# Investigation of $TiO_x$ as carrier selective contact for crystalline silicon solar cells

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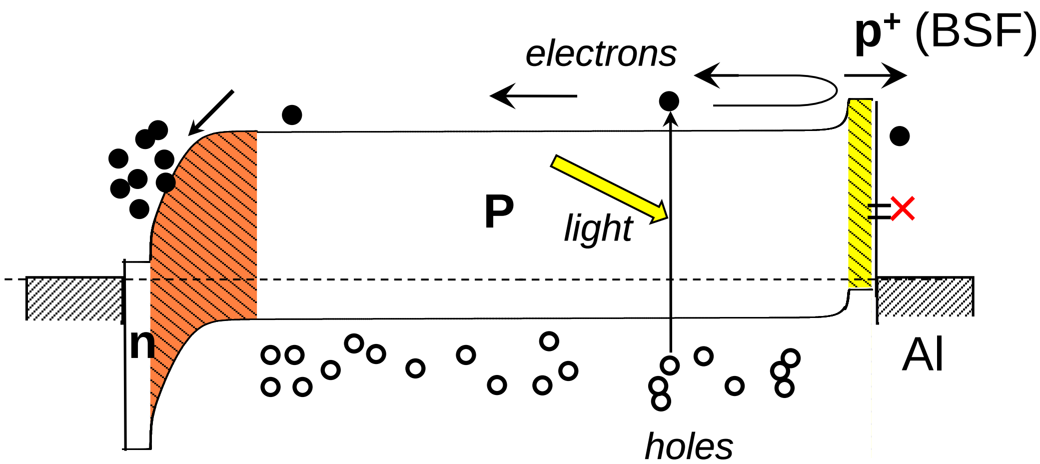
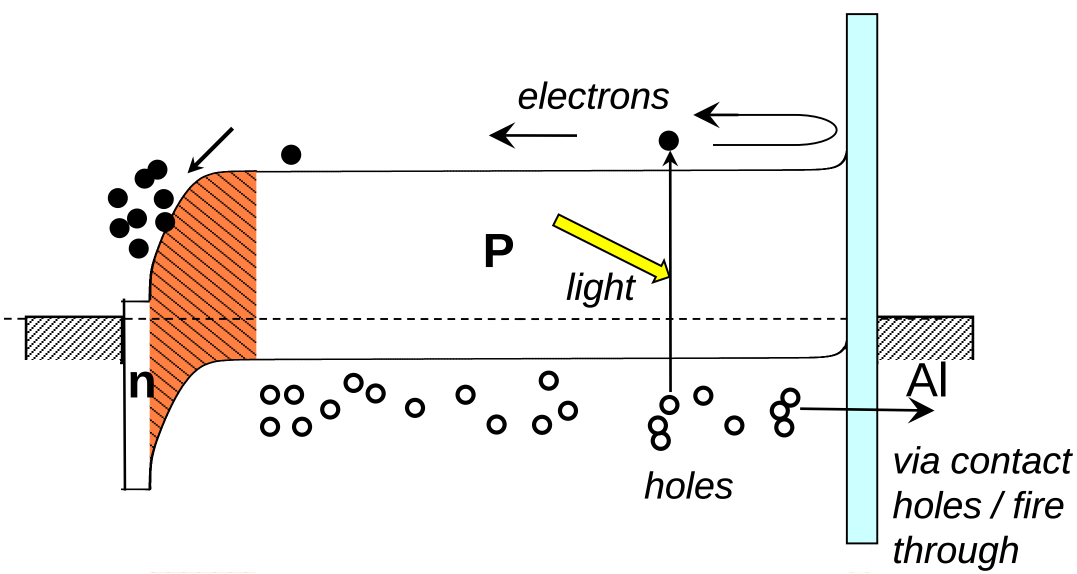
This work has been done during the stay of T. Matsui at Fraunhofer ISE.

# Industrial solar cells based on P-type c-Si




Al-BSF (Back Surface Field)

- Simplest process and most widely used
- Direct Si-metal contact limits efficiency due to poor passivation.
- η<20%



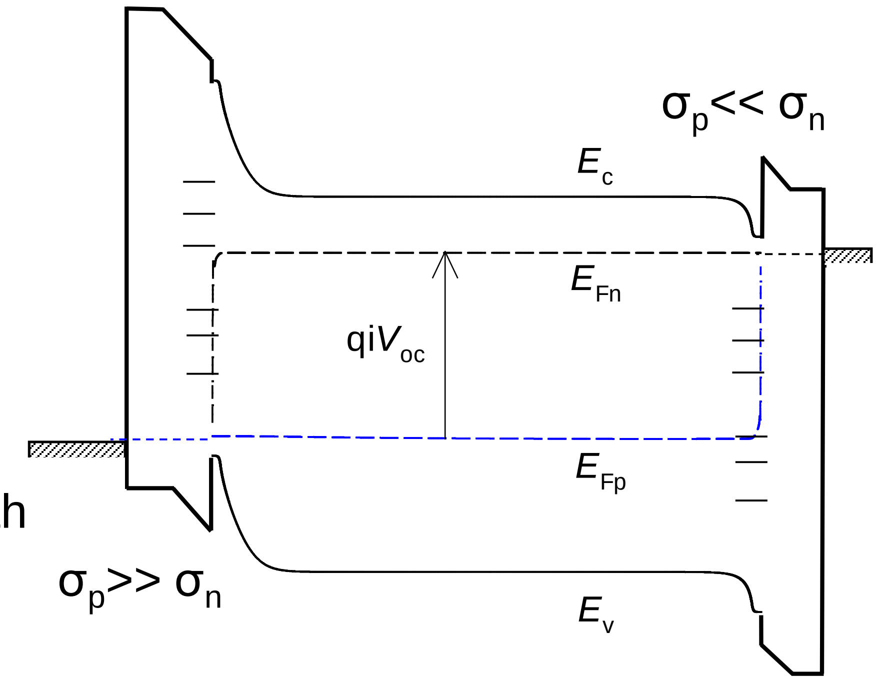

PERC (Passivated Emitter and Rear Cell)

- Passivated c-Si rear surface by $SiO_2$, $SiN_x$, $Al_2O_3$, etc.
- Partial Si-metal contact remains.
- η=22.6% Mono, η=21.3% Multi

Trina Solar press releases.

# Towards higher efficiency

1. N-type wafer (longer lifetime, high-*T* tolerance)
2. Completely avoiding silicon-metal contact
3. Semiconducting passivation layer
4. **Carrier selective contact**




e.g.,

- Silicon heterojunction (SHJ) solar cells with doped/undoped a-Si:H stack

  26.6% (IBC-SHJ), 25.1% (std. SHJ)

  K. Yoshikawa *et al*. SiliconPV 2017 (2017), Nature Energy **2**, 17032 (2017).

- Tunnel oxide passivated contact (TOPcon)

  25.7% (TOPcon applied to rear)

  A. Richter *et al*. SiliconPV 2017 (2017).

# Various carrier selective contacts

Carrier selectivity reflects how efficiently i$V_{oc}$ (Fermi-level splitting) is being extracted to the external circuit.

- *h* contact : High work function material

  e.g., *p*-type Si, $MoO_x$, $WO_x$

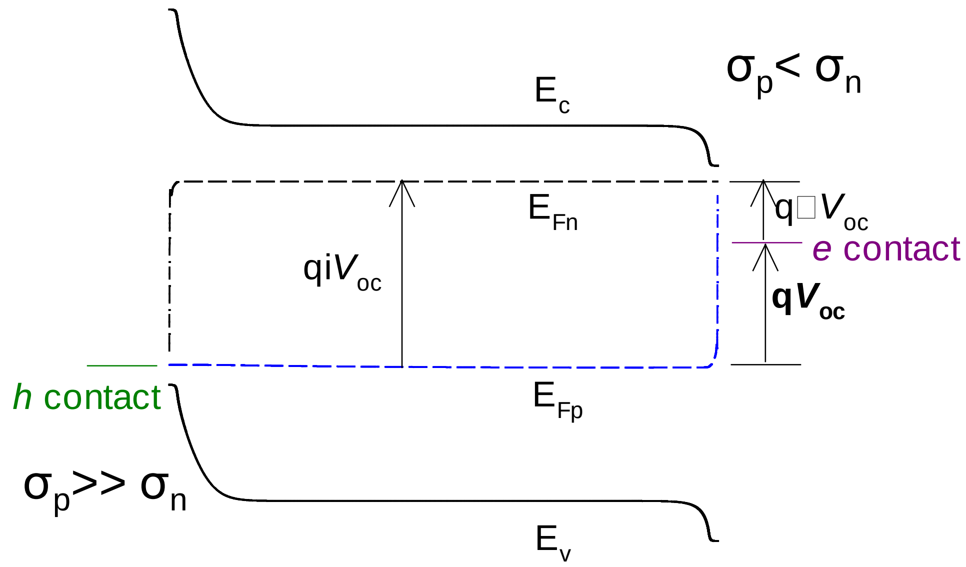
  $\sigma_p \gg \sigma_n$ (hole selective)

- *e* contact : Low work function material

  e.g., *n*-type Si, $TiO_x$, LiF, MgF

  $\sigma_p \ll \sigma_n$ (electron selective)

- Non-ideal contact results in a $V_{oc}$ loss.
- Efficient (non-Si) electron contact has been lacking.



# $TiO_x$ as electron selective contact

- $TiO_x$ ($TiO_2$) electron contact by thermal-ALD provides η=21.6% (ANU) .

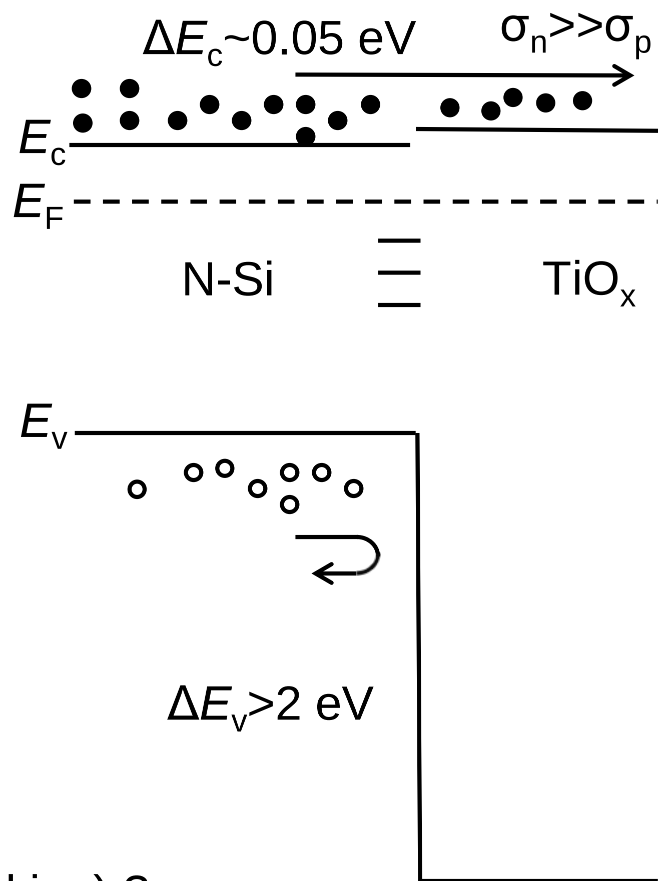
  X. Yang *et al*. Adv. Mater. **28**, 5891 (2016).

- In general, electron selectively originates from the asymmetric band offset at the N-Si/$TiO_x$ interface.

  S. Avasthi *et al*. Appl. Phys. Lett. **102**, 203901 (2013).

- Nevertheless, it was suggested that $TiO_x$ contains negative fixed charge, which might be detrimental for electron contact.

  B. Liao *et al*. Appl. Phys. Lett. **104**, 253903 (2014).
  J. Cui *et al*. SOLMAT **158**, 115 (2016).

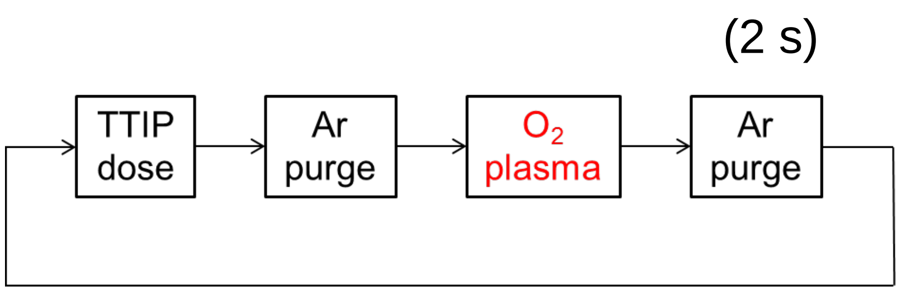



## Research objective / open issues

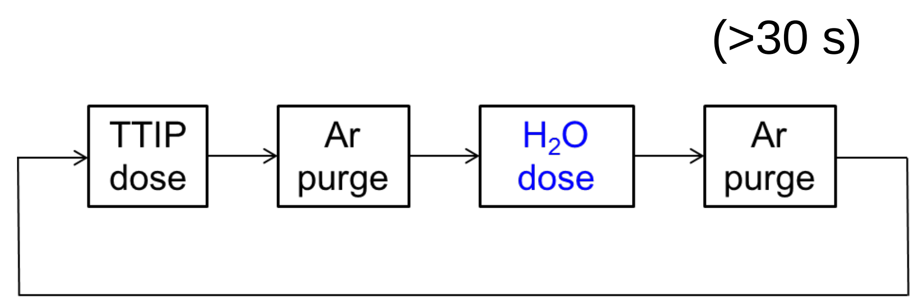
- Is $TiO_x$ an ideal electron contact (a perfect hole blocking) ?
- Is selectivity simply determined by band alignment?
- Any induced c-Si band bending by $TiO_x$?
- Carrier selectivity should be evaluated independent of surface passivation quality (e.g., external $V_{oc}$ vs. i$V_{oc}$) . M. Bivour *et al*. IEEE JPV **4**, 566 (2014).

# $TiO_x$ by atomic layer deposition (ALD)

- Titanium precursor: **TTIP** (Titanium tetraisopropoxide)
- Oxidation : plasma ($O_2$) or thermal ($H_2O$)
- Similar growth rate saturation (~0.045 nm/cycle) for both ALD processes
- Substantially longer $t_{purge}$ needed for thermal (>30 s) than for plasma (2 s)
- Refractive index differs slightly (plasma: $n$=2.40, thermal: $n$=2.32 @λ=632 nm).



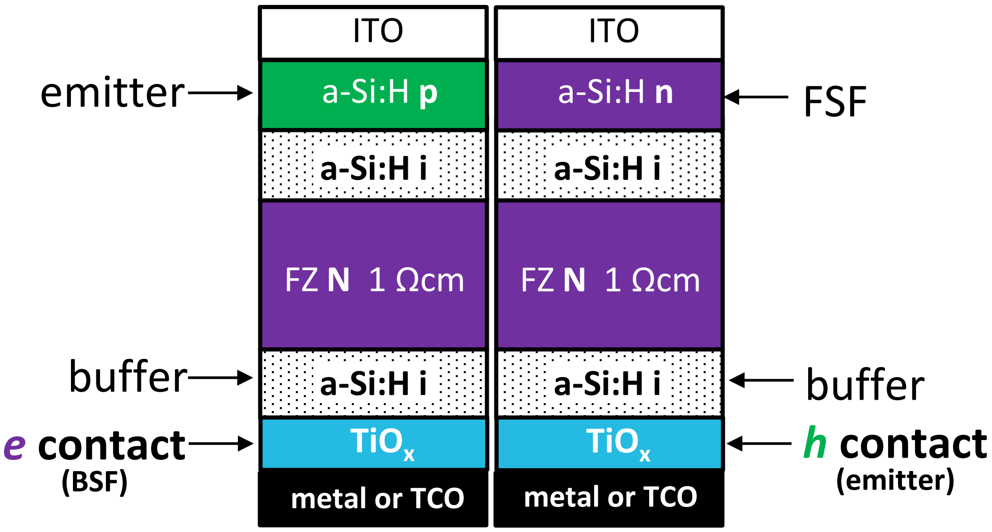

plasma-ALD




thermal-ALD

# Sample strucutres and characterization

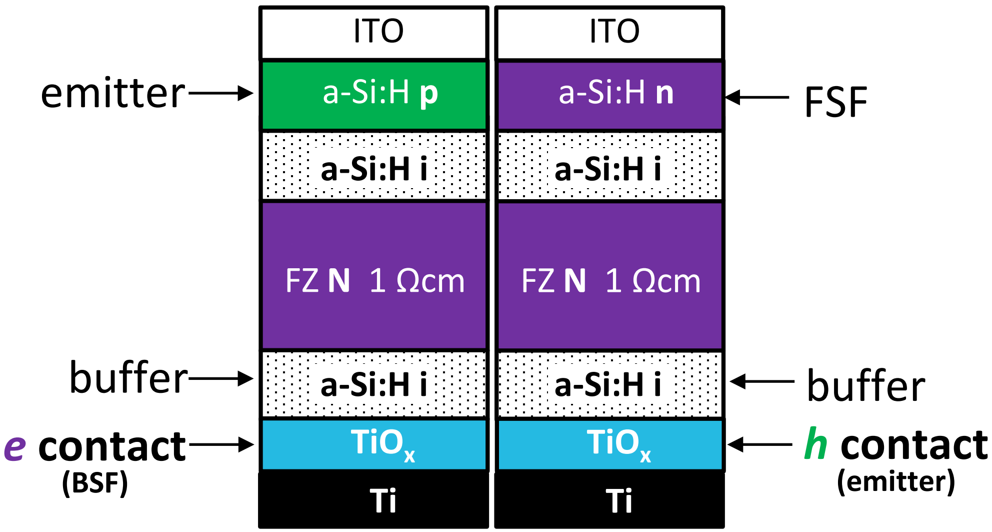
**$TiO_x$ as rear contacts in solar cell precursors**




**$TiO_x$ by plasma- and thermal-ALD**

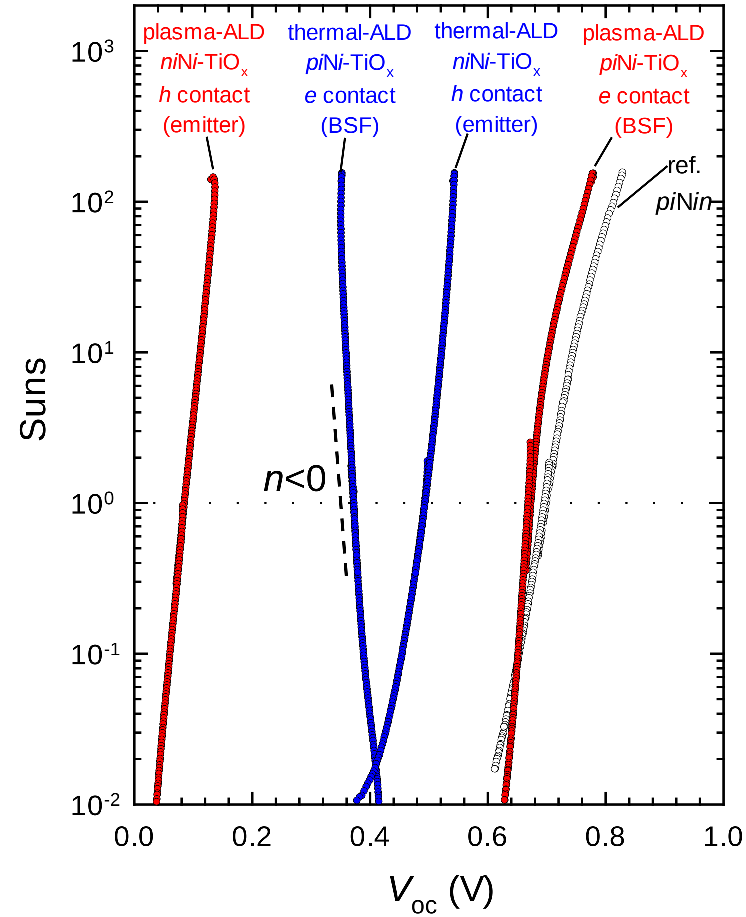
- **a-Si:H (i) buffer** between Si and $TiO_x$ to maintain surface passivation unchanged
- **6-nm-thick $TiO_x$** deposited by plasma- or thermal-ALD at rear
- **$TiO_x$ either as *e* contact (BSF) or *h* contact (rear emitter)**
- Various capping materials (**Ti, Al, ITO, Pd**) examined on top of $TiO_x$
- Front emitter and front-surface-field (FSF) by a-Si:H heterojunction (p-i , n-i)
- Suns-$V_{oc}$, Surface photovoltage (SPV), QSSPC

# Suns-$V_{oc}$ measurements




**$TiO_x$ by plasma- and thermal-ALD**

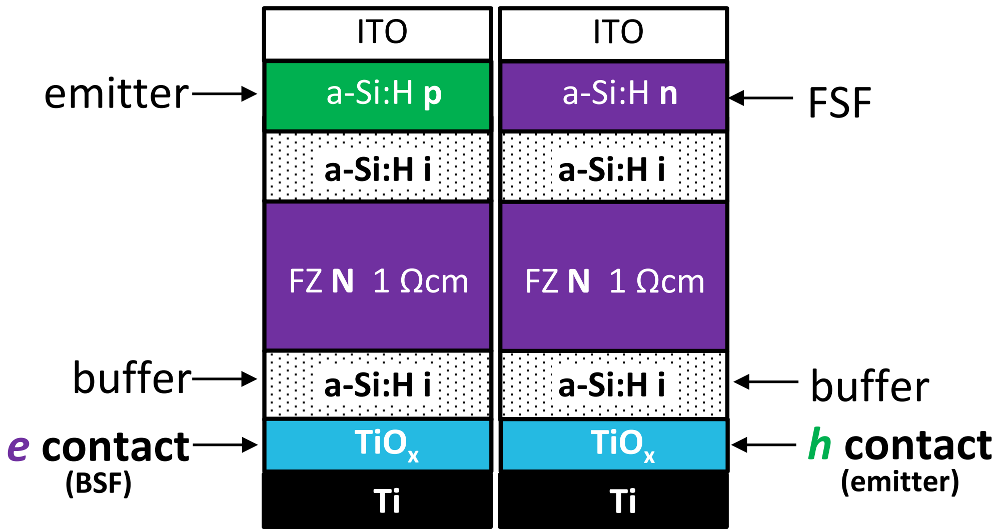
$TiO_x$/**Ti** contact



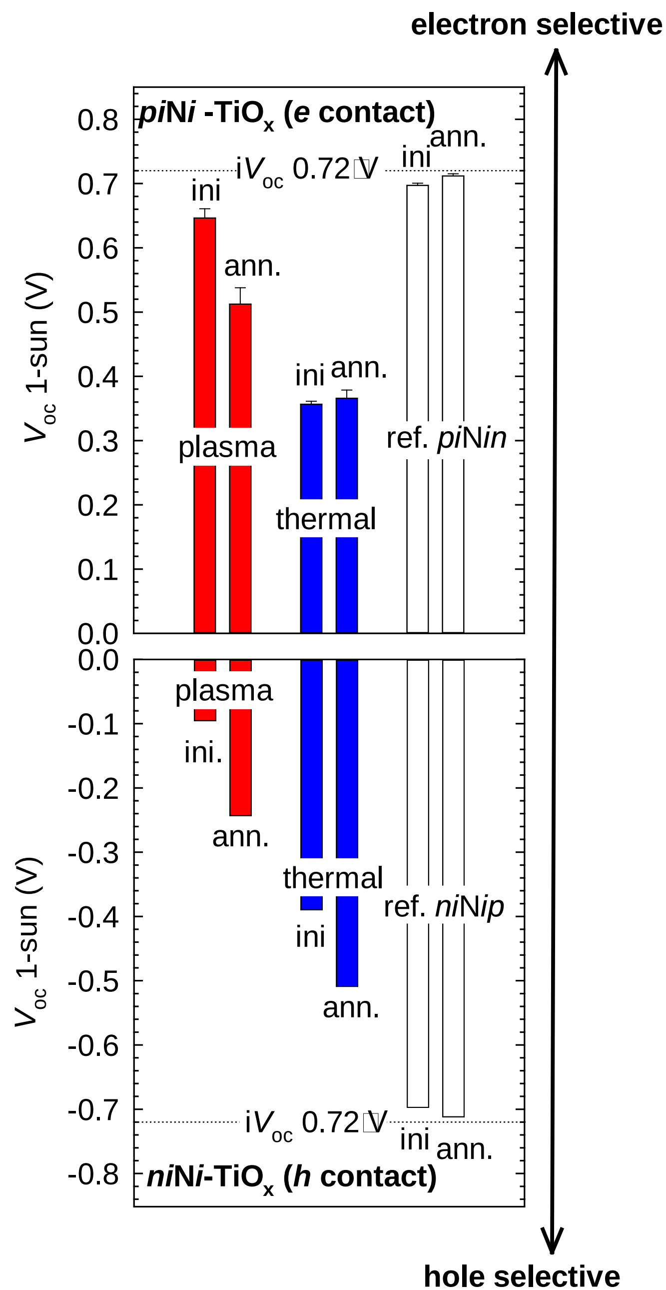

- Significant variation in suns-$V_{oc}$ curve depending on the $TiO_x$ ALD process
- Thermal-ALD $TiO_x$ used as an electron contact (BSF) results in a negative slope in the suns-$V_{oc}$ curve.
- Negative ideal factor ($n$<0) at low illuminations indicates the presence of a non-ideal barrier at Si/$TiO_x$/Ti contact.

S. W. Glunz *et al.*, Proc. 22nd EUPVSEC pp.849-853 (2007).
M. Bivour *et al.*, IEEE J. Photovoltaics **4**, 566 (2014).

# Suns-$V_{oc}$ measurements

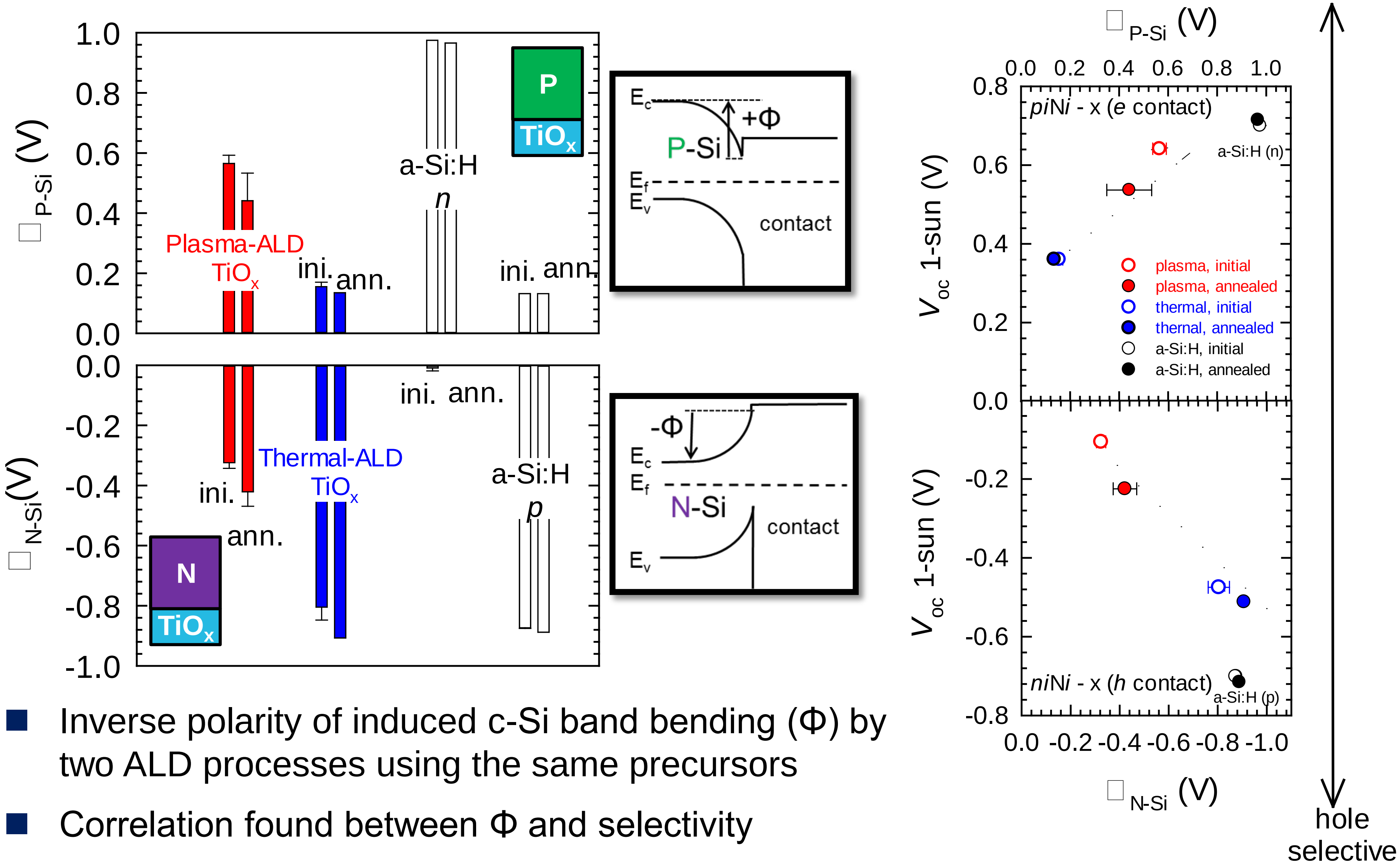



**$TiO_x$ by plasma- and thermal-ALD**



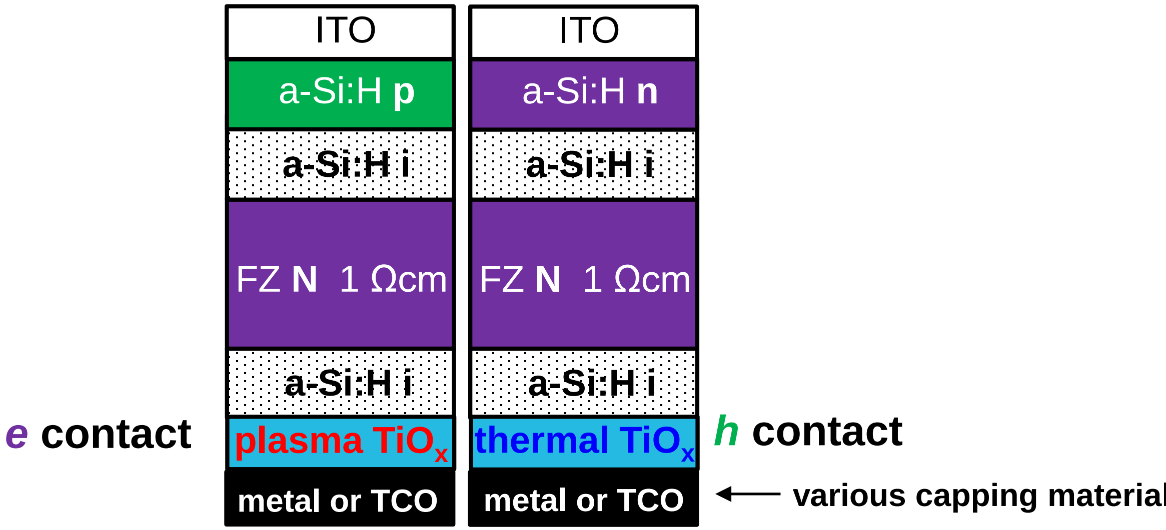

- $V_{oc}$ (1-sun) as a figure of merit of carrier selectivity
- Plasma-ALD $TiO_x$ : electron selectivity
- Thermal-ALD $TiO_x$ : hole selectivity
- Similar trend observed for P-base
- Post-annealing declines electron selectivity but enhances hole selectivity.

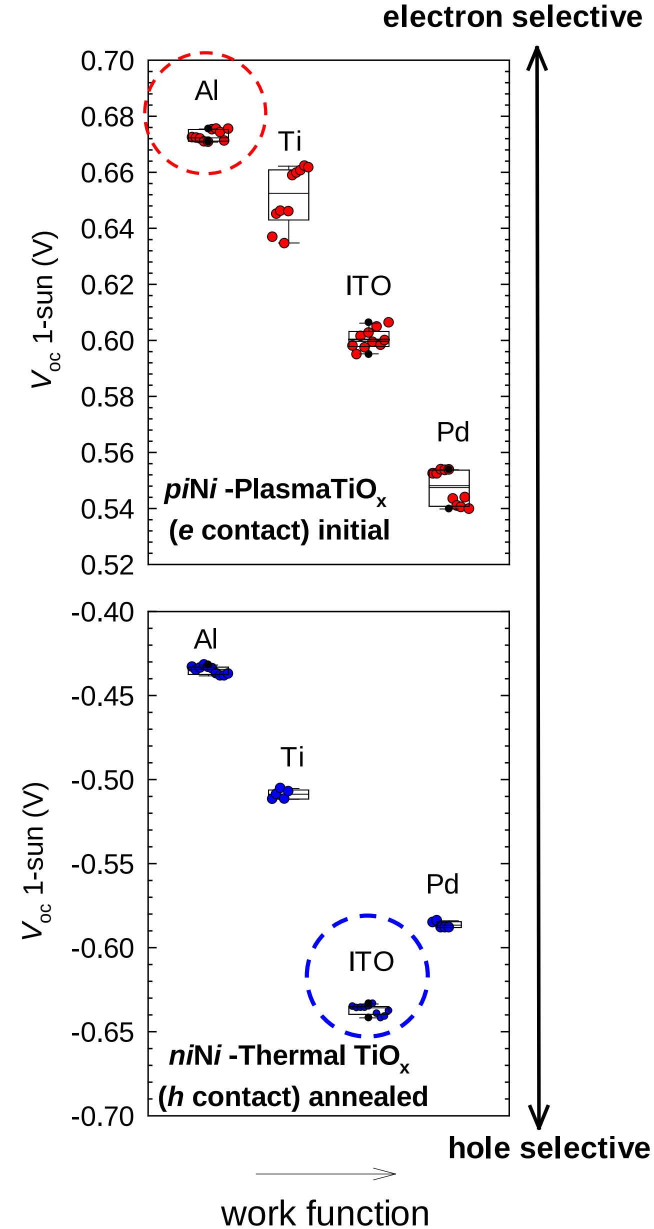
# SPV measurement




- Inverse polarity of induced c-Si band bending (Φ) by two ALD processes using the same precursors
- Correlation found between Φ and selectivity

# Influence of metal (TCO) contact




- Carrier selectivity is significantly influenced by the work function (WF) of the capping layer material (Al: 4.2 eV, Ti: 4.3 eV, ITO: 4.8 eV, Pd: 5.4 eV).

  WF of metals: CRC Handbook of Chemistry and Physics (92nd ed.) pp.12-124.

  WF of ITO: A. Klein *et al*., Thin Solid Films **518**,1197 (2009)..

- Screening length of $TiO_x$ is well above the thickness.
- As a result, carrier selectivity can be tuned from electron ($V_{oc}$~680 mV) to hole contact ($V_{oc}$~650 mV).

# Summary

- $TiO_x$ layers were deposited by plasma- and thermal-ALD.
- Inverse behavior in terms of carrier selectivity/induced c-Si band bending

  Plasma ALD: electron selective contact

  Thermal ALD: hole selective contact
- Carrier selectivity is widely tunable from electron selective ($V_{oc}$ ~680 mV) to hole selective ($V_{oc}$ ~650 mV), depending on ALD process, post annealing and WF of metal (TCO) contact.
- It suggests that carrier selectivity is governed by the effective work function and/or the fixed charge of $TiO_x$ rather than by the asymmetric band offsets at the Si/$TiO_x$ interface (induced-junction-like classical MS/MIS).
- Strong influence of capping layer might be an issue for realizing high-η device (e.g., $TiO_x$/TCO/metal *e* contact).

# Acknowledgements

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