Hydrogen Transport from Dielectrics to *poly*-Si/SiO$_x$ Passivating Contacts Measured by Mass Spectrometry and Vibrational Spectroscopy

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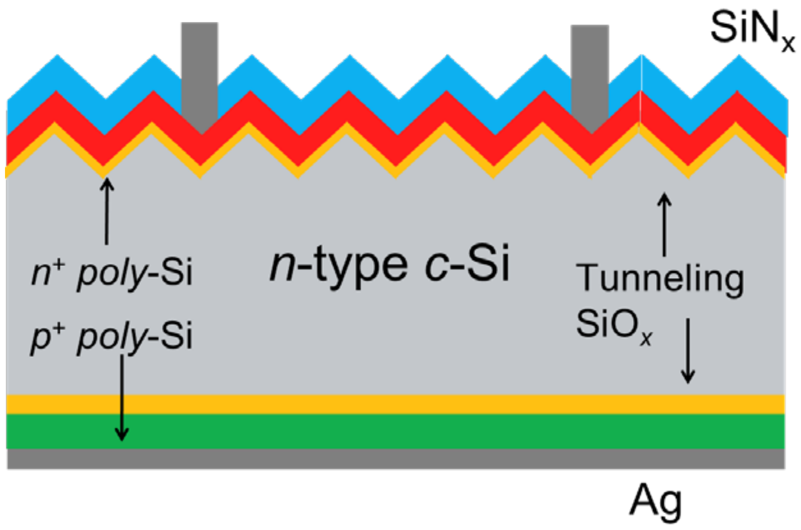
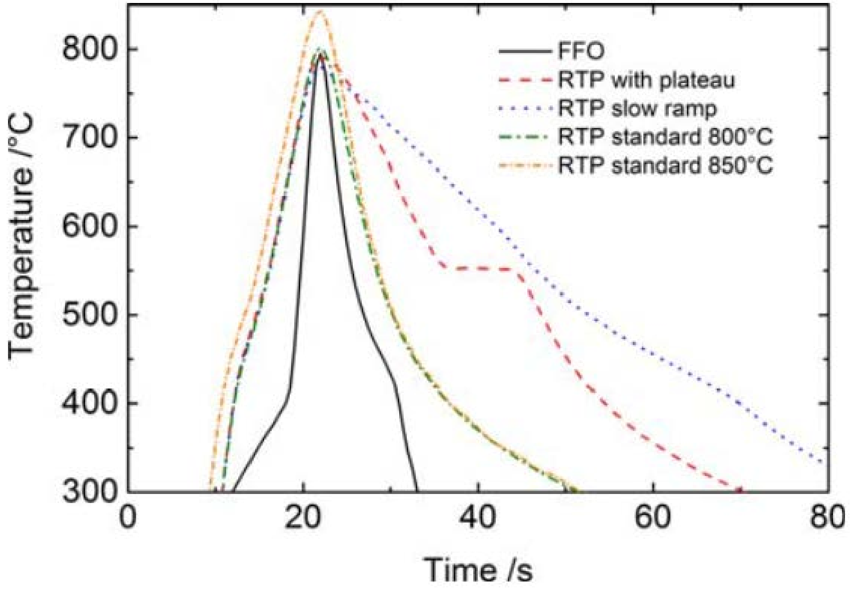
Passivating Contacts and Contact Firing

poly-Si/SiO$_x$ Passivating Contact



*i*V$_{oc}$ (mV)	As-dep	Fired	400 °C Annealed
SiN$_x$/*poly*-Si/*c*-Si	540	590	570
Al$_2$O$_3$/*poly*-Si/*c*-Si	545	650	737

Contact Firing

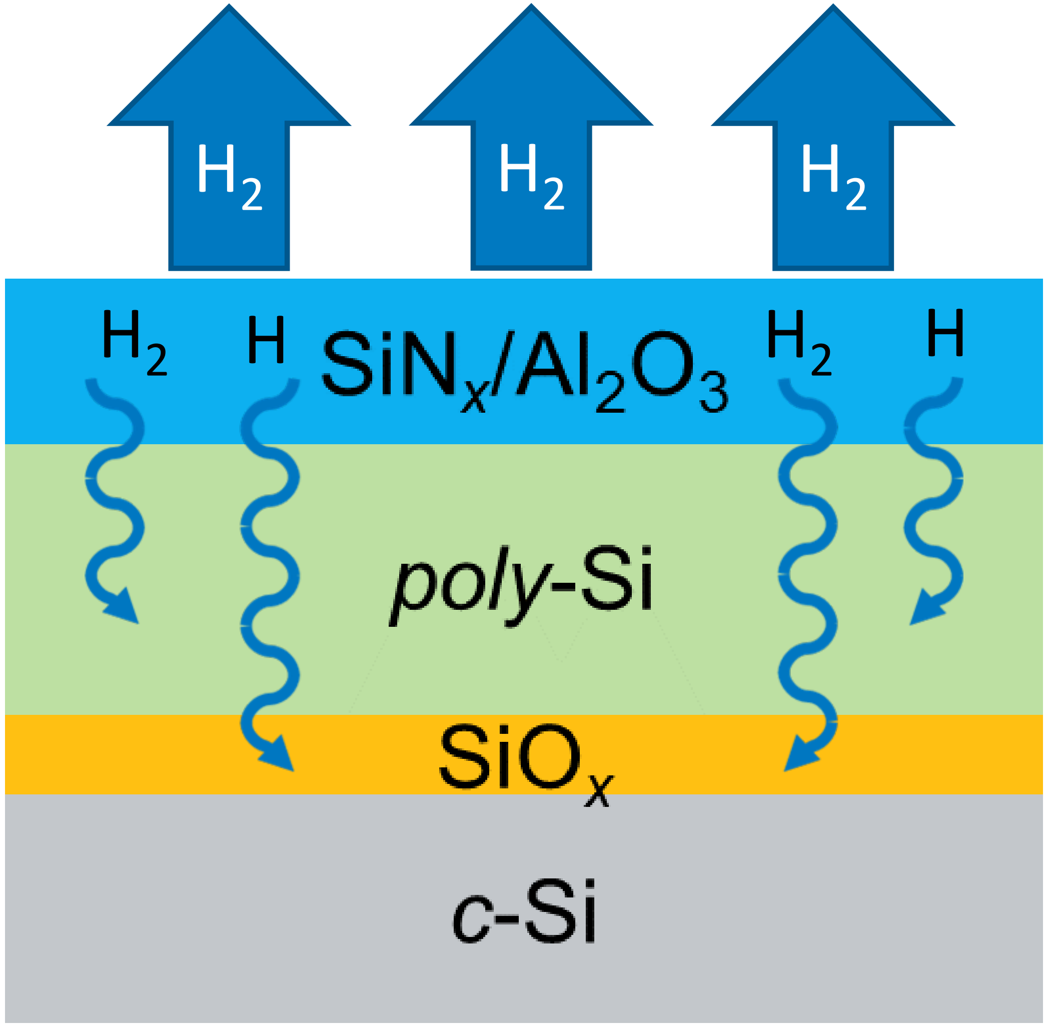


Eberle (2016), Phys. Status Solidi-R

Rapid heating and cooling causes H release from dielectrics

SiN$_x$ does not passivate nearly as well as Al$_2$O$_3$

How Does Hydrogen Reach the Interface from Al_2O_3 and SiN_x?



- SiO_x passivates *c*-Si well, but interface still has dangling bonds
- H mobilizes in Al_2O_3 and SiN_x at T>~400 °C, allowing for diffusion through structure

Meyer (2021), ACS Appl. Nano Mater. **11** 1363-1369

- H diffuses to defects in *poly*-Si, the SiO_x/*c*-Si interface, and into the wafer bulk
- H can be beneficial, but can also create defects such as LeTID

Meyer (2021), Energy Environ. Sci. **14**, 5416-5422

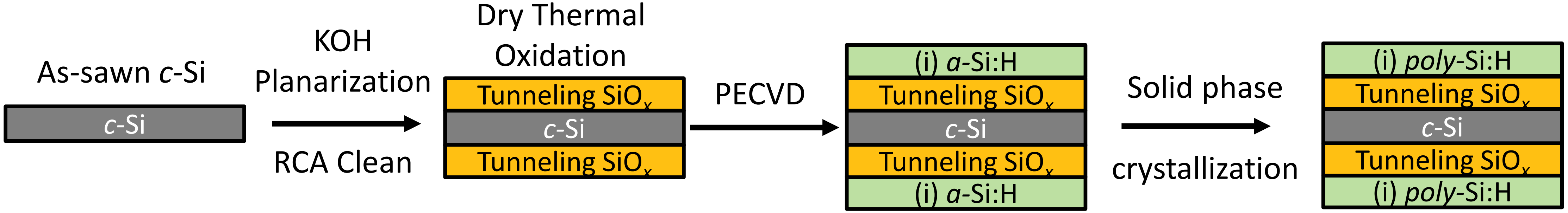
- Al_2O_3 can act as diffusion barrier to prevent H migration

Yang (2022), IEEE J. Photovolt. **12**, 259-266
Jafari (2021), IEEE J. Photovolt. **11**, 1363-1369
Varshney (2019), IEEE J. Photovolt. **10**, 19-27

- Oxides provide O-containing species to aid SiO_2 passivation

Benoit (2007), Microelectron. Eng. **84**, 2169-2172
Devine (1996), Thin Solid Films **286**, 317-320

Sample Fabrication Process Flow



As-sawn *c*-Si

c-Si

KOH Planarization

RCA Clean

Dry Thermal Oxidation

Tunneling SiO_x

c-Si

Tunneling SiO_x

PECVD

(i) *a*-Si:H

Tunneling SiO_x

c-Si

Tunneling SiO_x

(i) *a*-Si:H

Solid phase

crystallization

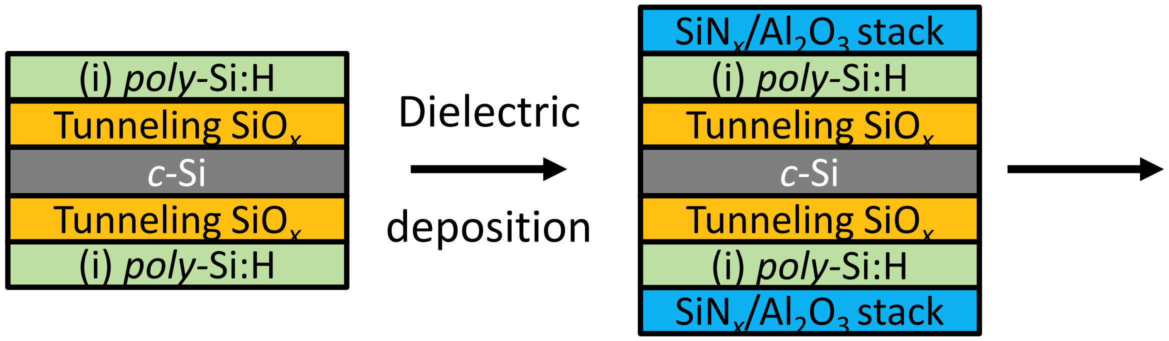
(i) *poly*-Si:H

Tunneling SiO_x

c-Si

Tunneling SiO_x

(i) *poly*-Si:H



(i) *poly*-Si:H

Tunneling SiO_x

c-Si

Tunneling SiO_x

(i) *poly*-Si:H

Dielectric

deposition

SiN_x/Al_2O_3 stack

(i) *poly*-Si:H

Tunneling SiO_x

c-Si

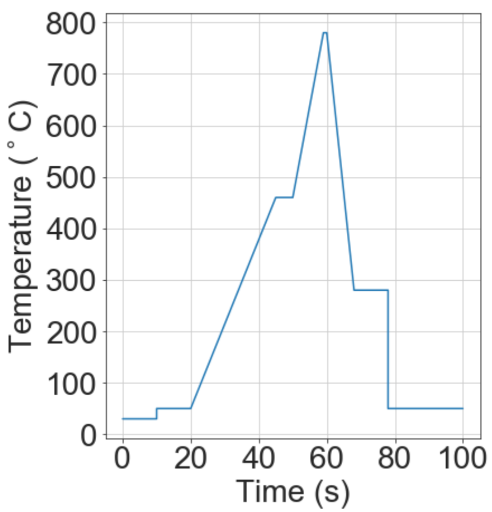
Tunneling SiO_x

(i) *poly*-Si:H

SiN_x/Al_2O_3 stack

Thermal Treatment

Fast firing 780 °C



Diagnostics

FTIR

-SiN_x Bonding

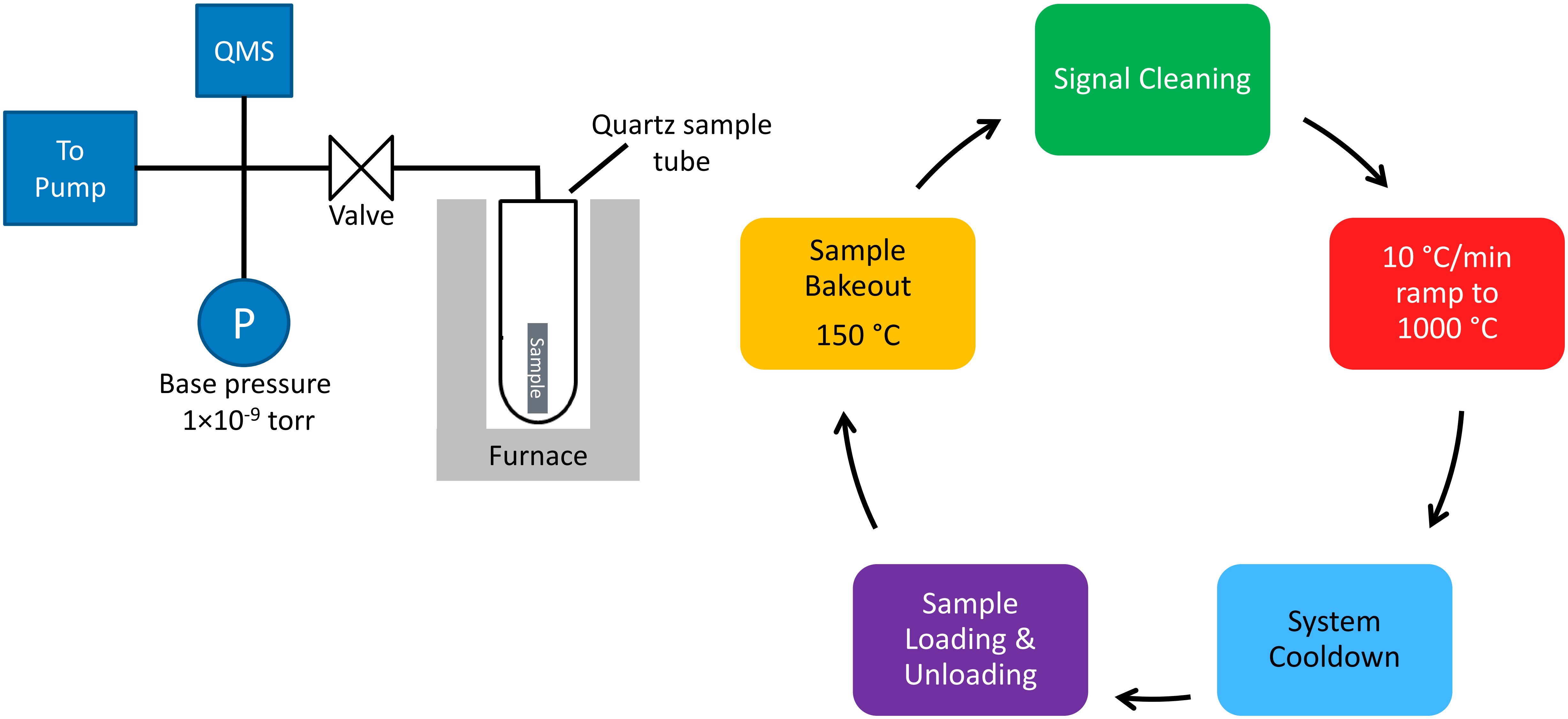
H_2 effusion

-Temperature dependence

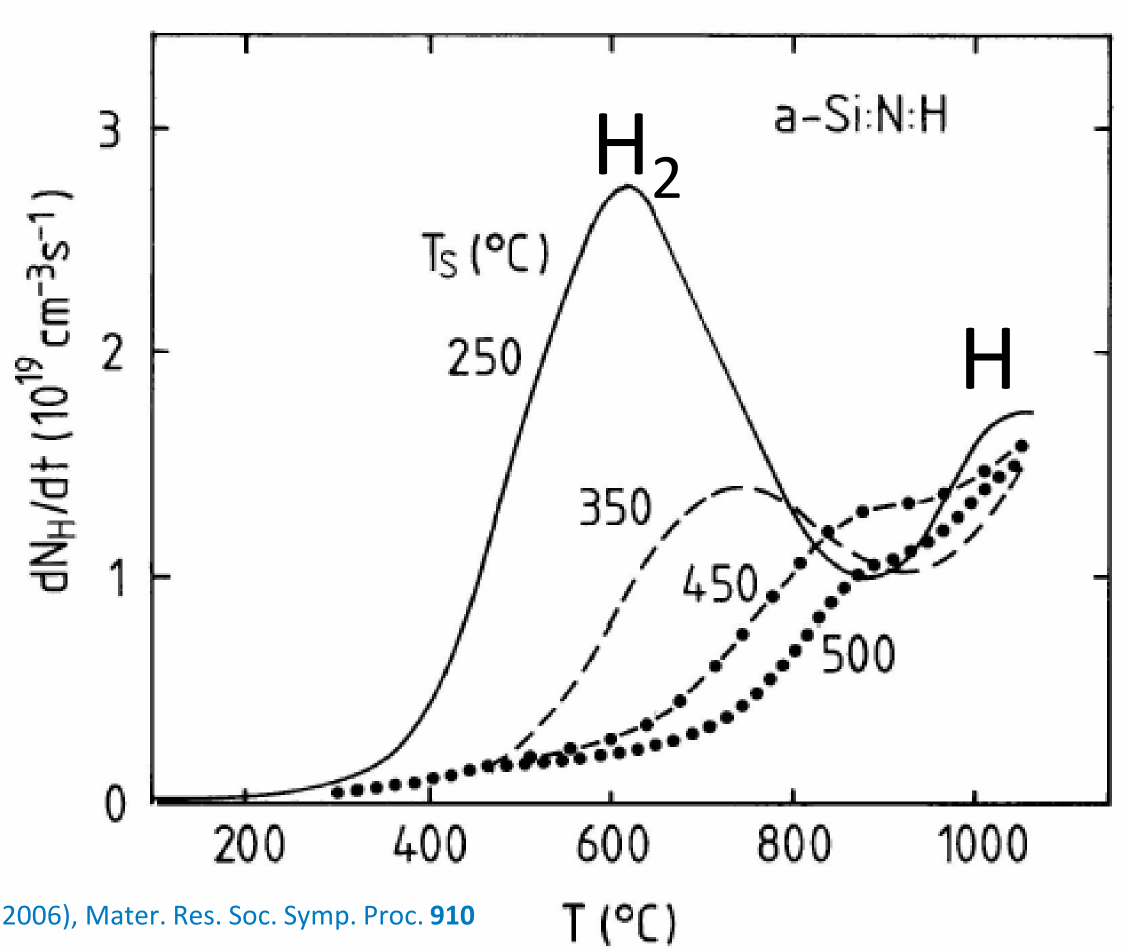
Sinton lifetime testing

-Passivation

Hydrogen Effusion Process Flow



Hydrogen Effusion Peaks from SiN_x Single Layer



Beyer (2006), Mater. Res. Soc. Symp. Proc. **910**

$$Si\text{-}H + Si\text{-}H \rightarrow Si\text{-}Si + H_2$$
$$Si\text{-}H + N\text{-}H \rightarrow Si\text{-}N + H_2$$

Benoit (2007), Microelectron. Eng. **84**, 2169-2172

- Low T: H_2 diffusion in void-rich SiN_x
- High T: atomic H diffusion in denser SiN_x
- Significant discussion in the literature regarding hydrogen diffusion in SiN_x
- Si-H and N-H bond restructuring to release H_2

Jafari (2021), IEEE J. Photovolt. **11**, 1363-1369

Kastner (1987), Disordered Semiconductors, 641-658

- Stability of Si-H vs N-H

Narikawa (1985), Jpn. J. Appl. Phys. **24**, 861-863

Morimoto (1983), Phys. Stat. Sol. (b) **119**, 715-720

  - N-H ~ 4 eV while Si-H ~ 3.3 eV
  - Si may take H from N-H bonds at high T

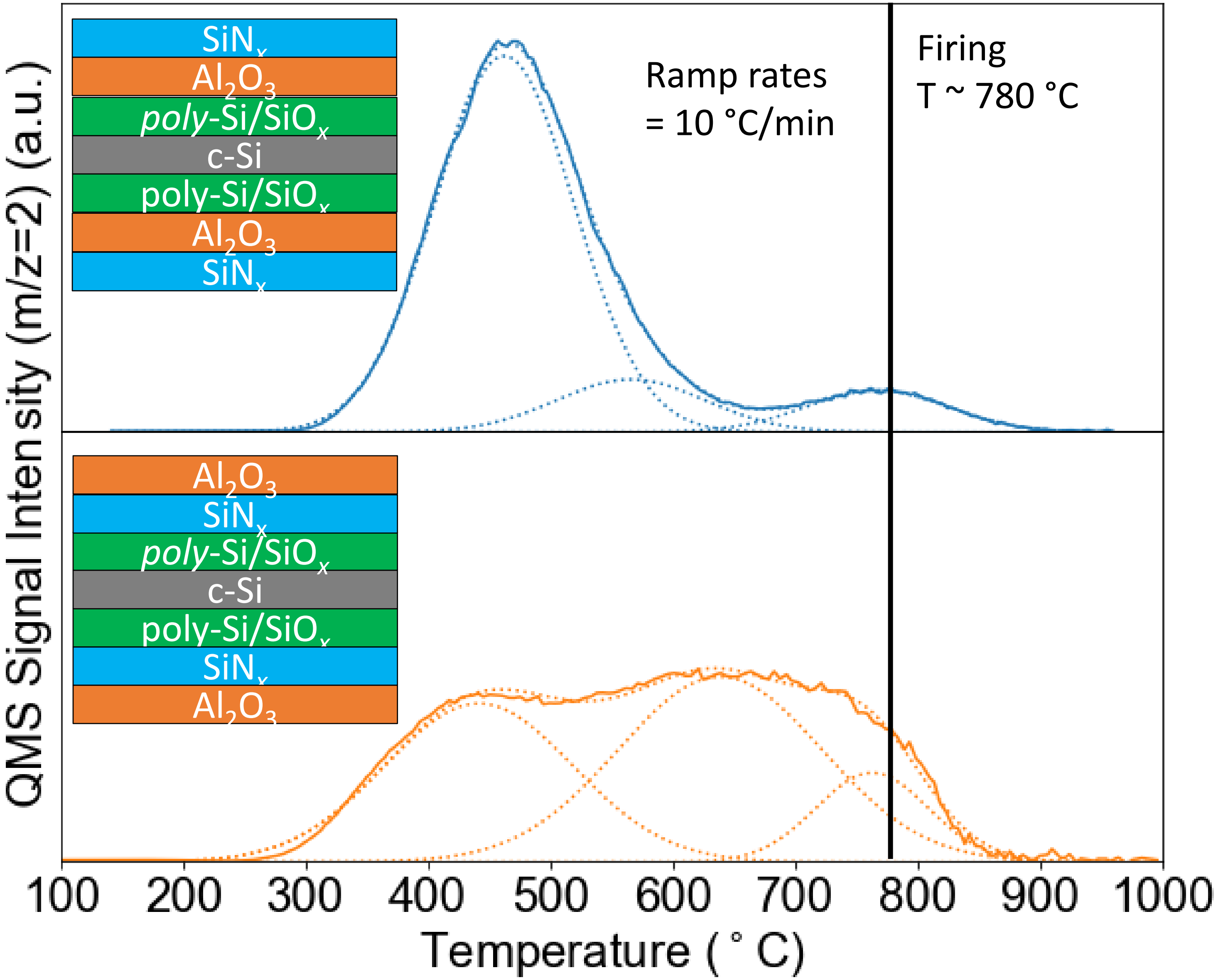
- Diffusion as molecular H_2 or atomic H

Cartier (1993), Appl. Phys. Lett. **63**, 1510-1512

Sheoran (2008), Appl. Phys. Lett. **92**, 172107

Boehme (2000), J. Appl. Phys. **88**, 6055-6059

Hydrogen Effusion Peaks from SiN_x/Al_2O_3 Stacks



- Total H effused does not change, as all is removed by 1000 C
- First curve looks very similar to our SiN_x only case – two main peaks
- Thermal stability would not change, but diffusion *through* Al_2O_3 is hampered
- Al_2O_3 is indeed a barrier layer, resulting in more H release around the peak firing temperature

Incremental Ramps Indicate Out-Diffusion Temperatures

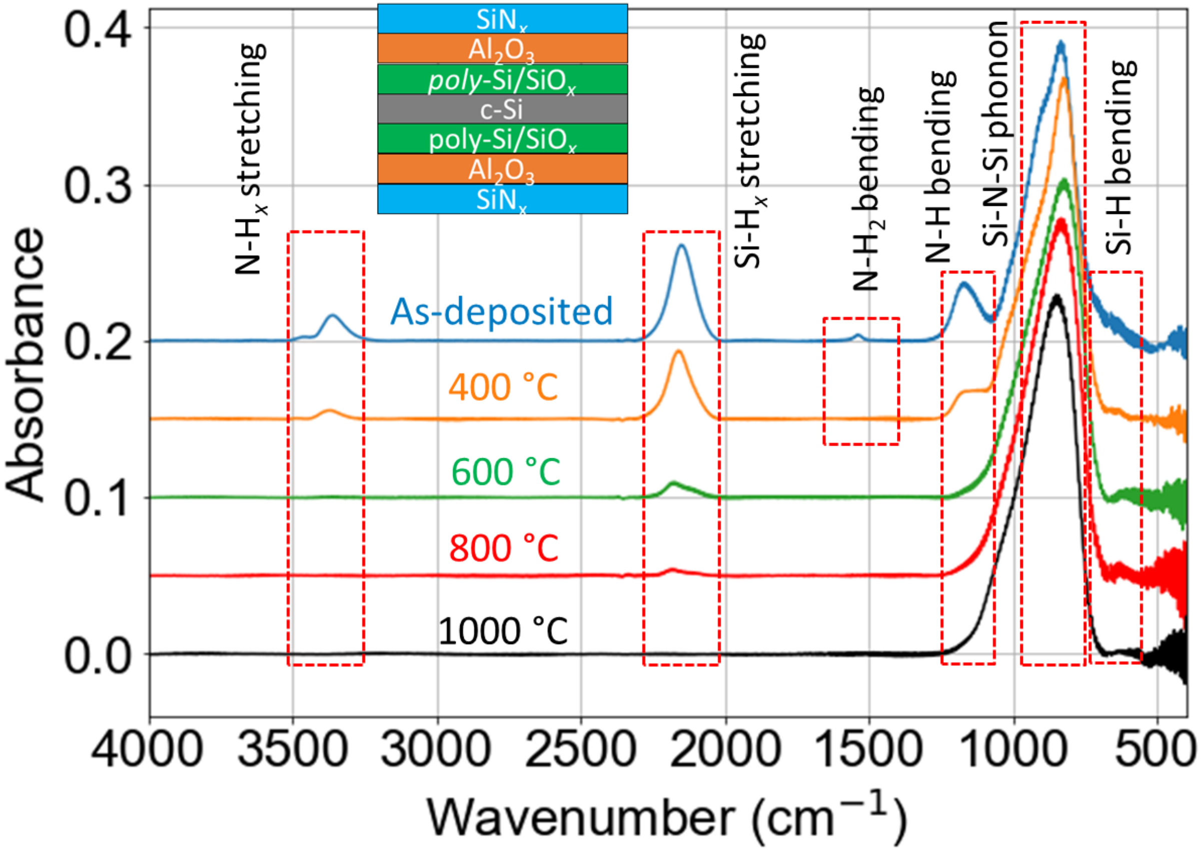
Deposit dielectric stacks → Measure FTIR

Heat to 400 °C @ 10 °C/min → Measure FTIR

Heat to 600 °C @ 10 °C/min → Measure FTIR

Heat to 800 °C @ 10 °C/min → Measure FTIR

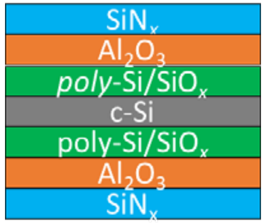
Heat to 1000 °C @ 10 °C/min → Measure FTIR



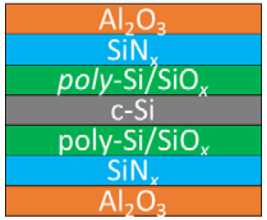
Measurement of sample bonding after elevated temperature relates H release to peak annealing temperature

Al_2O_3 Cap Retains H Up to Higher Temperatures

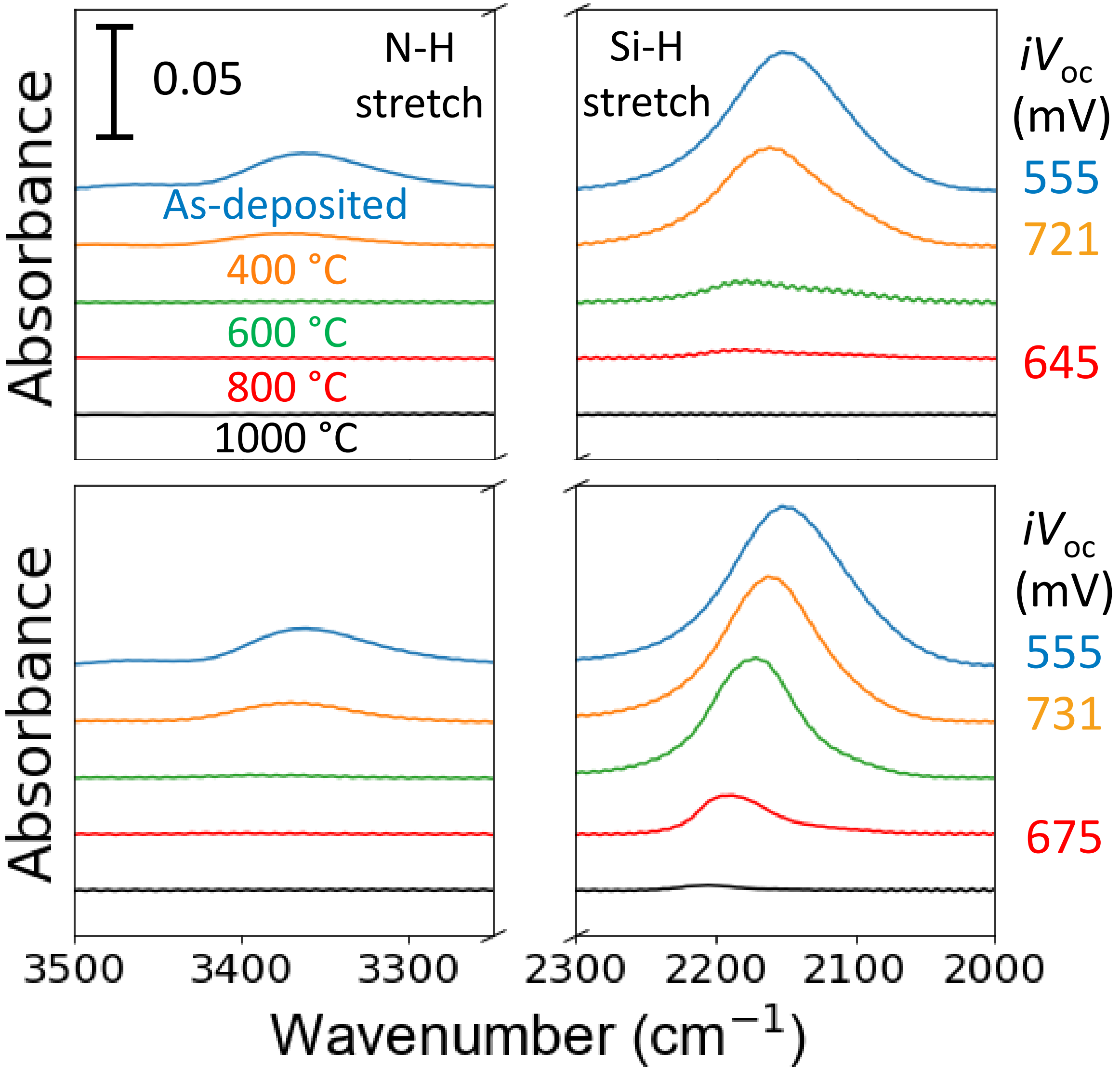
- Without Al_2O_3 cap, most hydrogen is lost by 600 °C
- With Al_2O_3 cap, hydrogen is retained up to 800 °C
- N-H bonds are lost before Si-H bonds
- Passivation is best with 400 °C anneal, worsens with firing
- Changes in the range 400-800 °C could be related to passivation



SiN_x
Al_2O_3
poly-Si/SiO_x
c-Si
poly-Si/SiO_x
Al_2O_3
SiN_x



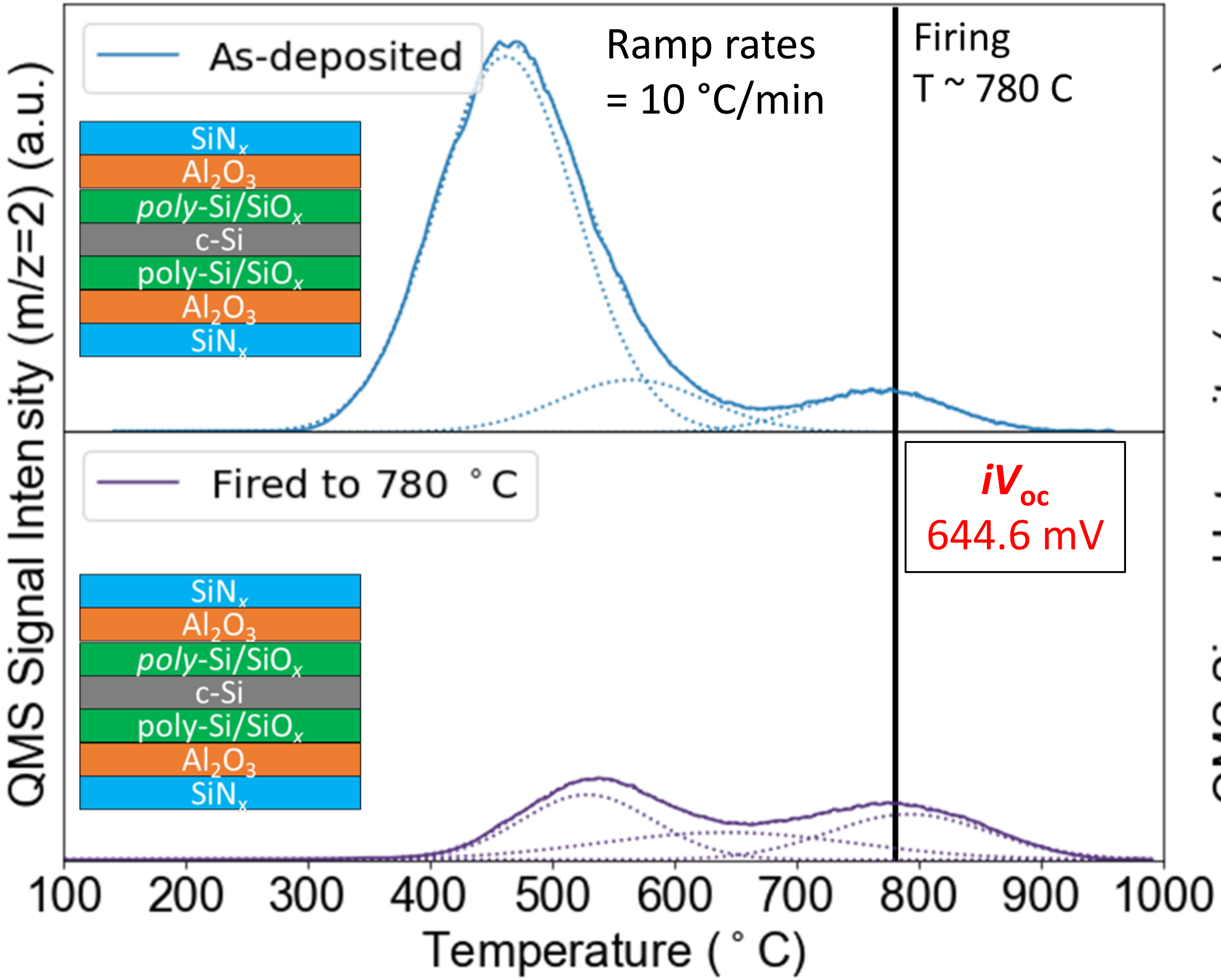
Al_2O_3
SiN_x
poly-Si/SiO_x
c-Si
poly-Si/SiO_x
SiN_x
Al_2O_3



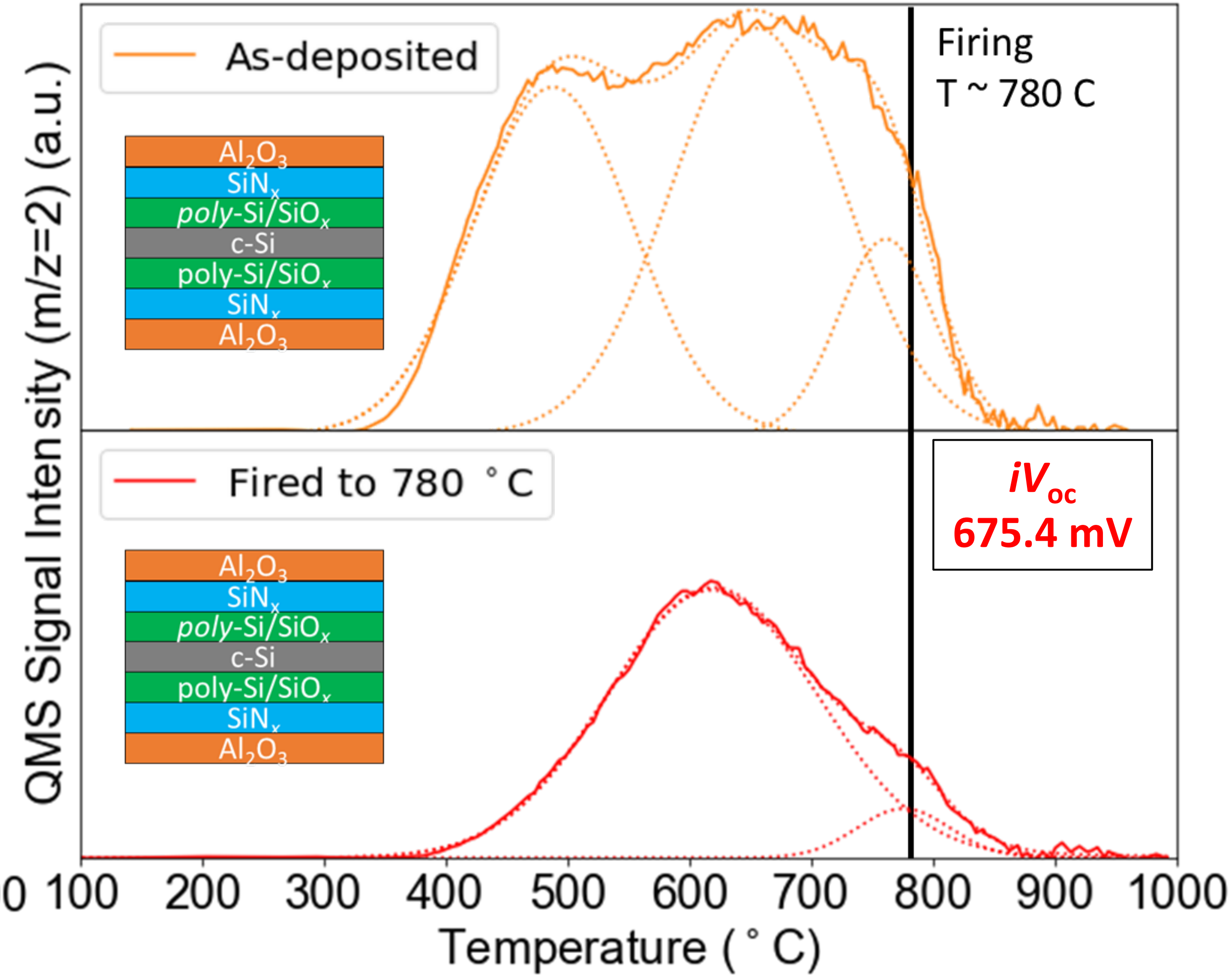
Stability of H in each film stack is better understood, but cannot be directly compared to firing

Stein (1979), J. Electrochem. Soc. **126**, 1750-1754

Firing Drastically Changes Effusion Profiles

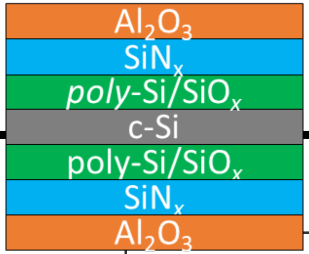


H content is drastically reduced, primarily from low-temperature peak

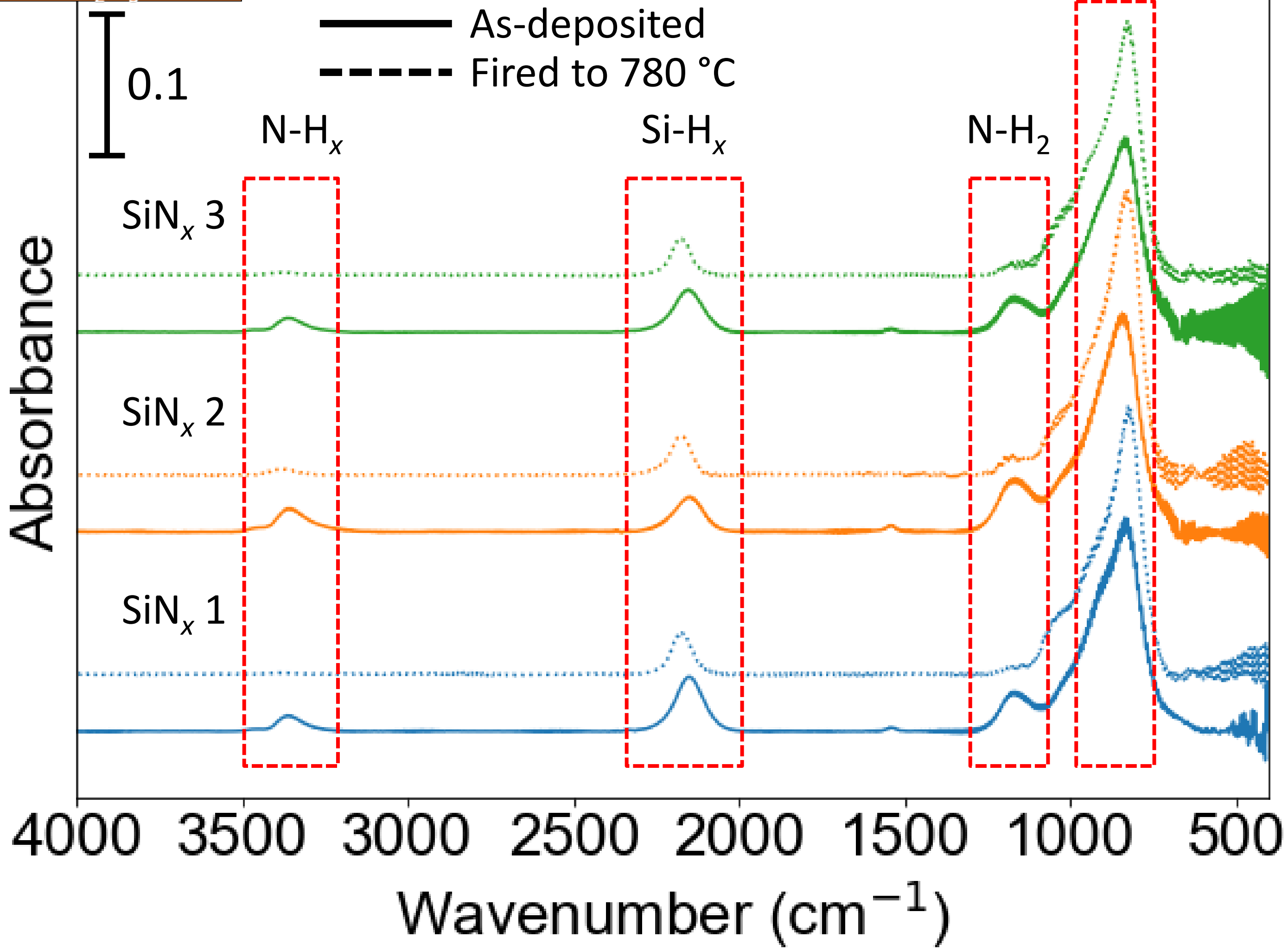


Change in SiN_x structure increases stability of H bonding within films

Morimoto (1983), Phys. Stat. Solidi (b) **119**, 715-720



Passivation of SiN_x Recipes Following Firing

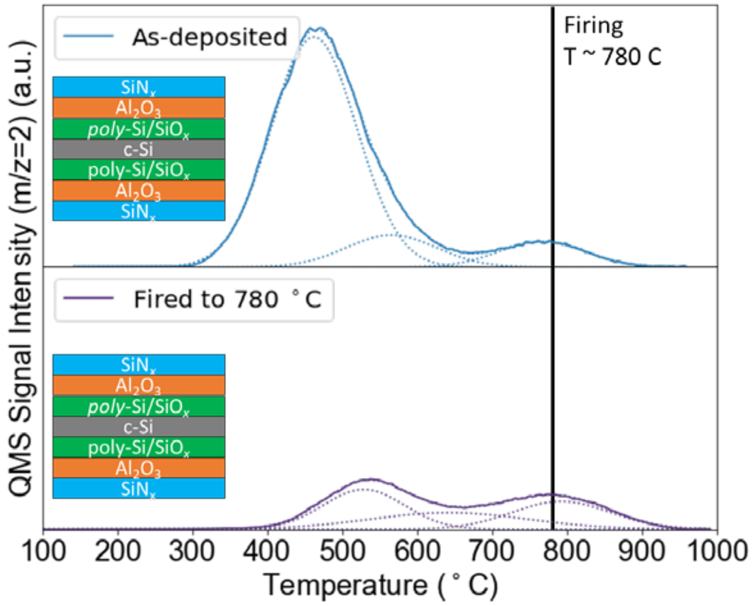


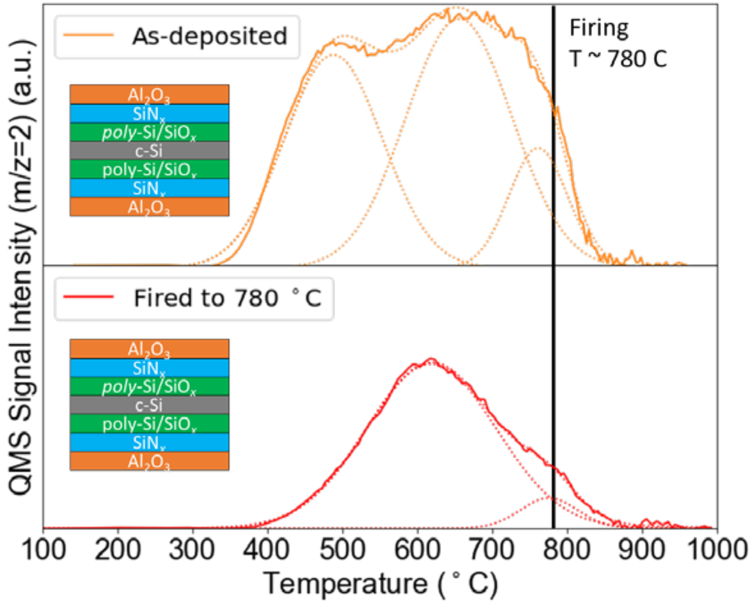
iV_{oc} (mV)		
SiN_x	As-dep	Fired
1	571	649
2	537	699
3	544	699

- N-H bonding lost in SiN_x 1, remains in 2 and 3
- Best passivation observed for SiN_x films where more H is retained in SiN_x

Summary

- SiN_x and Al_2O_3 dielectric stacks on *poly*-Si/SiO_x release hydrogen upon heating; H likely migrates to the SiO_x/*c*-Si interface
- Al_2O_3 prevents effusion of H_2 at lower temperatures and shifts the peak H_2 release temperature
- Restructuring of SiN_x during firing increases stability of Si-H bond through increased N back-bonding
- Passivation quality is correlated to amount of H released close to the peak firing temperature





Concluding Question

- What species passivates the SiO_x/*c*-Si interface?
- Atomic or molecular hydrogen?
- Other species such as O, O_2, OH, or H_2O?

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NREL Si PV Group

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- Caroline L. S. de Souza
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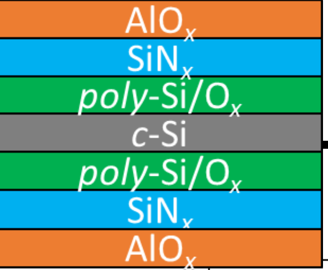
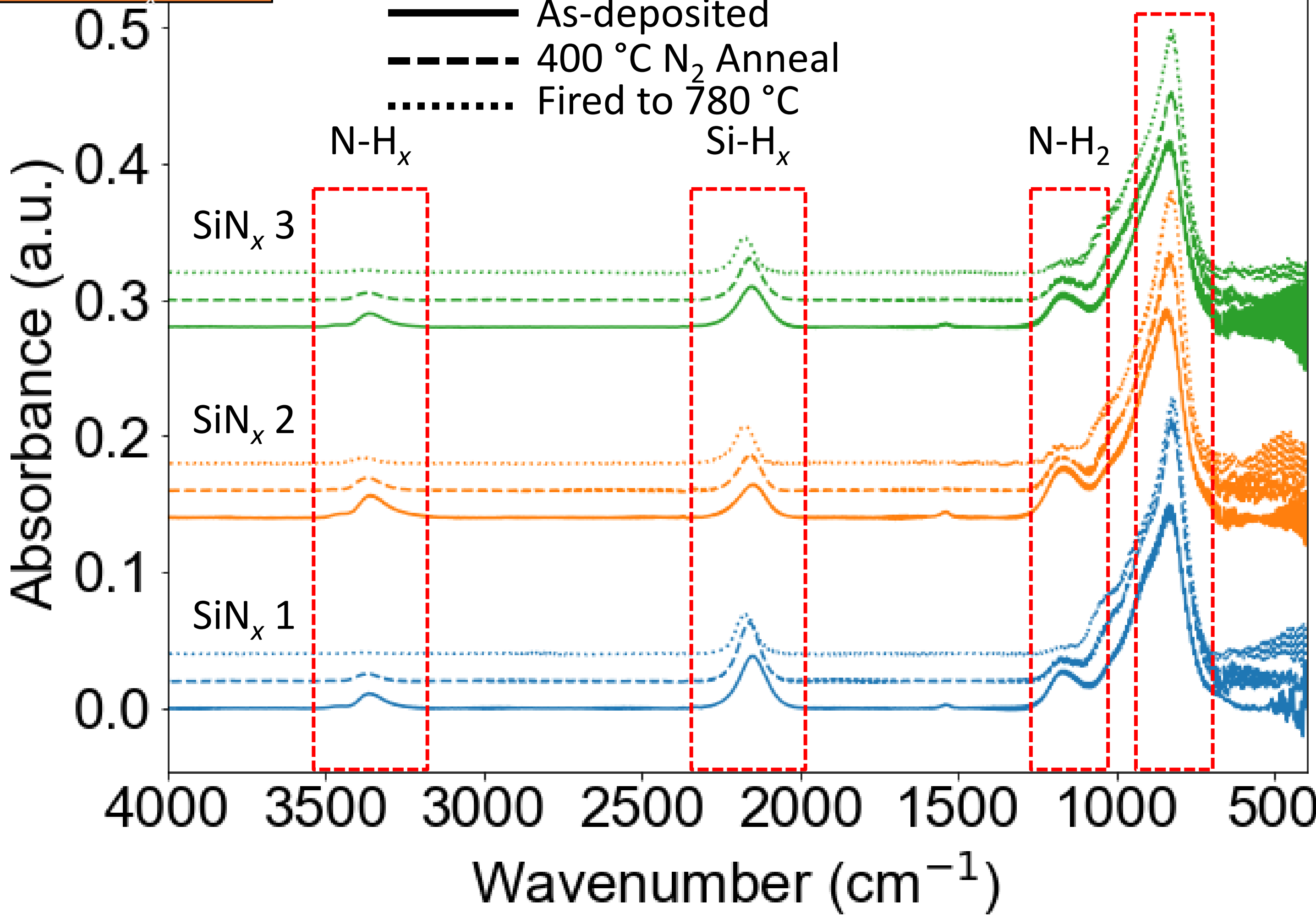
Fast Firing vs 1 hr 400 °C Anneal in N_2





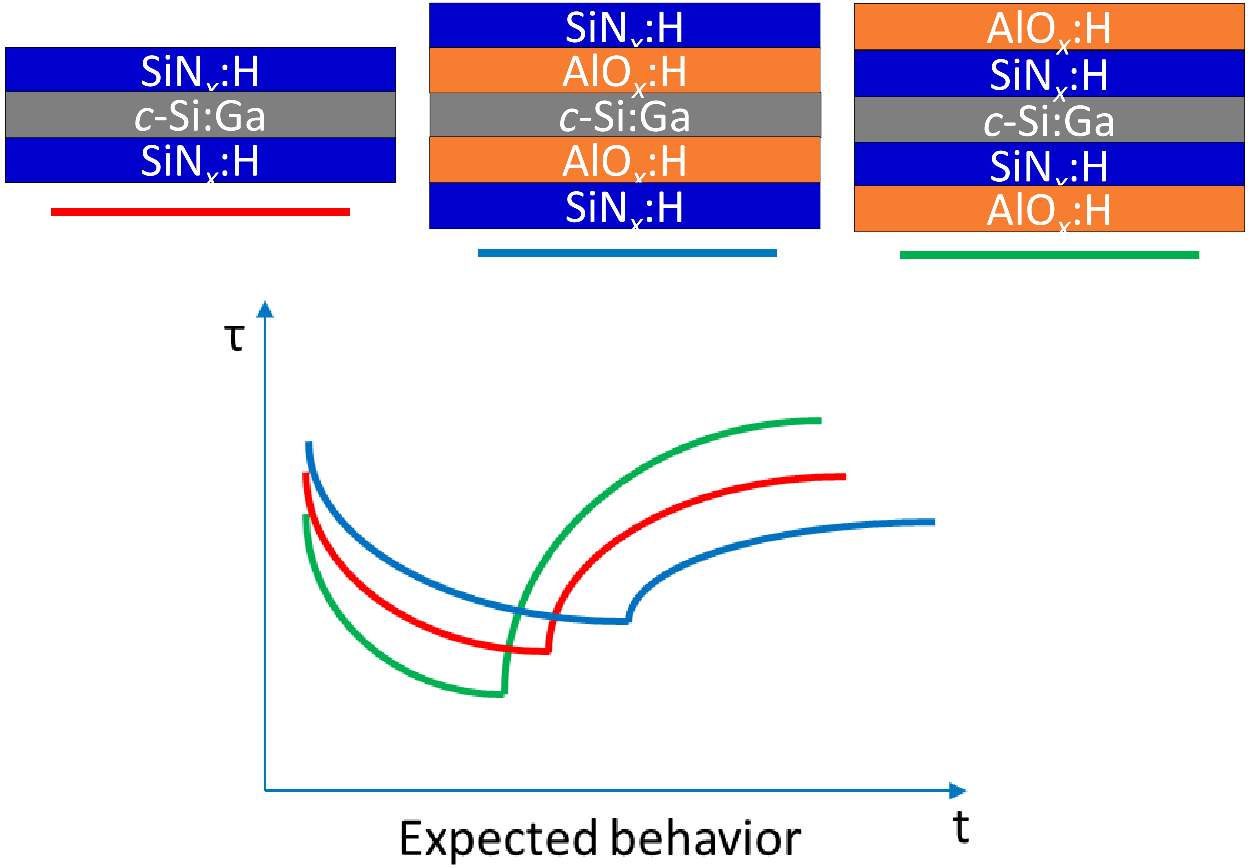
***iV_{oc}* (mV)**			
SiN_x	As-dep	Fired	N_2 Anneal
1	571	649	728
2	537	699	737
3	543	699	670

- Ambient H not needed – sufficient amount of bonded H exists in these stacks
- Expect to see more N-H bonding in Paul's SiNx, which has best passivation condition
  - We do see this, but why not clear difference in KOH, which is "bad"?

After this is mostly just data

Future Investigations: H Injection for LeTID

- **H has been proven as the source of LeTID**
- **Control amount of H injection and thus, degradation with AlOx interlayers**
- **More H should degrade faster, regenerate higher**

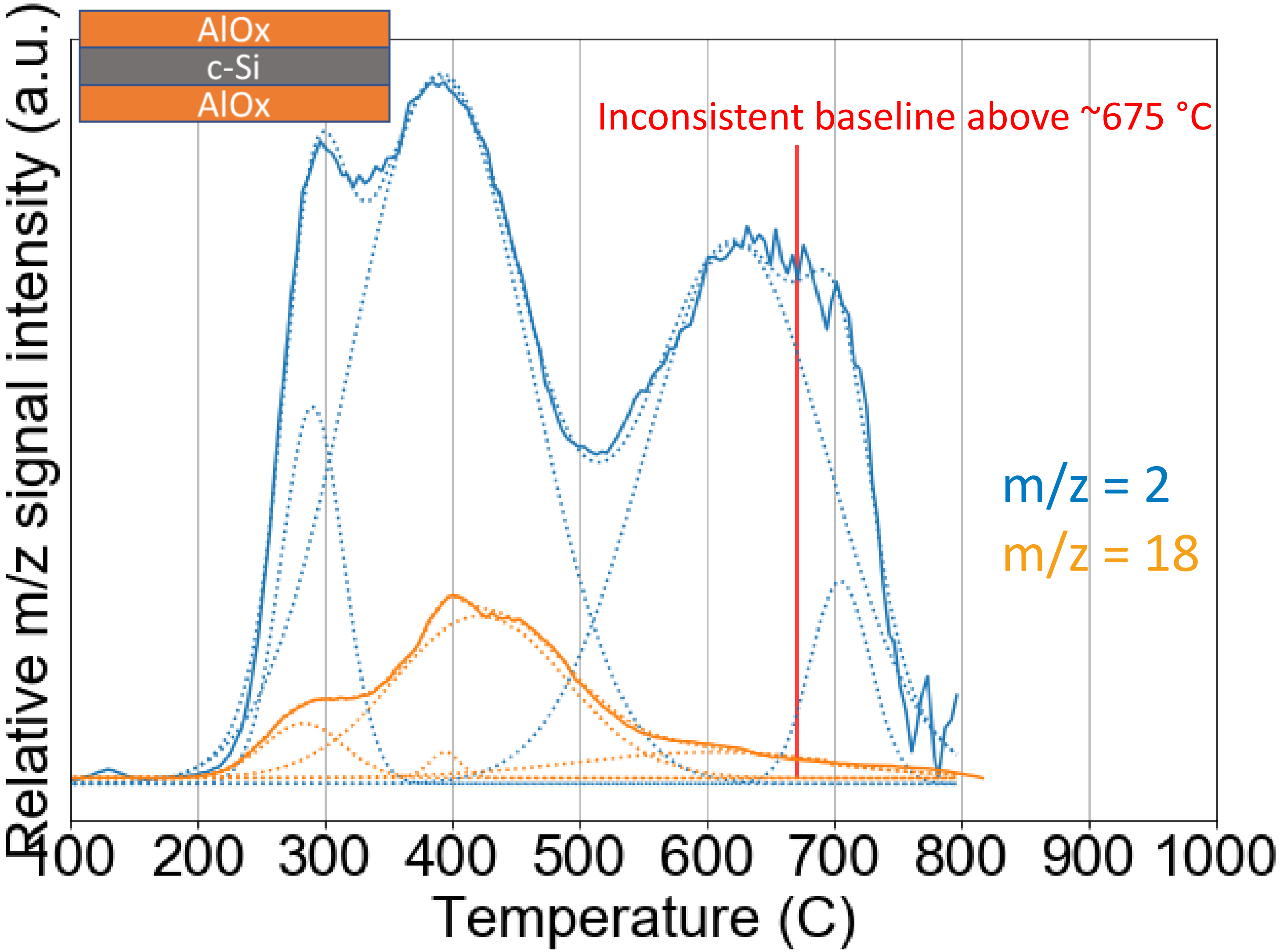


Expected behavior

Increased H injection from AlOx cap should result in faster degradation, followed by increased degradation

Meyer (2022), Energy Environ. Sci.

AlO_x H effusion and N_2 Annealing Passivation



- Passivation with AlO_x at ~ 400 °C provides better passivation than SiN_x
- Effusion curves show m/z = 2 correlates well with m/z = 18 up to ~ 500 °C
- Additional peak exists between annealing and firing temperature

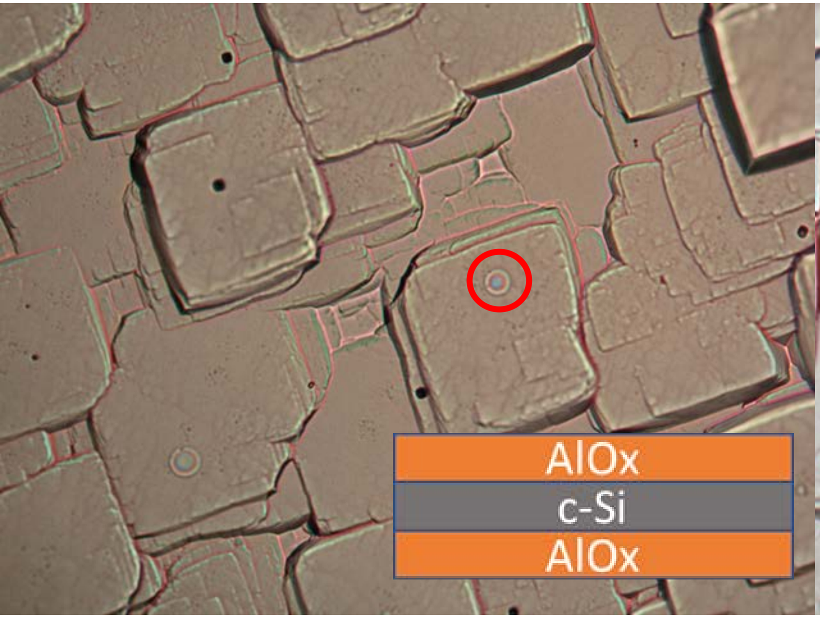
Dingemans (2012), J. Appl. Phys.

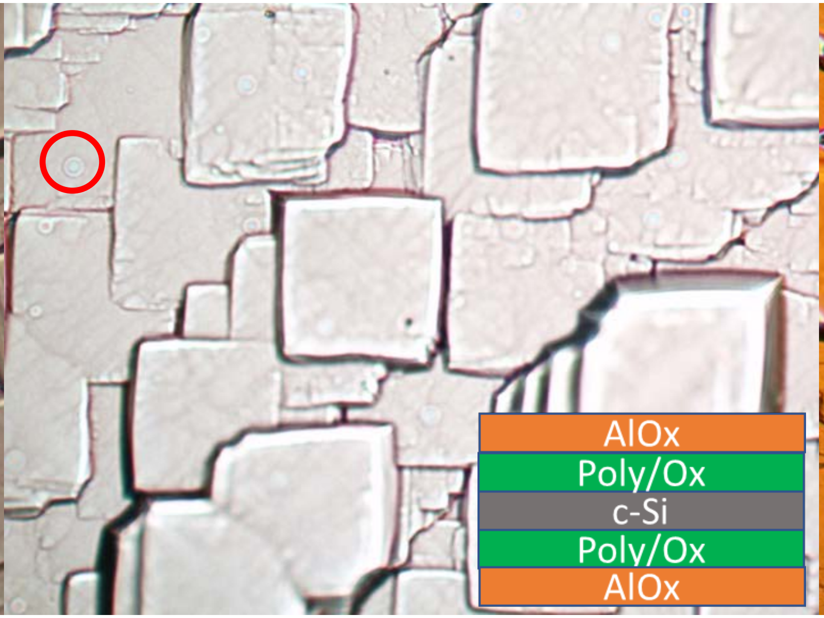
iVoc data for structures

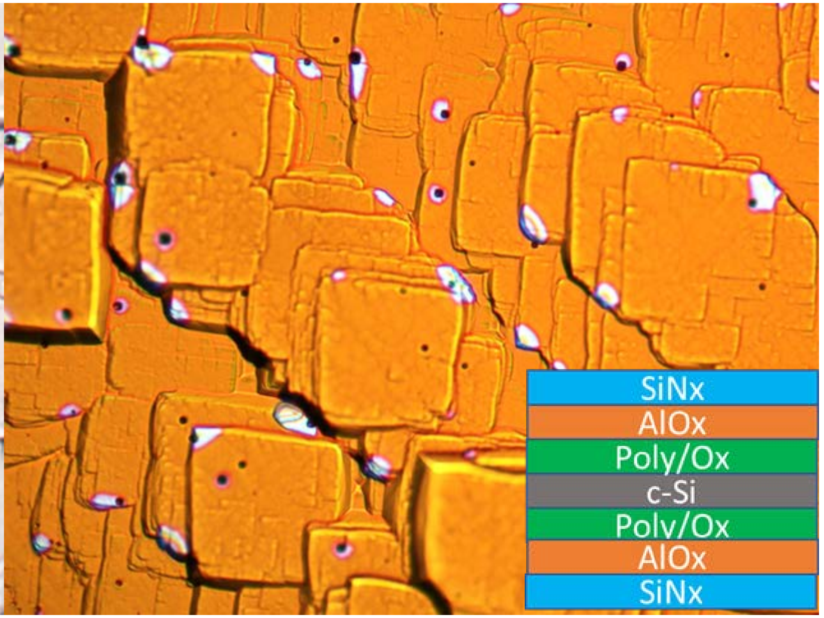
Sample type	As-dep	Fired	FGA’d	FGA’d & Fired
AlOx/c-Si	645	700	726	720
SiNx/c-Si	620	590	676	590
Poly/c-Si	535	525	567	560
SiNx/poly/c-Si	540	590	570	586
AlOx/poly/c-Si	545	650	737	716
AlOx/SiNx/poly/c-Si	555	675	731	701
SiNx/AlOx/poly/c-Si	555	645	721	686
Tempress SiNx/p-poly/c-Si	625	670	660	680

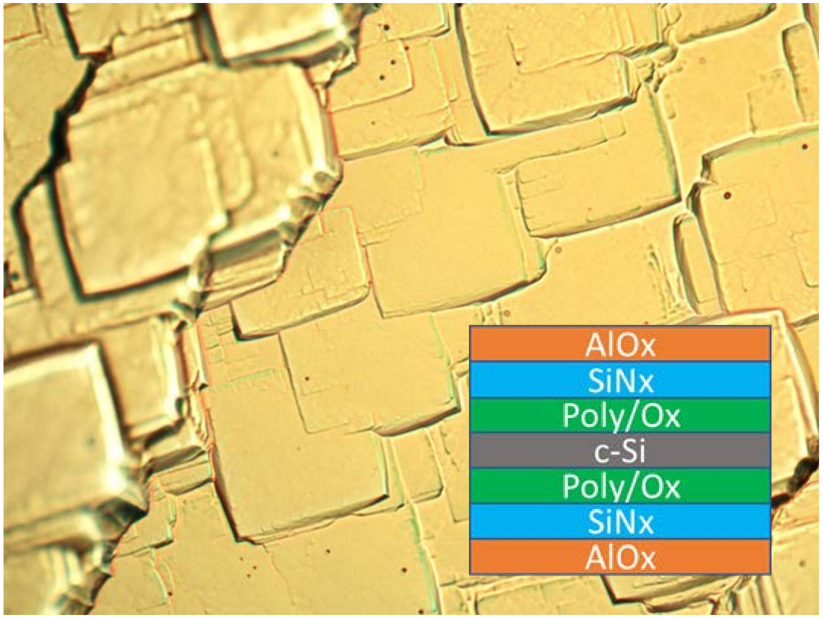
COMPONENT INFORMATION/ BACKUP SLIDES

Blistering on AlOx films



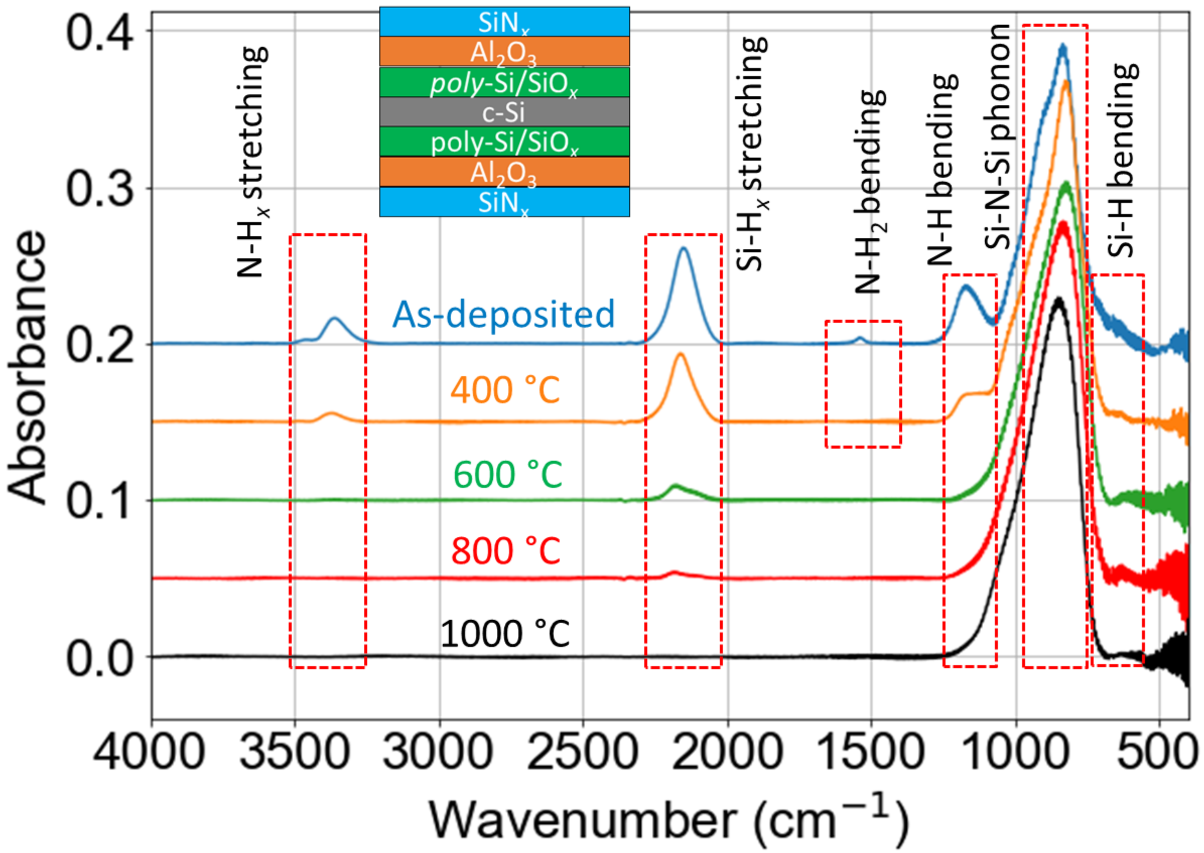


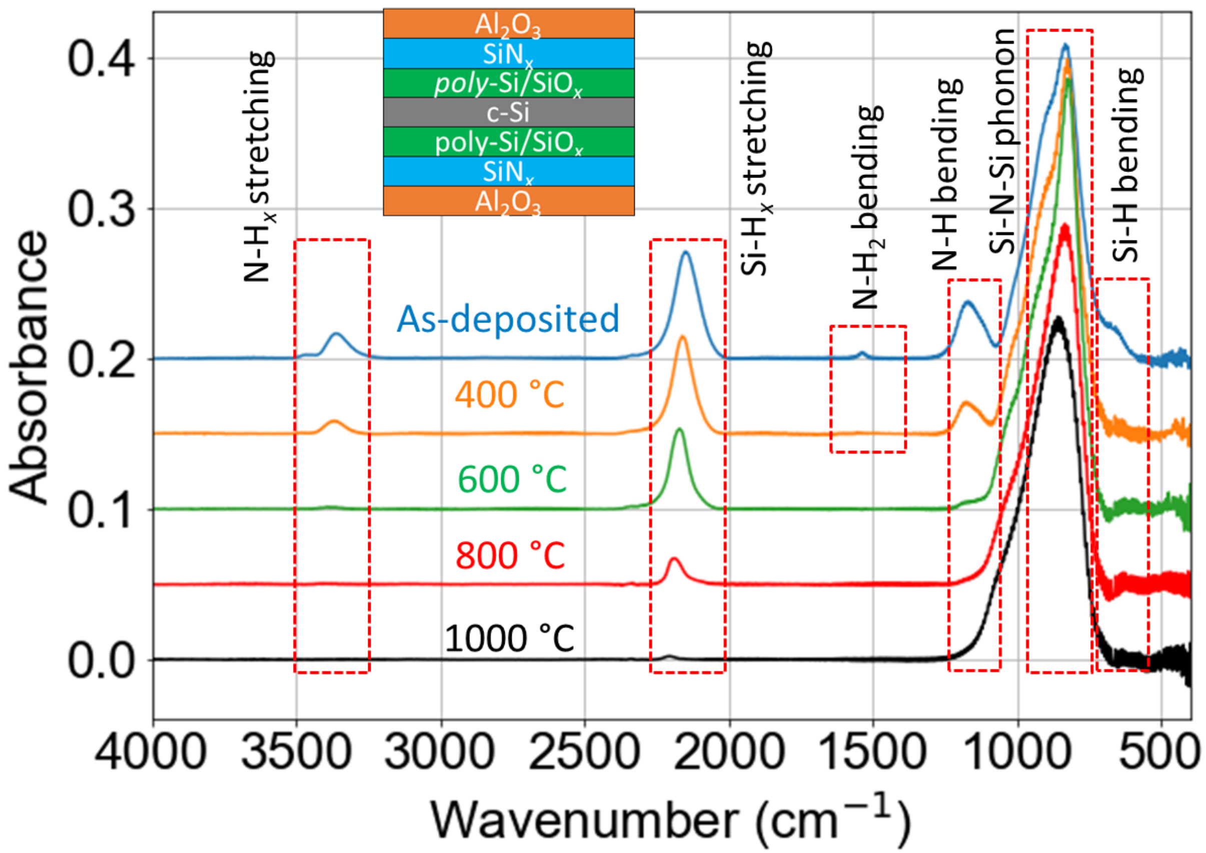




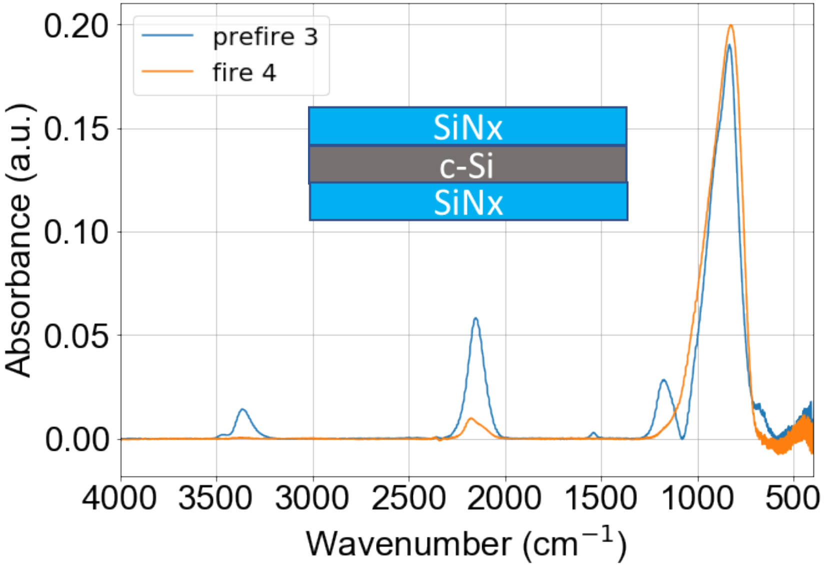
- Bill expressed concern that AlOx films > few nm blister after firing (he was right)
- Not sure that this would have effect on our FTIR or effusion measurements
- Blisters appear to be deflated (not exploded)
- Blisters don’t appear when AlOx is capping layer

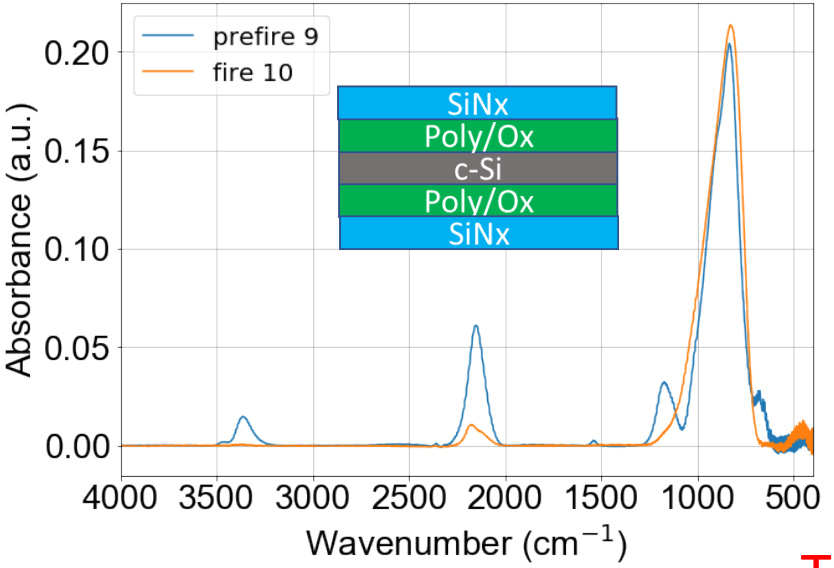
FTIR spectra after incremental temperature ramps



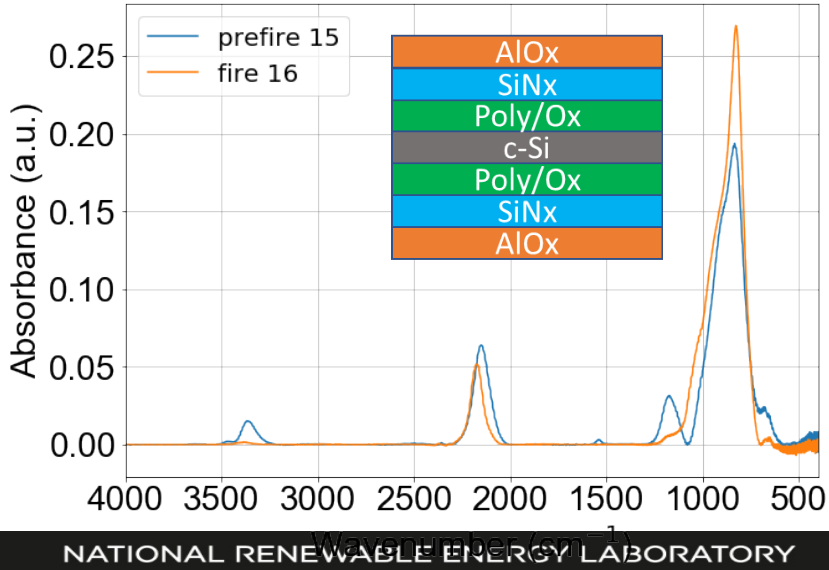


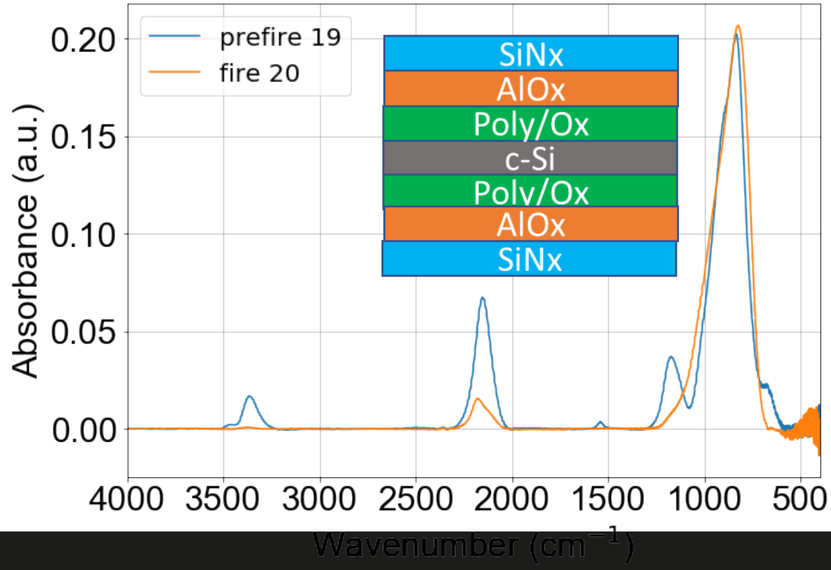
FTIR of fired samples vs unfired

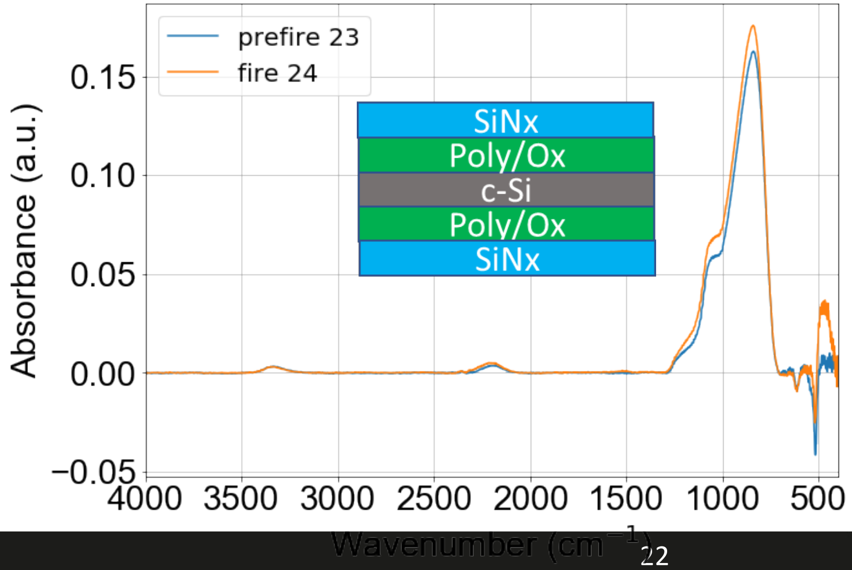




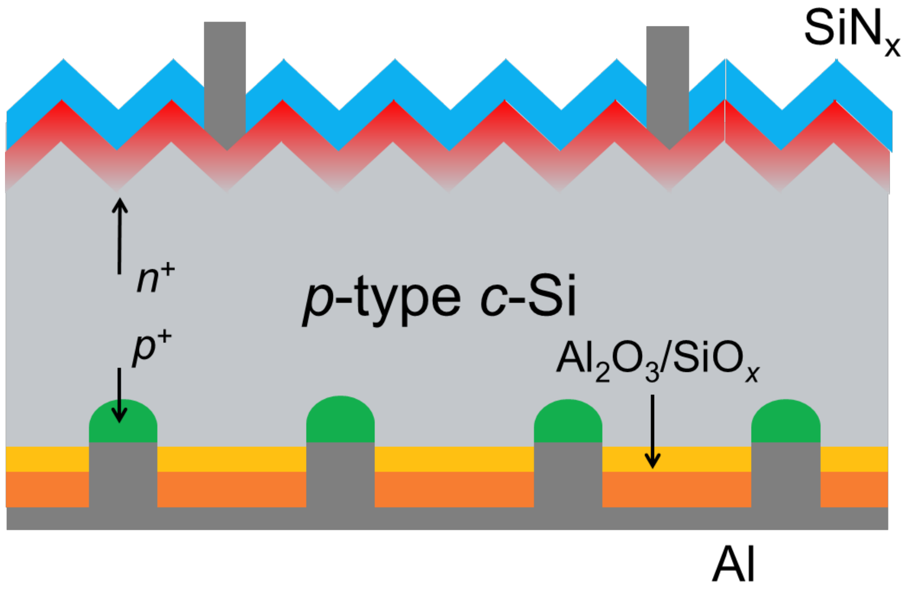
Tempress







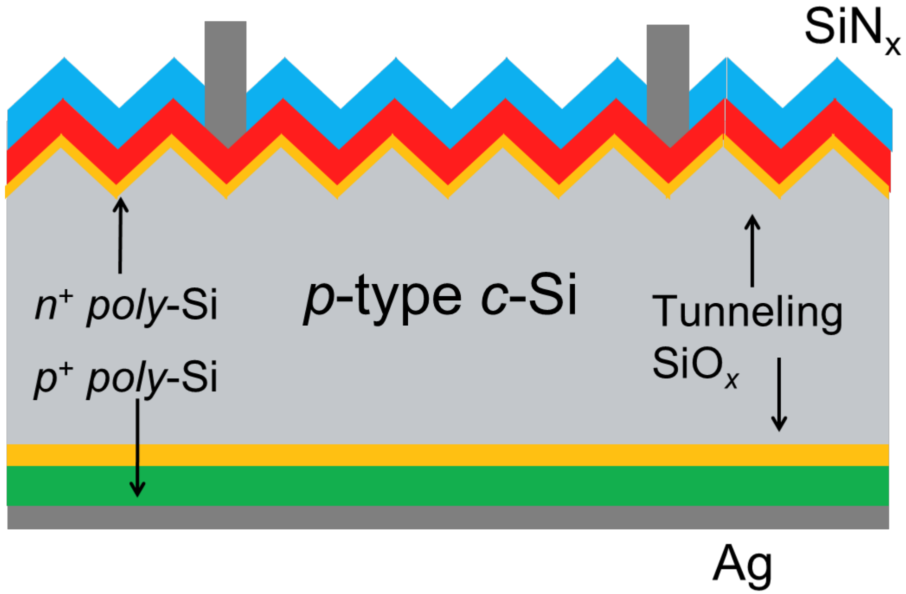
Drastic Passivation Difference Between Al_2O_3 and SiN_x



Green (2015), Sol. Energ. Mat. Sol. C.

PERC

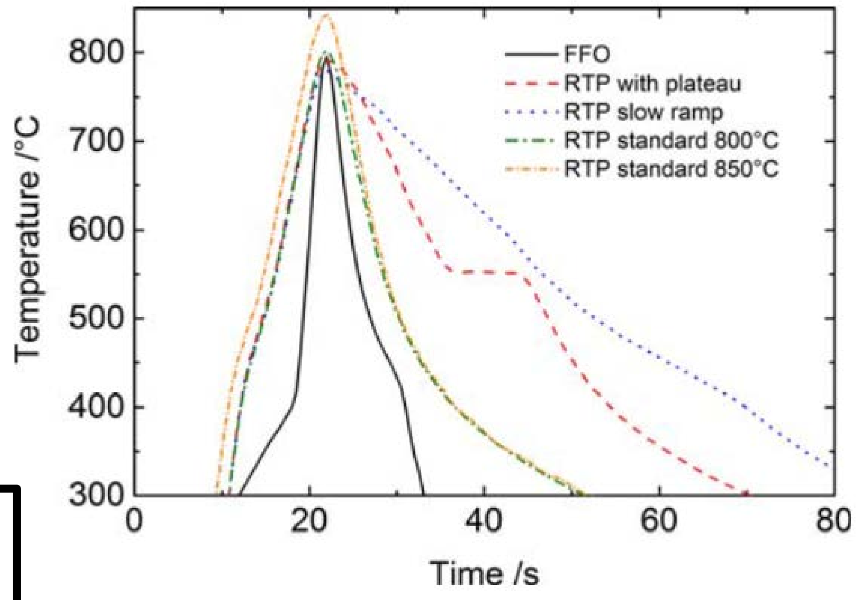
- Industry standard
- Low $J_{0,surface}$
- Improved transport



poly-Si/SiO_x Passivating Contact

- Industrial future
- No metal/*c*-Si contact
- Better transport

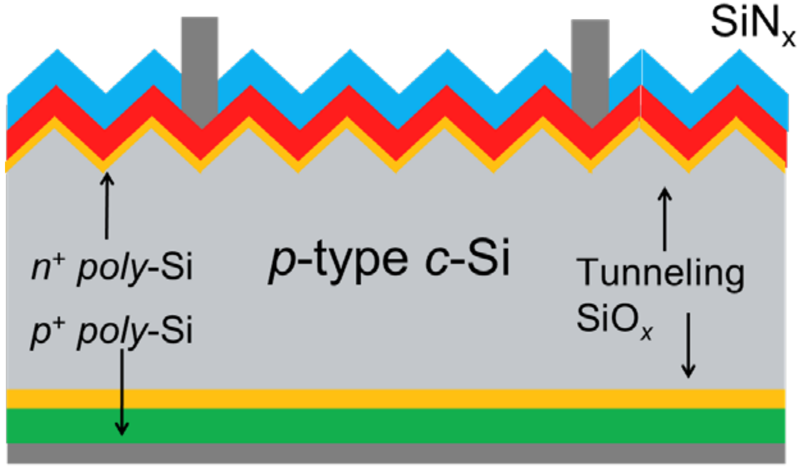
Contact Firing



Rapid heating and cooling causes H release from dielectrics

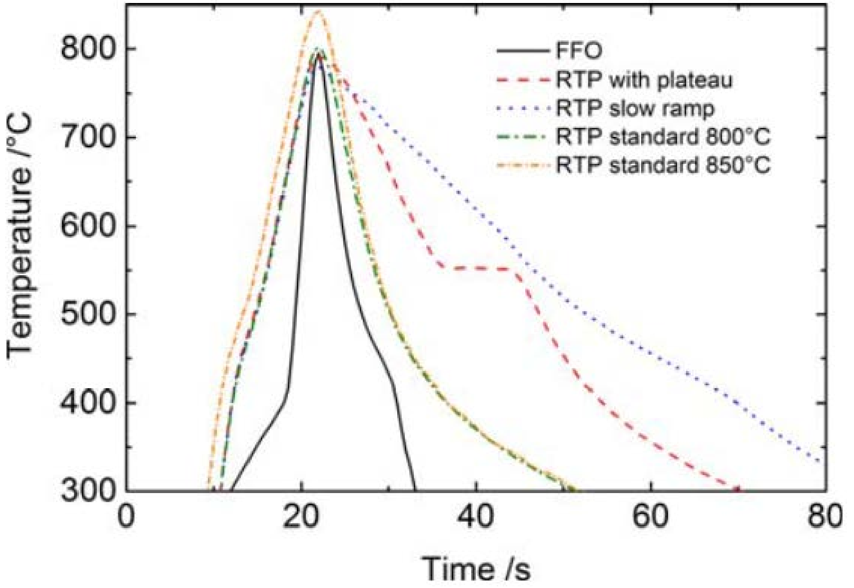
Eberle (2016), Phys. Status Solidi-R

Firing of Cells Requiring H-rich Dielectrics



poly-Si/SiO$_x$ Passivating Contact

Contact Firing

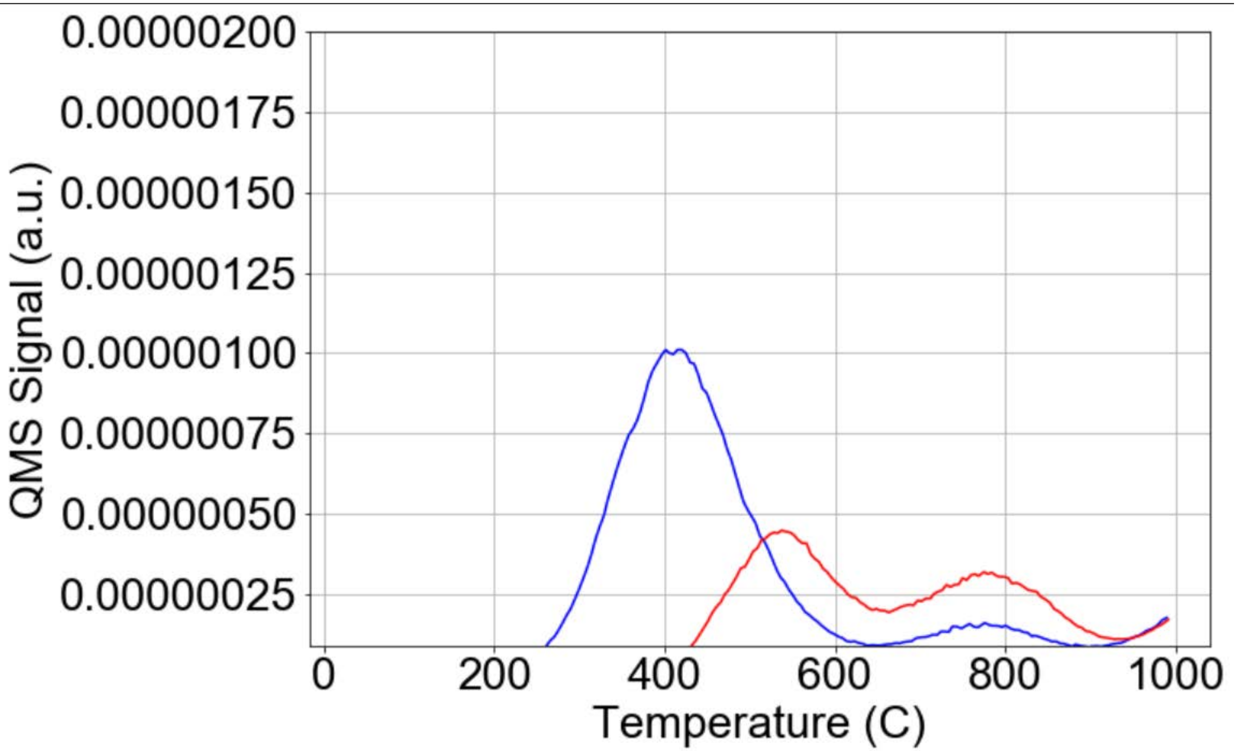


Eberle (2016), Phys. Status Solidi-R

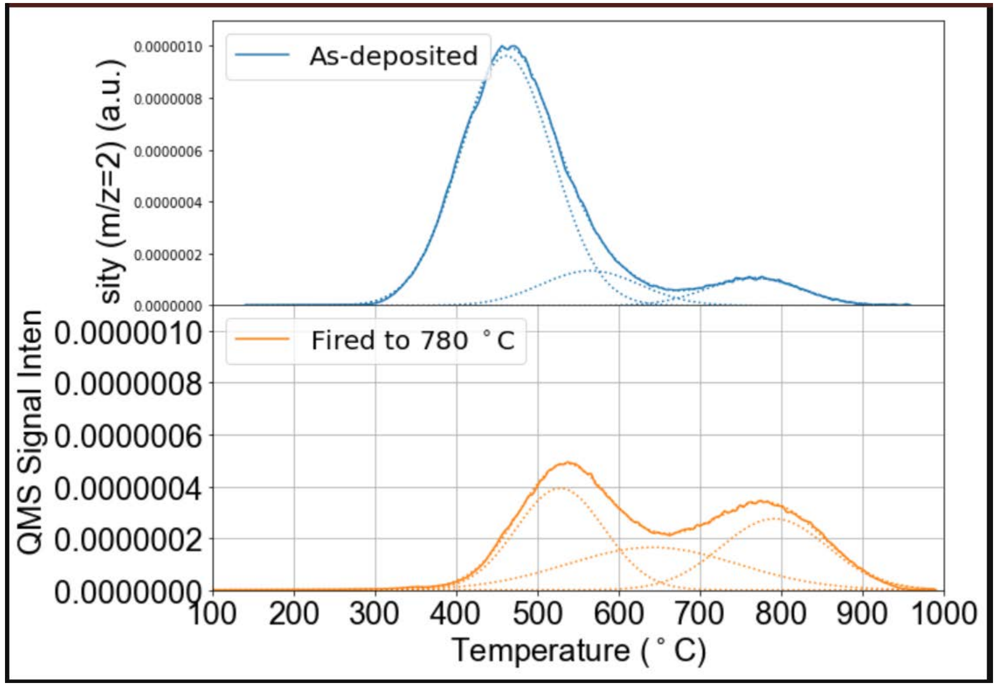
iV_{oc}	As-dep	Fired	400 °C Annealed
SiN$_x$/*c*-Si	620	590	676
Al$_2$O$_3$/*c*-Si	645	700	726
SiN$_x$/*poly*-Si/*c*-Si	540	590	570
Al$_2$O$_3$/*poly*-Si/*c*-Si	545	650	737

Rapid heating and cooling causes H release from dielectrics

SiN$_x$ does not passivate nearly as well after firing as Al$_2$O$_3$, despite also providing H to SiO$_x$/*c*-Si interface – why?



0.00000200
0.00000175
0.00000150
0.00000125
0.00000100
0.00000075
0.00000050
0.00000025
QMS Signal (a.u.)
0
200
400
600
800
1000
Temperature (C)



As-deposited
Fired to 780 ° C
QMS Signal Intensity (m/z=2) (a.u.)
0.0000010
0.0000008
0.0000006
0.0000004
0.0000002
0.0000000
100
200
300
400
500
600
700
800
900
1000
Temperature (° C)