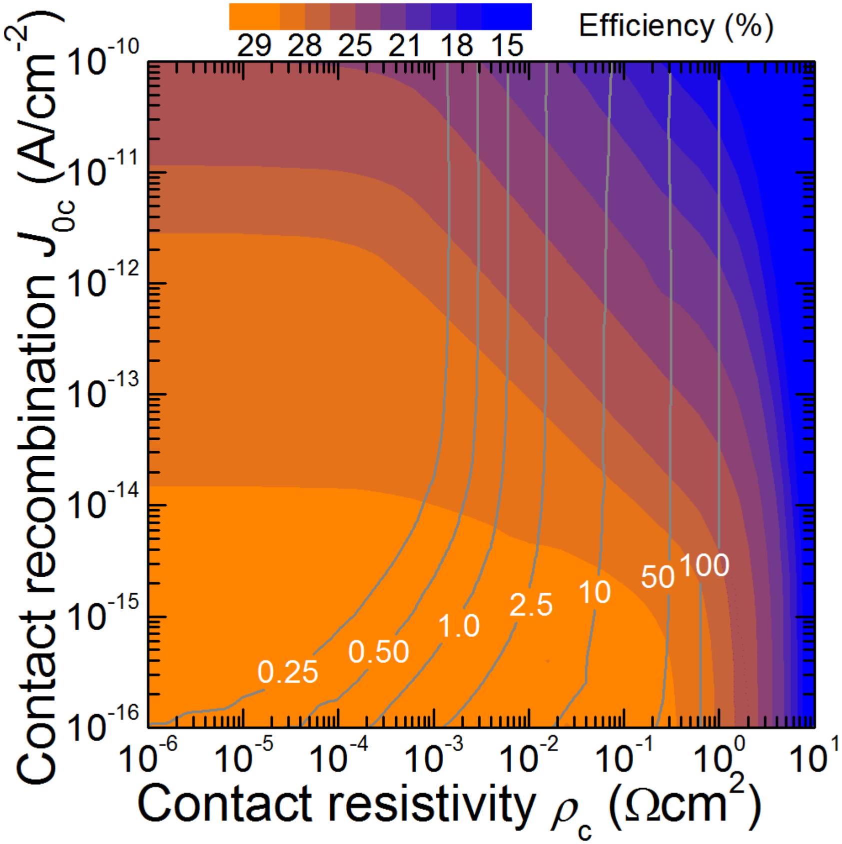
Contact recombination J_{0c}

•Indicates the conductivity presented to the **non-collected** carrier

Contact configuration

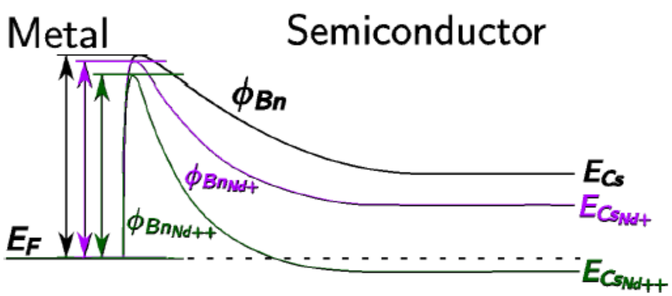
•Can further modulate the conductivities by adjusting the contact geometry

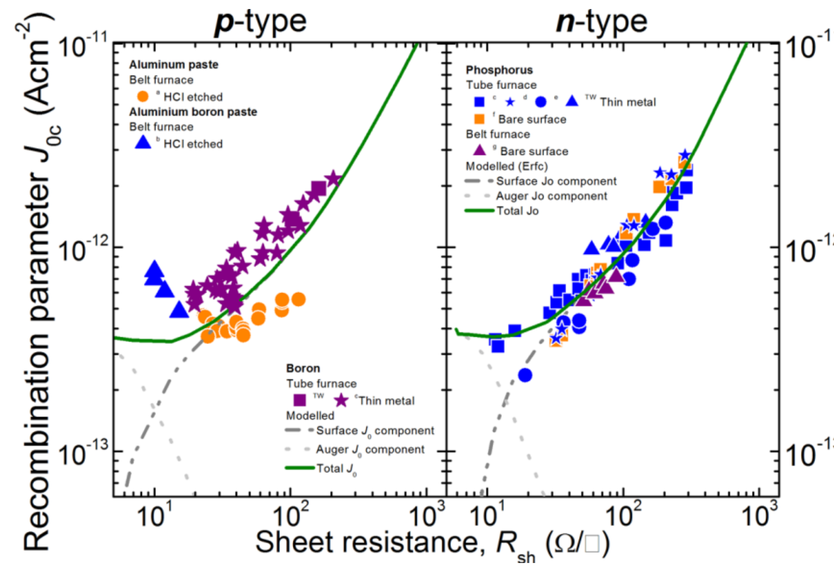


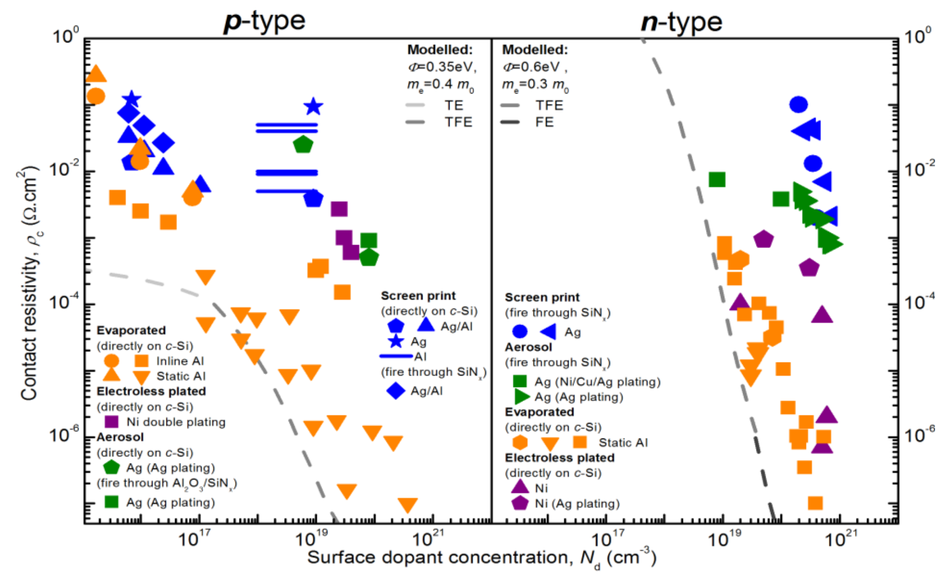


The priorities are all wrong

- **Direct metal contacts exhibit poor selectivity**
  - Large barrier heights (resistive)
  - High recombination
- **<u>Need to dope</u>**

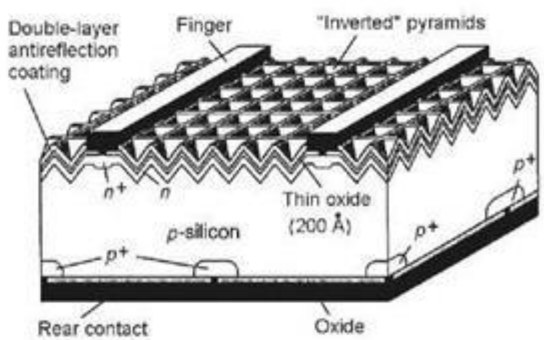






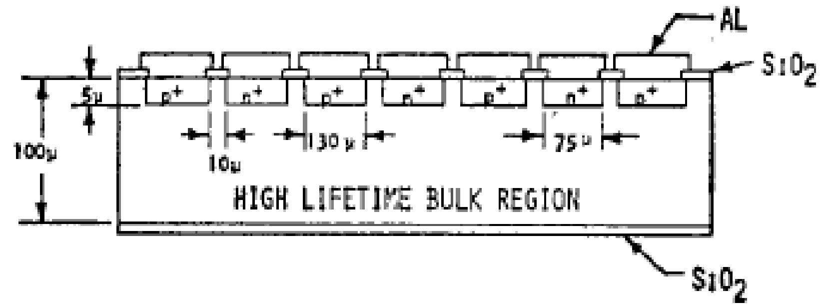
Solution: confine the contacts

- **Direct metal contacts exhibit poor selectivity**
  - Large barrier heights (resistive)
  - High recombination
- **<u>Need to dope</u>**
- **Efficiency potential demonstrated by 25% PERC/PERL cell (UNSW)**

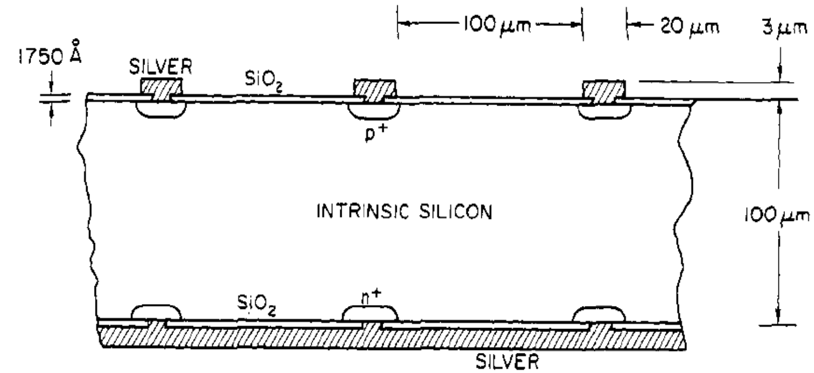


J. Zhao et al., *APL* **(1998)**

- **Make the contacts as small as possible**
- **Passivate the other surfaces**
- **Maximise absorption**



Schwatrz and Lammert, *IEDM* **(1975)**



R. M. Swanson, *IEDM* **(1978)**

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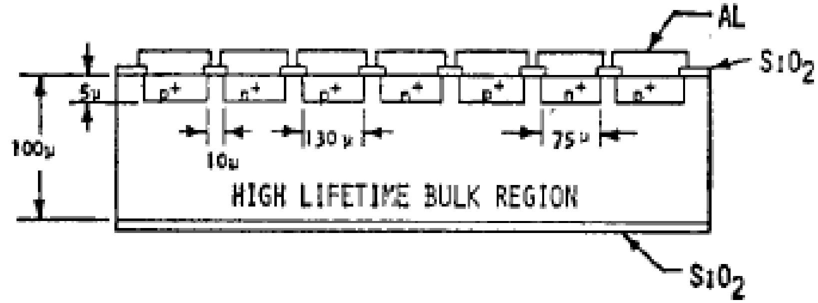
APPROACHING THE 29% LIMIT EFFICIENCY OF SILICON SOLAR CELLS

Richard M. Swanson
SunPower Corporation

NEEDED—NEW CONTACTS

None of the above discussed contacts permit cell efficiency over 25%. What is needed is a new contact that has J_0 less than 5 fA/cm^2 and makes good majority carrier contact. Two such contacts are needed, one for electrons and one for holes.



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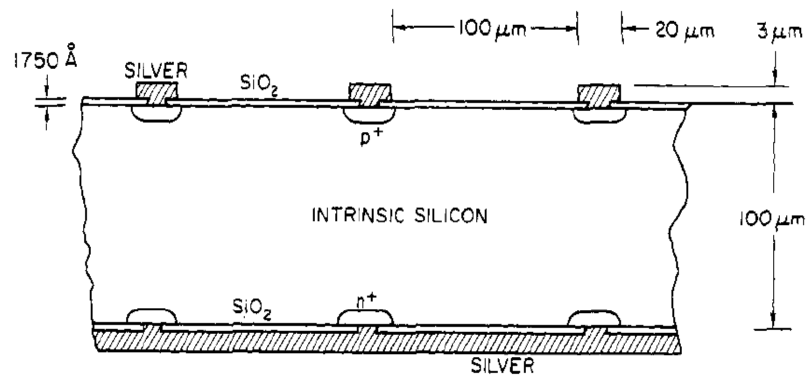
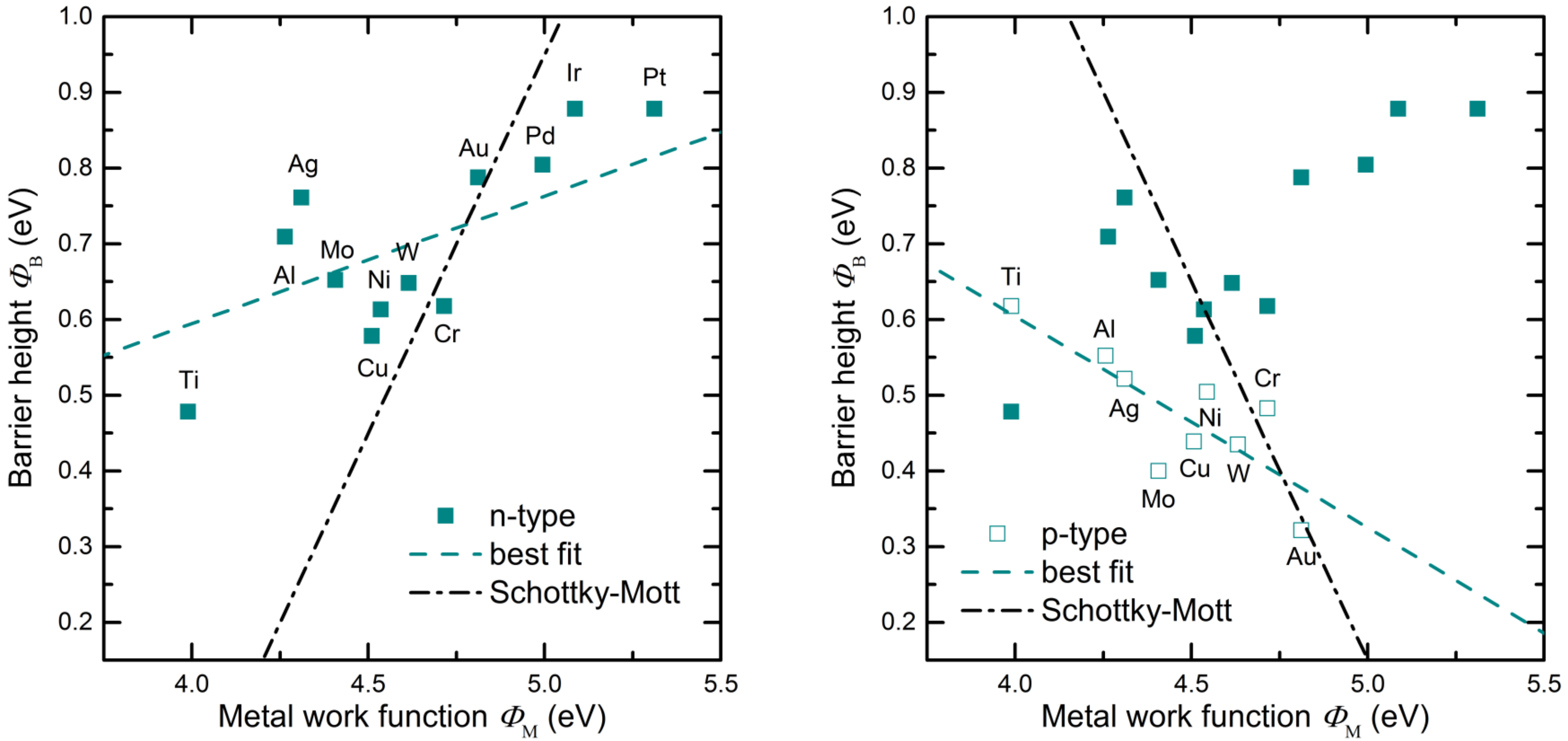


R. M. Swanson, *IEDM* **(1978)**

Fermi level pinning

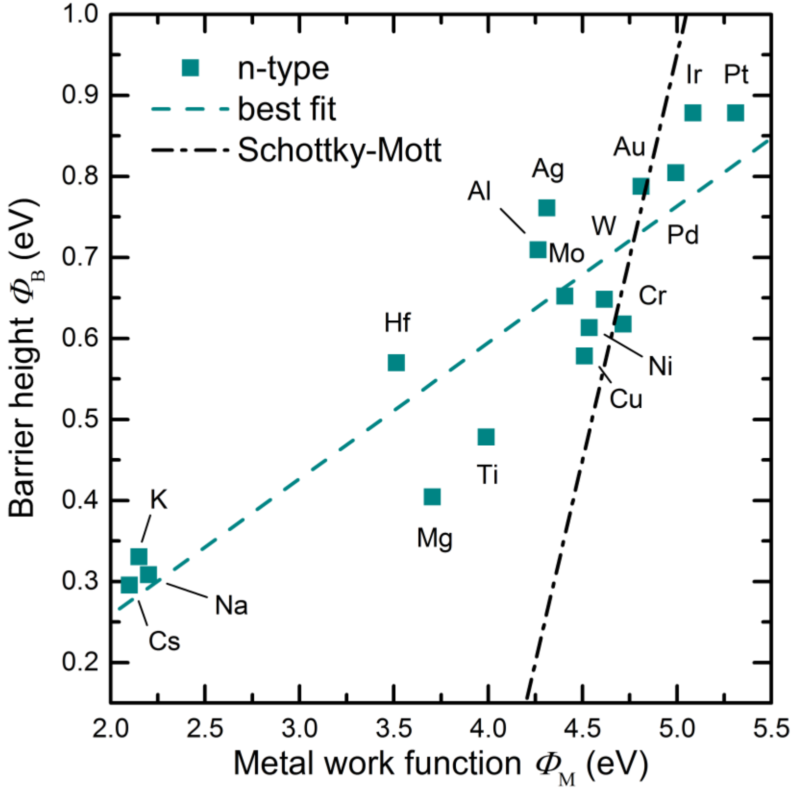
- **Harder to contact n-type silicon because of Fermi level pinning**
  - due to interface defects
  - typical barrier height > 0.7 eV for Al and Ag contacts
- **lower barriers tend to form at the p-type silicon / metal interface**
  - typical barrier height < 0.6 eV



source: D. K. Schroder and D. L. Meier, *IEEE Trans. Electron Devices*, 1984.

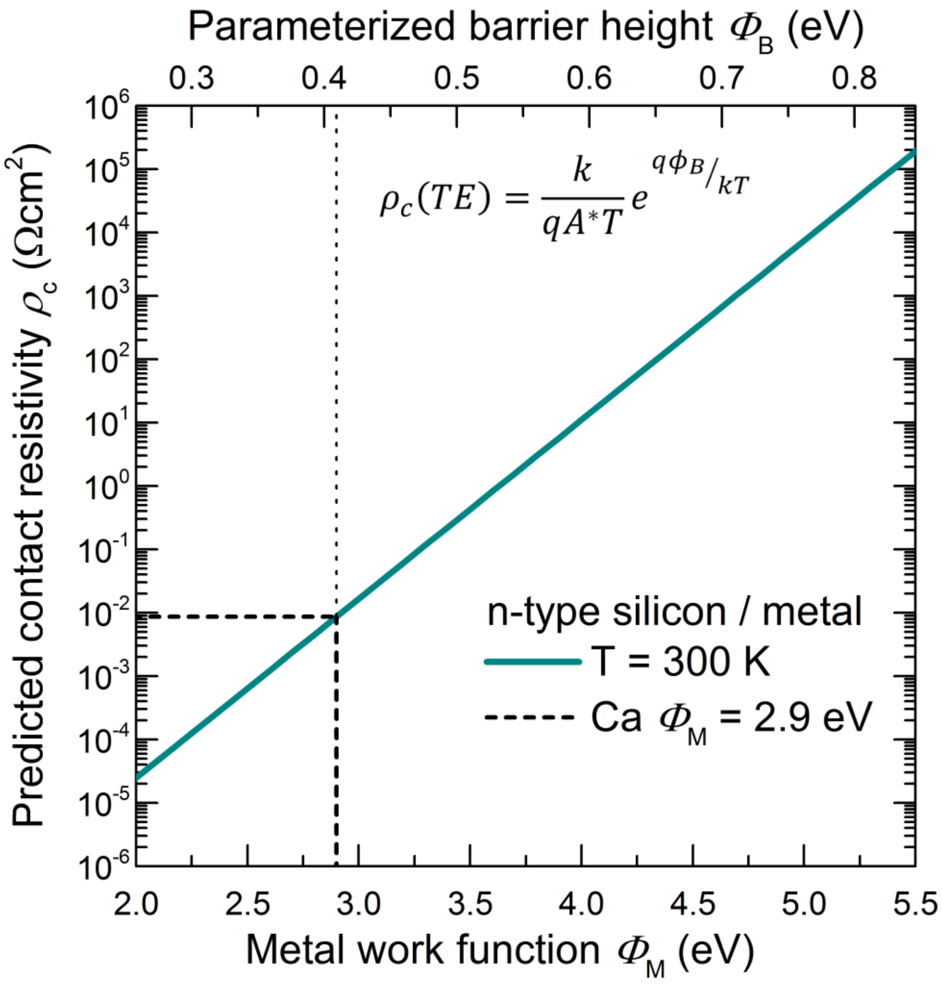
‘Extreme’ work functions needed

- **Harder to contact n-type silicon because of Fermi level pinning**
  - due to interface defects
  - typical barrier height > 0.7 eV for Al and Ag contacts
- **lower barriers tend to form at the p-type silicon / metal interface**
  - typical barrier height < 0.6 eV
- **low barriers possible with low metal work function**



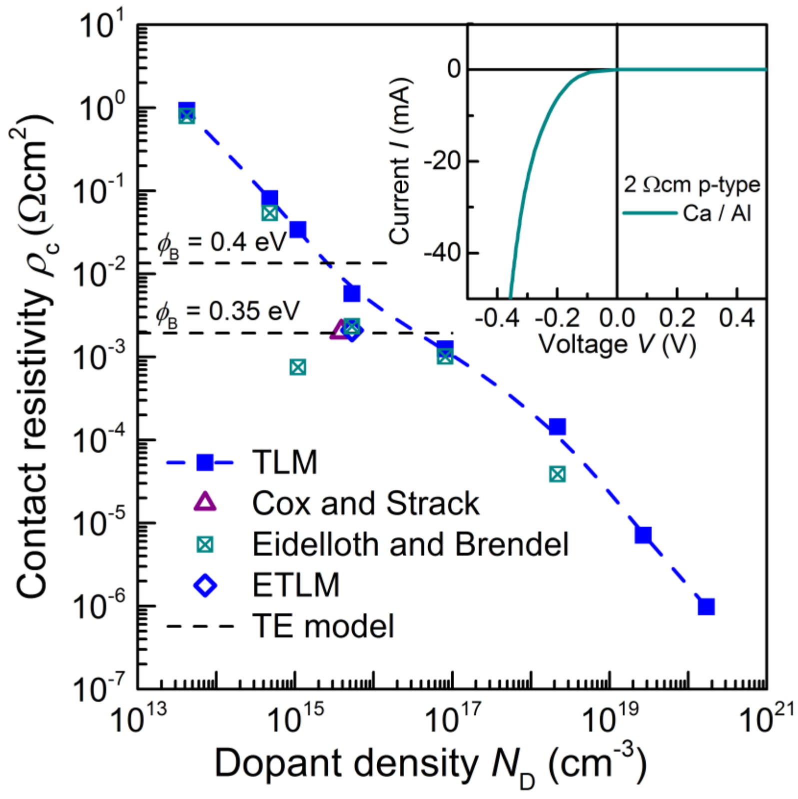
Proof-of-concept: Ca

- **Using a linear parameterization we can predict barrier height formation vs metal work function**
  - input into thermionic emission model
  - can predict dopant-free contact resistivity
- **Calcium work function ~ 2.9 eV**
  - common electrode in OPV
  - predicted ρ_c < 10 mΩcm^2
  - predicted ϕ_B ~ 0.4 eV



Calcium contacts

- **Ohmic contact over all phosphorus dopant densities**
- **ρ_c ~ 2-6 mΩcm^2 on (undiffused) 1 Ωcm n-type Si**
  - similar to screen printed Ag on phosphorus diffused n$^+$
- **rectifying contact to p-type**
  - small barrier for electrons means large barrier for holes

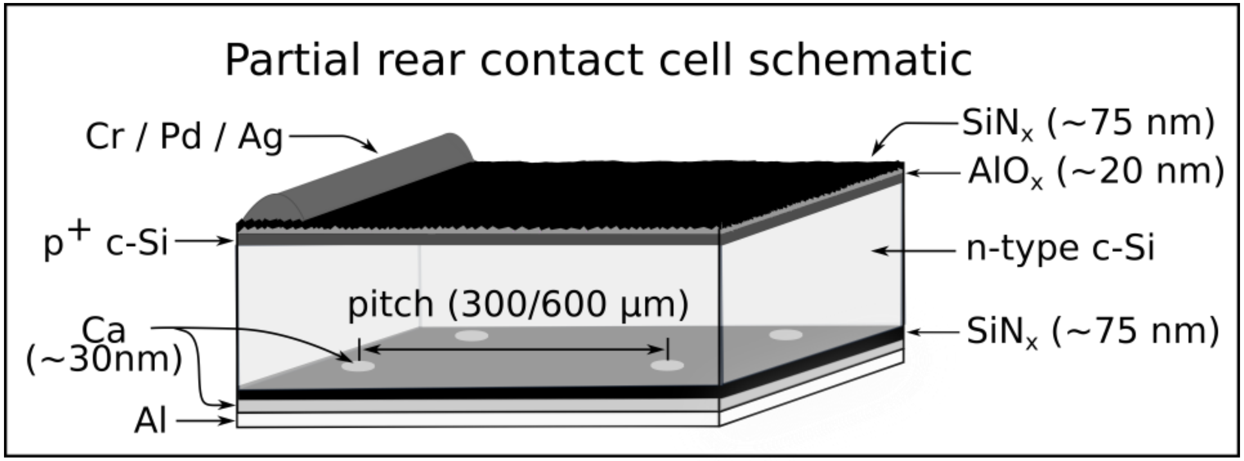


Allen, T. G., et al., PiP, 2017

N-type PERC cells

- **4 PERC cells fabricated**
  - differing wafer resistivity 9.9 and 0.9 Ωcm
  - differing rear contact pitch (and so contact fraction) (1.26% and 0.32%)

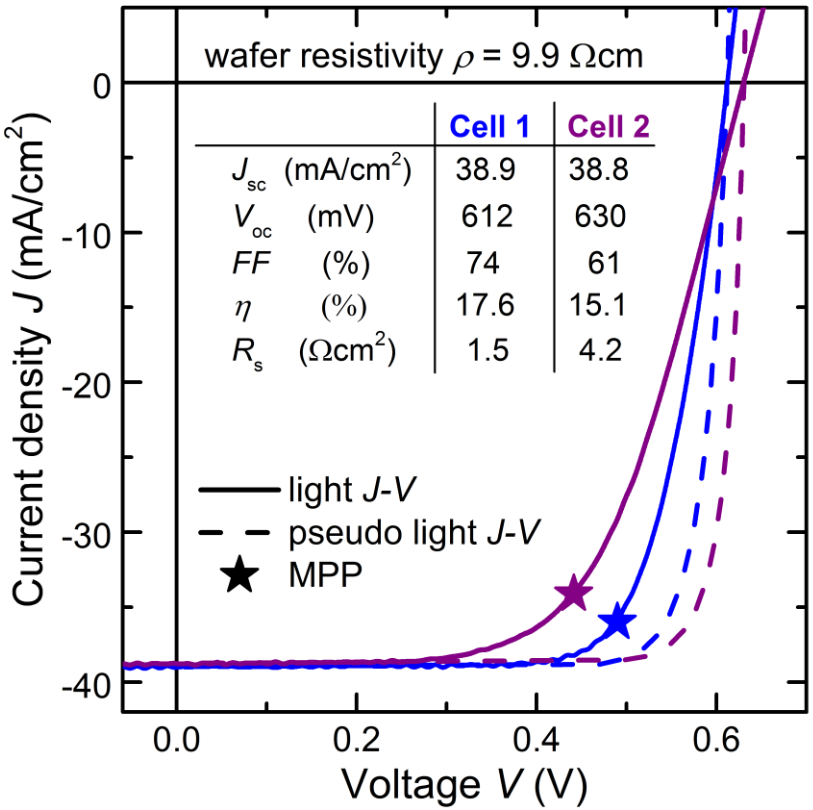
	contact fraction	
wafer ρ	1.26%	0.32%
9.9 Ωcm	Cell 1	Cell 2
0.9 Ωcm	Cell 3	Cell 4



N-type PERC cells

- **low dopant density**
  - $N_D = 4.5 \times 10^{14}$ cm^{-3}
- **high R_s for both cells**
- **low V_{oc}**
  - due to recombination at the contacts
- **Cell 1 (larger contact fraction)**
  - **η = 17.6%**

	contact fraction	
wafer ρ	1.26%	0.32%
9.9 Ωcm	**Cell 1**	**Cell 2**
0.9 Ωcm	Cell 3	Cell 4

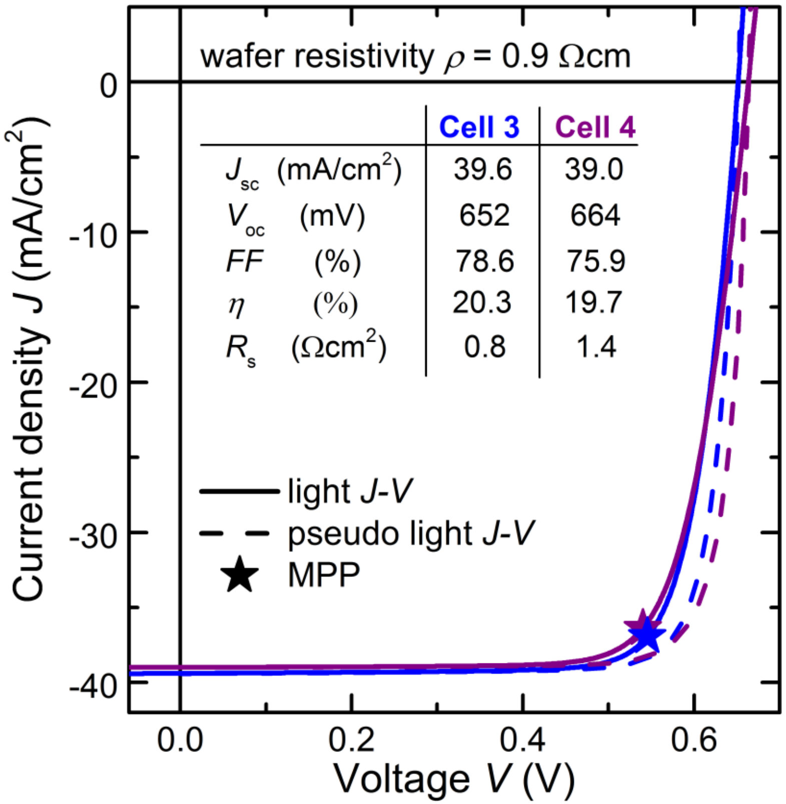


Allen, T. G., et al., PiP, 2017

N-type PERC cells

- **moderate dopant density**
  - $N_D = 5.4 \times 10^{15}$ cm^{-3}
- **improvement in all device performance metrics**
  - much higher V_{oc}
  - much lower R_s
- **Cell 3 (larger contact fraction)**
  - ***η* = 20.3%**

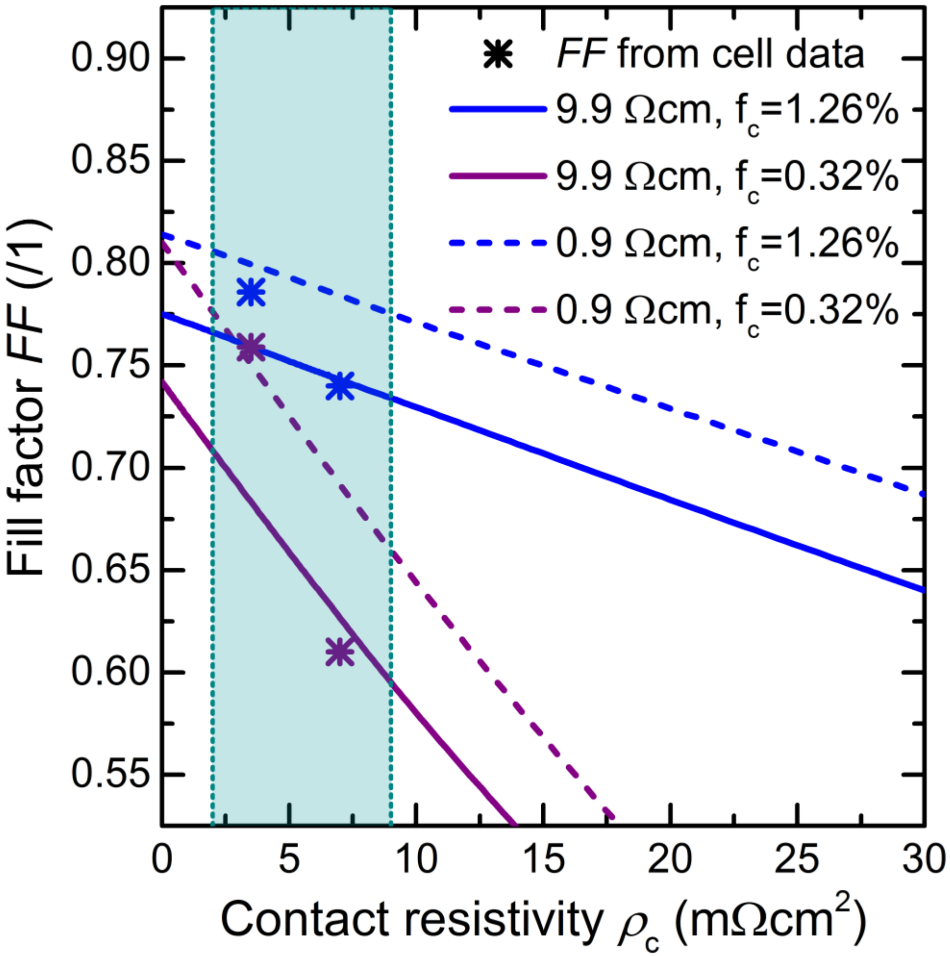
	contact fraction	
wafer ρ	1.26%	0.32%
9.9 Ωcm	Cell 1	Cell 2
0.9 Ωcm	**Cell 3**	**Cell 4**



Allen, T. G., et al., PiP, 2017

Confirming ρ_c

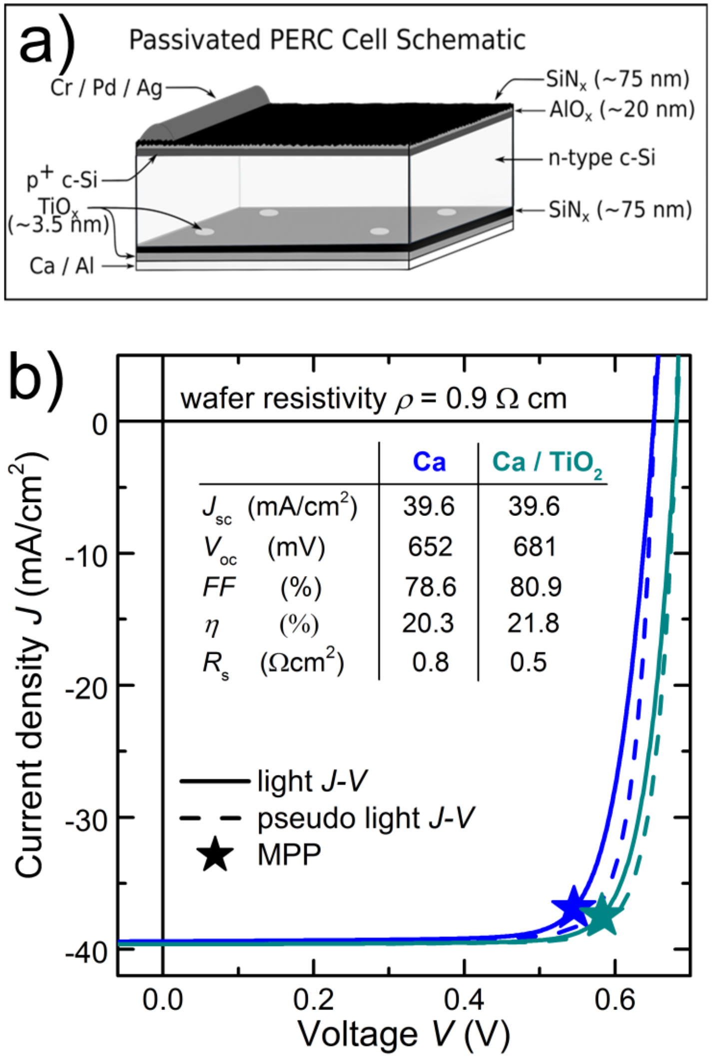
- **Modelling in QSCell_PRC**
- **low f_c cells sensitive to ρ_c**
- **rear contact ρ_c ~ 5 +/- 3 mΩcm^2**
  - contact resistivity only slightly higher on 9.9 Ωcm wafer
  - consistent with thermionic emission model
    - previous ρ_c results due to bulk resistance effects



Allen, T. G., et al., PiP, 2017

Passivated PERC cells

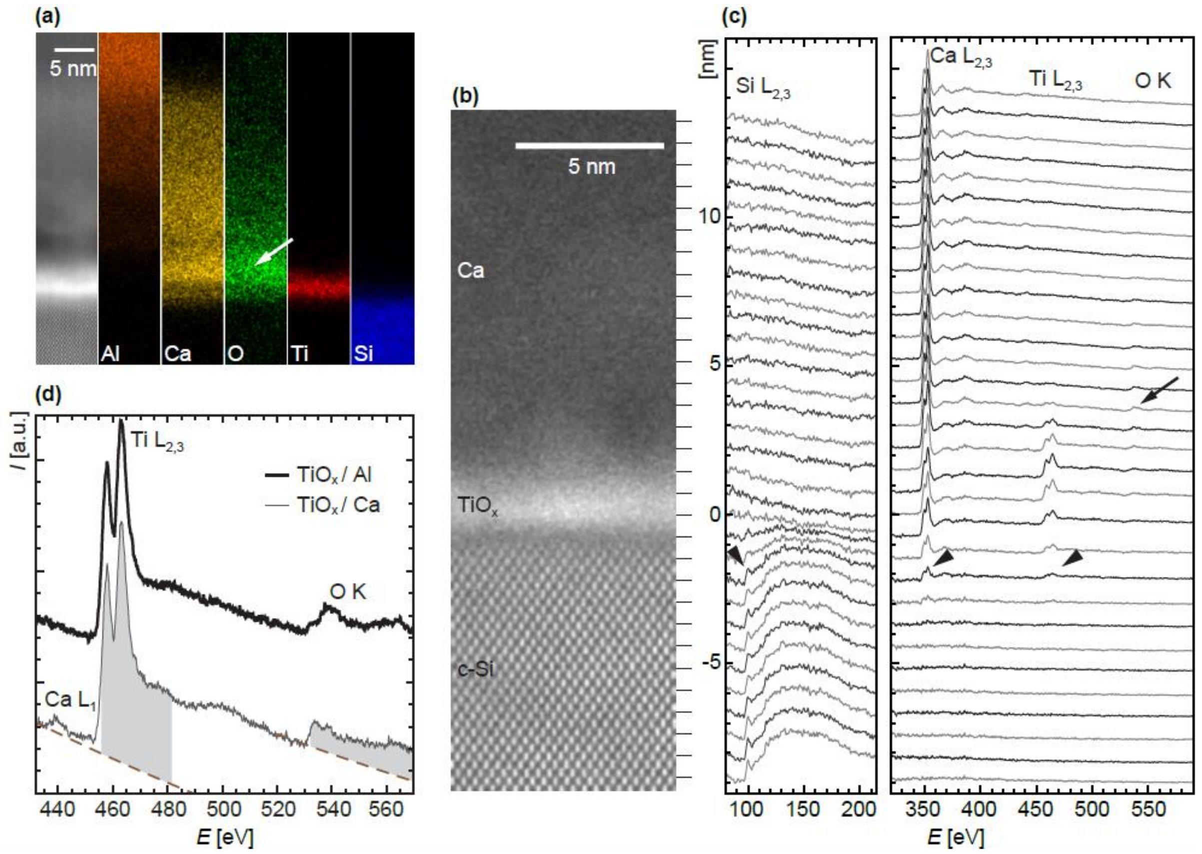
- **similar structure as Cell 3**
  - ρ = 0.9 Ωcm
  - f_c = 6%
- **insertion of a passivating TiO_2 interlayer (~3.5 nm)**
  - increase cell voltage
  - decrease series resistance
    - improvement in rear contact resistivity?
  - ***η* = 21.8%**
- **Other interlayers were less successful:**
  - GaO_x and a-Si



Allen, T. G., et al., Adv. En. Mat., 2017

A closer look at the contact

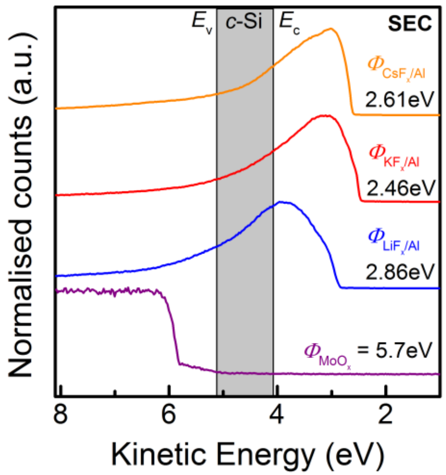
- **TiO_2 (as deposited)**
- **Oxygen accumulates at Ca / TiO_x inteface**
  - Reducing TiO_2 to TiO
  - Also for Al / TiO_x contacts
- **Ca diffusion toward Si interface**
  - Low WF of Ca relative to Al lowers contact resistance

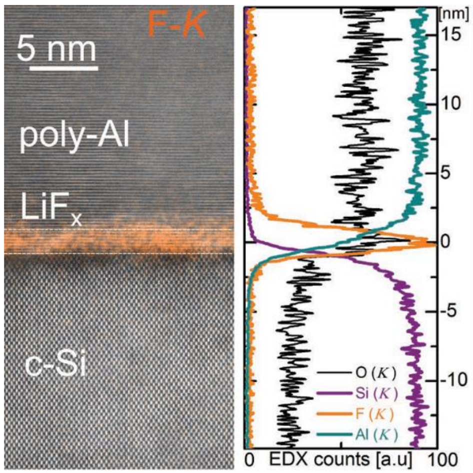


Allen, T. G., et al., Adv. En. Mat., 2017

Another approach: LiF / Al

- **Instead of using a low work function metal, lower the work function of Al**
  - Thermally evaporated LiF / Al stack
  - $\phi \sim 2.9$ eV
  - transparent ($E_g > 6.8$ eV)





Bullock, J., et al, Adv. Energy Mater, 2016

Bullock, J., et al, Nature Energy, 1, 15031, 2016

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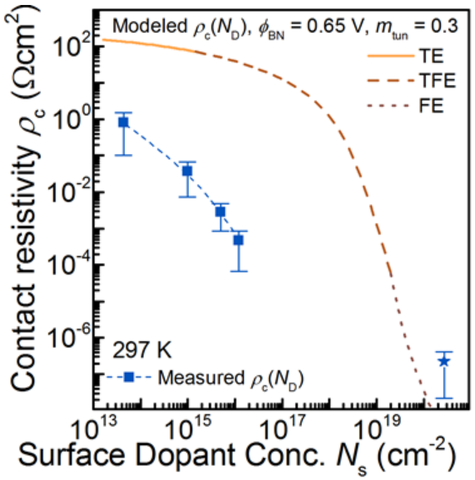
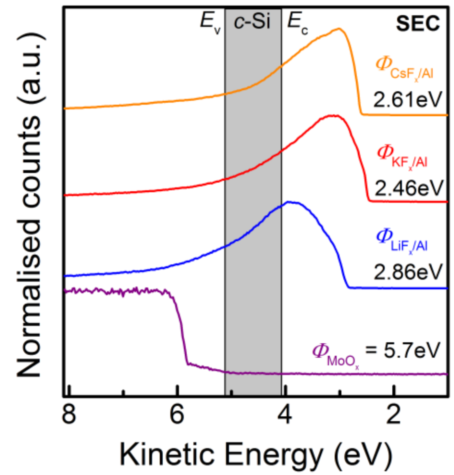
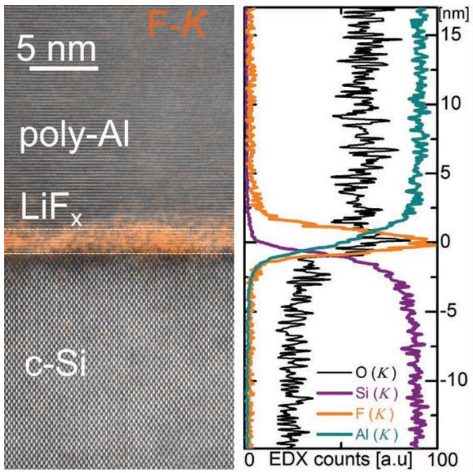
  - transparent (E_g > 6.8 eV)
- **ρ_c ~ 1 mΩcm² (1 Ωcm n-type)**







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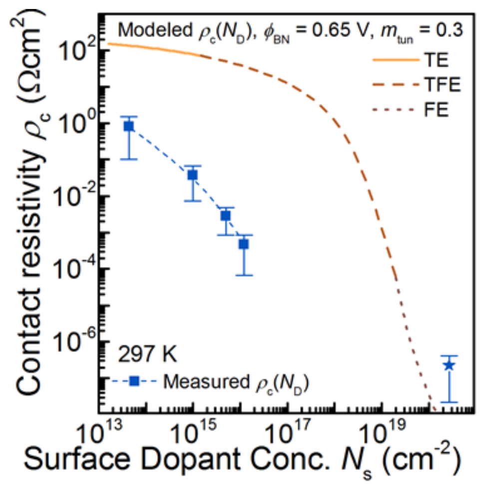
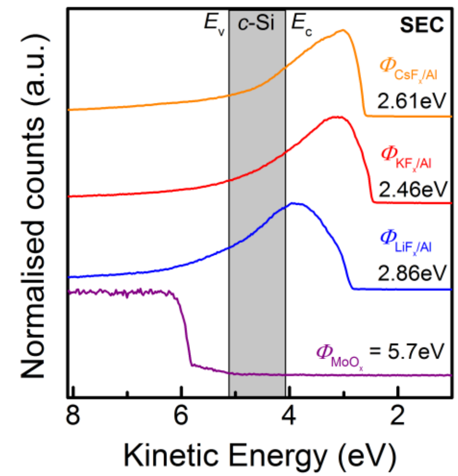
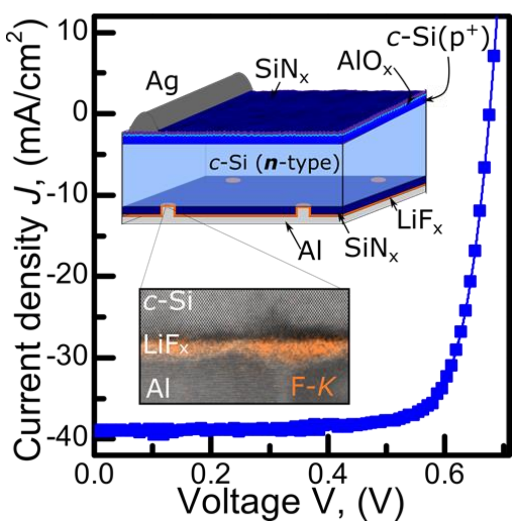
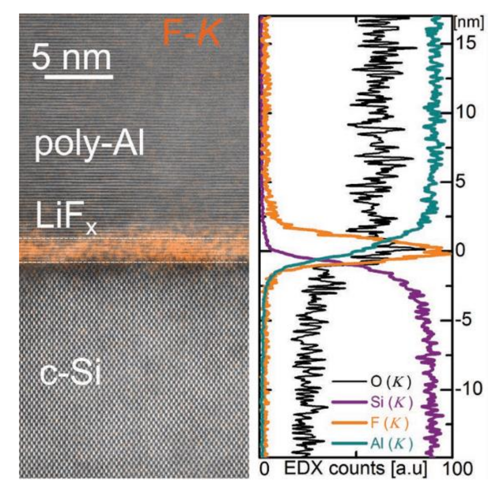
  - Thermally evaporated LiF / Al stack
  - ϕ ~ 2.9 eV
  - transparent (E_g > 6.8 eV)
- **ρ_c ~ 1 mΩcm² (1 Ωcm n-type)**
- **LiF / Al PERC cell**
  - f_c ~ 1%
  - ρ = 1 Ωcm
- **Higher voltage than Ca PERC cells**
  - V_{oc} = 676 mV
  - contact SRV < 10^4 cm/s
- ***η* = 20.6%**







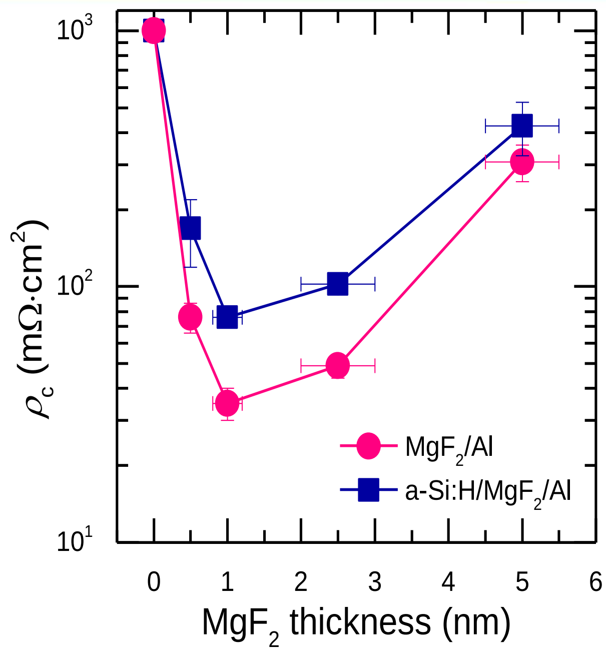


V_{oc} = 676 mV, J_{sc} = 38.9 mA/cm², FF = 78.9, η = 20.6%

Bullock, J., et al, Adv. Energy Mater, 2016
Bullock, J., et al, Nature Energy, 1, 15031, 2016

Another approach: MgF_2 / Al

- **Instead of using a low work function metal, lower the work function of Al**
  - Thermally evaporated MgF_2 / Al stack
  - ϕ ~ 3.5 eV
- **direct Si ρ_c ~ 35 mΩcm^2**
- **with a-Si ρ_c ~ 80 mΩcm^2**
  - J_0 ~ 10 fA/cm^2



Wan, Y., et al, ACS Appl. Mater. Interfaces, 2016

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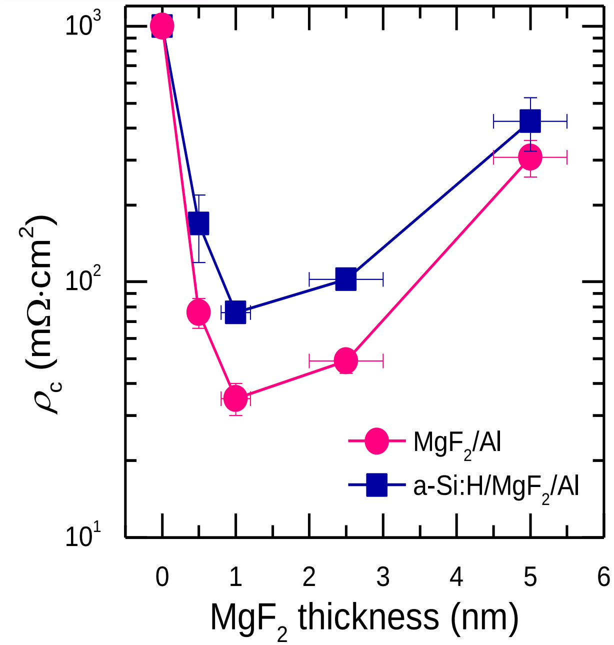
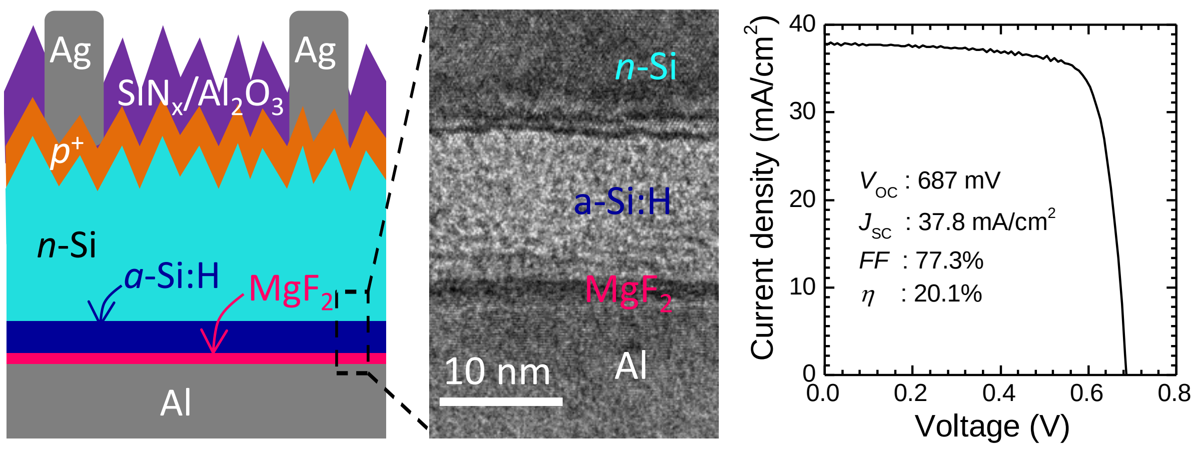
  - ϕ ~ 3.5 eV
- **direct Si ρ_c ~ 35 mΩcm²**
- **with a-Si ρ_c ~ 80 mΩcm²**
  - J_0 ~ 10 fA/cm²
- **Full rear area a-Si / MgF_2 / Al**
- **V_{oc} = 687 mV**
- **η = 20.1%**

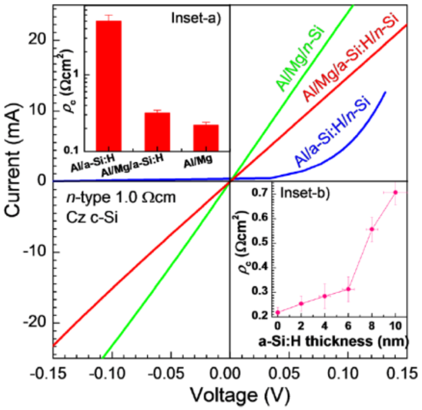


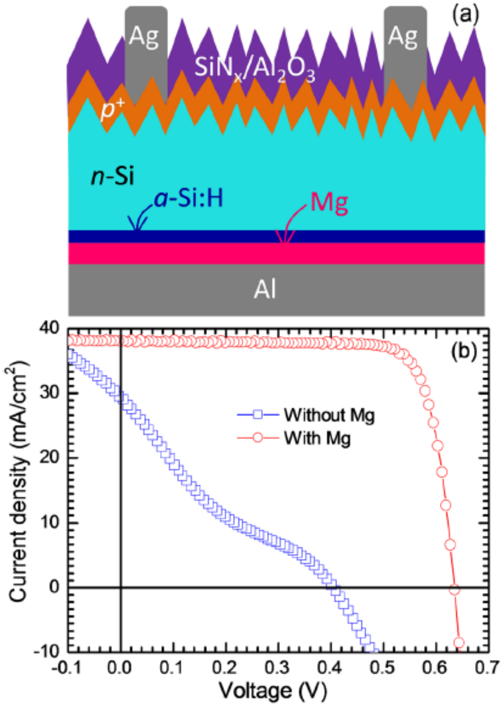


Wan, Y., et al, ACS Appl. Mater. Interfaces, 2016

Also Mg…

- **Similar approach to Ca**
  - Potentially more stable and easier to evaporate
  - ϕ ~ 3.7 eV
- **direct Si ρ_c ~ 220 mΩcm^2**
- **with a-Si (6 nm) ρ_c ~ 310 mΩcm^2**
- **Full rear area a-Si / Mg / Al**
- **V_{oc} = 637 mV**
  - Degradation of voltage due to interaction with a-Si layer?
- **η = 19.0%**





	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
Without Mg	405.0	29.5	18.2	2.2
With Mg	636.6	38.0	78.4	19.0

Wan, Y., et al, APL, 2016

Wan, Y., et al., Adv. En. Mat., 2016

Also Mg, and MgO_x…

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King Abdullah University of Science and Technology
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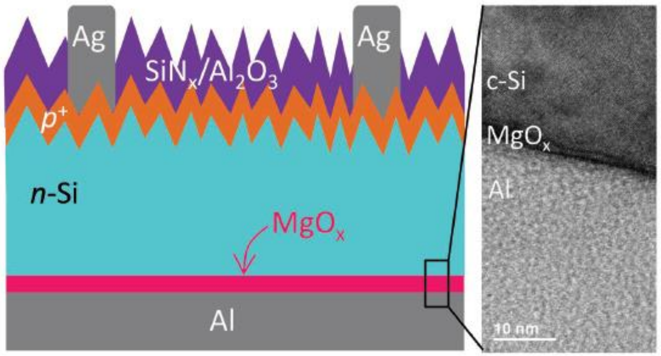
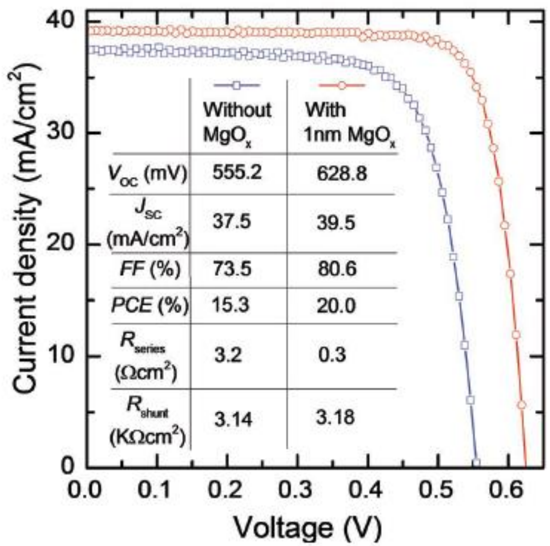
- **Similar approach to MoOx**
  - Thermal evaporation from powder source
  - O vacancy defect band
  - $MgO_{0.75}$ (from XPS)
- **MgOx (1 nm) / Al ρ_c ~ 18 mΩcm^2**
- ***η* = 20.0%**
  - Stable up to 400 C
  - Poor passivation





Wan, Y., et al, APL, 2016
Wan, Y., et al., Adv. En. Mat., 2016

Also Mg, and MgO_x, and others…

	Contact Characteristics			Deposition details
	IV behavior	Extracted ρ_c (mΩcm^2)	Extraction method	
Electron contacts				
c-Si(n)/**TiO_x**/Al	Ohmic	30	C&S	TiOx (Thermal ALD, 230ºC, titanium tetraisopropoxide / water, 2.8nm)
c-Si(n)/**TiO_x**/LiF_x/Al	Ohmic	490	C&S	TiOx (Thermal ALD, 230ºC, titanium tetraisopropoxide / water, 6 nm).
c-Si(n)/**TaO_x**/Al	Non-linear	N/A	N/A	ALD, 250ºC tantalum ethoxide / water, 10nm
c-Si(n)/**ZnO_x**/Al	Non-linear	N/A	N/A	ALD, 200ºC, diethylzinc / water, 10nm
c-Si(n)/**SnO_x**/Al	Non-linear	N/A	N/A	TE, powder source, ~1Å/sec, ~10^{-5} mbar, 15 nm
c-Si(n)/**LiF_x/**Al	Ohmic	~1	C&S	TE, powder source, ~1Å/sec, ~10^{-6} mbar, ~1.5 nm
c-Si(n)/**CsF_x**/Al	Ohmic	~1	C&S	TE, powder source, ~1Å/sec, ~10^{-6} mbar, ~1.5 nm
c-Si(n)/**KF_x**/Al	Ohmic	7.6	C&S	TE, powder source, ~1Å/sec, ~10^{-6} mbar, ~1.5 nm
c-Si(n)/**C_{60}**/Al	Ohmic	~200	C&S	TE, powder source, ~1Å/sec, ~10^{-5} mbar, ~5 nm
c-Si(n)/**CsO_x**/Al	Ohmic	1.8	C&S	TE, CsCO3 powder source, ~1Å/sec, ~10^{-5} mbar, 2 nm
Hole contacts				
c-Si(p)/**MoO_x**/Pd/Ag	Ohmic	~1	C&S	TE, powder source, ~1Å/sec, ~10^{-6} mbar, ~10nm
c-Si(p)/**PEDOT:PSS/**Pd/Ag	Ohmic	50	C&S	LPD, spin coated, Heraeus 4083, ~50nm
c-Si(p)/**CuPc**/Au/Ag	Ohmic	~300	TLM	TE, powder source, ~1Å/sec, ~10^{-5} mbar, 25 nm
c-Si(p)/**CuSCN**/Al	Ohmic	58	TLM	LPD, spin coated, 10mg/mL CuSCN in dipropyl sulphate
c-Si(p)/**CuO_x:N**/Pd/Ag	Ohmic	11	C&S	Reactive sputtered, ~8nm

- **Keep an eye out for an upcoming review paper for updated cell results…**

Bullock et. al., IEEE PVSC., Portland, 2016

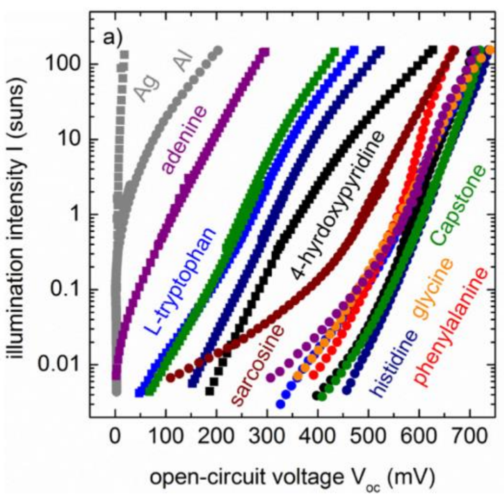
What's next?

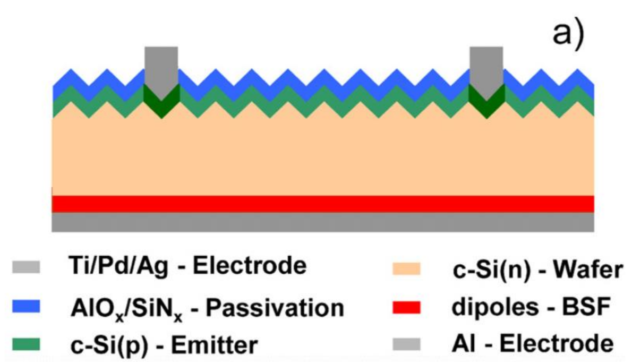
How Molecules with Dipole Moments Enhance the Selectivity of Electrodes in Organic Solar Cells – A Combined Experimental and Theoretical Approach

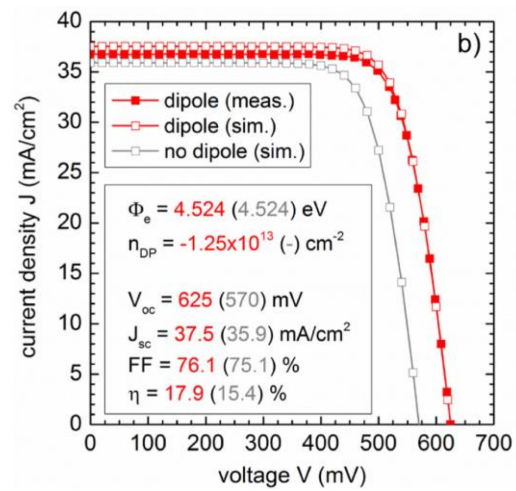
Uli Würfel, Martin Seßler, Moritz Unmüssig, Nils Hofmann, Mathias List, Eric Mankel, Thomas Mayer, Günter Reiter, Jean-Luc Bubendorff, Laurent Simon, and Markus Kohlstädt*

Electron-selective contacts via ultra-thin organic interface dipoles for silicon organic heterojunction solar cells

Christian Reichel, Uli Würfel, Kristina Winkler, Hans-Frieder Schleiermacher, Markus Kohlstädt, Moritz Unmüssig, Christoph A. Messmer, Martin Hermle, and Stefan W. Glunz







Conclusion

- **Many materials out there!**
  - We learnt a lot over a very short time period
  - Read widely! (Think creatively but critically)
- **Passivation is critical (and hard)**
  - Success likely to come from leveraging off materials like a-Si and SiOx
- **Stability is largely overlooked**
  - Any material must be stable for 20+ years

Join the team:
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https://ksc.kaust.edu.sa/Pages/Home.aspx
Internship, Masters, PhD, Postdoc…

THANK YOU!

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