Department of Materials
Semiconductor and Silicon Photovoltaics Group

UNIVERSITY OF OXFORD

Extrinsic surface passivation of silicon solar cells

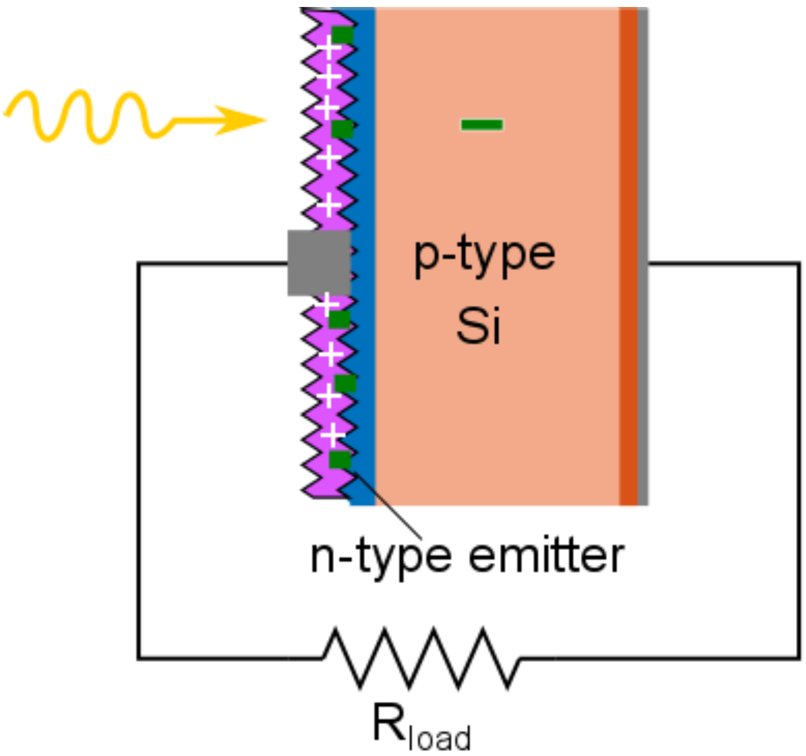
Ruy Sebastian Bonilla

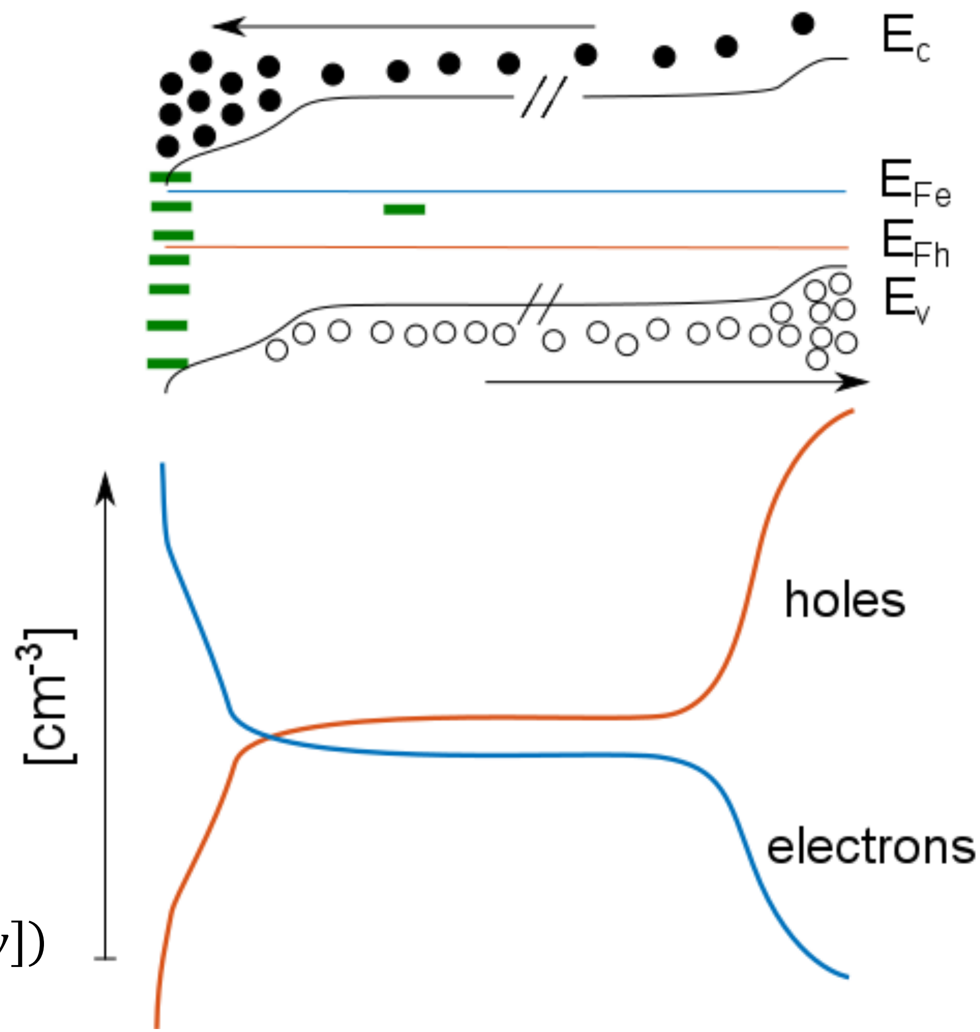
Content

- Surface recombination basics

1. Key aspects on the dielectric-silicon interface
2. Consistent surface recombination metrics
3. Intrinsic vs Extrinsic surface passivation
4. Potential of charge-assisted (field-effect) passivation
5. Damage free plasma hydrogenation

Surface recombination in silicon





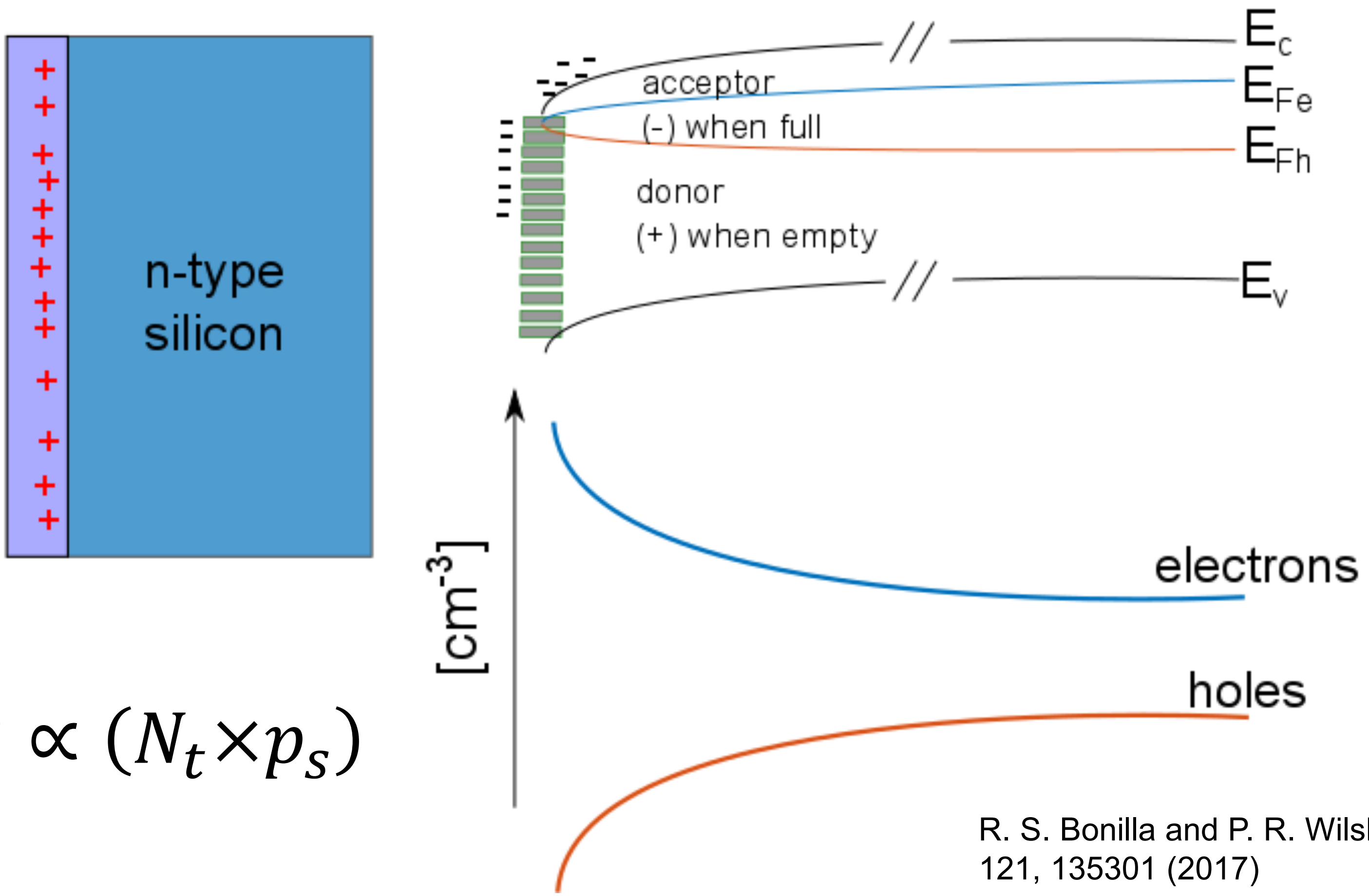
Shockley–Read–Hall recombination rate:

$$R_1 = \frac{np - n_{ie}^2}{\frac{p+p_1}{\sigma_n N_t v_{th}} + \frac{n+n_1}{\sigma_p N_t v_{th}}} \propto (N_t \times [minority])$$

The silicon-dielectric interface

- So far the two typical key elements to recombination at the silicon surface are:
  - The concentration of trap states (CHEMISTRY)
  - The concentration of carriers: n_s, p_s (CHARGE)
- Two other key aspects:
  - Nature of interface states
  - Their ability to capture carrier ($\sigma_{n,p}$)

The silicon-dielectric interface



$$R \propto (N_t \times p_s)$$

R. S. Bonilla and P. R. Wilshaw J. Appl. Phys. 121, 135301 (2017)

The silicon-dielectric interface

- The ability of states to capture carriers

Shockley–Read–Hall recombination rate:

$$R_1 = \frac{np - n_{ie}^2}{\frac{p + p_1}{\sigma_n N_t v_{th}} + \frac{n + n_1}{\sigma_p N_t v_{th}}}$$

At the surface
Surface Recombination Velocity

$$S_{eff} = \frac{1}{\Delta n} \frac{n_s p_s - n_{ie}^2}{\frac{p_s + p_1}{S_{n0}} + \frac{n_s + n_1}{S_{p0}}}$$

$$S_{n0} = D_{it} \sigma_n v_{th}$$

$$S_{p0} = D_{it} \sigma_p v_{th}$$

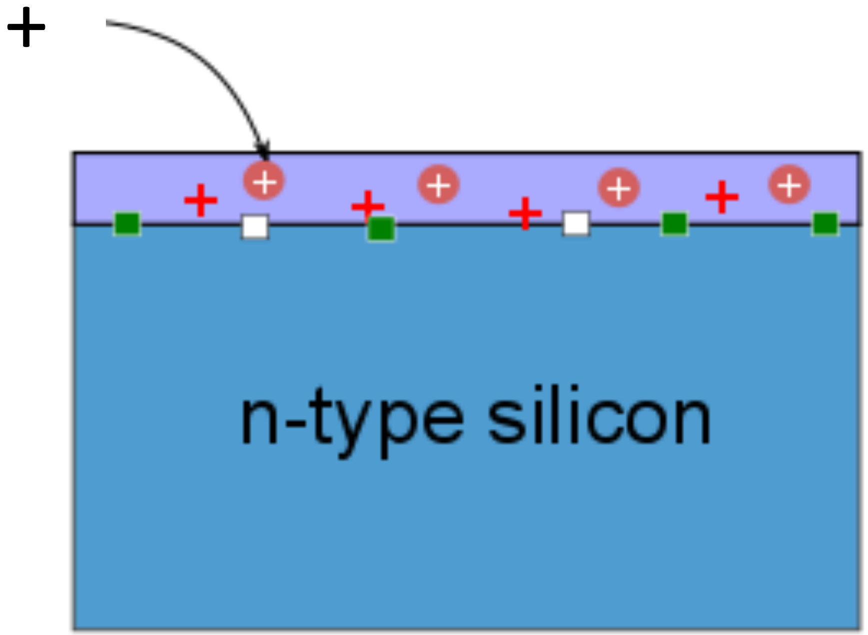
Surface recombination metrics

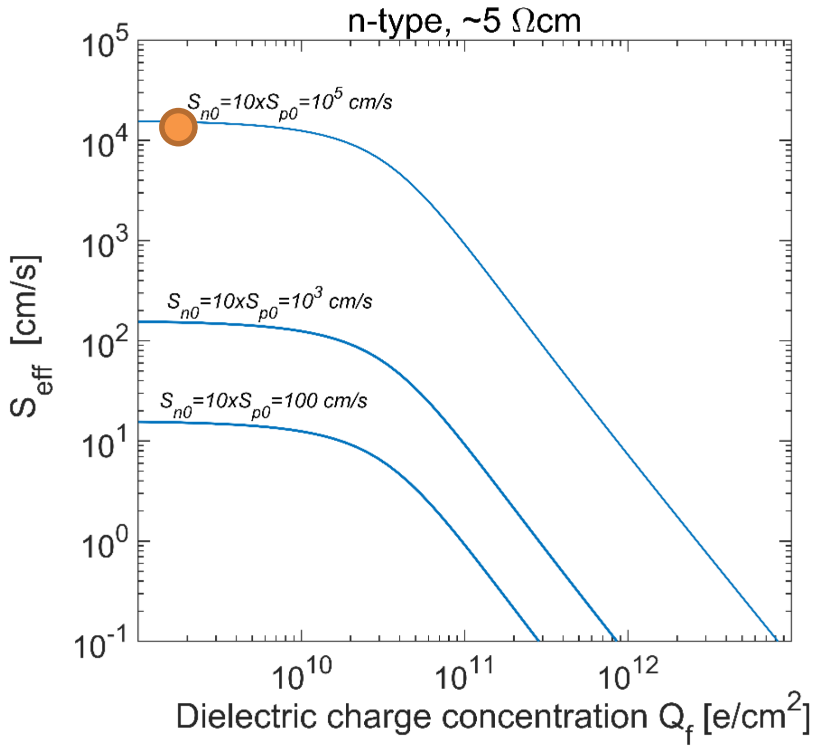
$$S_{eff} = \frac{1}{\Delta n} \frac{n_s p_s - n_{ie}^2}{\frac{p_s + n_i}{S_{n0}} + \frac{n_s + n_i}{S_{p0}}} \qquad J_{0,surf} = \frac{q n_{ie}^2}{\frac{p_s + p_1}{S_{n0}} + \frac{n_s + n_1}{S_{p0}}}$$

K. R. McIntosh and L. E. Black J. Appl. Phys. 116, 014503 (2014)

Approximation	S_{eff}	J_{0S}
Negligible Q such that $n_s = n_d$	S_{p0}	$q \frac{S_{p0}}{n_d} n_{ie}^2$
Low Q, low injection	$S_{p0} \exp\left[\frac{-Q}{\sqrt{kT\epsilon_{Si}N_D}}\right]$	$q \frac{S_{p0}}{n_d} \exp\left[\frac{-Q}{\sqrt{kT\epsilon_{Si}N_D}}\right] n_{ie}^2$
Large positive Q (strong accumulation)	$S_{p0} n_d \frac{2kT\epsilon_{Si}}{Q^2}$	$q\, S_{p0} \frac{2kT\epsilon_{Si}}{Q^2} n_{ie}^2$
Large negative Q (strong inversion)	$S_{n0} n_d \frac{2kT\epsilon_{Si}}{Q^2}$	$q\, S_{n0} \frac{2kT\epsilon_{Si}}{Q^2} n_{ie}^2$

Intrinsic vs Extrinsic passivation





$$\Delta n = 10^{15}\ \mathrm{cm}^{-3}$$

Single interface mid-gap defect:

$$S_{eff} = \frac{1}{\Delta n}\frac{n_s p_s - n_{ie}^2}{\frac{p_s + n_i}{S_{n0}} + \frac{n_s + n_i}{S_{p0}}}$$

$$Q_{it} = 10^{11}\ e/cm^2$$

Surface Passivation

- **CHARGE** is essential to obtain good surface passivation!
- **Intrinsic** passivation
  - That due to the dielectric film in the *as deposited* state
  - Chemical and FEP (Charge-assisted)

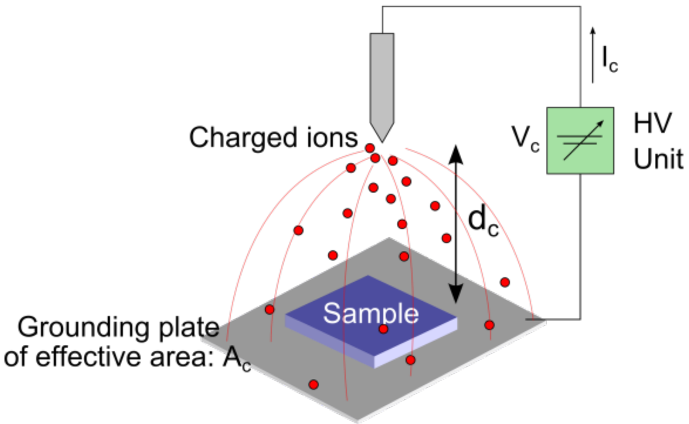
$$R_s \propto D_{it} \times \sigma_p \times p_s$$

- Chemistry and charge ***difficult to*** optimise
  - Limited by the deposition process

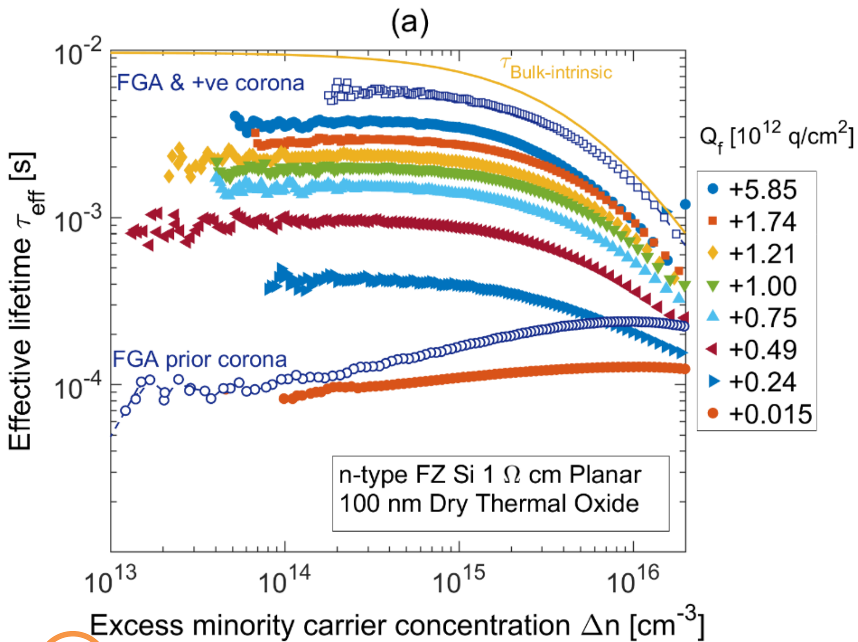
- If charge deposited ***after*** the film deposition (**extrinsic**) ***it can be*** optimised independent of chemistry

Potential of Extrinsic Passivation

- Externally added charge to the dielectric *after* deposition –e.g. Corona charge:



Sinton transient PCD

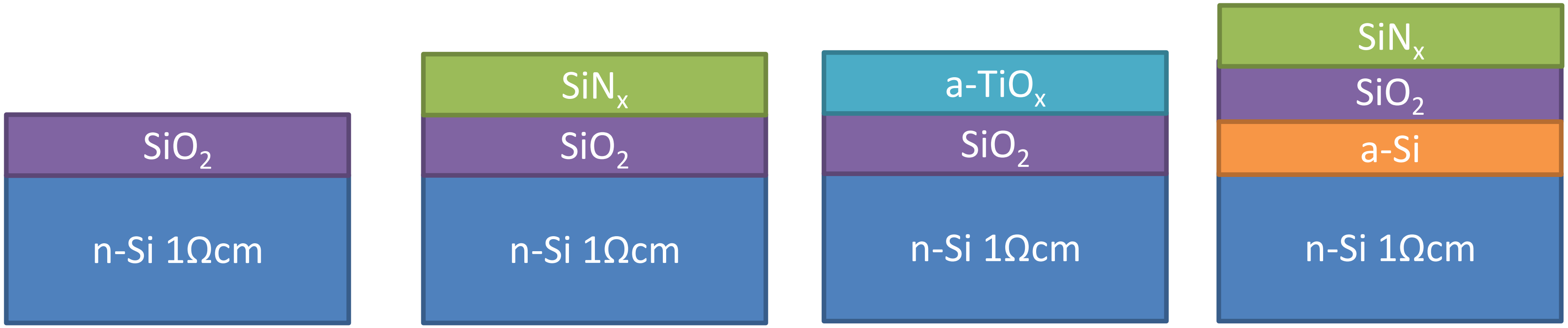


R.S. Bonilla et al. Applied Surface Science 412 (2017) 657–667

$$\frac{1}{\tau_{eff}} = \left(\frac{1}{\tau_{Rad}} + \frac{1}{\tau_{Au}} + \cancel{\frac{1}{\tau_{SRH}}}\right) + \frac{2S}{W}$$

1.42 cm/s @ $\Delta n = 10^{15}$ cm^{-3}

Potential of Extrinsic Passivation



S_{eff}=1.42 cm/s | 0.15 cm/s | 1.2 cm/s | 0.01 cm/s

4%H anneal: 0.6 cm/s

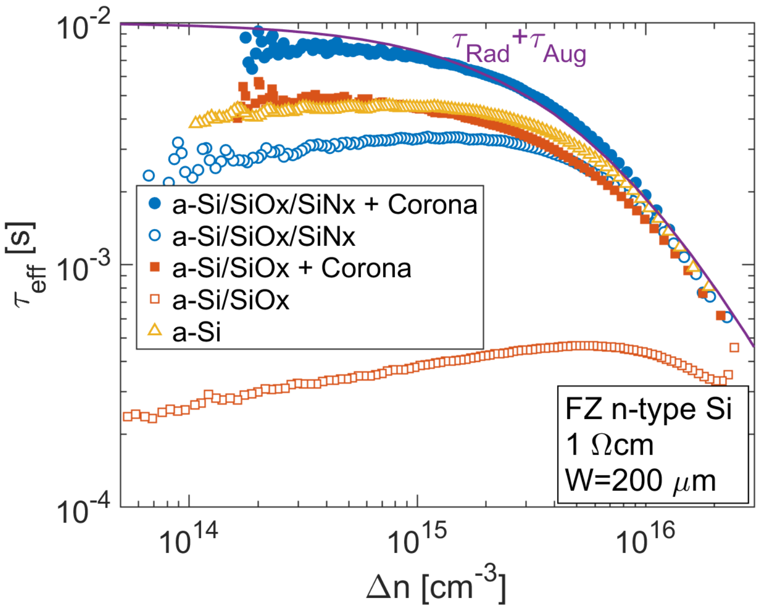
H passivation: 0.17 cm/s

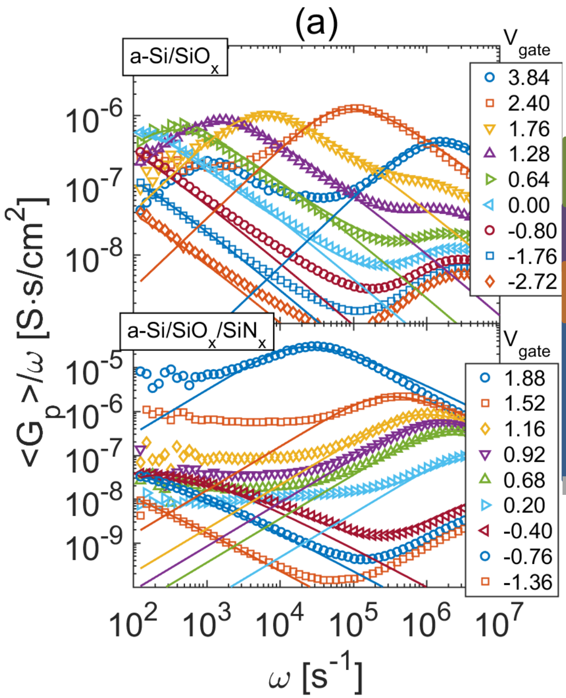
Bonilla et. al. Phys. Status Solidi A 214, No. 7, 1700293 (2017)

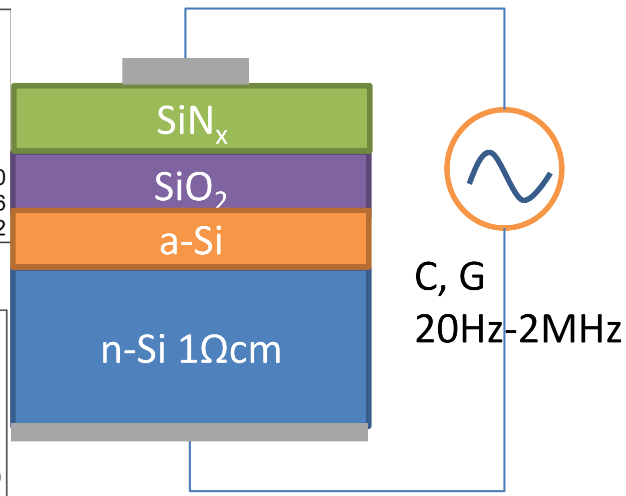
$\Delta n=10^{15}$ cm^{-3}

Potential of Extrinsic Passivation

a-Si/SiOx/SiNx



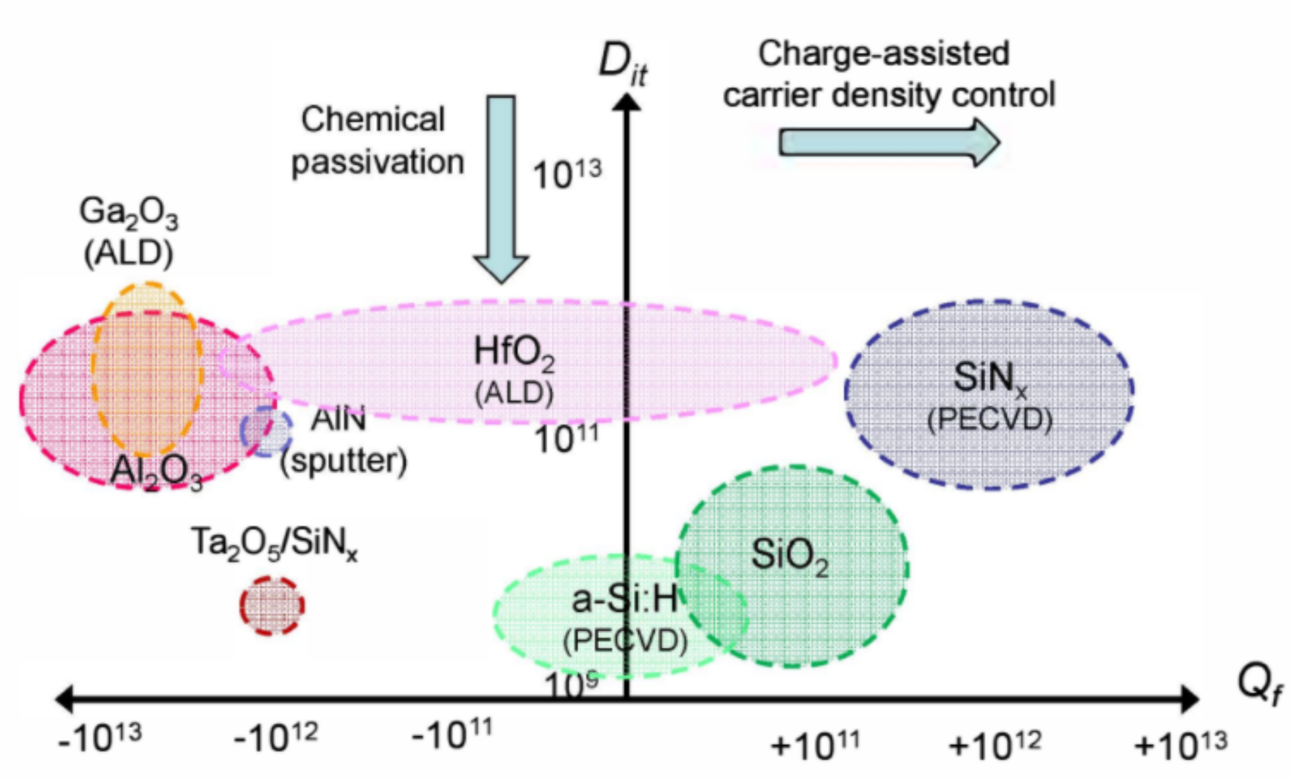




$$R_s \propto D_{it} \times \sigma_p \times p_s$$

R. S. Bonilla et al. Phys. Status Solidi RRL 11, No. 1 (2017)

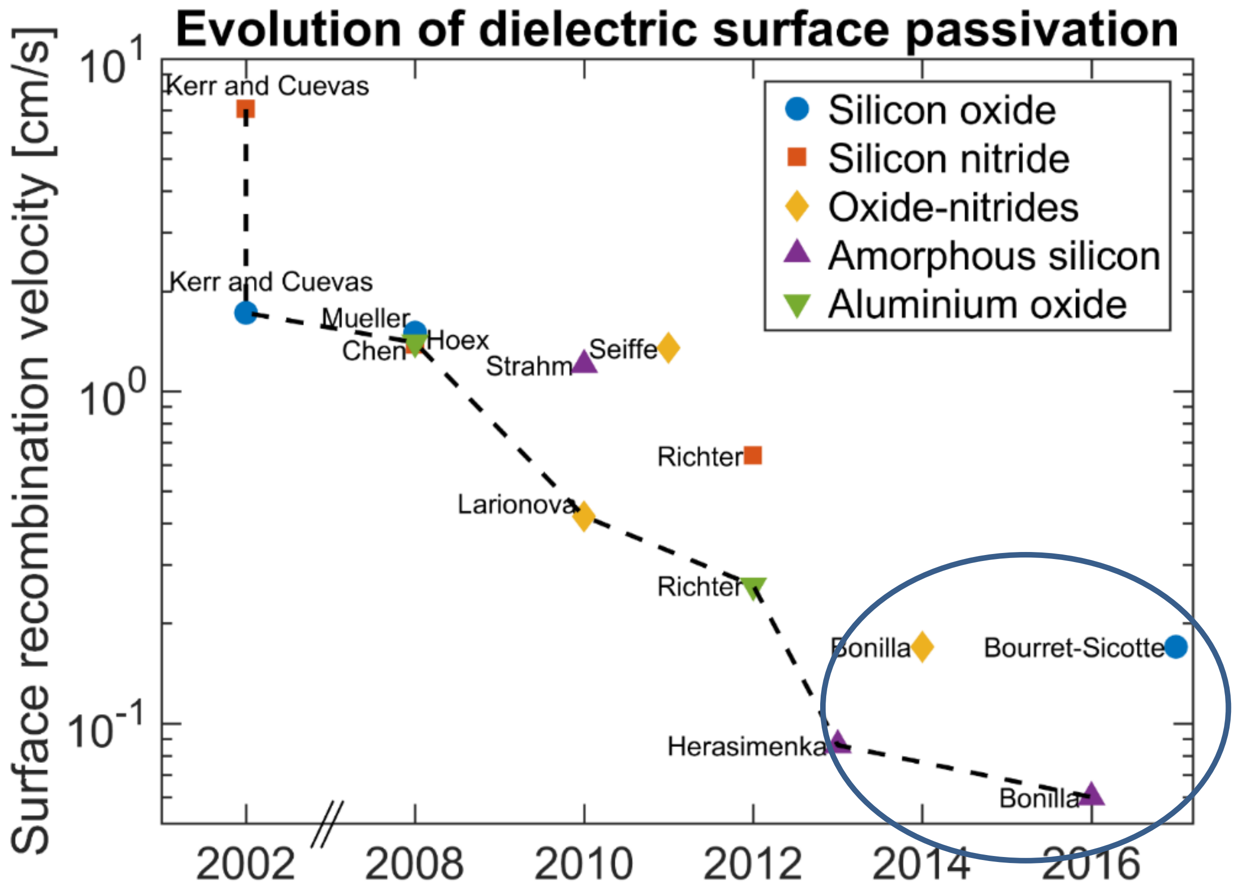
State-of-the-art



A. Cuevas et al. IEEE PVSC 2015, 6pp

State-of-the-art

Proof of concept:
Corona Discharge



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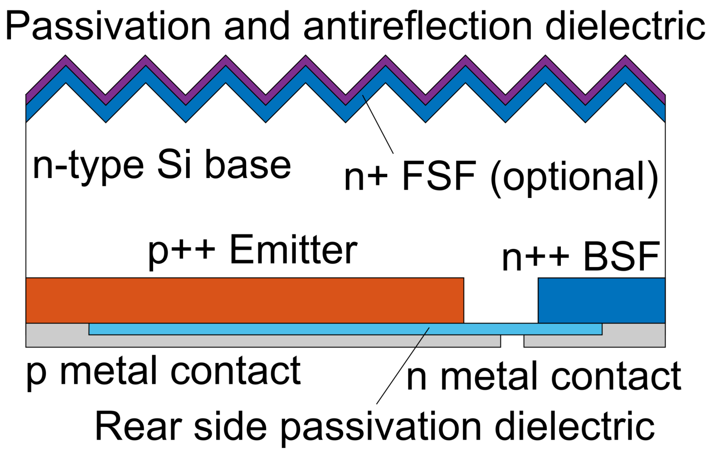
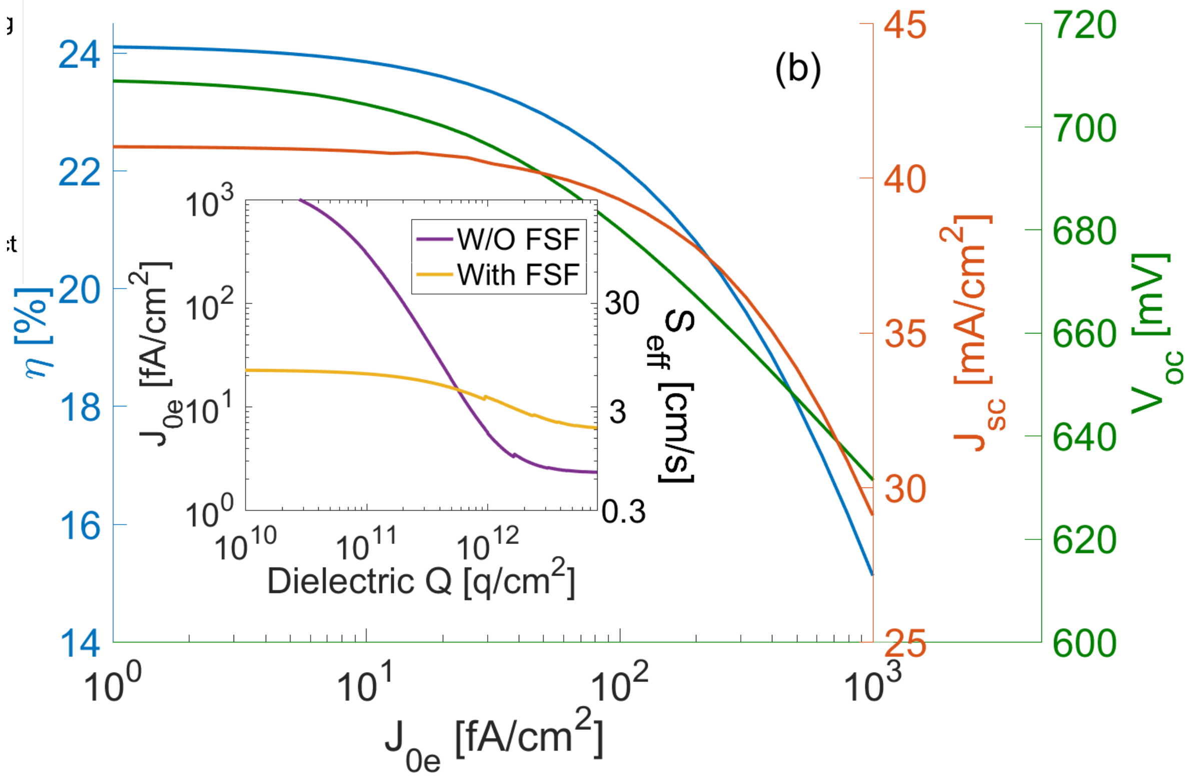
Bonilla et. al. Phys. Status Solidi A 214, No. 7, 1700293 (2017)

Extrinsic Field Effect Passivation

- Charge added to the dielectric *after* deposition greatly improves passivation.
- It allows optimisation of FEP independently of chemical passivation
- How important is it for a solar cell?

Field Effect Passivation in cell performance (Quokka)





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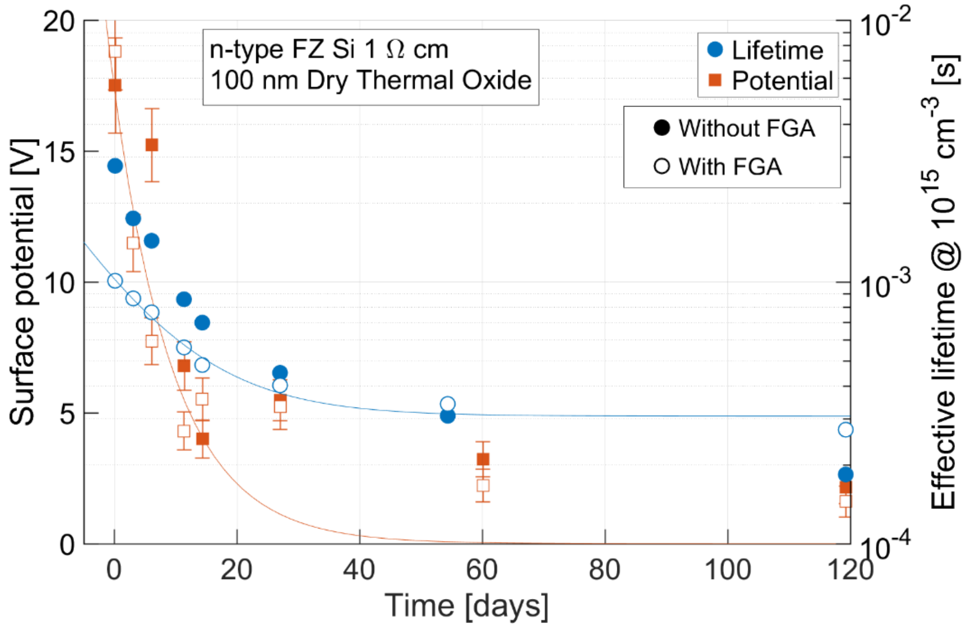
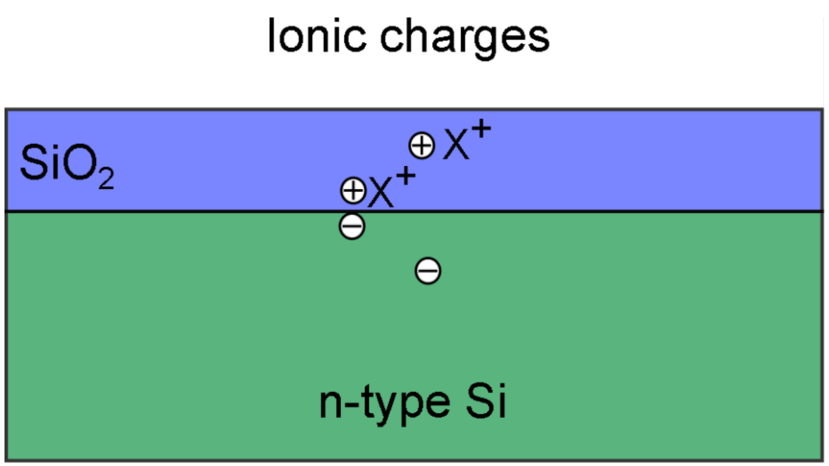
But… Is this Charge Stable?

- Corona discharge ...



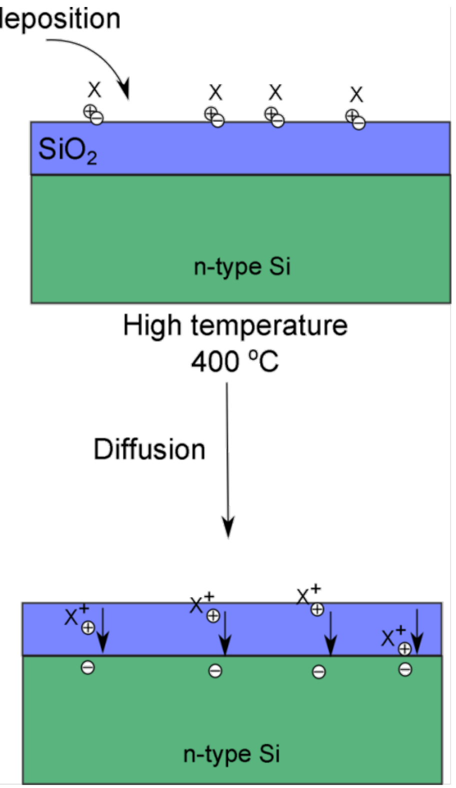
Ionic field effect passivation

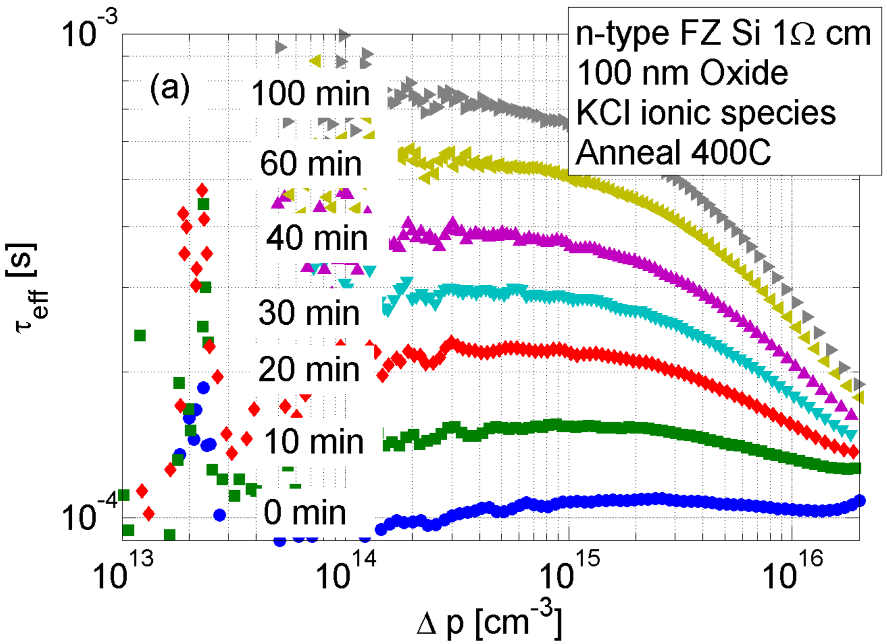
- Charge is introduced into dielectric films at high temperature and then permanently quenched in place by cooling to room temperature



Ionic field effect passivation

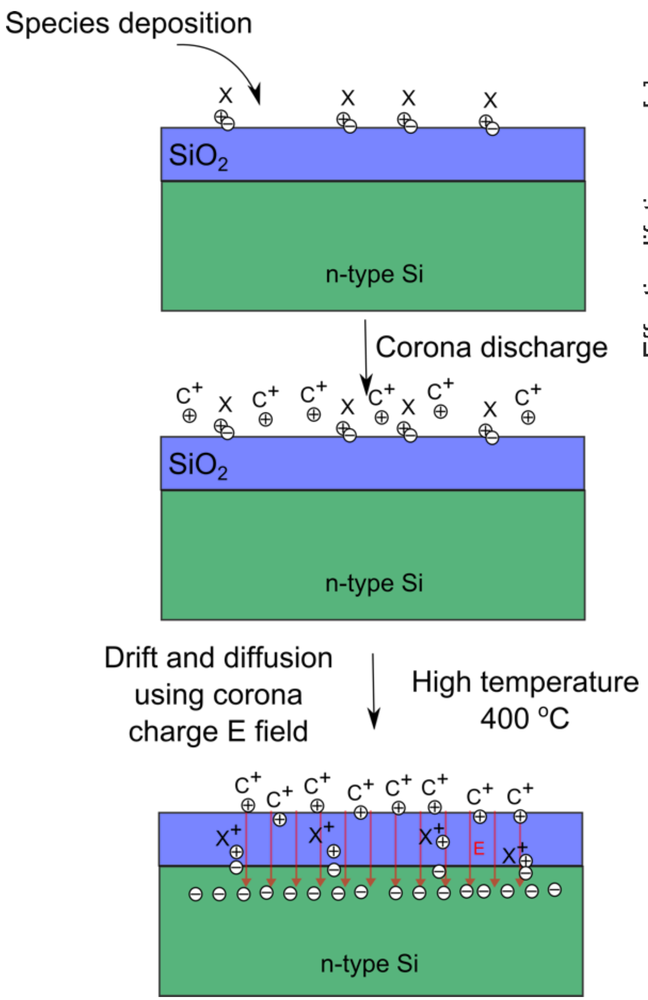
- Diffusion of Potassium ions into SiO2

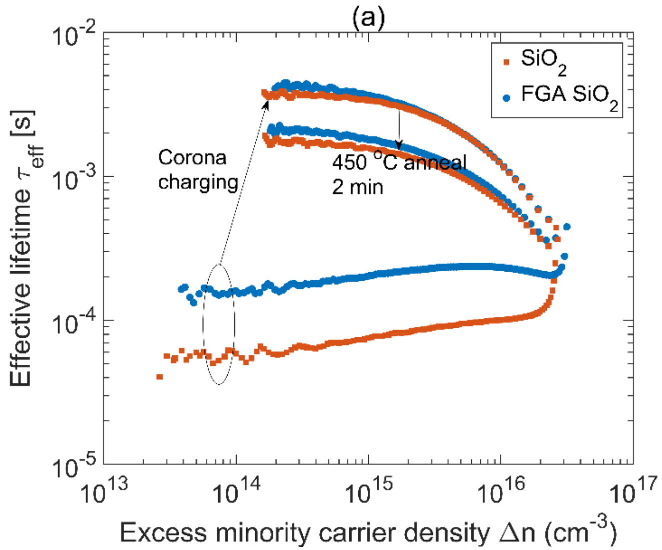


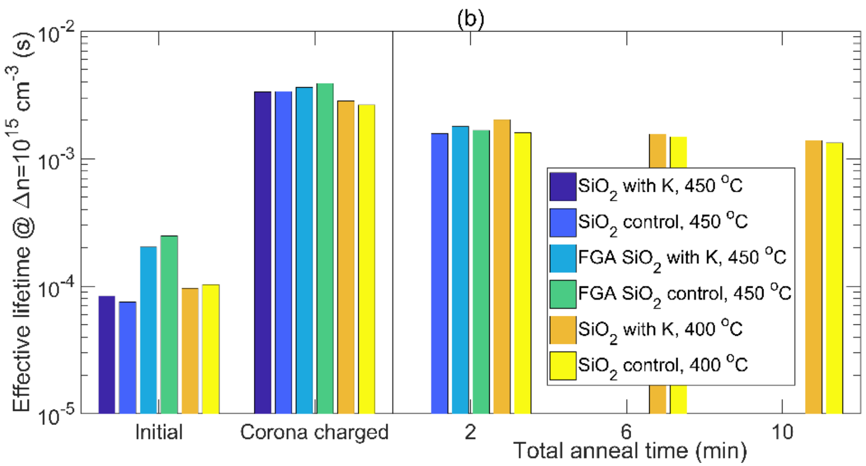


Bonilla et al. Solid State Phenomena Vol. 242 (2016) pp 67-72

Diffusion + Drift of Potassium in SiO_2

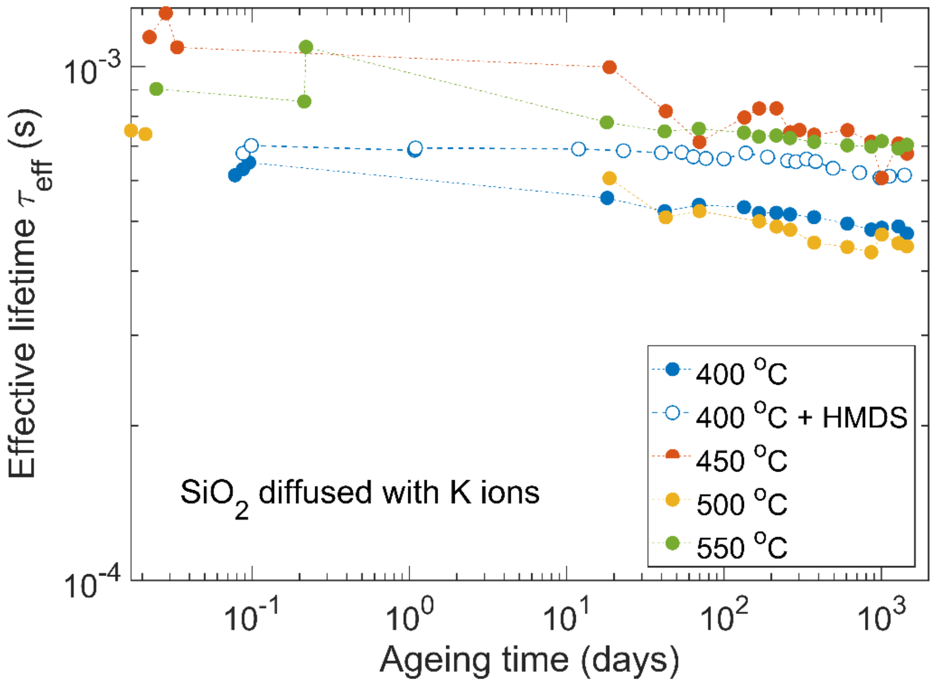




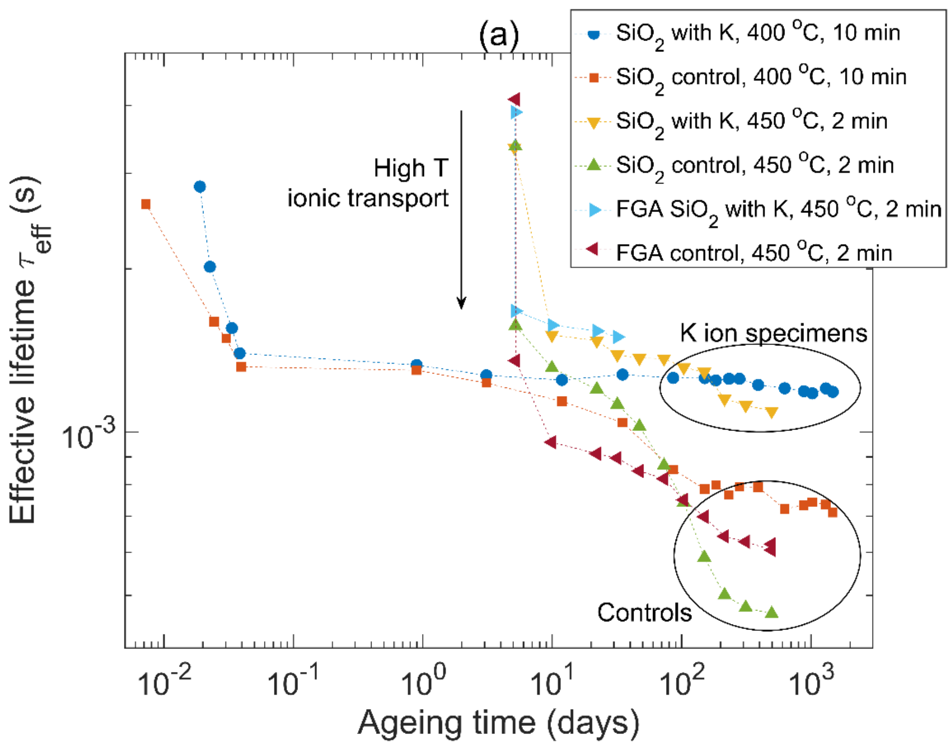


Long term stability of ion-charged SiO_2

Diffusion



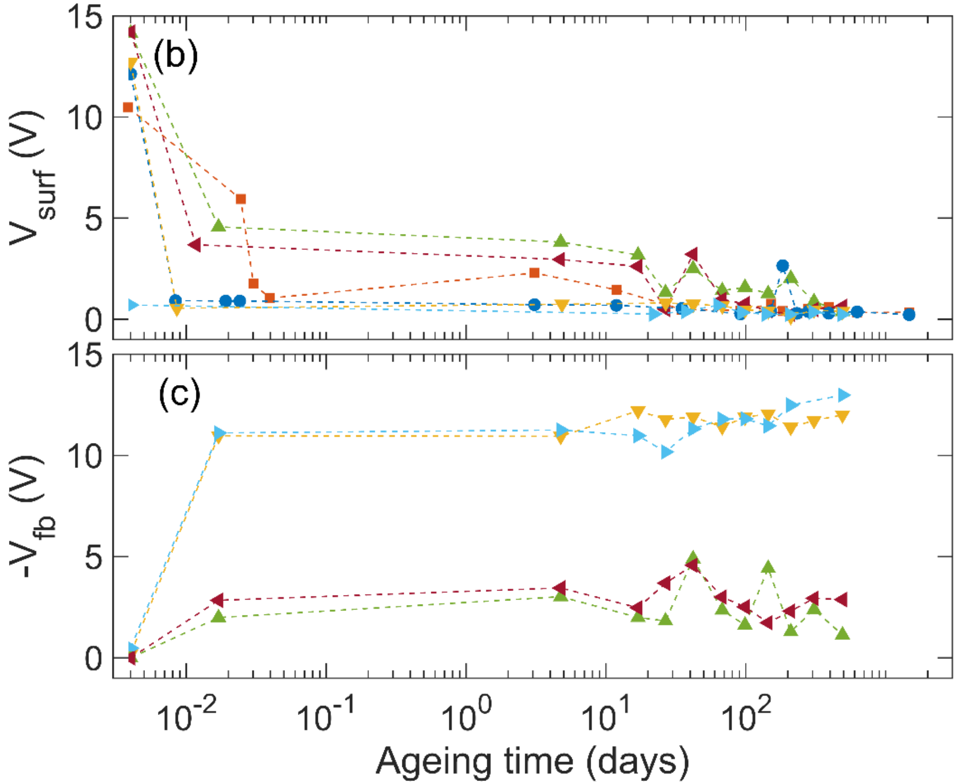
Diffusion + Drift



Long term stability of ion-charged SiO_2

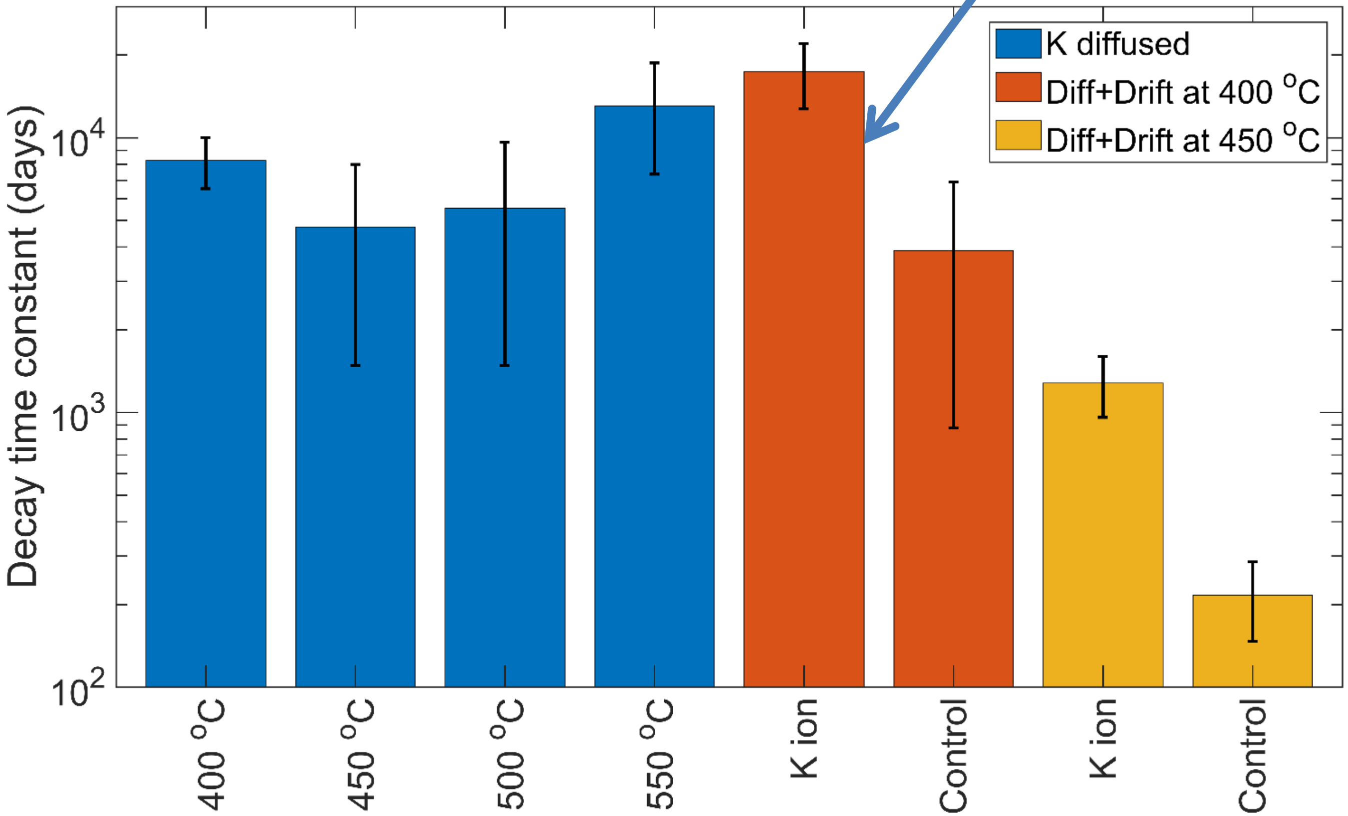
Diffusion + Drift

Direct measurement of charge concentration using kelvin probe and capacitance-voltage



Long term stability of ion-charged SiO_2

Exceeding 10k days
~ 30 Years



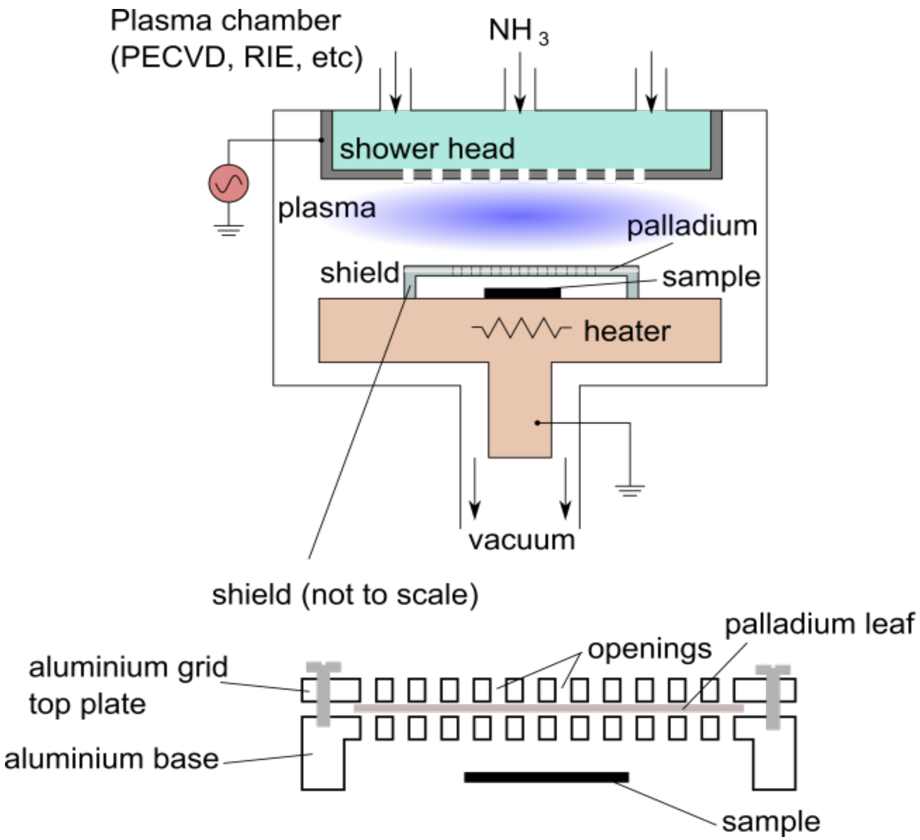
Towards industrially compatible extrinsic passivation
(fast and cost-effective)

- **Field effect**
  - Stabilise charge using ions: lab conditions >4 years, *likely indefinite*. But, as yet, slightly worse passivation
  - Working conditions stability: to be tested
  - Compatibility of process: K ions, others possible
  - Industrial deposition technique for ions
  - Process temperature: 450-550 C
  - Speed of process: currently 1-2 mins, but possible in seconds

Extrinsic Hydrogen Passivation

- Hydrogen is effective at passivating defects and dangling bonds at the surface or in the bulk of silicon wafers
- Industrially – dielectrics + firing
- Research – Forming Gas anneals, Remote Hydrogen Plasma

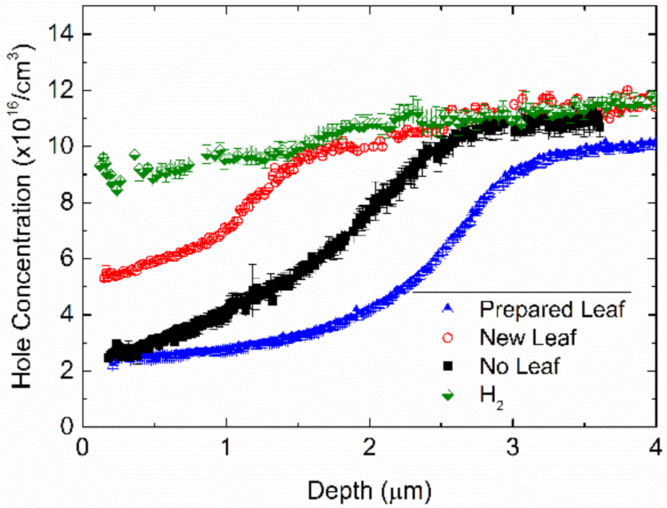
Shielded Hydrogen Passivation



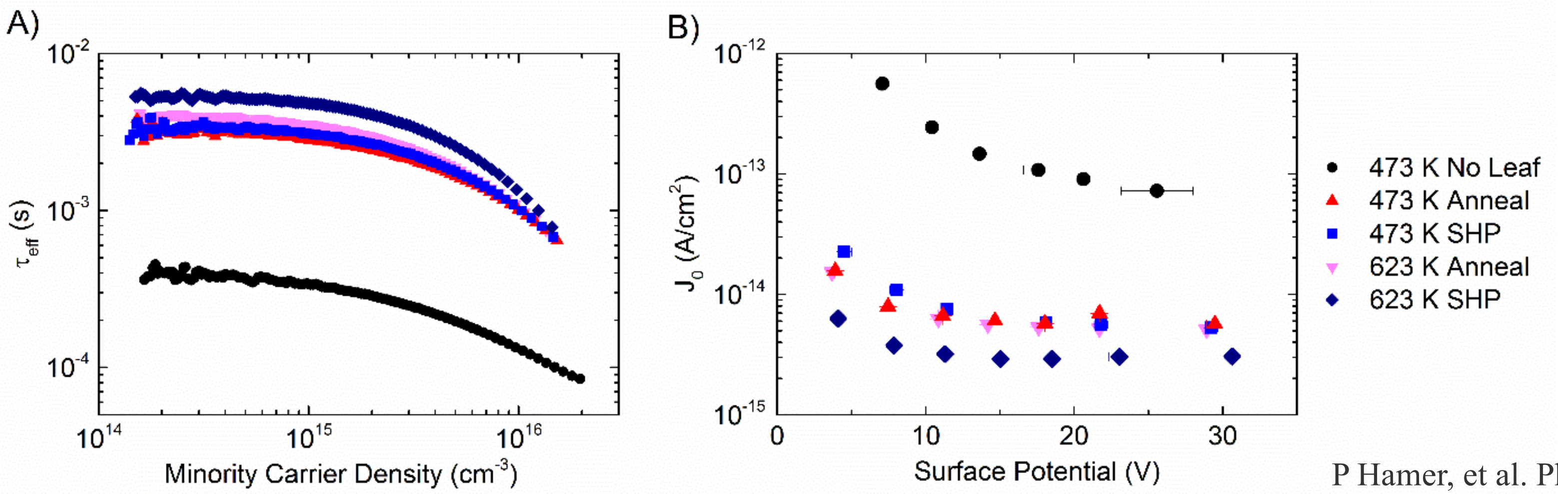
- Uses a plasma source of atomic hydrogen
- A thin palladium "shield" is inserted between the plasma and the sample
- Protects against UV, high energy particles
- Damage free plasma hydrogenation

P Hamer, et al. Phys. Status Solidi RRL 11, 2017

SHP - Results



eCV measurements of active boron concentration vs depth after 20 min exposure at 200 ^oC.



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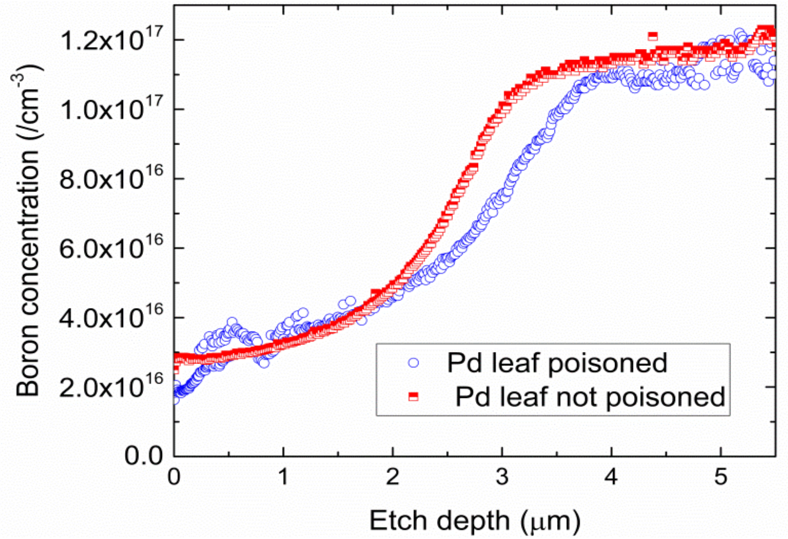
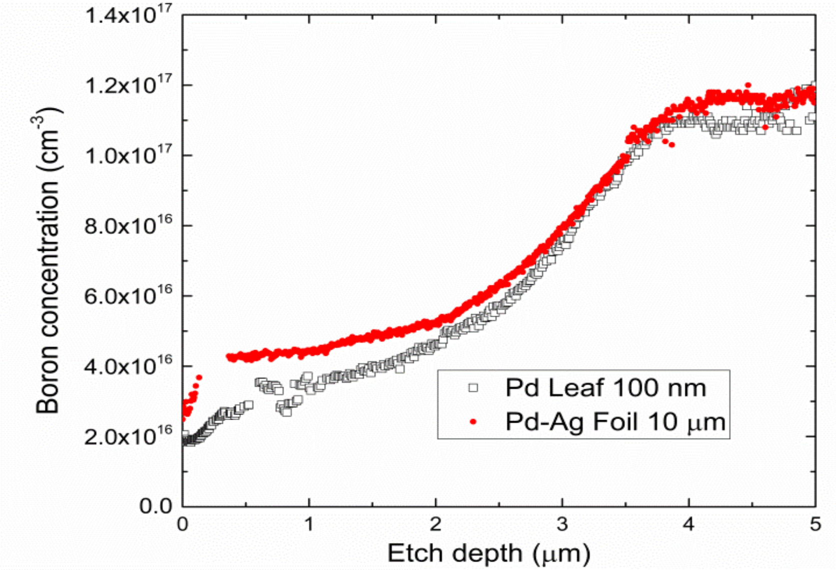
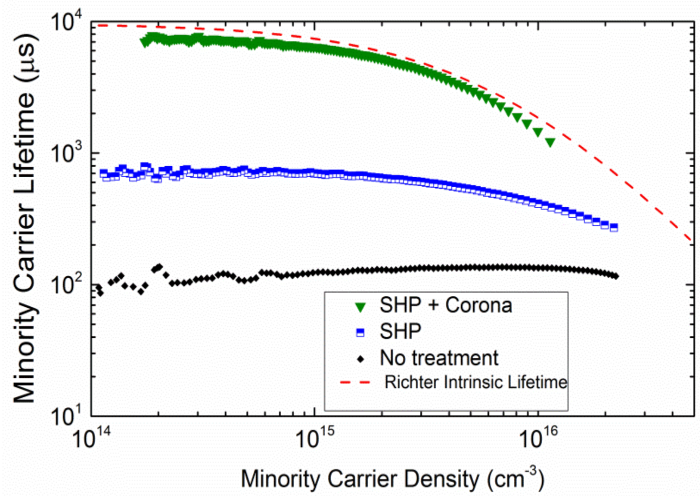
Poisoning and Thicker Foils





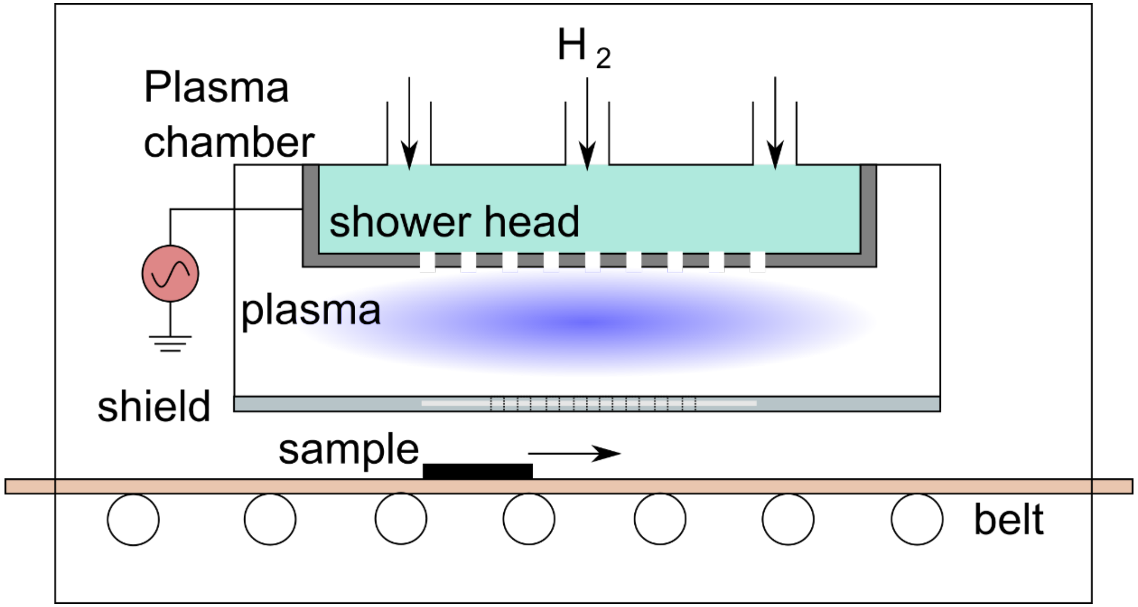


eCV plots using leaves with and without “poisoning”.

eCV plots using a 100 nm thick “leaf” and a 10 µm thick Pd/Ag “foil”.

Bourret-Sicotte, et al. Phys. Status Solidi A 214, No. 7 (2017)

Industrial Application



- Potential for in-line processing
- Quick, damage-free hydrogen exposure
- Potential for:
  - low temperature processing,
  - passivation without firing dielectrics,
  - passivation of carrier selective contacts.

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Summary

- Understanding of dielectric surface passivation
- Extrinsic FEP can be very effective. SRV<0.1 cm/s
  - It is also independent from the chemical and optical properties of the dielectric.
  - Possible combination with damage free hydrogenation
- Progress towards ***stable***, fast, commercial, extrinsic field effect passivation.

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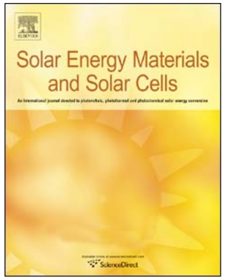

Call for Papers: Special Issue on Surface and Interface Passivation in Crystalline Silicon Solar Cells

-Fundamentals and new concepts of silicon surface passivation
-Novel thin film dielectrics and deposition technology
-Modelling and characterisation methods of surface charge dynamics
-Review papers on surface passivation using AlOx, SiOx and SiNx
-Implementation of passivation technology into solar cell manufacturing
-Passivated hole and electron selective contacts