Nuclear Reaction Profiling unraveling the incorporation of water in SiO_2/SiC structures

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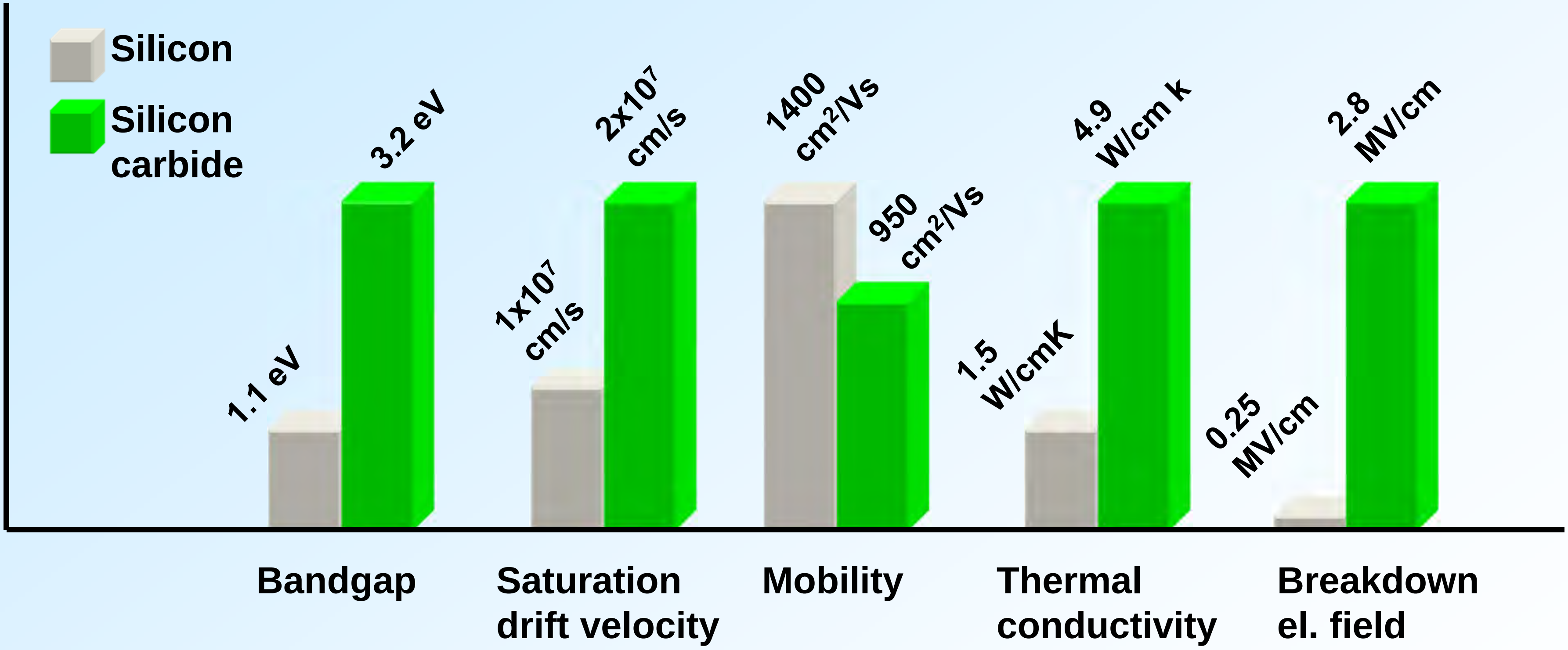
HRDP 2016

Why SiC?



- high temperature
- high voltage

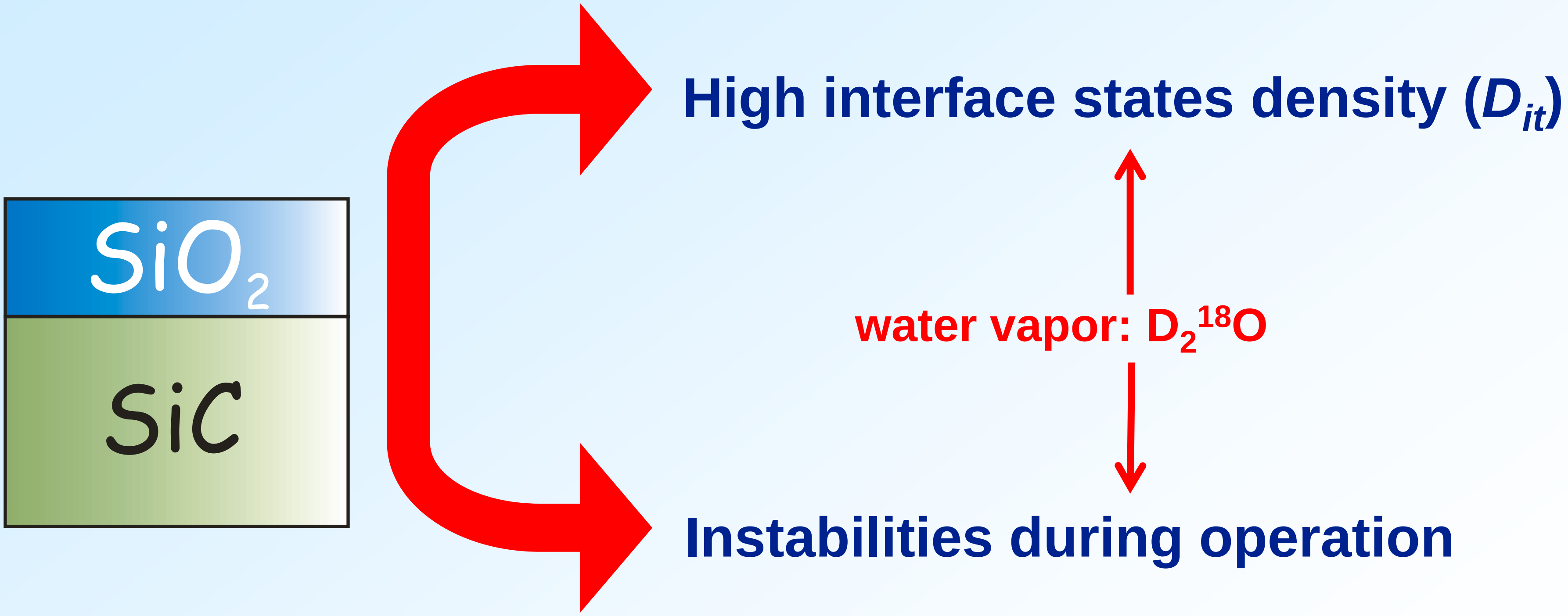
- high power
- high frequency

•SiO_2 native oxide → thermal oxidation

Water related problems in microelectronics

- ❑ humidity in a clean room fabrication facility is between 30 and 50%
- ❑ negative oxide charge buildup near the SiO_2/Si interface
- ❑ increases in the interface state density already reported for SiO_2/Si
- ❑ negative-bias-temperature instabilities attributed to water related species at the SiO_2/Si interface

Challenges in SiC technology



High interface states density (D_{it})

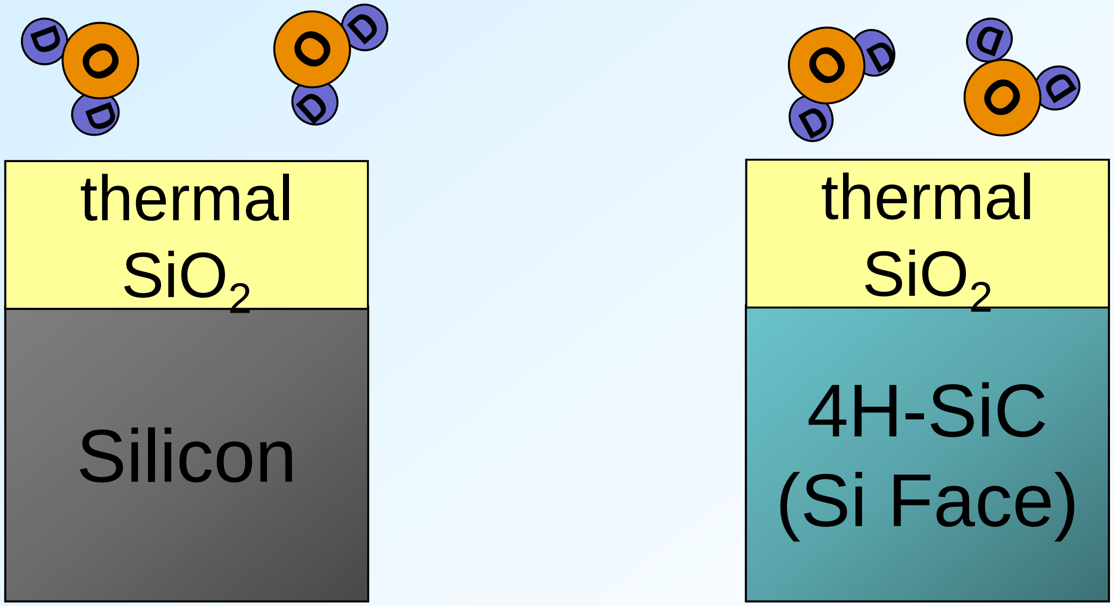
water vapor: $D_2{}^{18}O$

Instabilities during operation

Water vapor incorporation in thermally grown SiO_2/Si and SiO_2/SiC:

- Isotopically enriched gas

- Nuclear reaction analyses

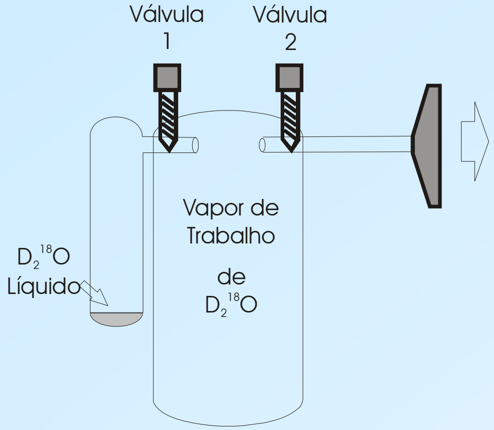


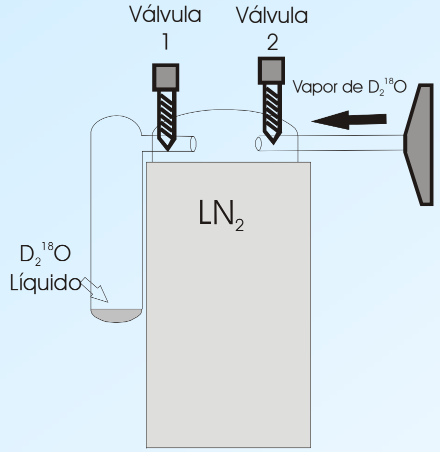
G.V. Soares *et al.* Appl. Phys. Lett. 95 (2009) 191912-1
G.V. Soares *et al.* Electrochem. Solid-State Letters, 13 (2010) G95
S.A. Corrêa *et al.* NIMB 273 (2012) 139

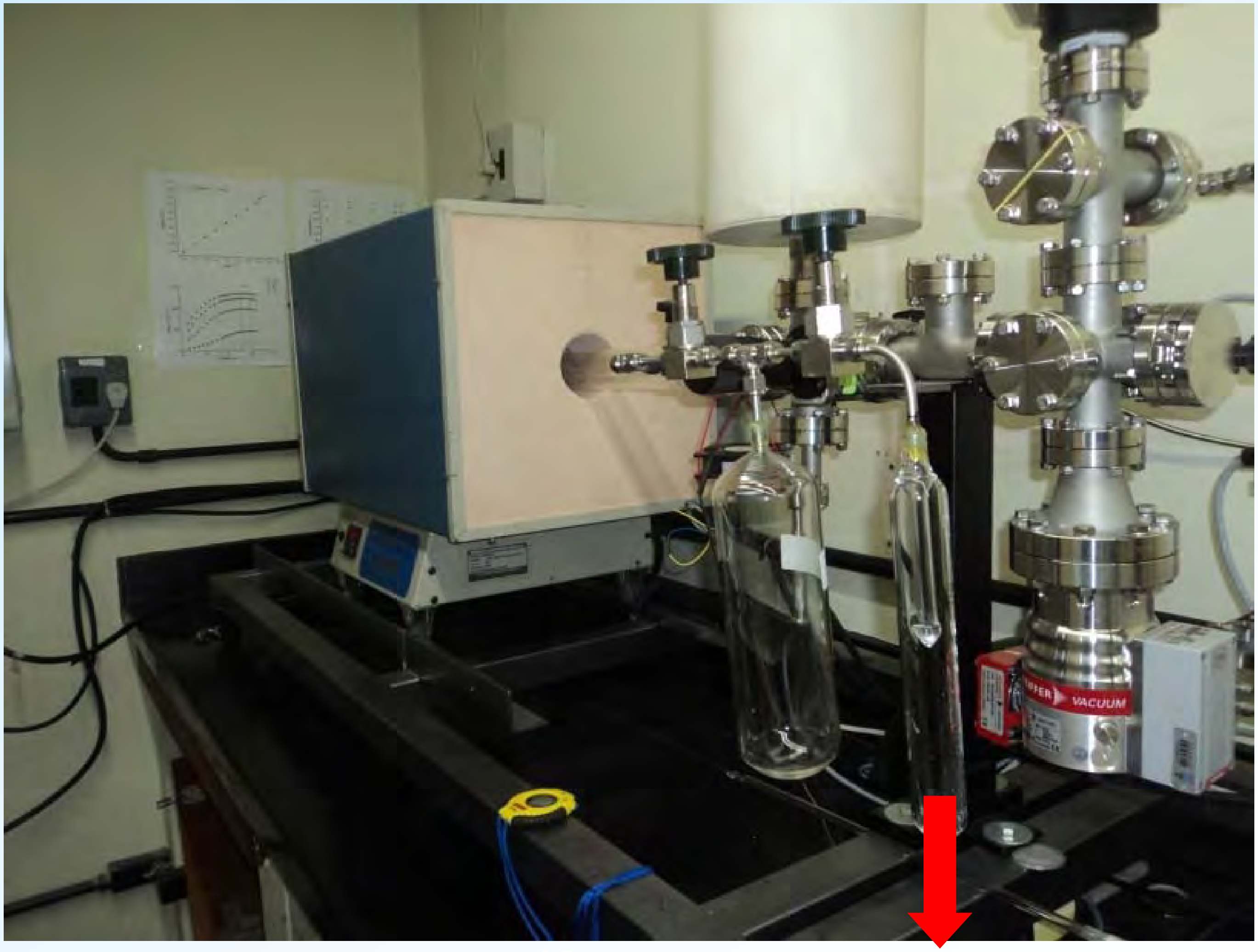
SiO_2 thermal growth: 1100°C, 100 mbar dry natural "$^{16}O_2$"

+ vacuum annealing: 10^{-7} mbar, 700°C, 30 min

Water vapor ($D_2{}^{18}O$) exposures: 1h, 200 – 800°C, 10 mbar





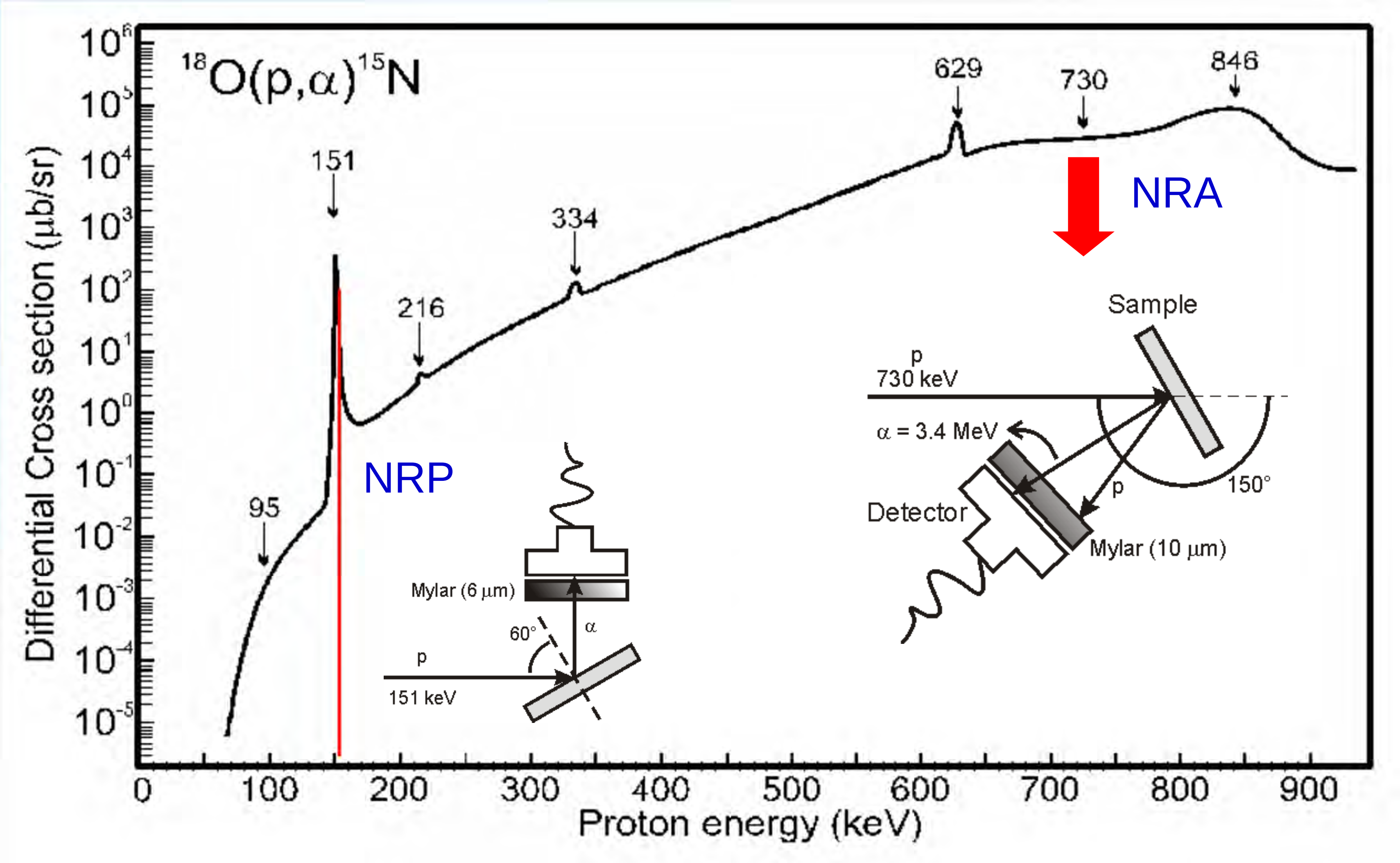


Water partial pressure in air of 30% humidity at 25°C

^{18}O : natural abundance of 0.2%

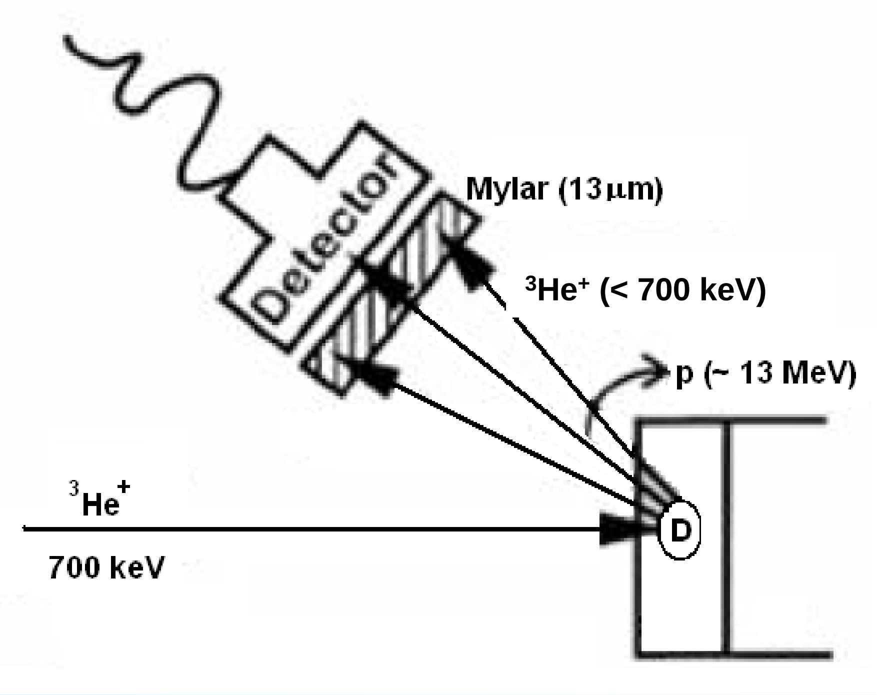
D : natural abundance of 0.015%

^{18}O quantification and profiling

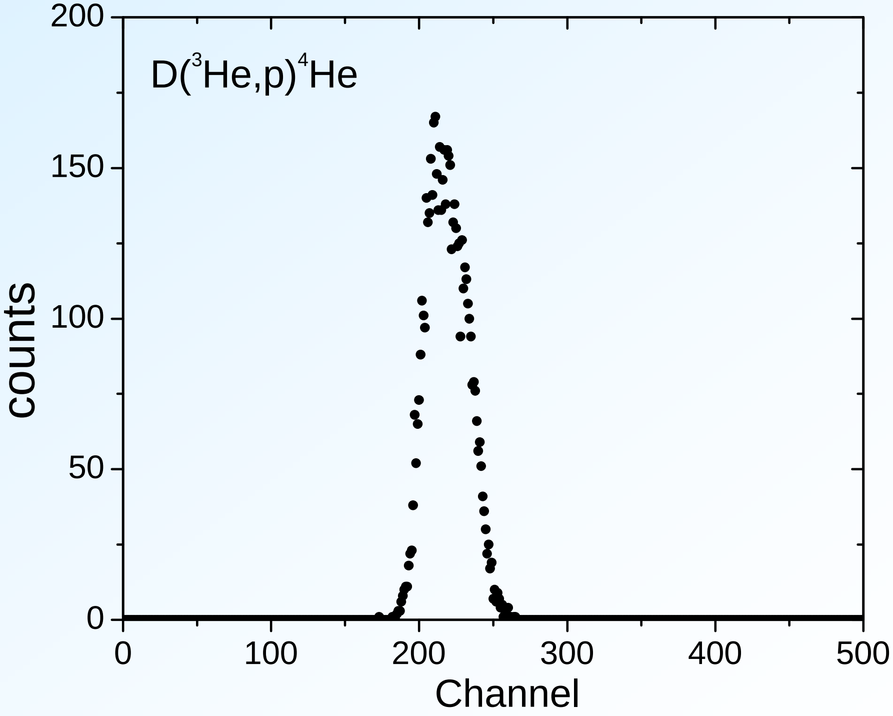


D quantification

D(^{3}He,p)^{4}He at 700 keV

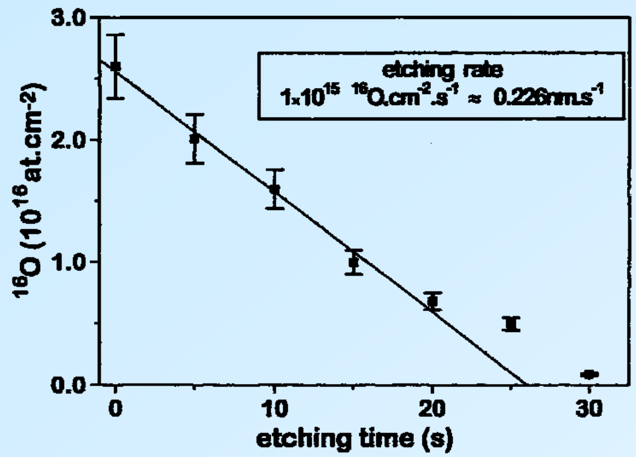


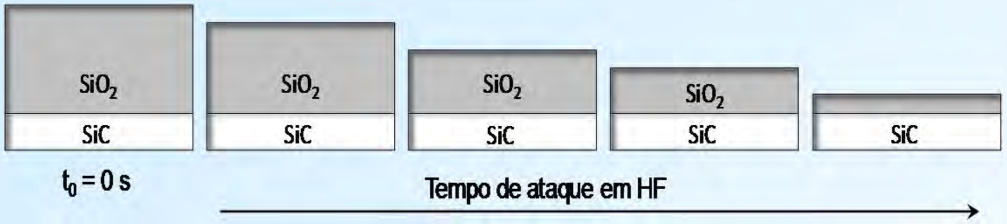
protons spectrum



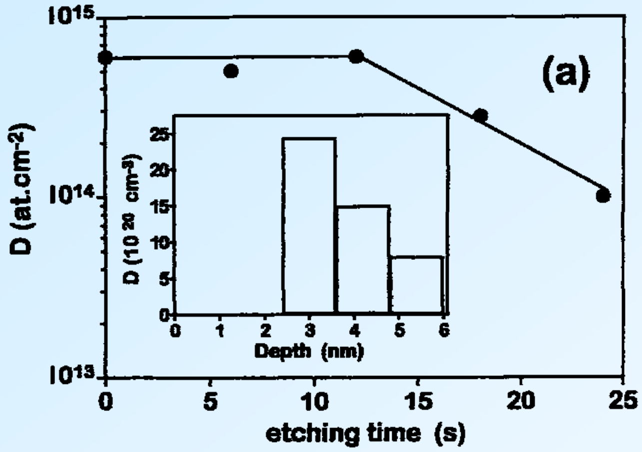
sensitivity ~ 4.0 x 10^{12} D.cm^{-2}

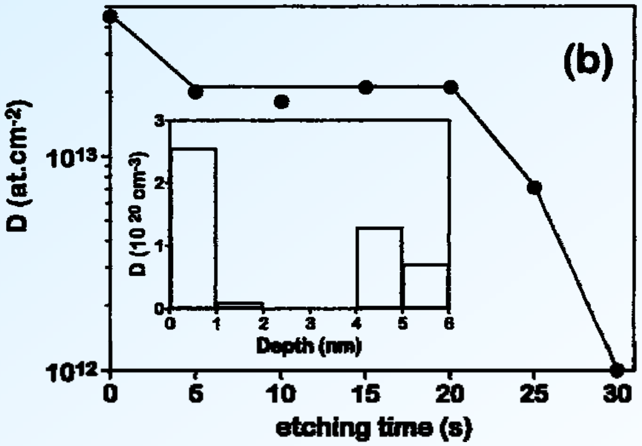
Accuracy: 10%





Areal density of O in Si dioxide films versus time of chemical dissolution in diluted HF-solution.





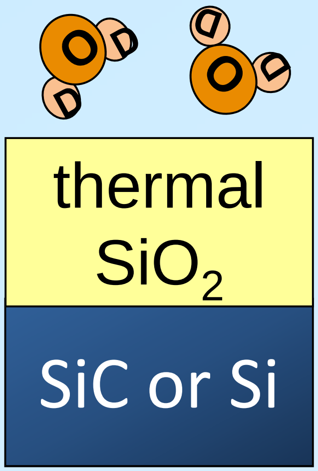
Areal densities of deuterium in **SiO_2 films on Si** as a function of chemical etching time. The corresponding **D profiles** determined by differentiation are shown in the insets:

(a) as-loaded with D_2;

(b) loaded with D_2 and annealed in vacuum at 450°C for 30 min.

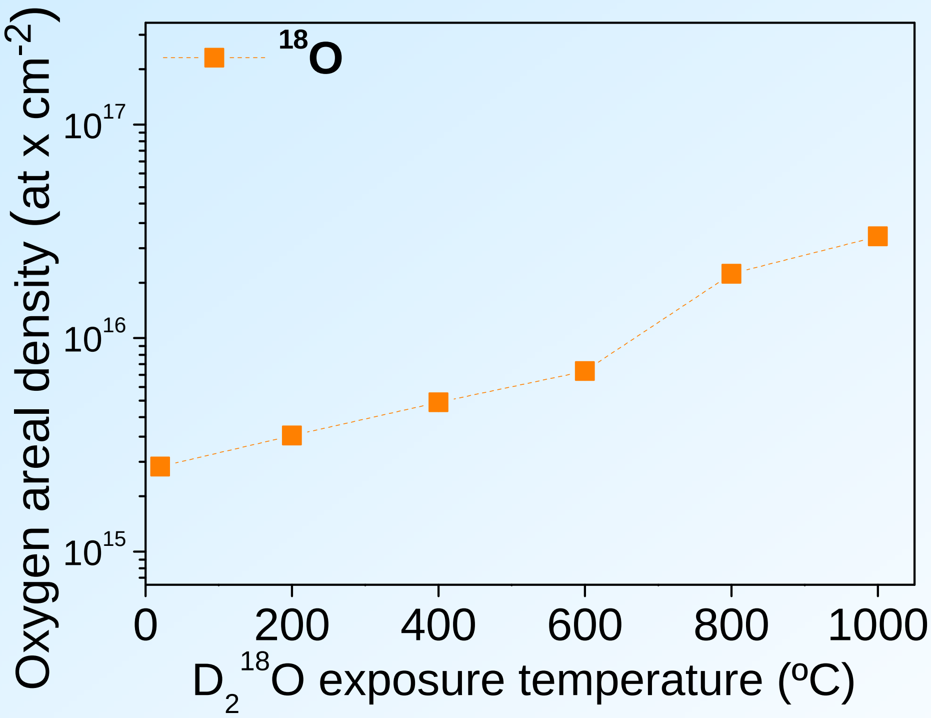
I.J.R. Baumvol Surface Science Reports 36 (1999) 1

^{18}O areal densities

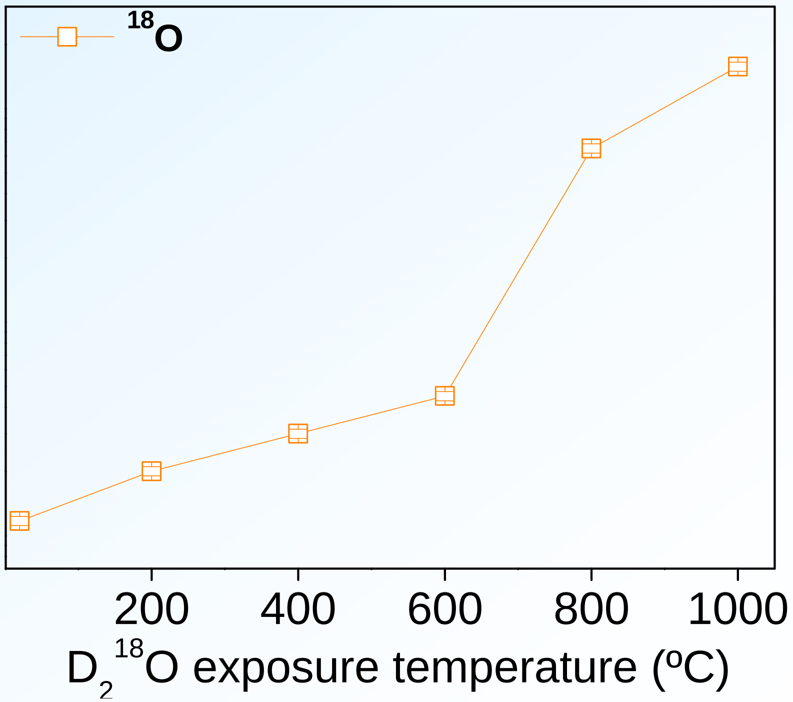


initial t_{ox} = 7 nm

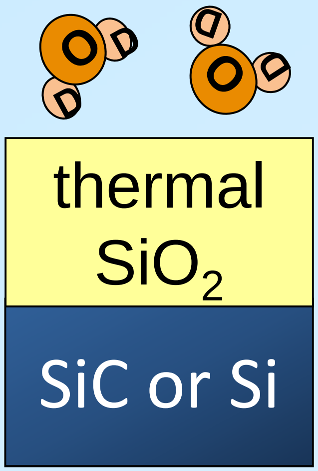
SiO_2/SiC



SiO_2/Si



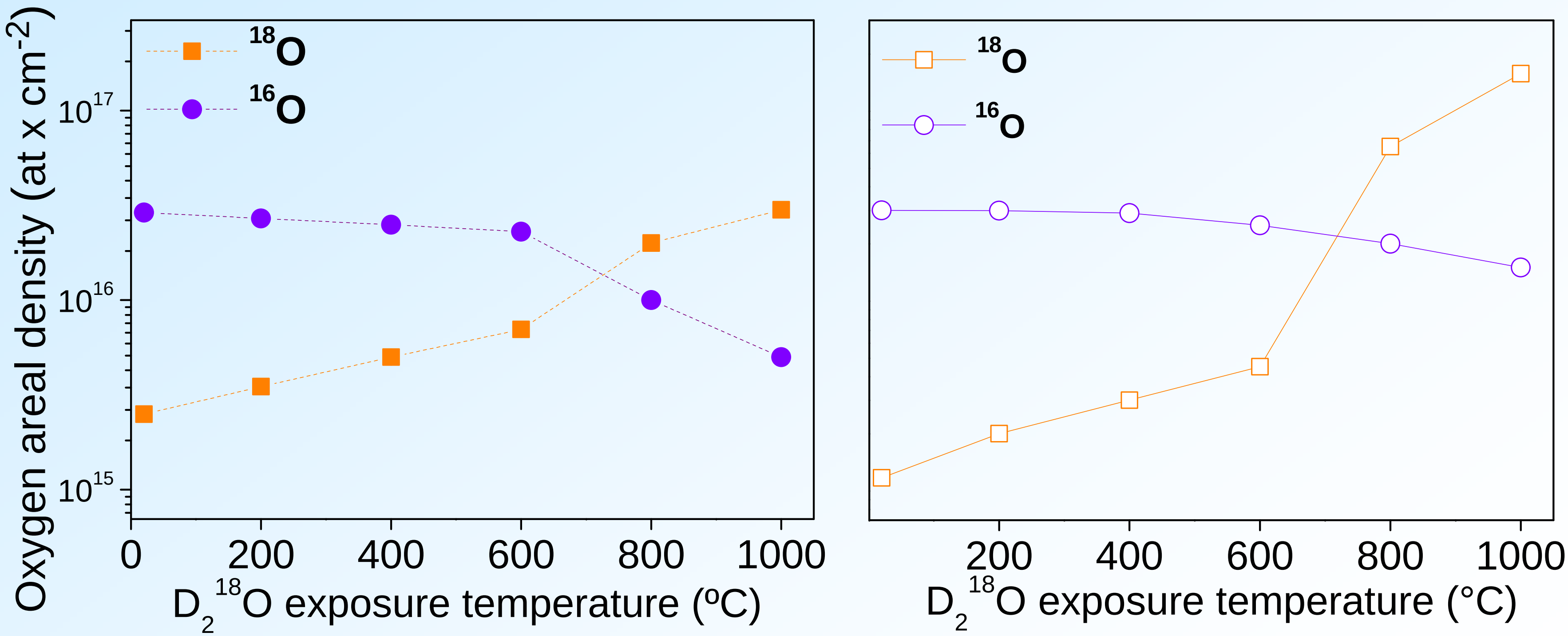
$^{18}O(p,\alpha)^{15}N$ @ 730 keV



thermal SiO_2

SiC or Si

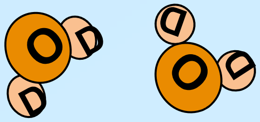
^{18}O and ^{16}O areal densities



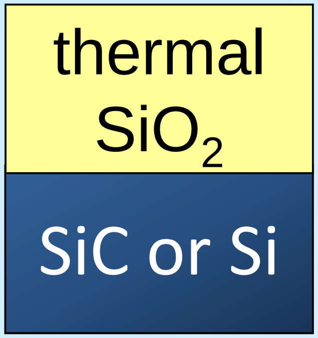
SiO_2/SiC

SiO_2/Si

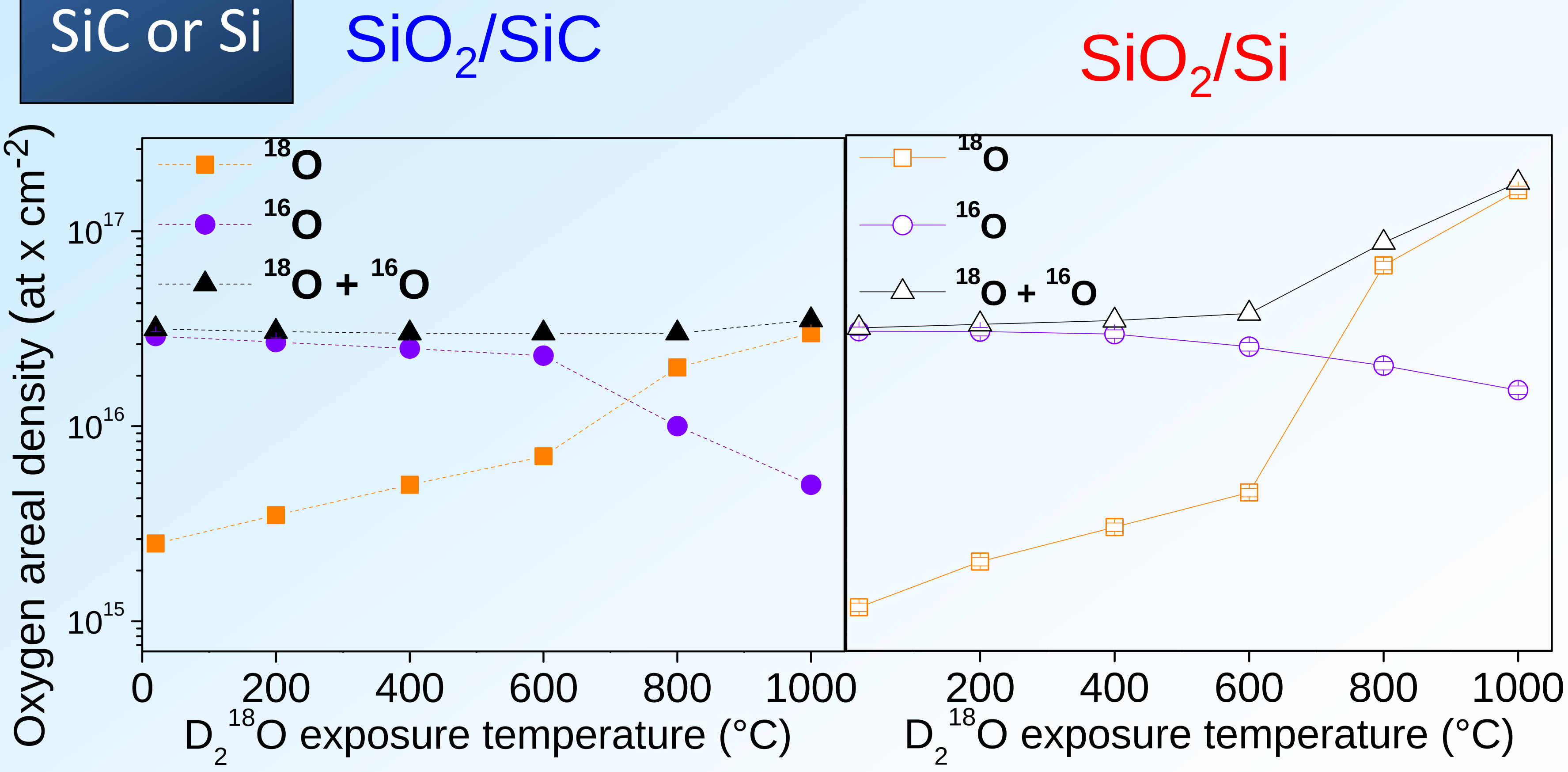
^{16}O: c-RBS, He^+ at 2 MeV



^{18}O and ^{16}O areal densities


thermal SiO_2

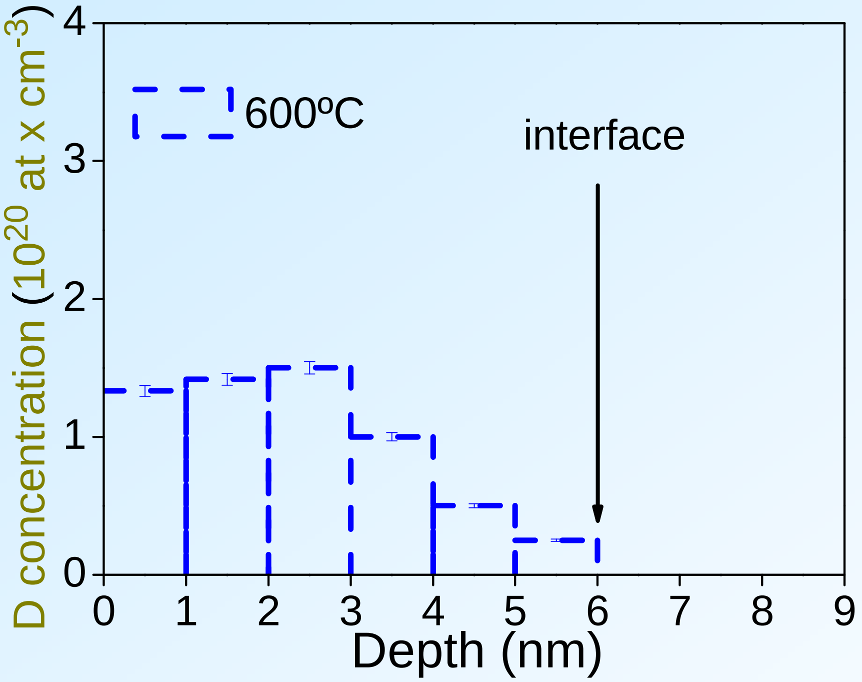
SiC or Si

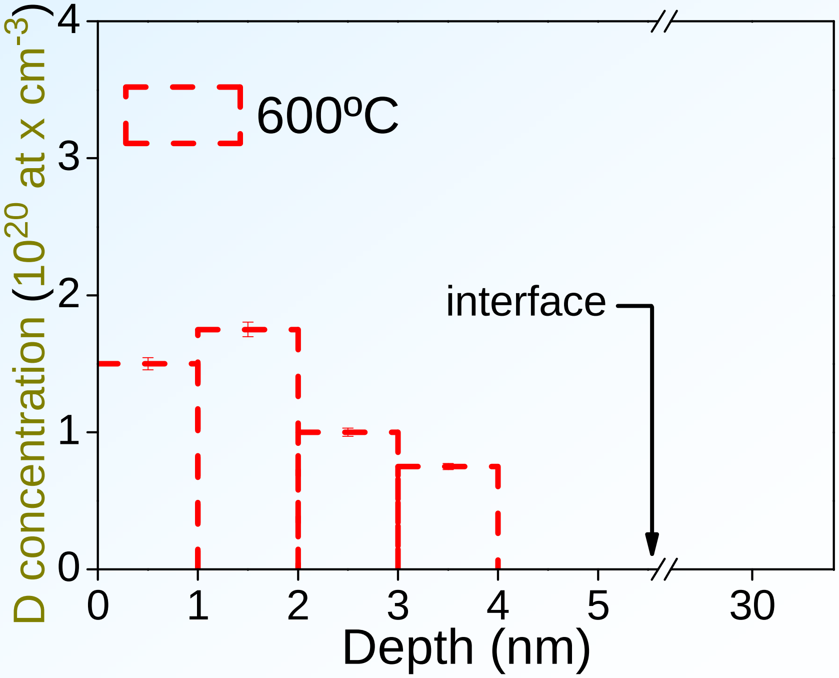


D profiles

in $Si^{16}O_2/SiC$ and in $Si^{16}O_2/Si$

initial t_{ox} = 6 nm T = 600ºC

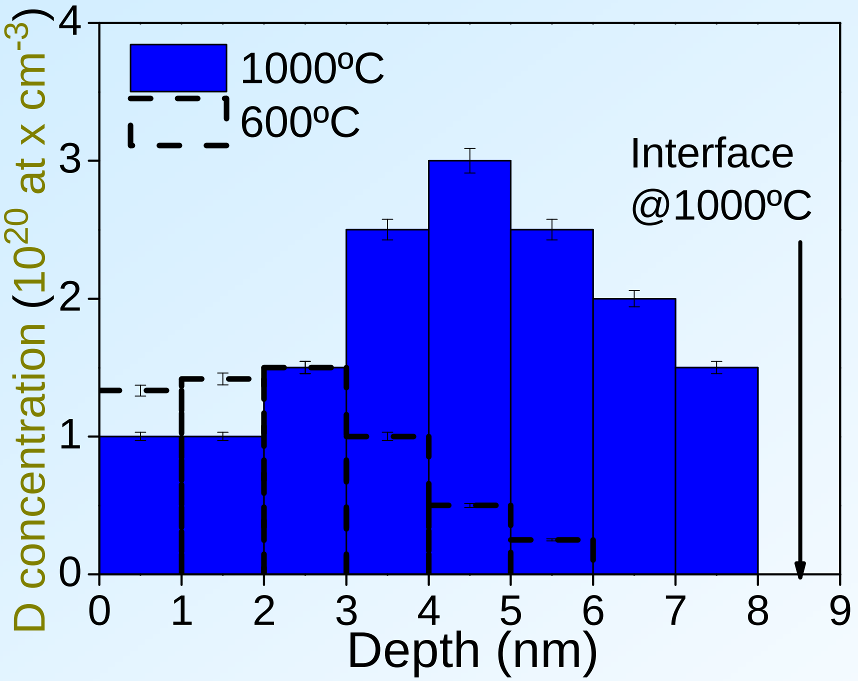


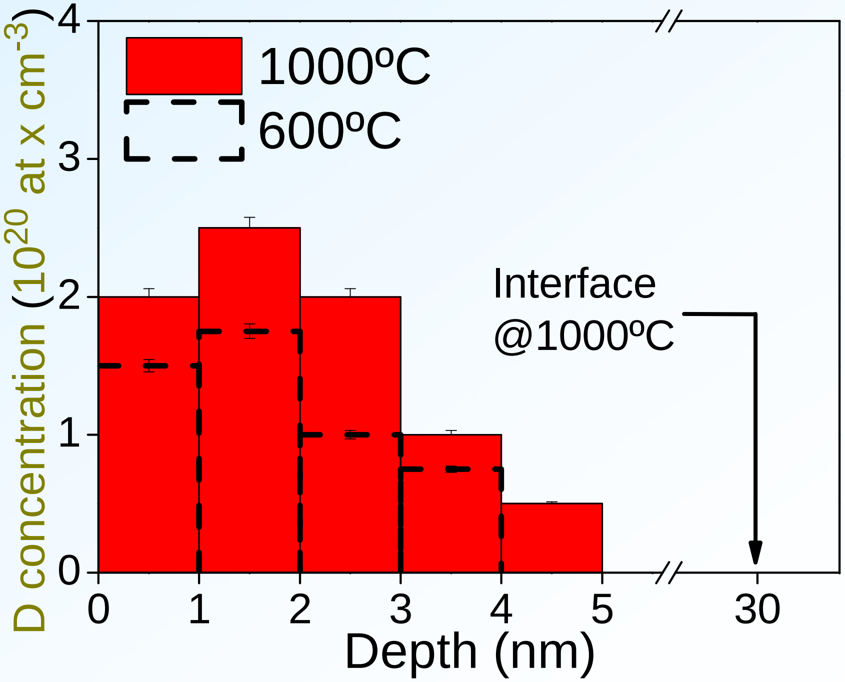


$D(^3He,p)^4He$ at 700 keV

D profiles

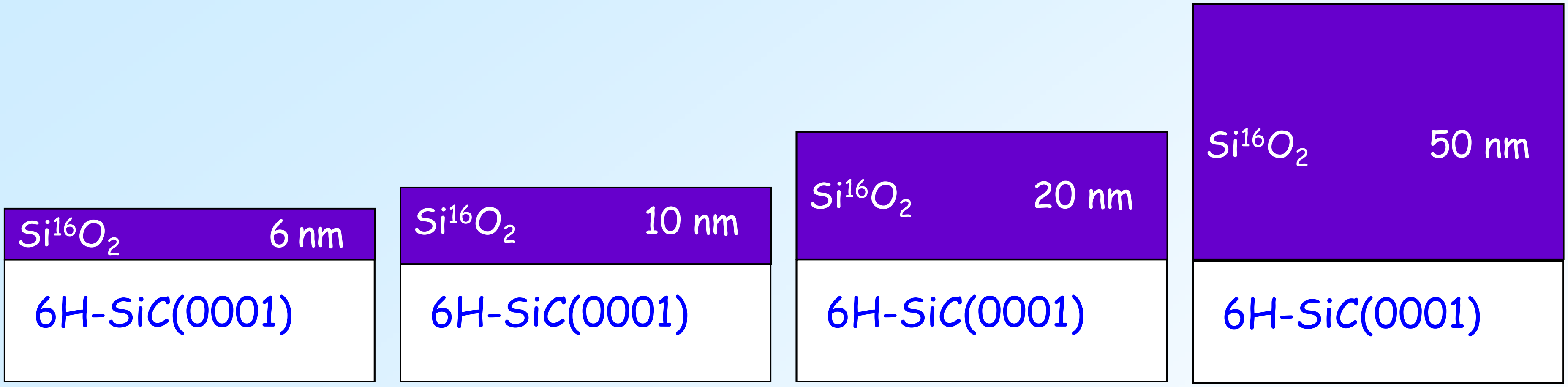
in Si^{16}O$_2$/SiC and in Si^{16}O$_2$/Si





D(^{3}He,p)^{4}He at 700 keV

Samples preparation



$Si^{16}O_2$ 6 nm

6H-SiC(0001)

$Si^{16}O_2$ 10 nm

6H-SiC(0001)

$Si^{16}O_2$ 20 nm

6H-SiC(0001)

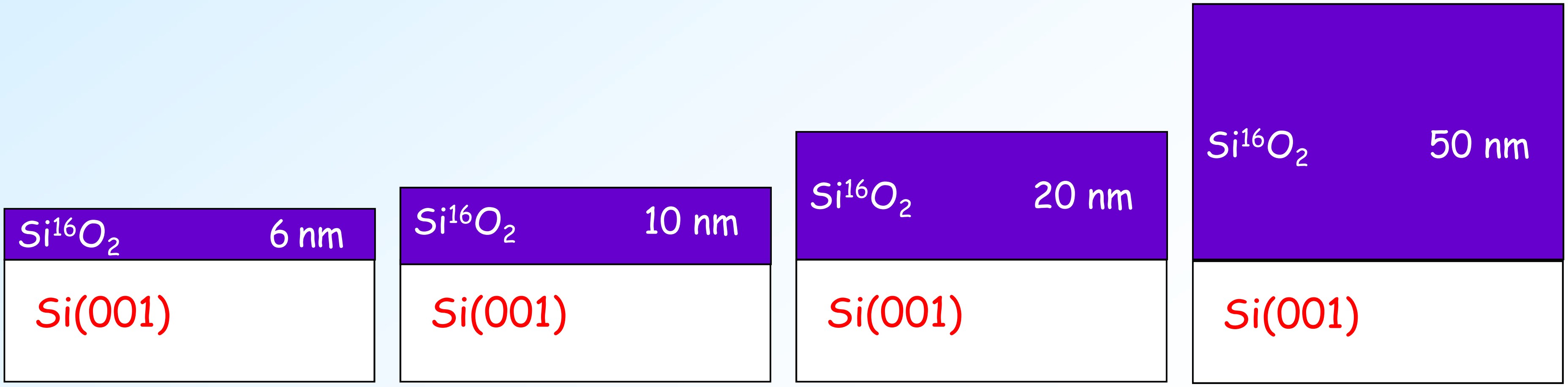
$Si^{16}O_2$ 50 nm

6H-SiC(0001)

1. SiO_2 thermal growth:
1100°C, 100 mbar dry $^{16}O_2$

2. Vacuum annealing:
700°C, 30 min

3. Water vapor ($D_2{}^{18}O$) exposure: 1h,
20 – 1000°C, 10 mbar



$Si^{16}O_2$ 6 nm

Si(001)

$Si^{16}O_2$ 10 nm

Si(001)

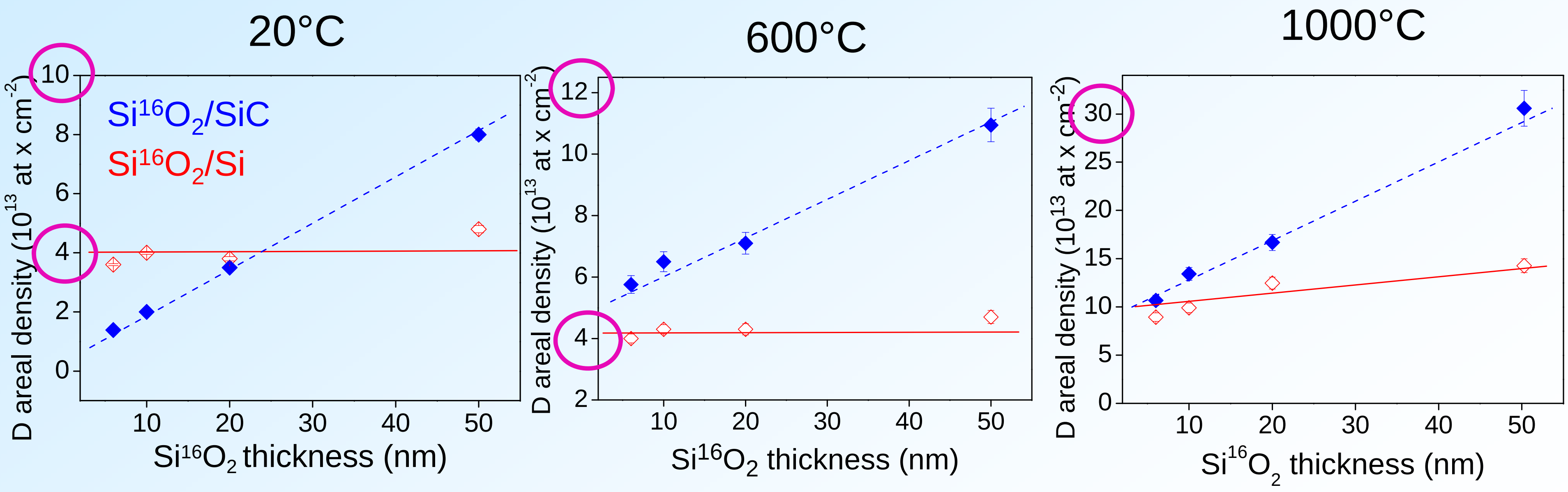
$Si^{16}O_2$ 20 nm

Si(001)

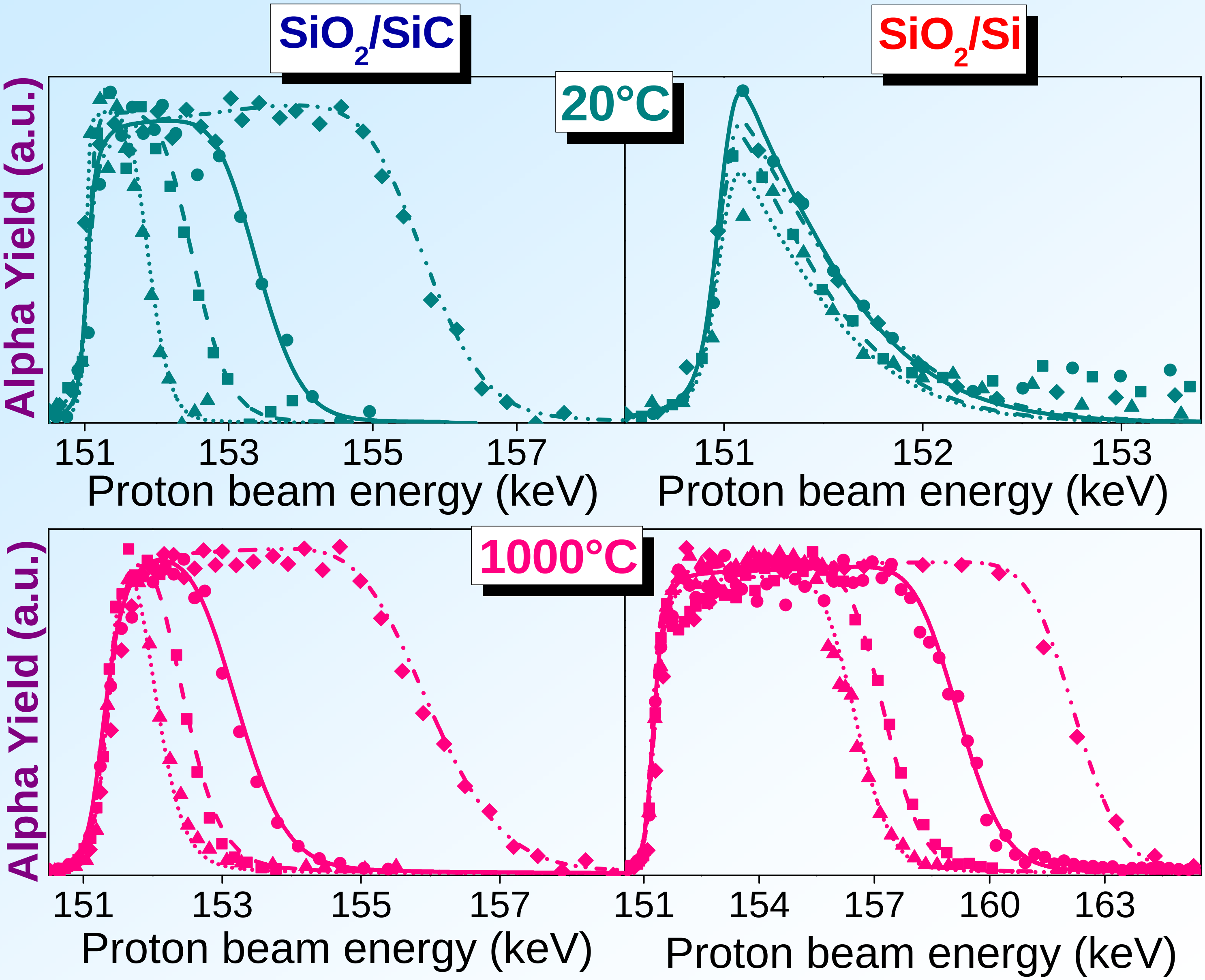
$Si^{16}O_2$ 50 nm

Si(001)

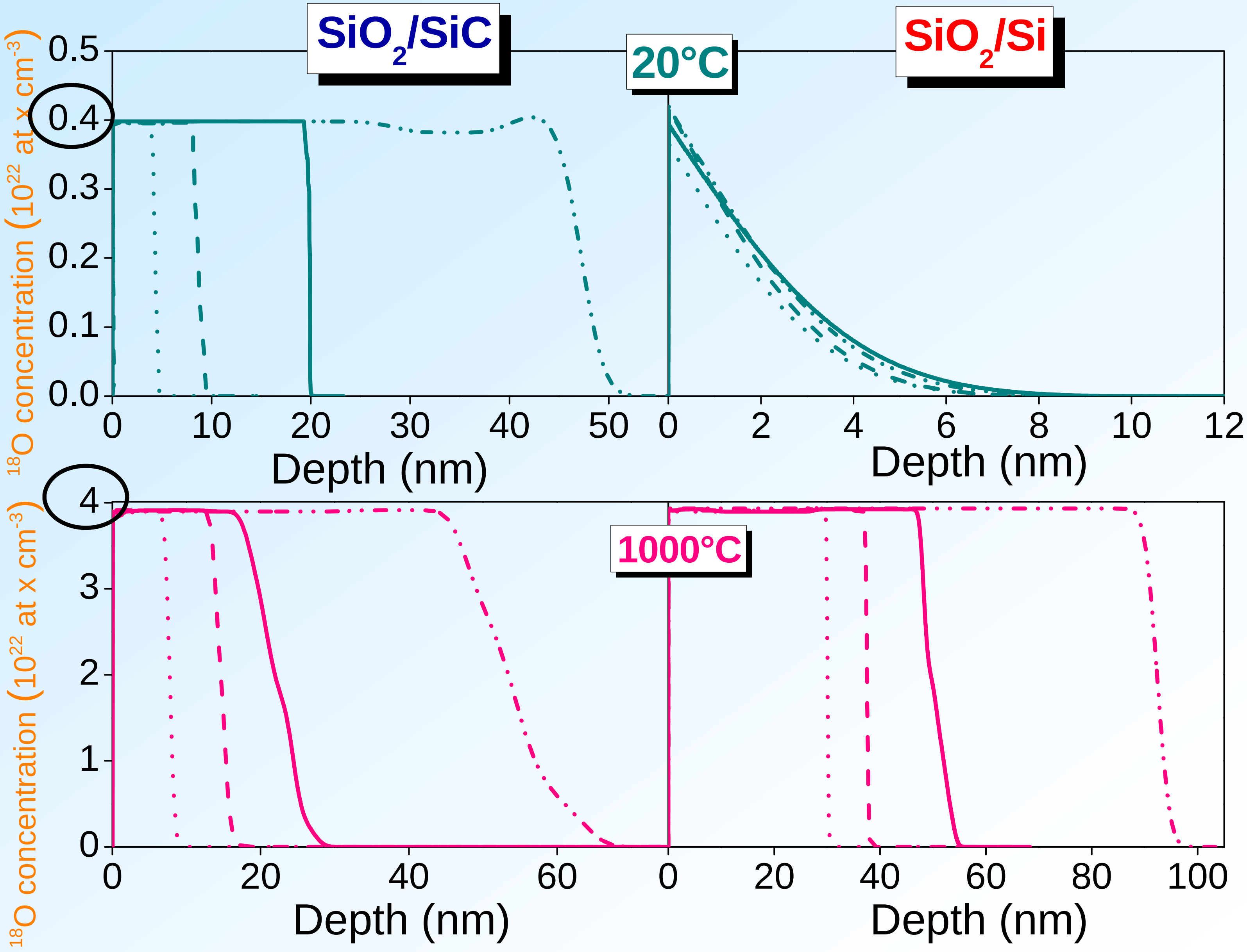
D incorporation for ≠ oxide film thickness



^{18}O excitation curves



^{18}O profiles



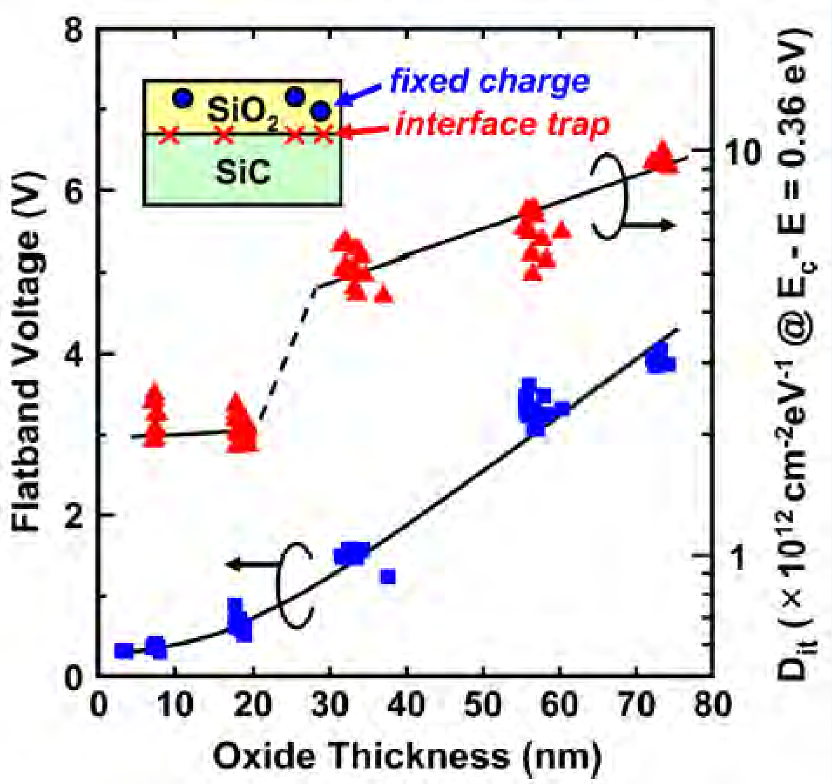
Partial conclusions

✓ In SiC samples, in any exposure temperature, **O** from water is incorporated in **all depths** of the oxide films, mainly by isotopic exchange, reaching the SiO_2/SiC interface, in contrast to SiO_2/Si.

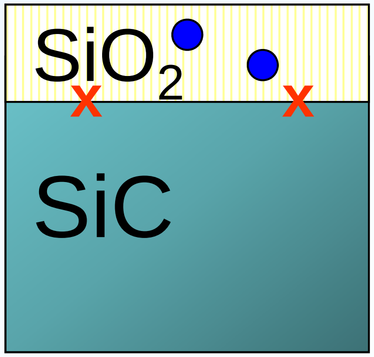
✓ In SiO_2/SiC, **D** is transported and incorporated in the **surface, bulk, and interface regions**, whereas in SiO_2/Si, it is observed only in **near-surface** regions of the oxide.

✓In SiO_2/SiC, the amount of incorporated **D** increases continuously with **temperature** and with **initial oxide thickness**, while in SiO_2/Si there is no such dependence.

Influence of thermal conditions in the quality of the SiO_2/SiC

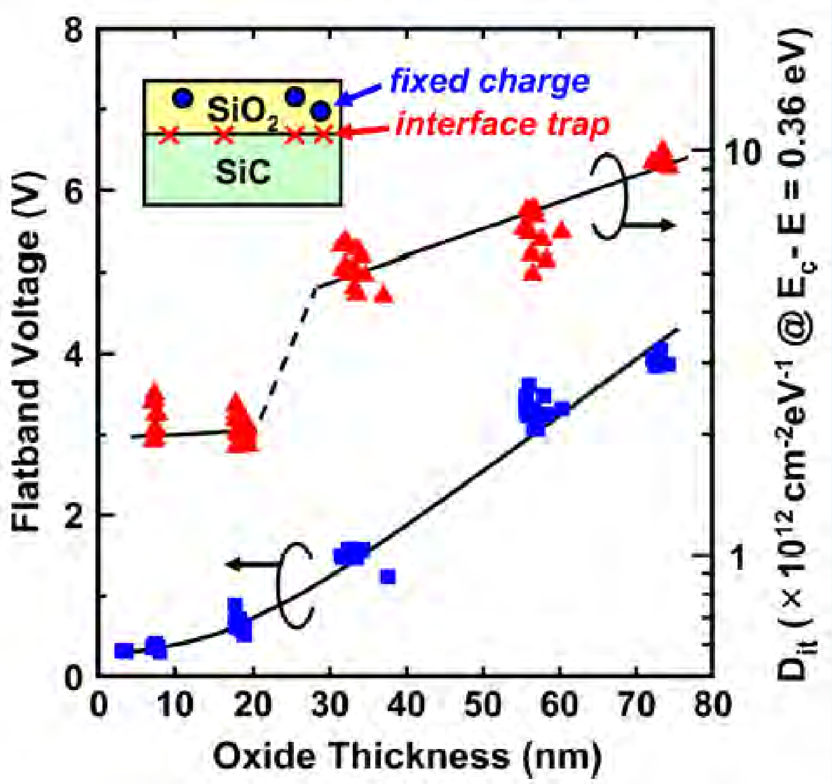


Longer oxidation times lead to higher D_{it} and negative fixed charges



H. Watanabe *et al.* Appl. Phys. Lett. 99, 021907 (2011)

Influence of thermal conditions in the quality of the SiO_2/SiC



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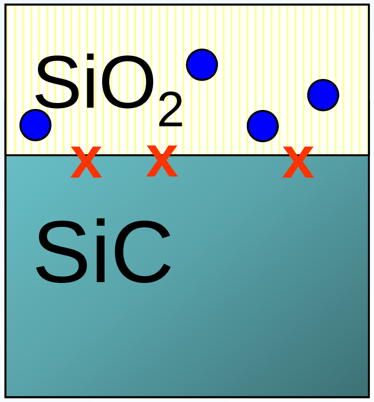

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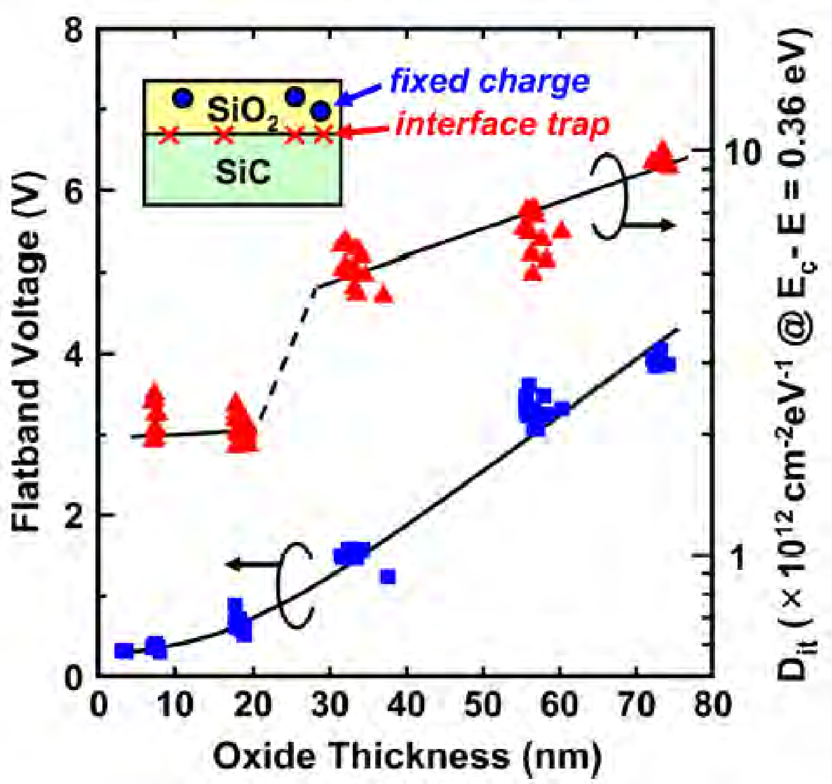

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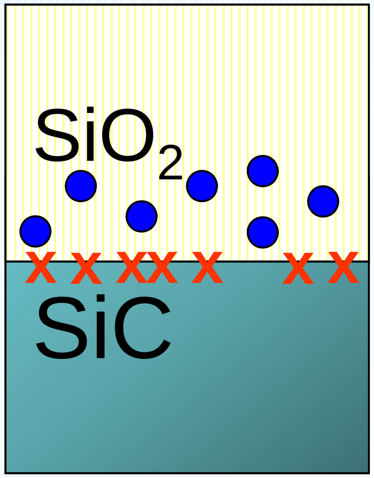
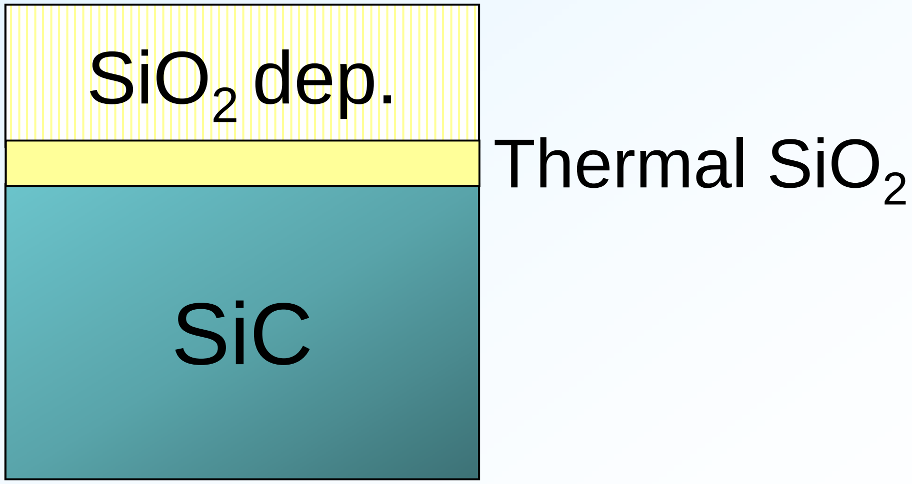


H. Watanabe *et al.* Appl. Phys. Lett. 99, 021907 (2011)

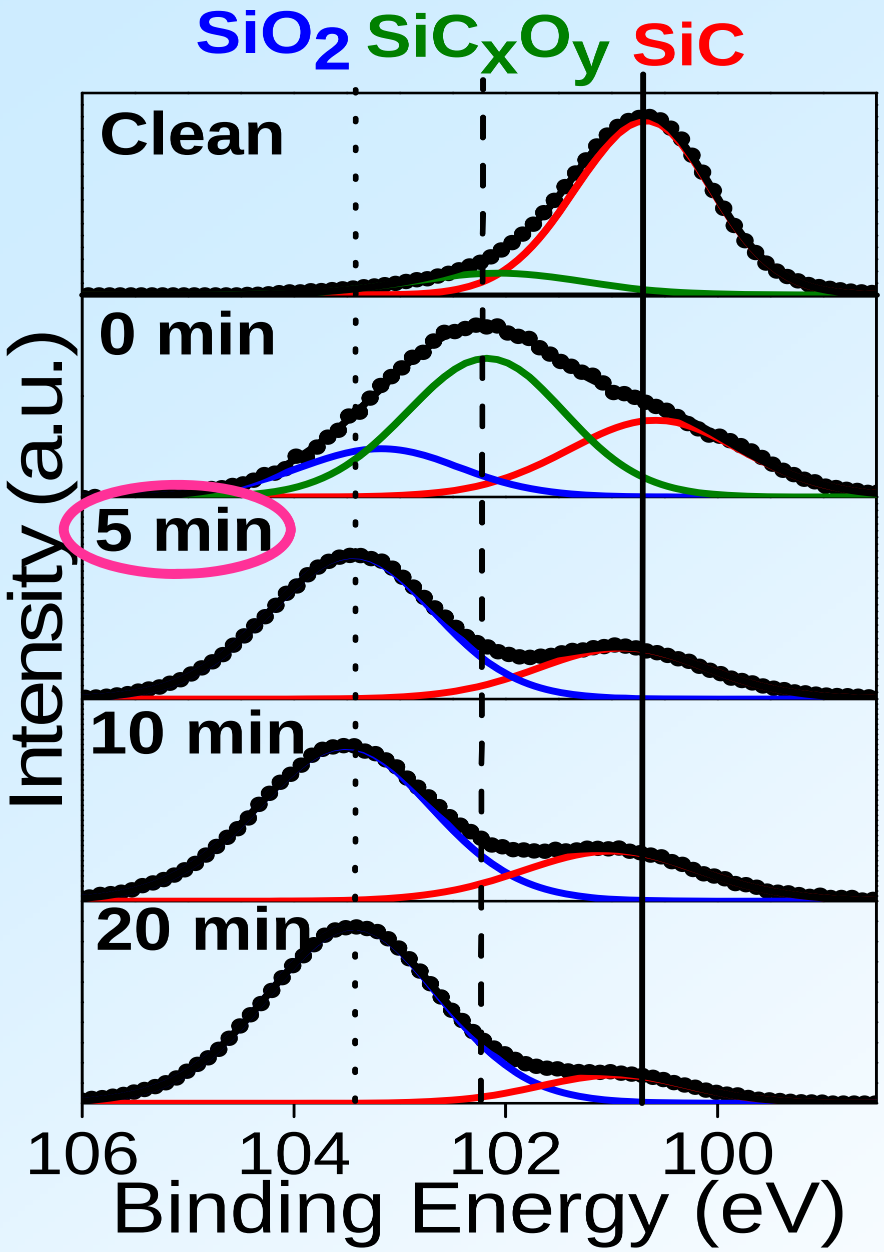
Alternative method to improve the SiO_2/SiC interface quality

Thermally grow a very thin and stoichiometric SiO_2 film to minimize the electrical degradation from the oxidation

Deposition of a SiO_2 film to obtain a thicker film



E. Pitthan *et al.* ECS Solid State Letters, 2 (2013) P8

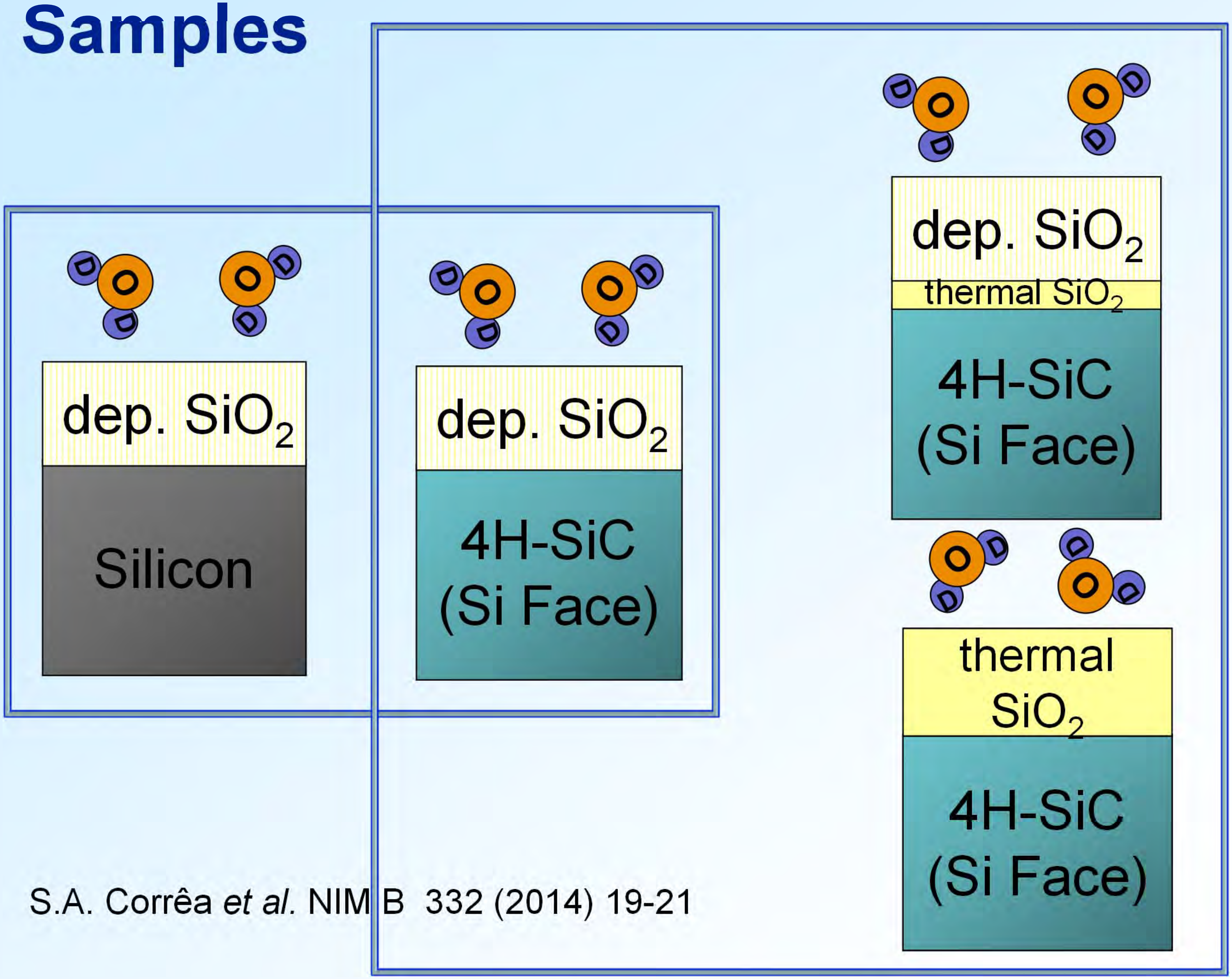


X-ray Photoelectron Spectroscopy

Si 2p photoelectron spectra at a take-off angle sensitive to the surface of **Si-faced 4H-SiC** samples thermally oxidized at 1100°C in 100 mbar of $^{18}O_2$ for different oxidation times, as indicated.

E. Pitthan *et al.*
ECS Solid State Letters, 2 (2013) P8

Samples



dep. SiO_2

Silicon

dep. SiO_2

4H-SiC (Si Face)

dep. SiO_2

thermal SiO_2

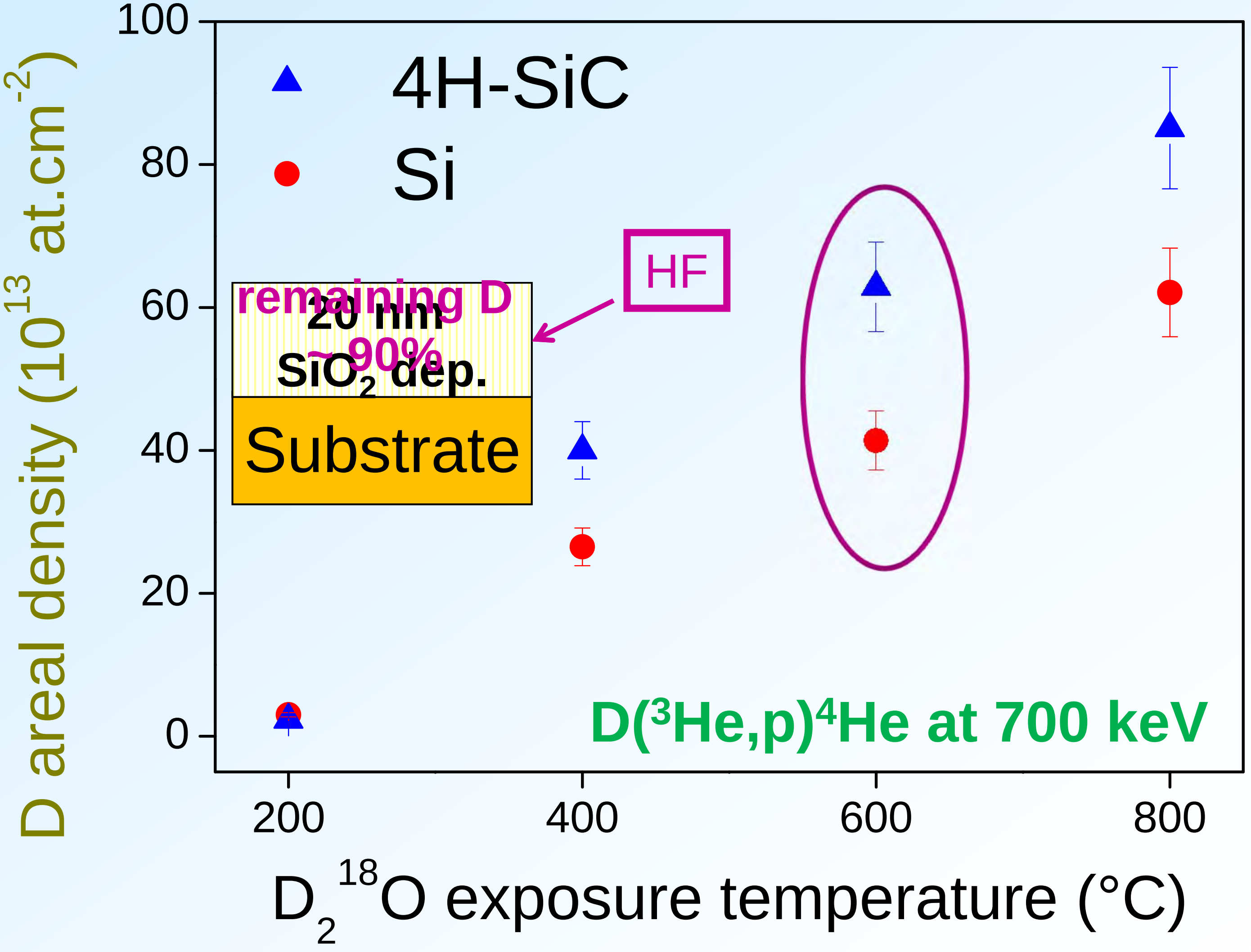
4H-SiC (Si Face)

thermal SiO_2

4H-SiC (Si Face)

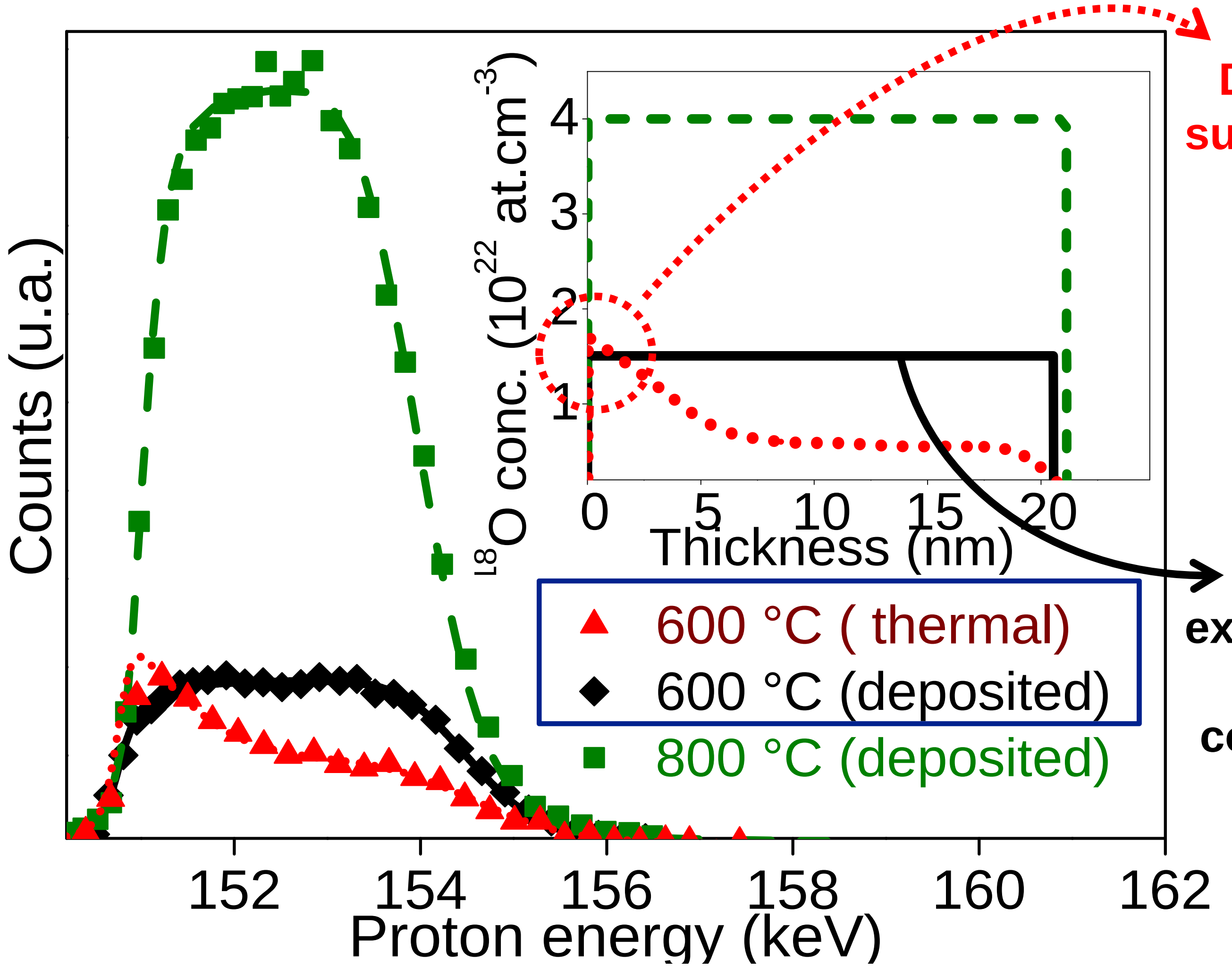
S.A. Corrêa *et al.* NIM B 332 (2014) 19-21

Influence of substrate and of temperature in $D_2{}^{18}O$ vapor incorporation



^{18}O profiles

SiO_2/SiC + 10 mbar $D_2{}^{18}O$, 1h



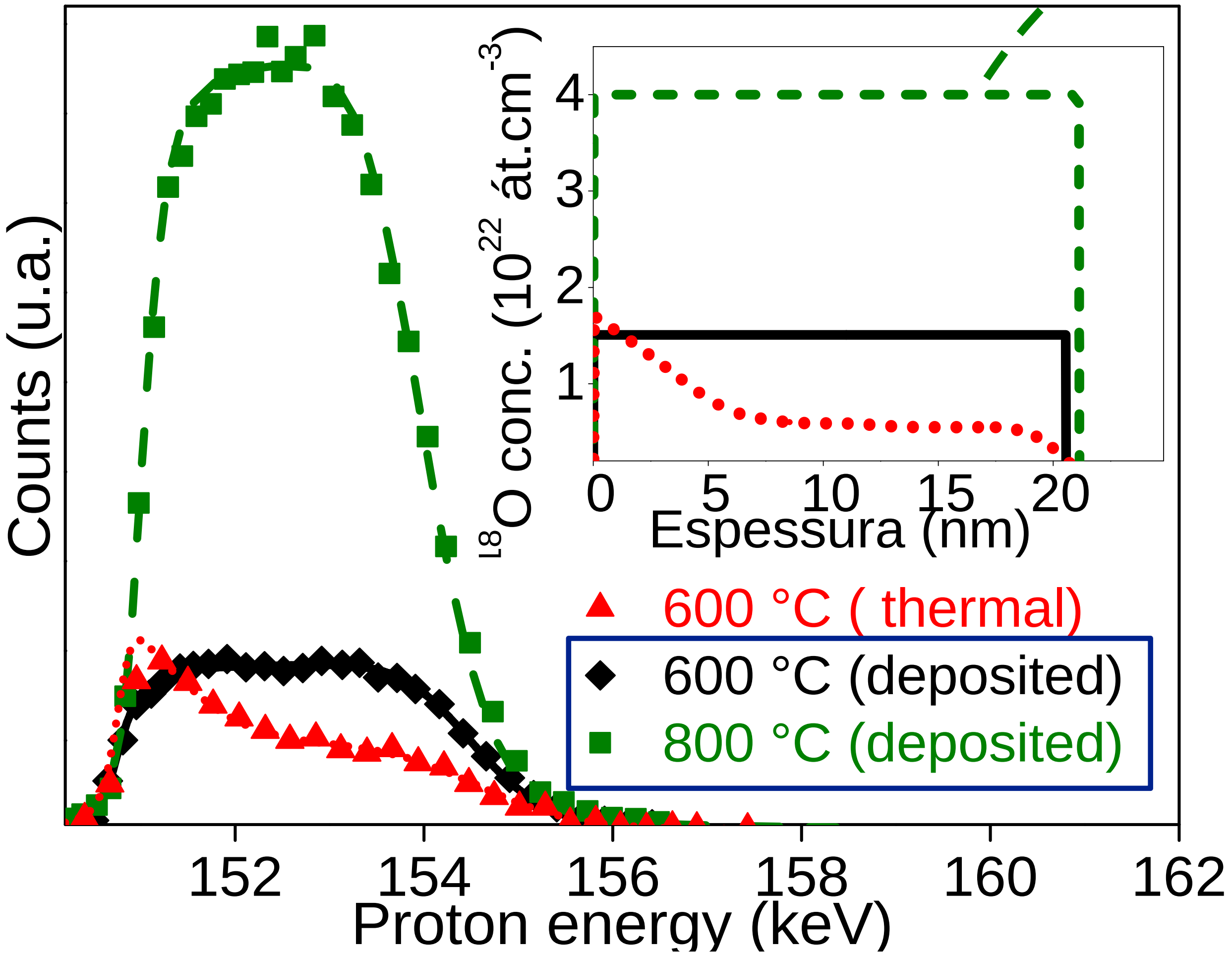
Defects present in the surface region of the film thermally grown

Larger O isotopic exchange in the *bulk* of the deposited film: larger concentration of defects?

E. Pitthan *et al.* Appl. Phys. Lett. 104 (2014) 111904

^{18}O profiles

SiO_2/SiC + 10 mbar $D_2{}^{18}O$, 1h



^{16}O-^{18}O total isotopic exchange

Similarly to the case of films thermally grown

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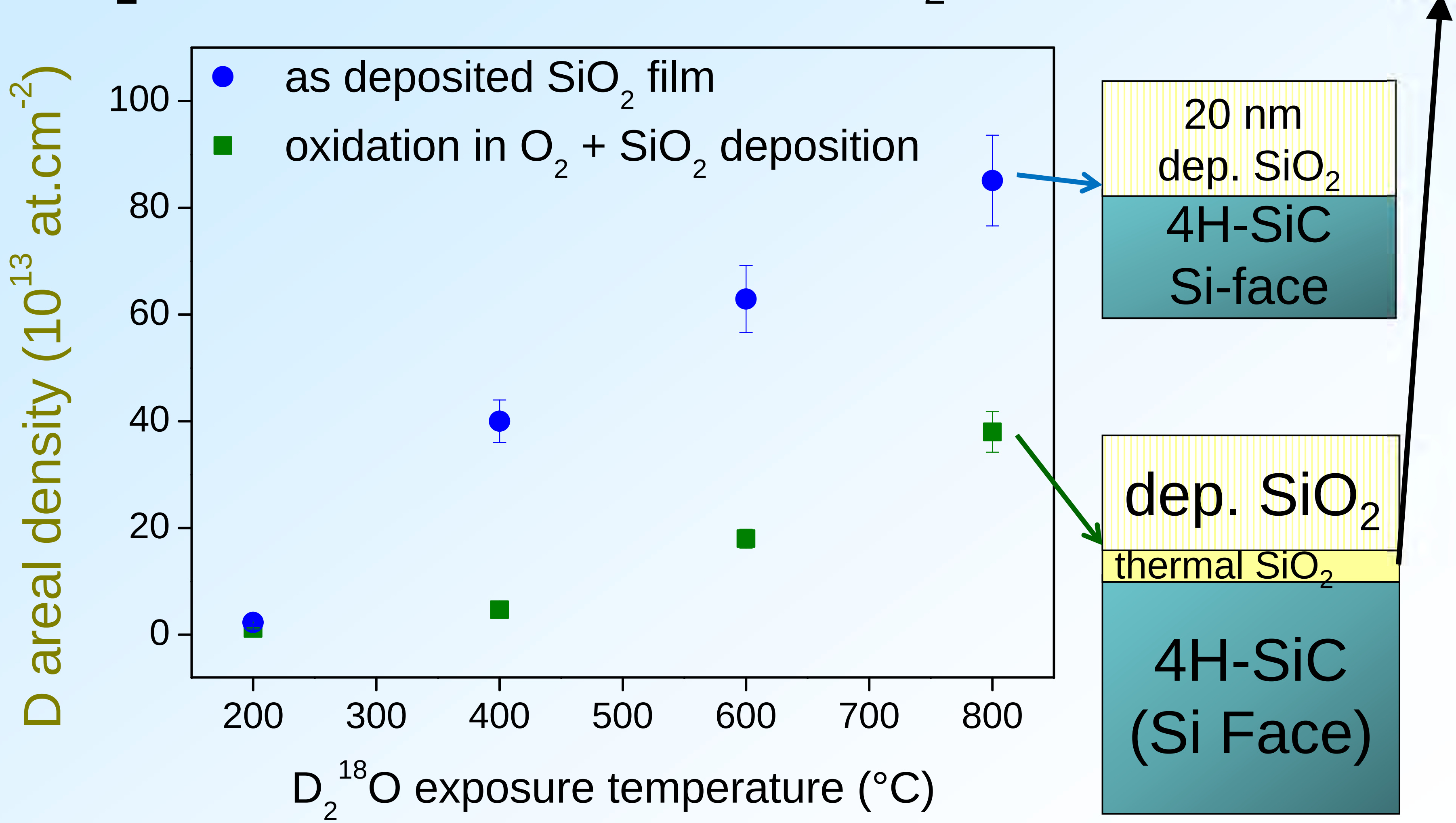
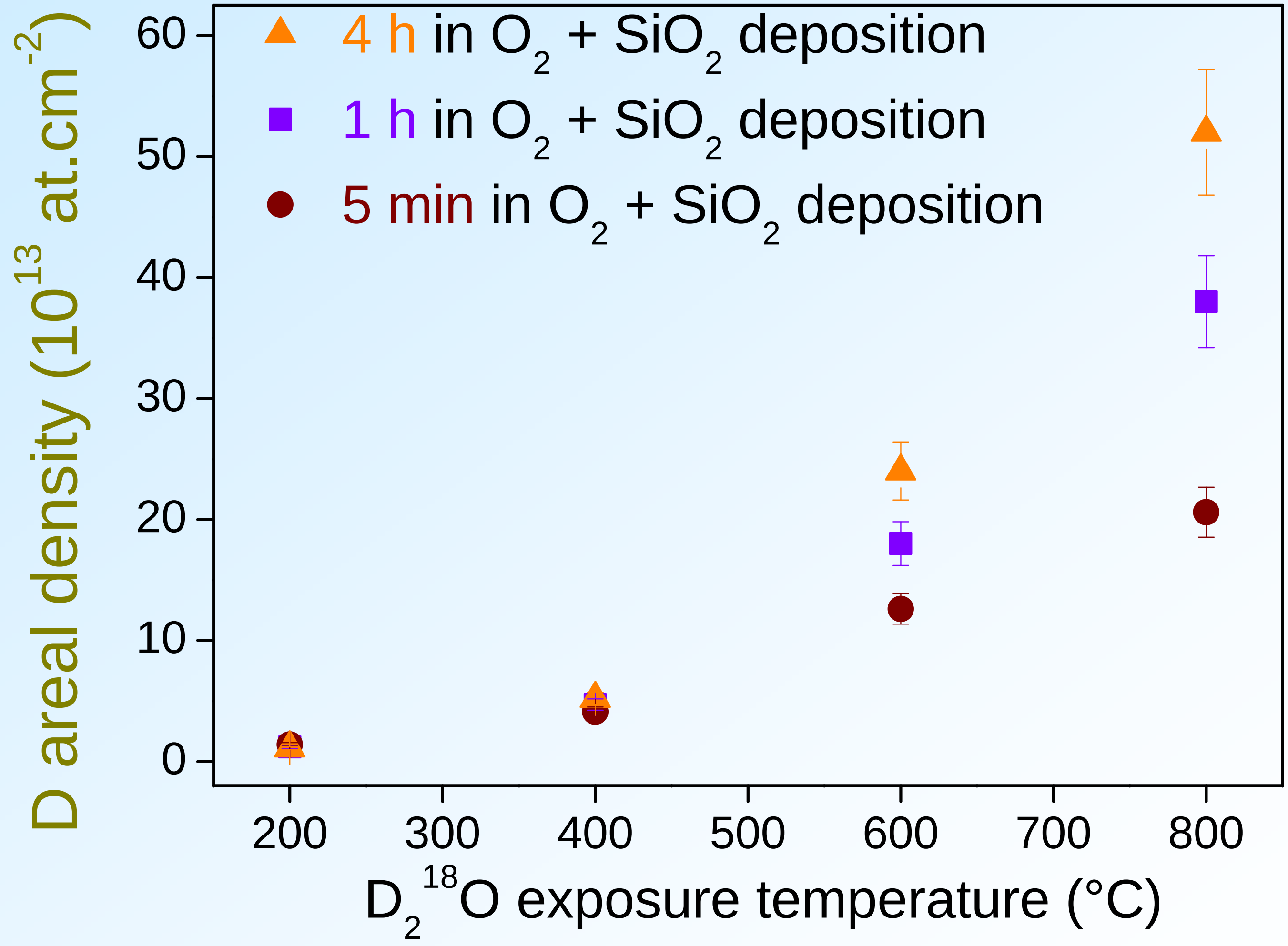
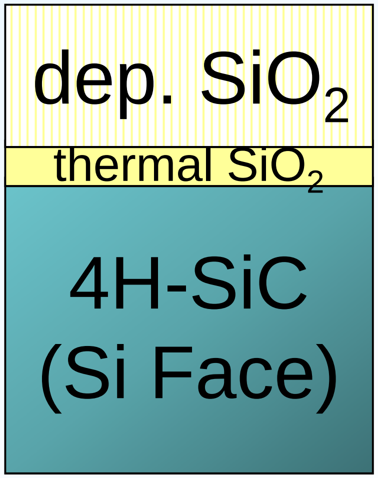
Effect of oxidation prior to the deposition

O_2: 1h in 100 mbar of **natural** O_2 @ 1100°C for 5 min



Pre-deposition oxidation times



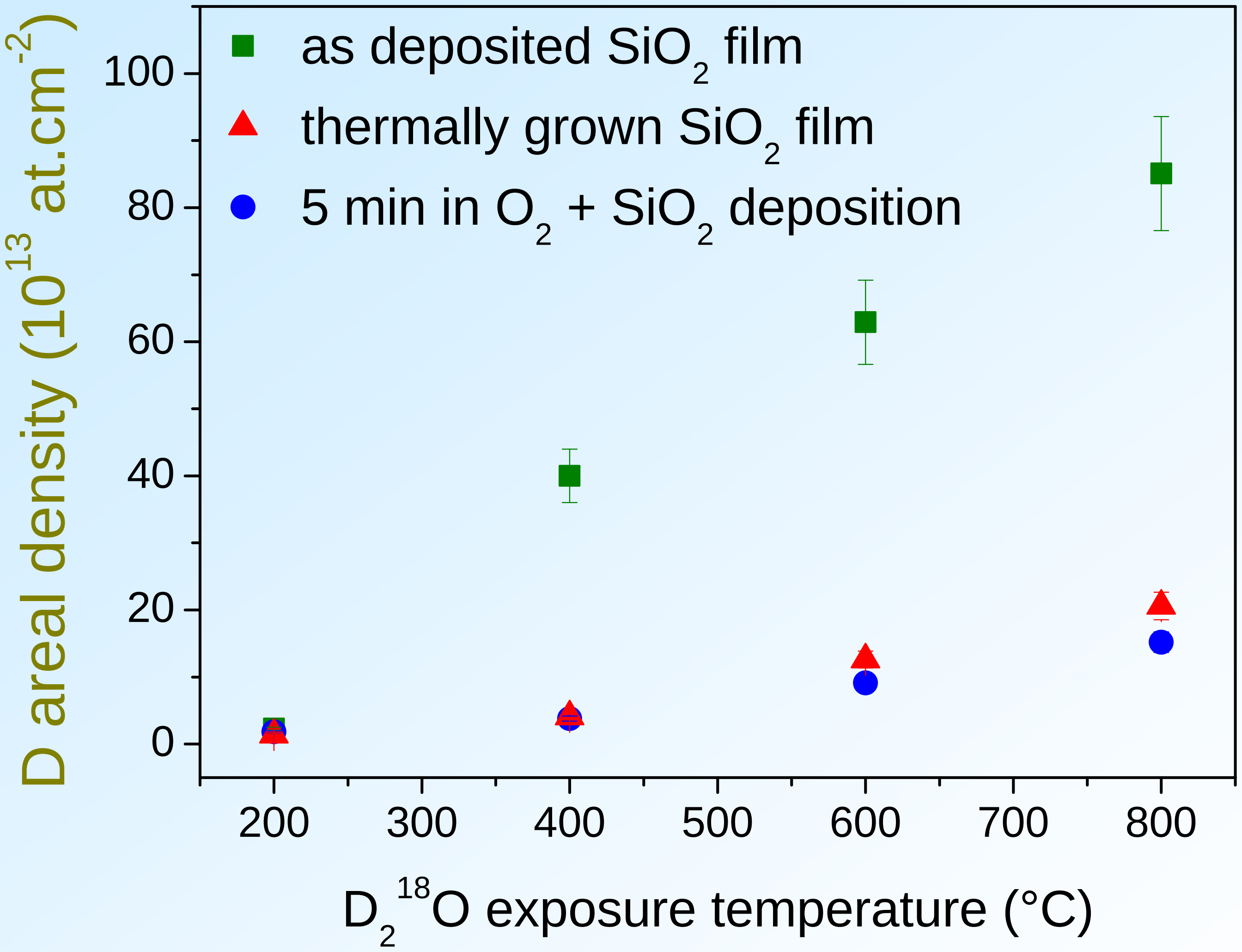


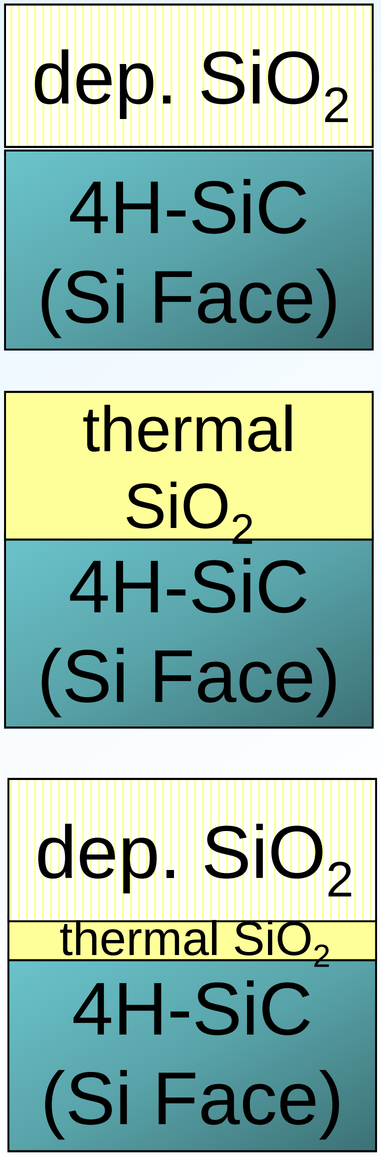
dep. SiO_2

thermal SiO_2

4H-SiC
(Si Face)

D incorporation for different routes





dep. SiO_2

4H-SiC (Si Face)

thermal SiO_2

4H-SiC (Si Face)

dep. SiO_2

thermal SiO_2

4H-SiC (Si Face)

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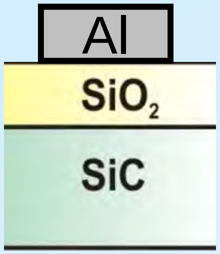
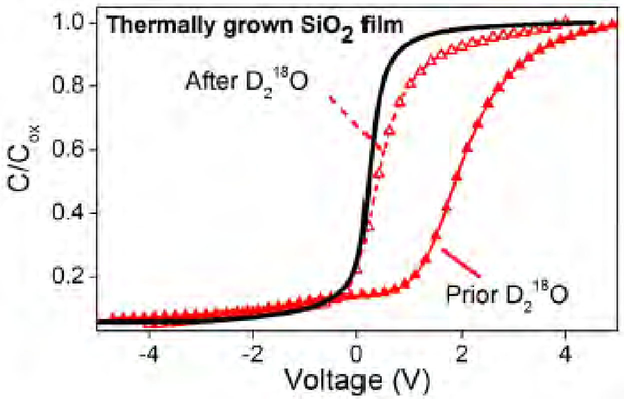
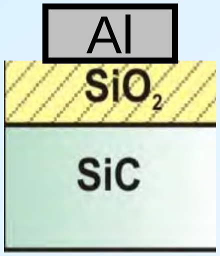
Interaction of $D_2{}^{18}O$ with SiO_2/SiC

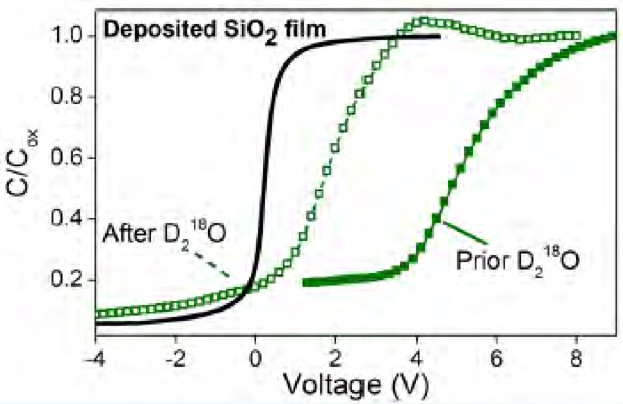
Oxidation in O_2



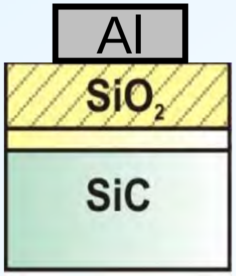


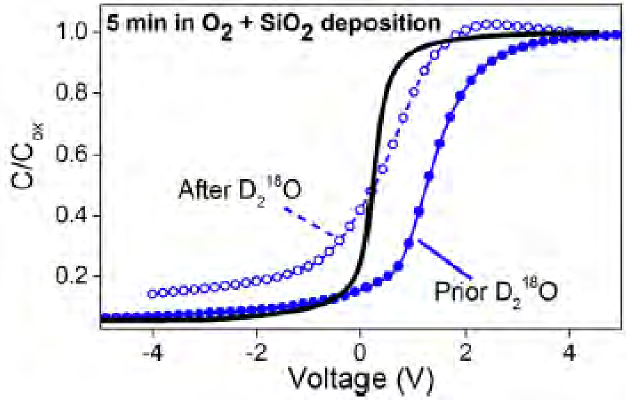
SiO_2 deposition





5 min oxidation
+ SiO_2 deposition





Significant reduction in the **negative effective charge** in **MOS capacitors** after $D_2{}^{18}O$ exposure

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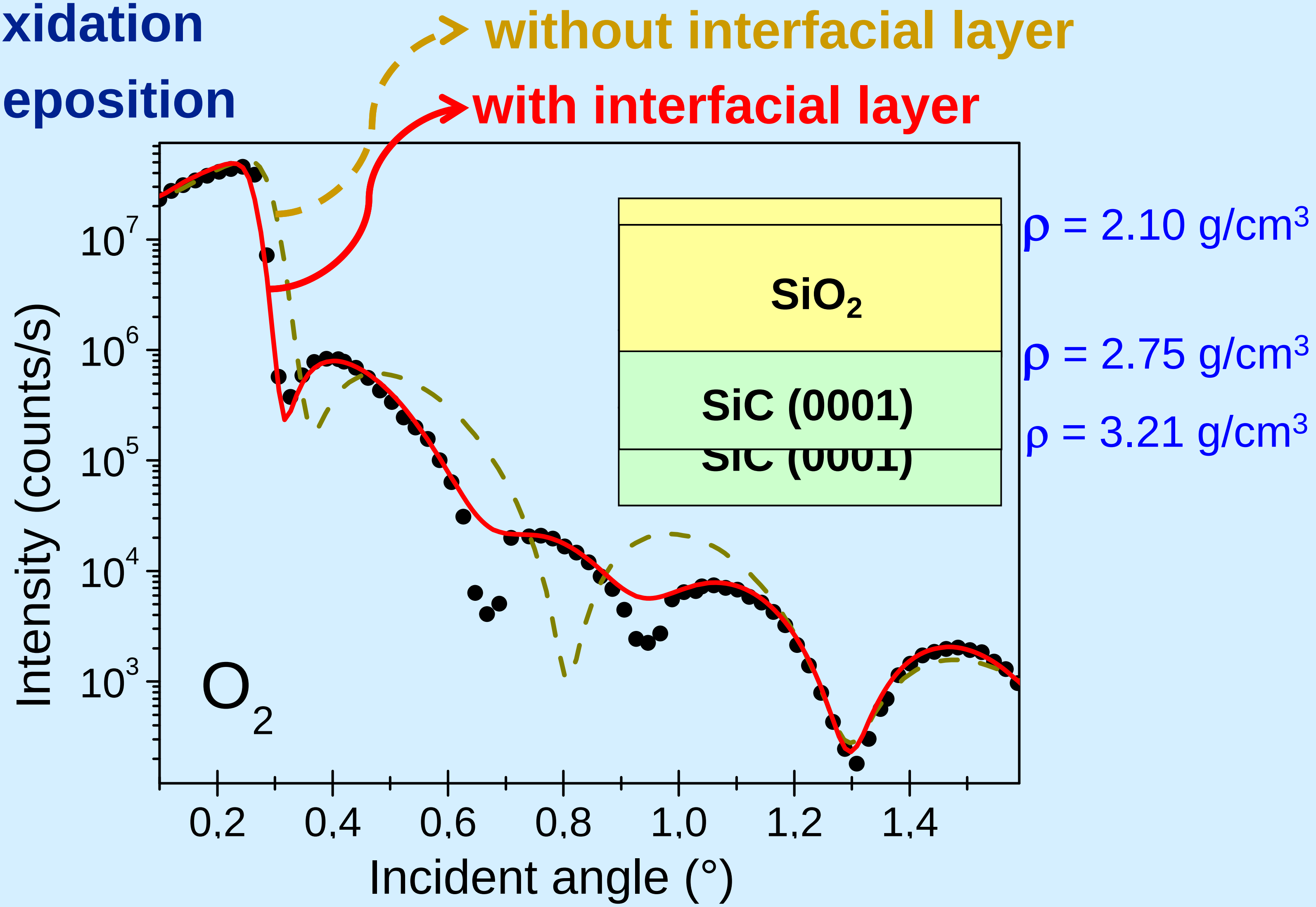
X-Ray Reflectivity (XRR)

5 min oxidation

+ SiO_2 deposition



without interfacial layer

with interfacial layer

ρ = 2.10 g/cm^3

ρ = 2.75 g/cm^3

ρ = 3.21 g/cm^3

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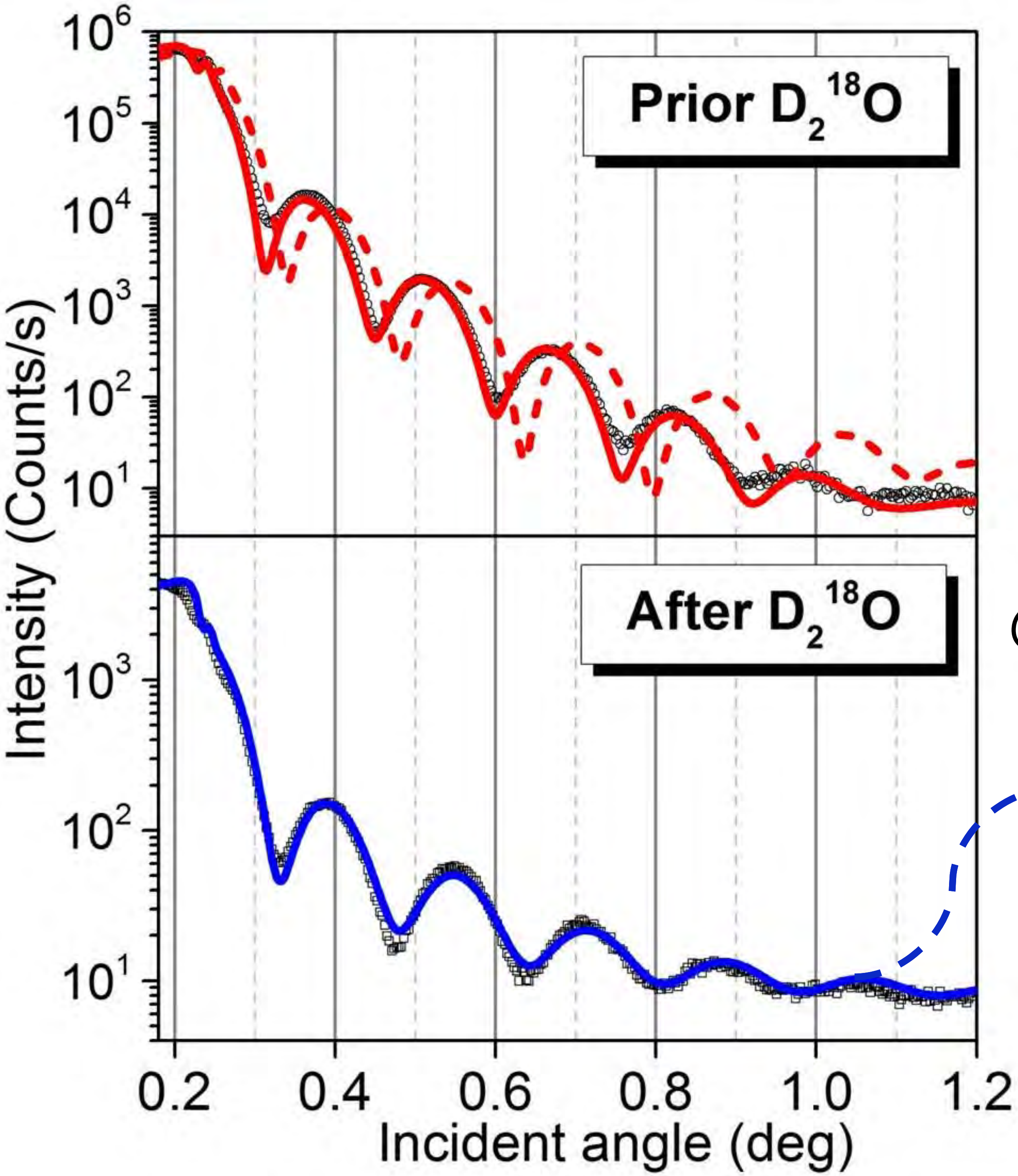
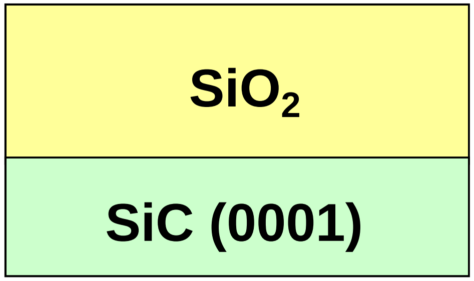


@ 800°C

without interfacial layer



SiO_2

SiC (0001)

Partial Conclusions

- ✓ **D** incorporation in **dep.SiO_2**/SiC and **dep.SiO_2**/Si structures occurs mainly in the SiO_2/semiconductor **interface region**
- ✓ Water vapor exposure at 800°C led to total **isotopic exchange** between **^{18}O** from water and **^{16}O** present in the **dep. SiO_2** film
- ✓ The thermal growth of SiO_2 prior to its deposition on SiC **reduced** the incorporation of **D**
- ✓ **D** incorporation **increases** with the oxidation **time** and exposure **temperature** for SiO_2/SiC
- ✓ The incorporation of **D** depends on the **route** employed to obtain SiO_2 films on SiC

General Conclusions

✓ The **route** employed to obtain SiO_2 films on SiC has a great influence in the incorporation of **O** and of **D** from water vapor exposures

✓ Larger incorporation of **D** ↔ larger amounts of **electrical defects**

✓ Water vapor exposures led to the removal of the **interfacial layer** between the SiO_2 film and SiC ↔ reduced the **effective negative charge** in all tested structures

✓ **High-Resolution Depth Profiling** techniques were crucial to unravel these facts

Acknowledgements

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Fapergs

Thank you !