Nuclear reaction analysis and narrow profiling

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Topics

- Introduction to Si and SiC
- Principles of Isotopic Tracing
- Principles of Nuclear Reaction Analyses: NRA and NRP
- Results on thermal oxidations of Si and SiC

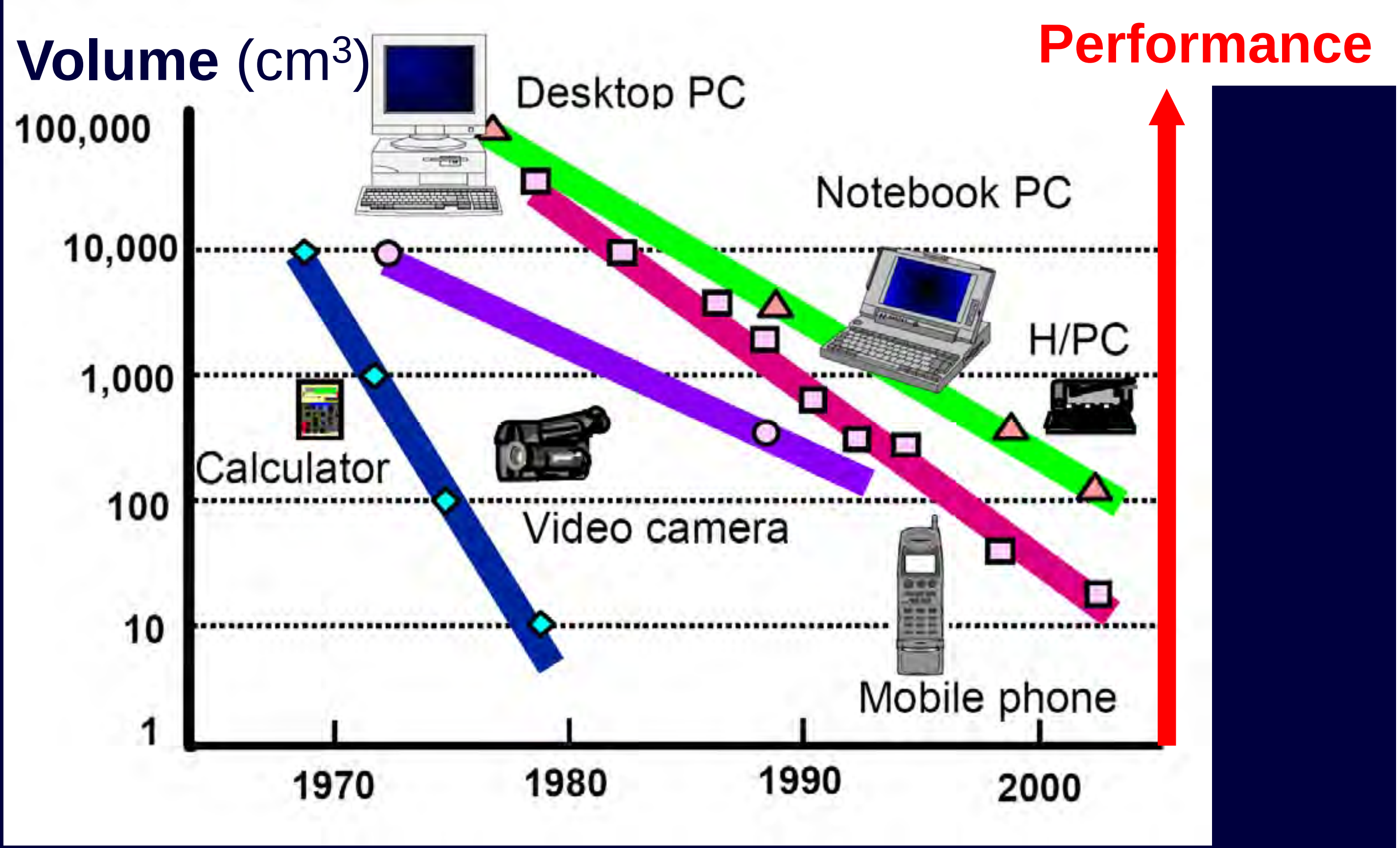
Advantages of Si

- Oxide film thermally grown (SiO_2)
  - Excelent electrical and thermodinamic characteristics
- SiO_2/Si interface
  - Low density of electrically active states

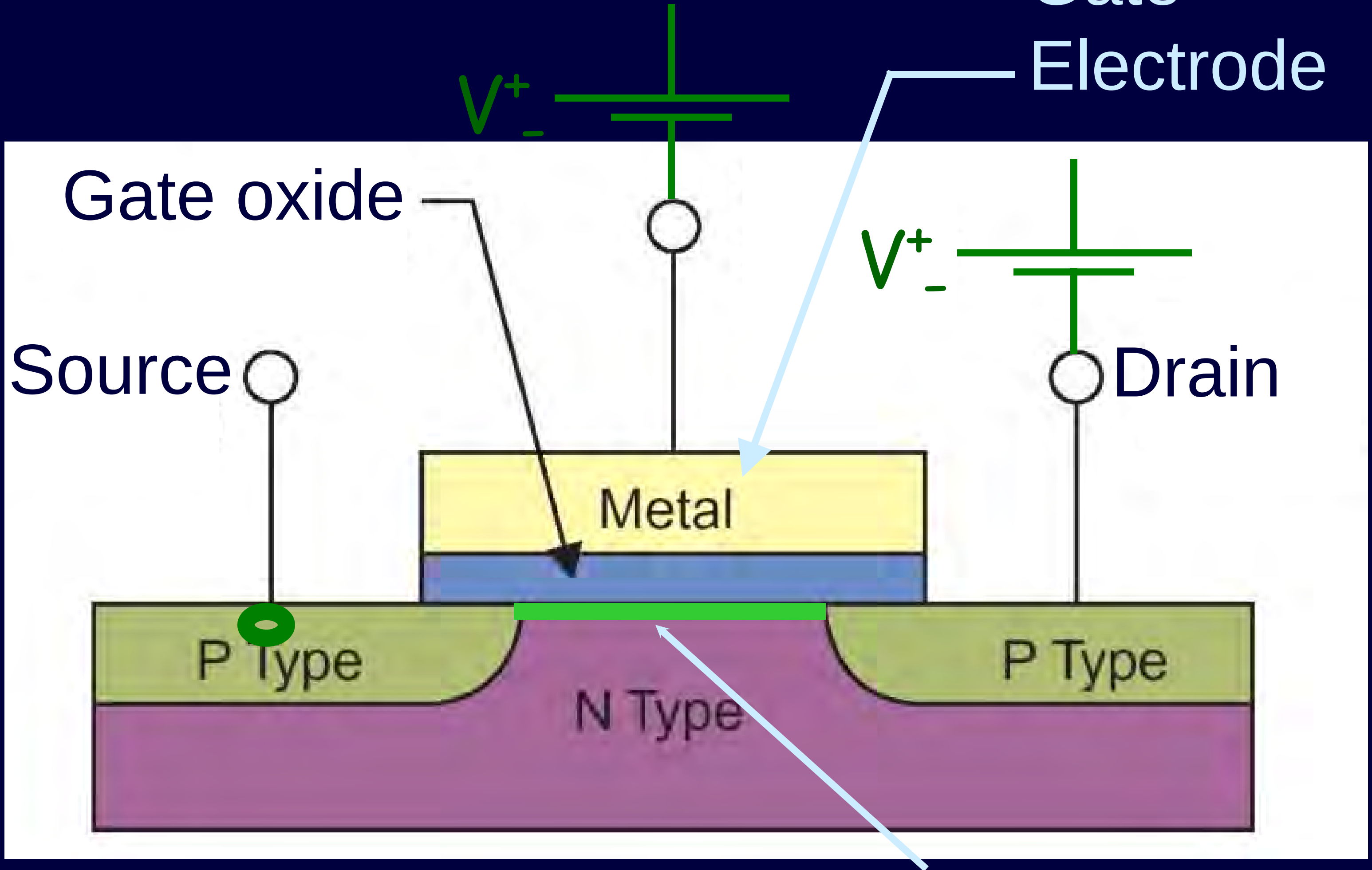

1993


2013

Silicon: the most widely used semicondutor in the microelectronic industry



MOSFET



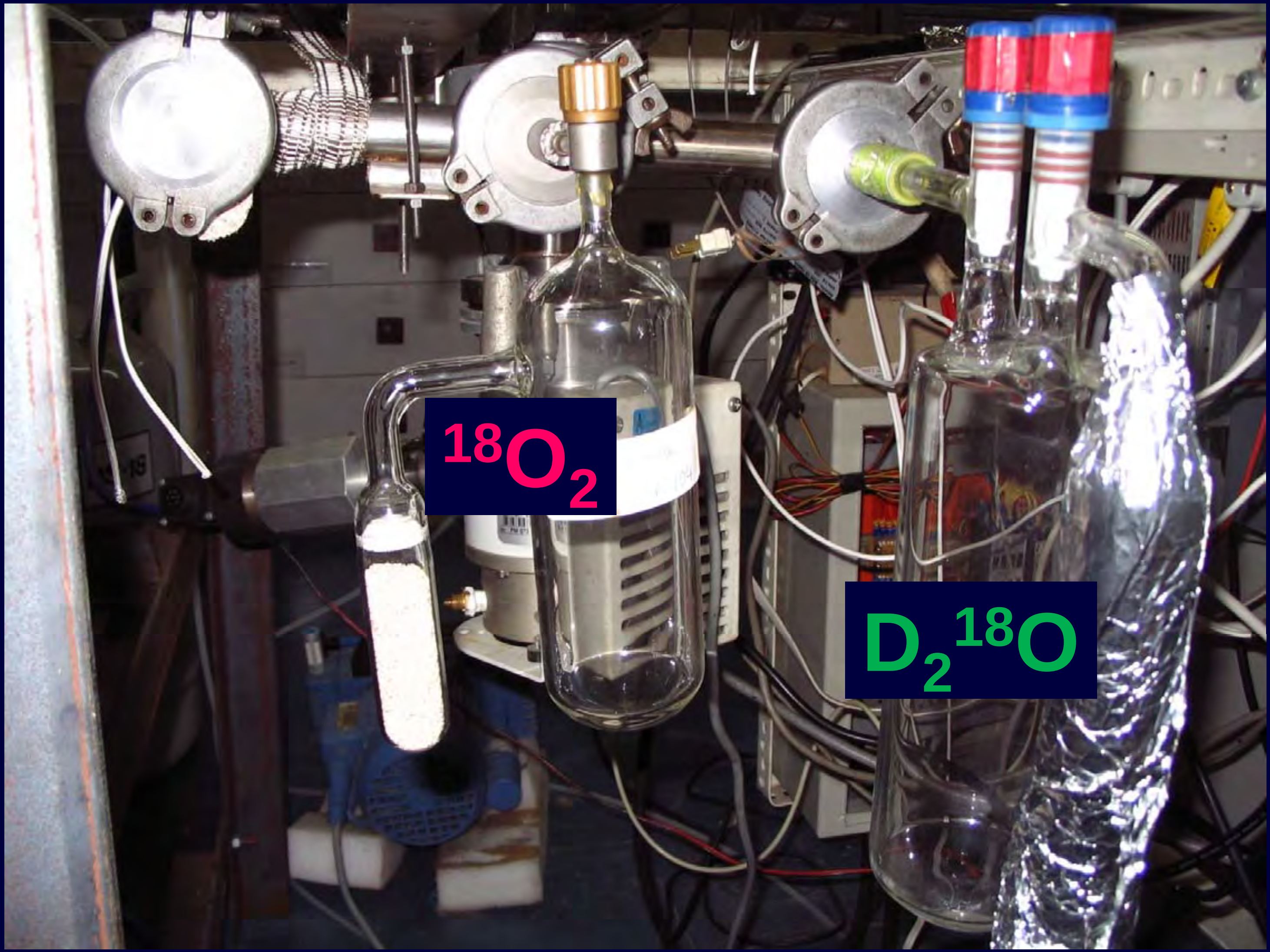
Gate Electrode

Dielectric/semicondutor interface (inversion layer)

From chip to transistor - Intel

Natural oxygen: 99,759% ^{16}O 0,204% ^{18}O 0,037% ^{17}O

Natural hydrogen: 99,985% ^{1}H 0,015% ^{2}H = D



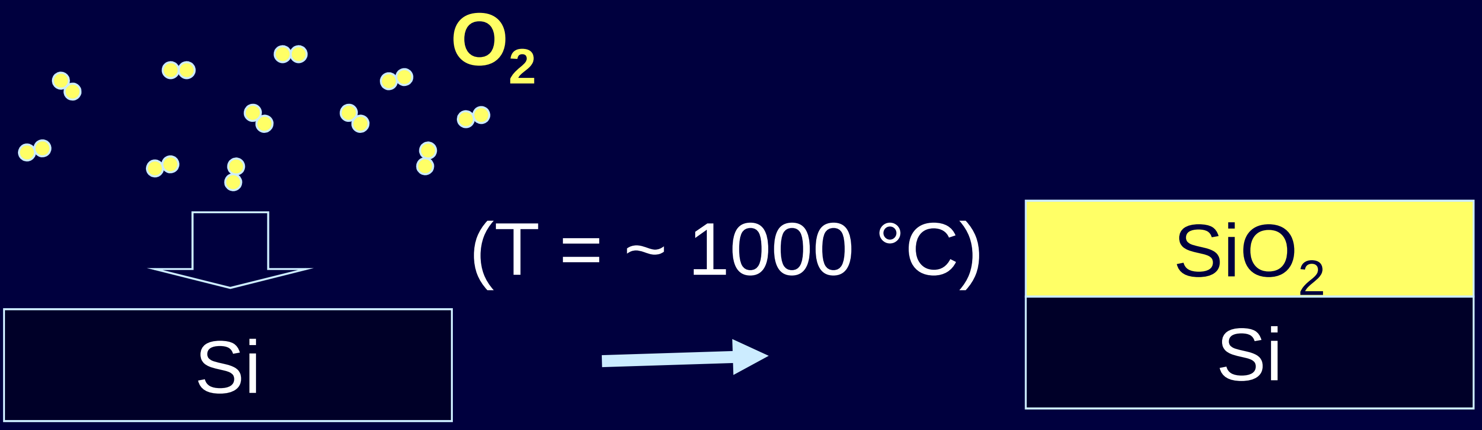
$^{18}O_2$ 97% ~U$ 1,000/L $D_2{}^{18}O$ ~US$ 2,000/mL

Static atmosphere reactor

Isotopic Tracing

*Using **isotopes** and **nuclear reactions** to understand the **atomic transport** during the Si thermal oxidation*

Oxidation in O_2 (natural abundance):



O_2

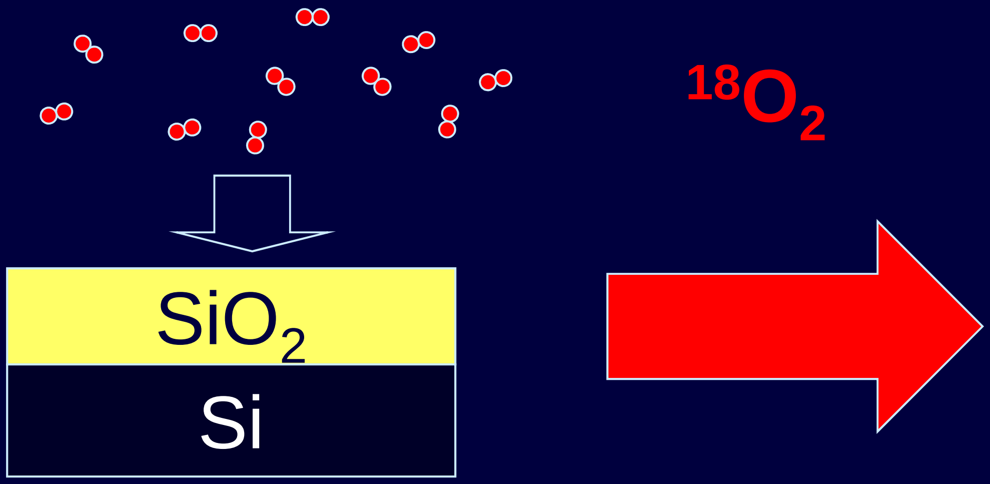
Si

(T = ~ 1000 °C)

SiO_2

Si

Oxidation in $^{18}O_2$

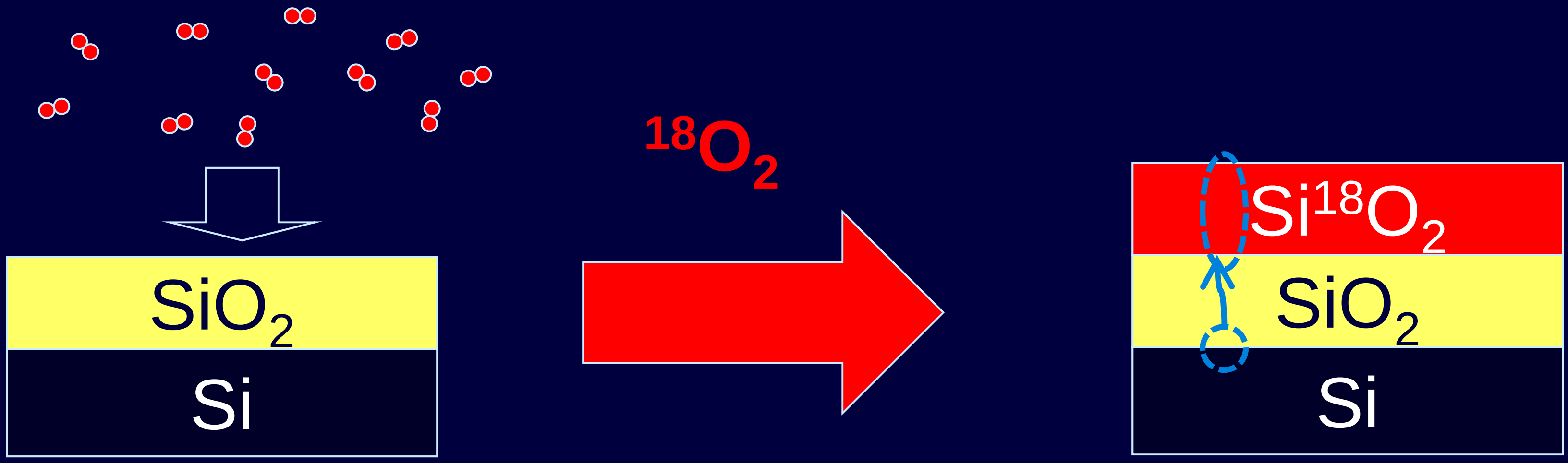


Who is the mobile species ?
O, Si, or both ?

Mobile species during oxidation

1st possibility:

Si is the mobile species



SiO_2

Si

$^{18}O_2$

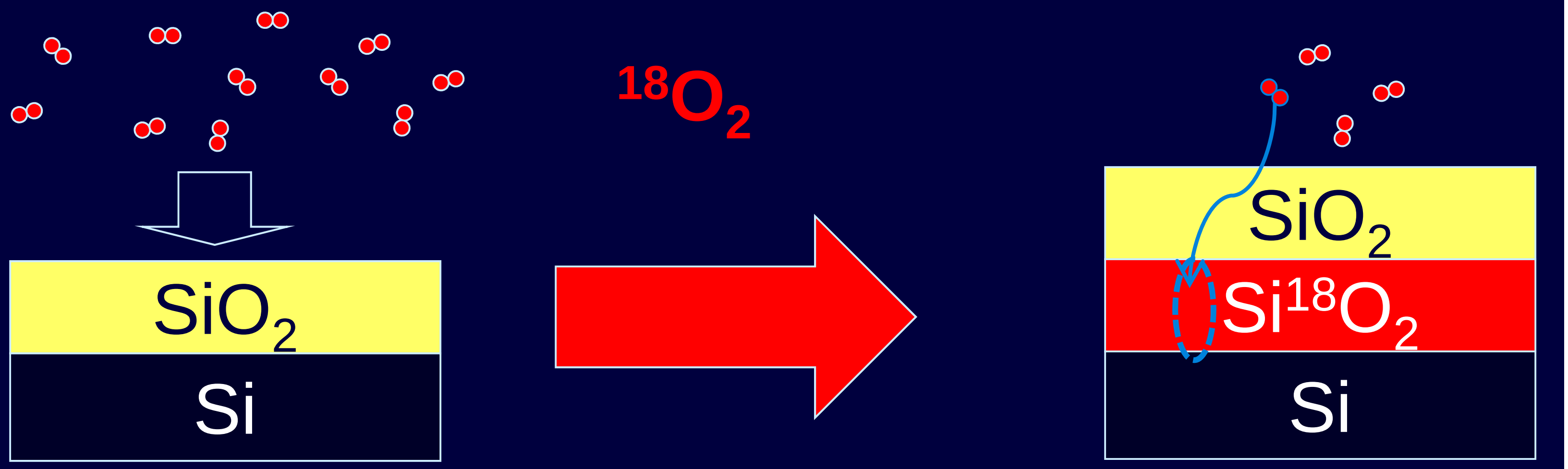
$Si^{18}O_2$

SiO_2

Si

Mobile species during oxidation

2nd possibility: **O is the mobile species**



$^{18}O_2$

SiO_2

Si

SiO_2

$Si^{18}O_2$

Si

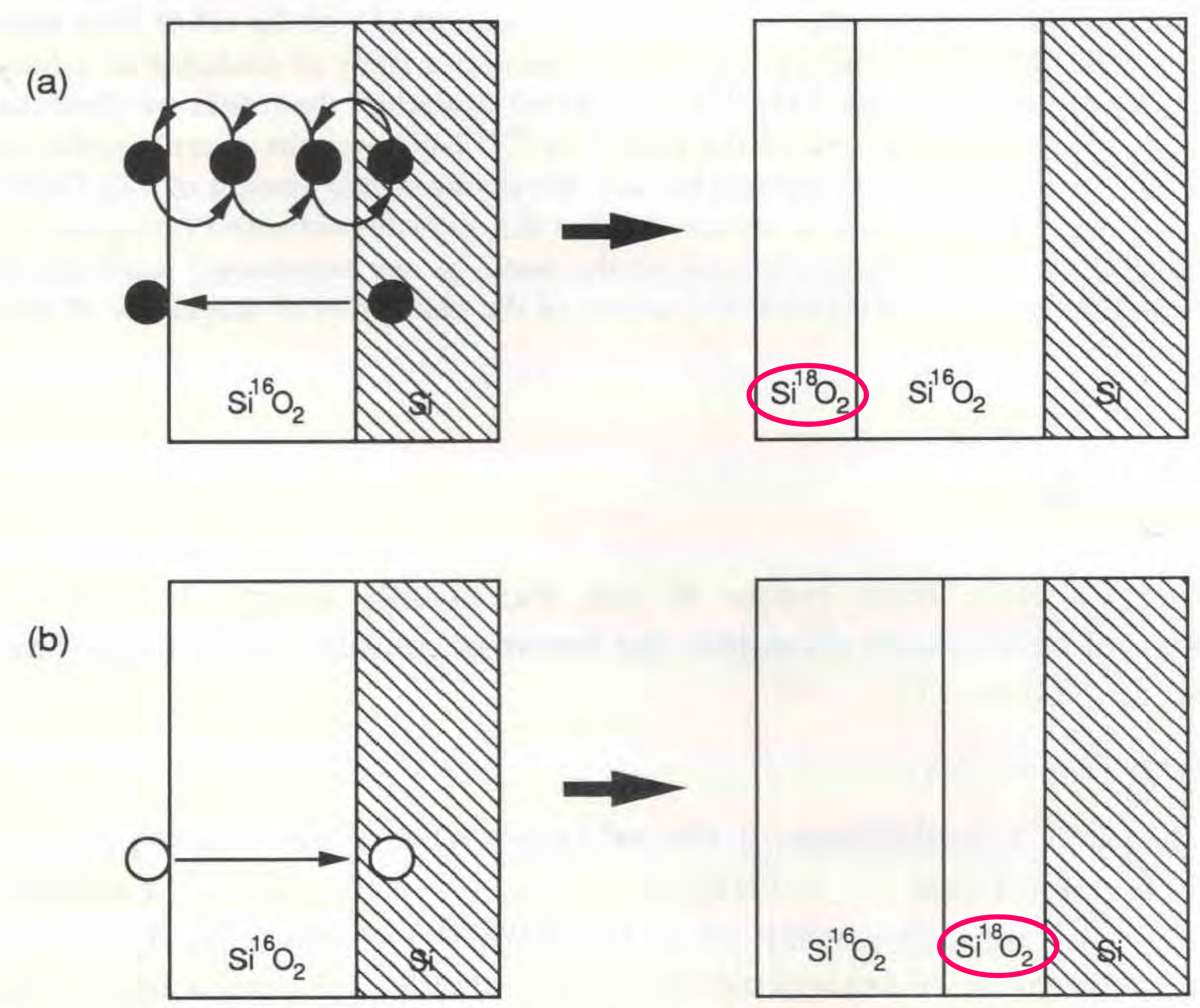
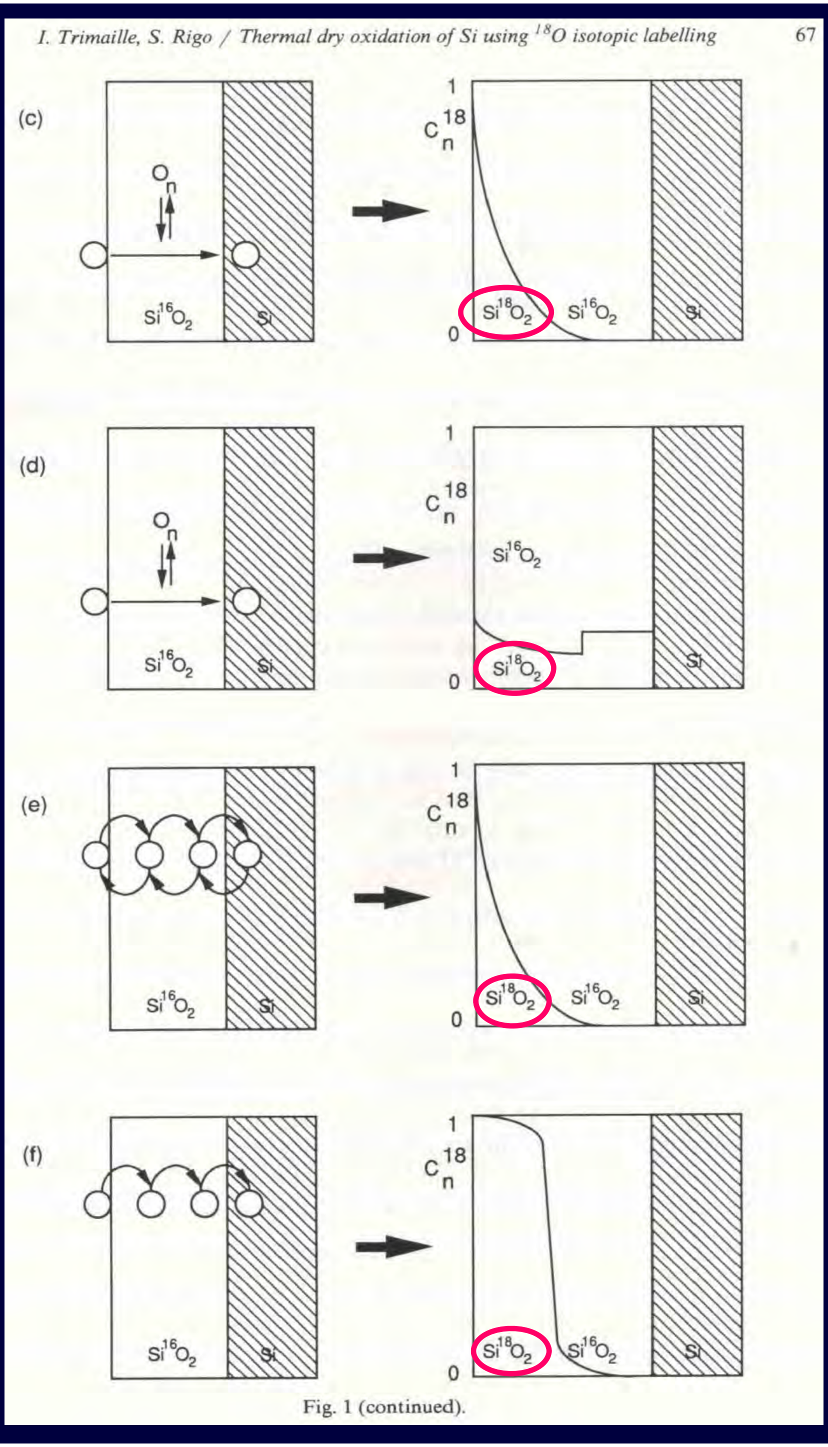


Fig. 1. Illustration of how the labelling technique can be used to identify the mobile species and their transport mechanism: (a) only silicon is mobile; (b) oxygen moves interstitially without reacting with the silica network; (c) oxygen moves interstitially while reacting with the silica network: case of isotopic quasi-equilibrium; (d) oxygen moves interstitially while reacting with the silica network: case far from isotopic quasi-equilibrium; (e) oxygen moves by a simple diffusion of network defects; (f) oxygen moves by migration of network defects in only one direction. Black dots stand for silicon, white dots for oxygen.

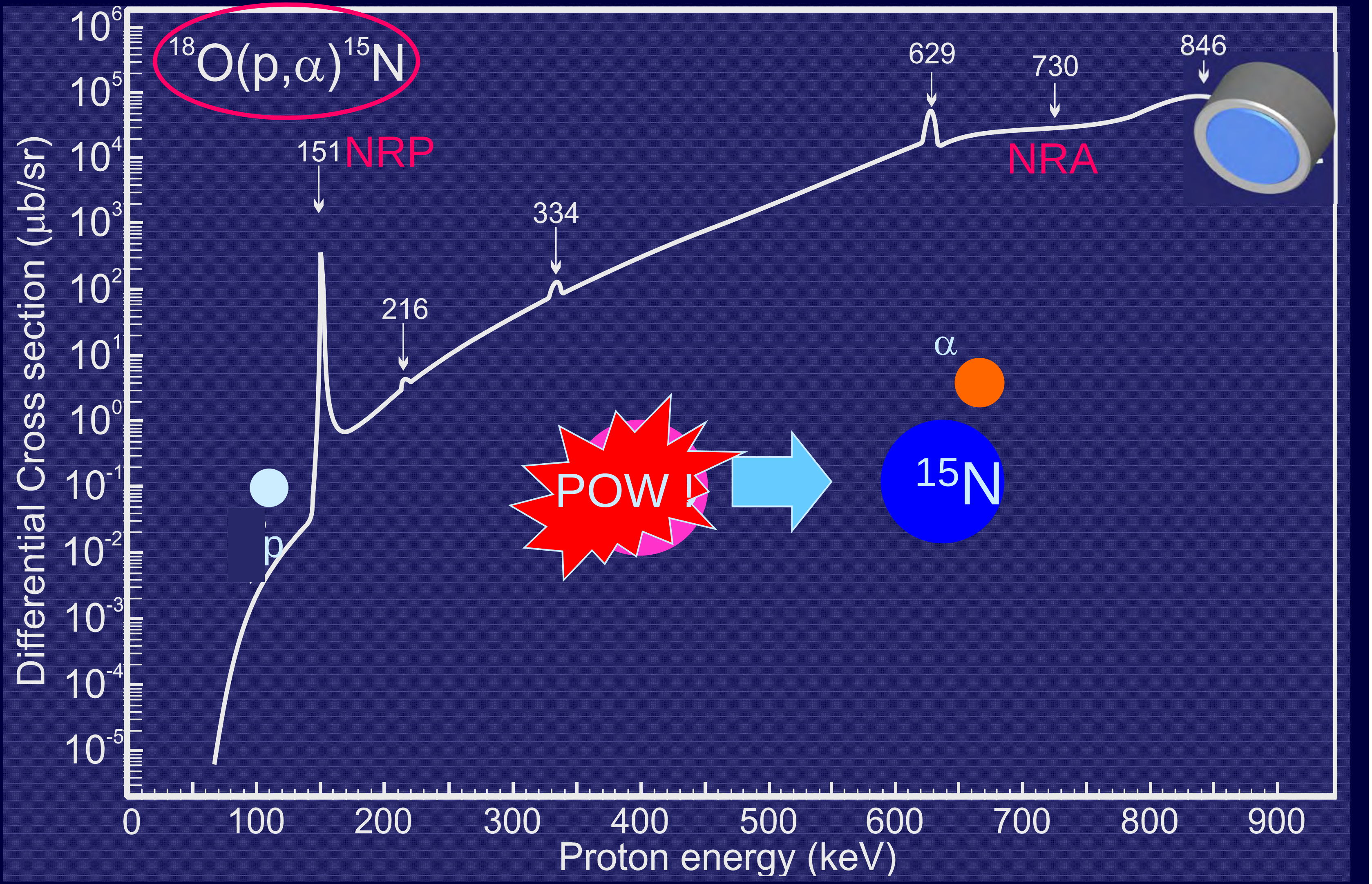


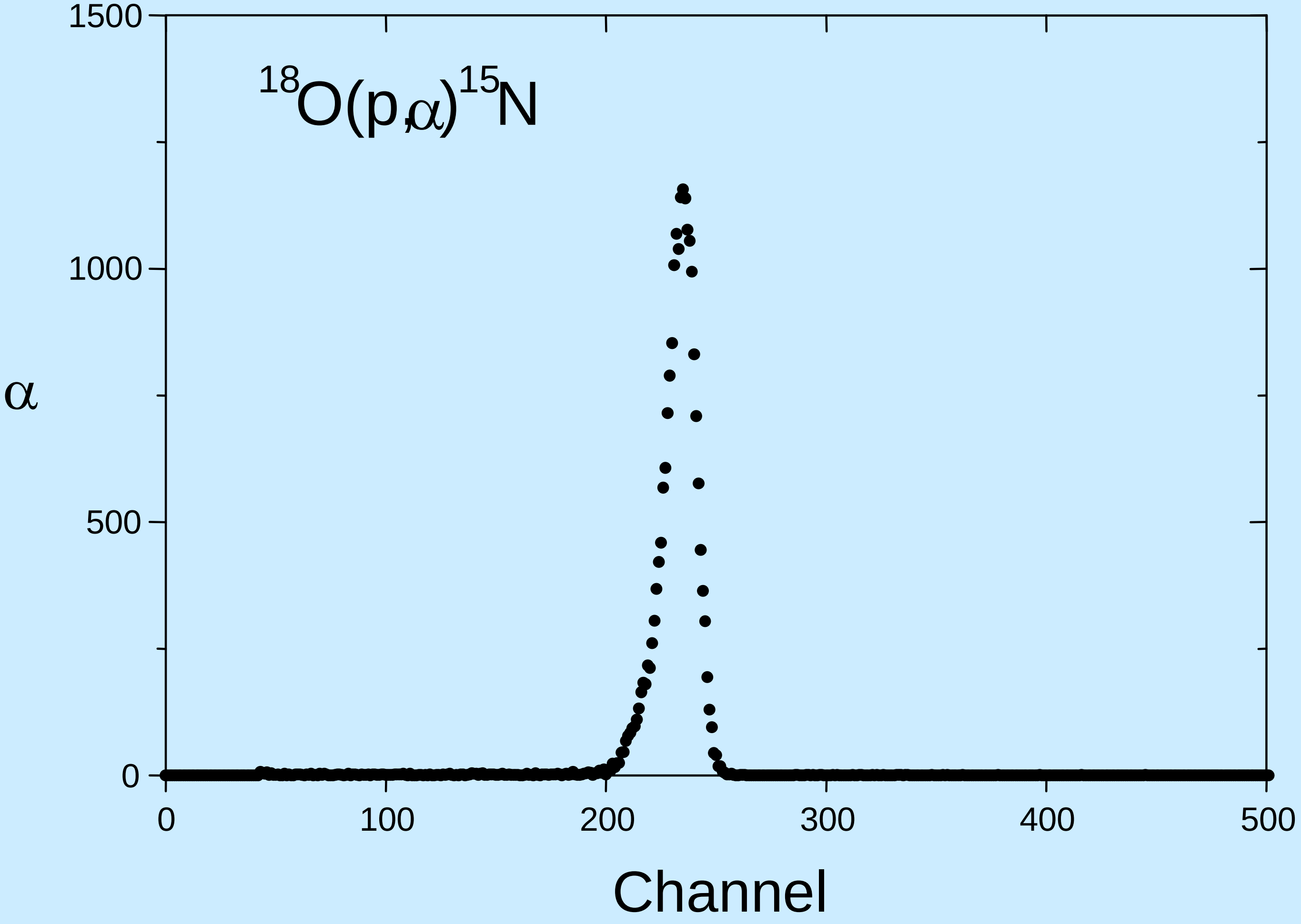
I. Trimaille, S. Rigo / Thermal dry oxidation of Si using ^{18}O isotopic labelling 67

Fig. 1 (continued).

Appl.Surf. Sci.
39 (1989) 65

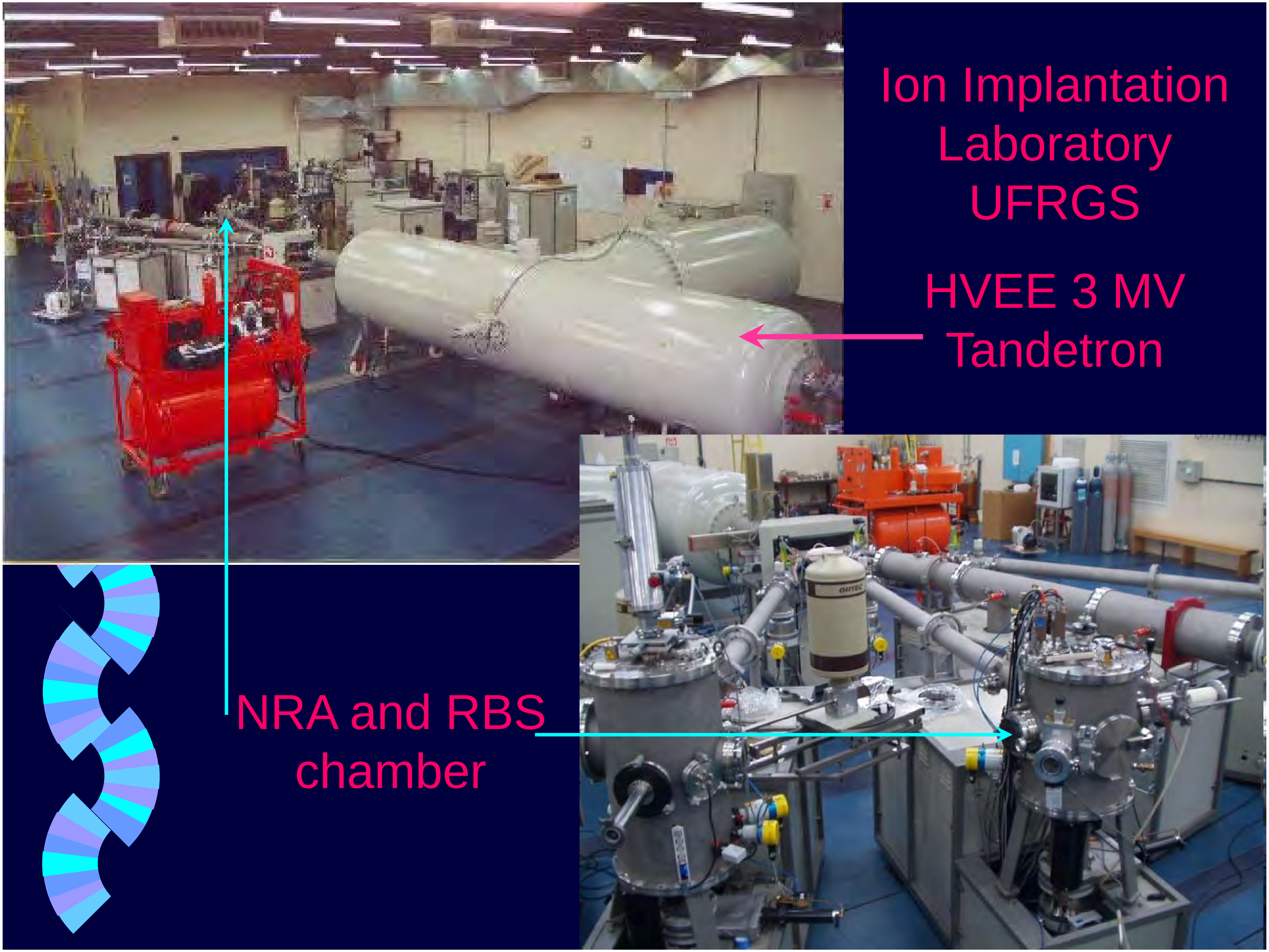
Nuclear Reactions





$^{18}O(p,\alpha)^{15}N$
1500
1000
500
0
α
0
100
200
300
400
500
Channel

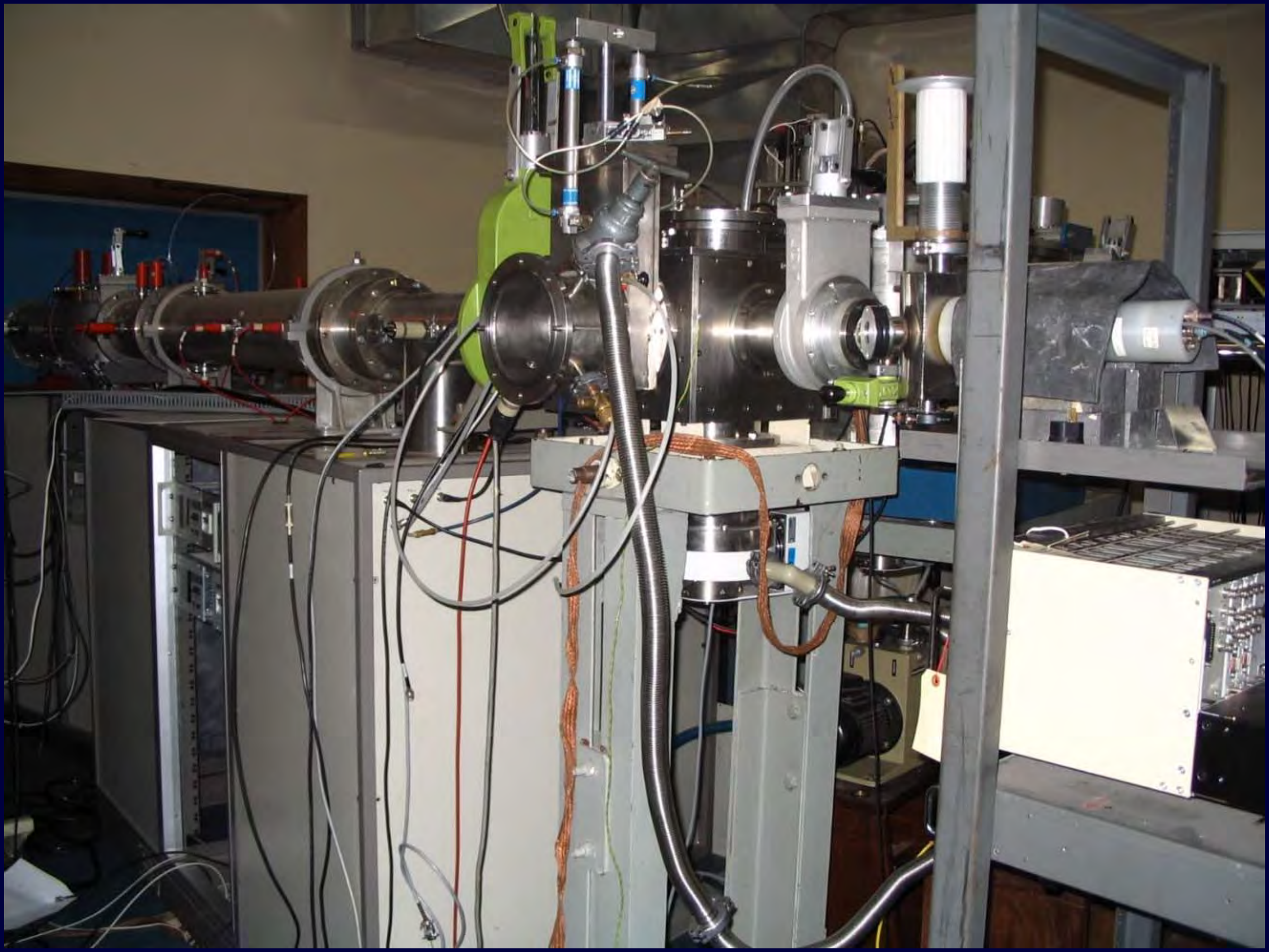
Ion Implantation Laboratory UFRGS



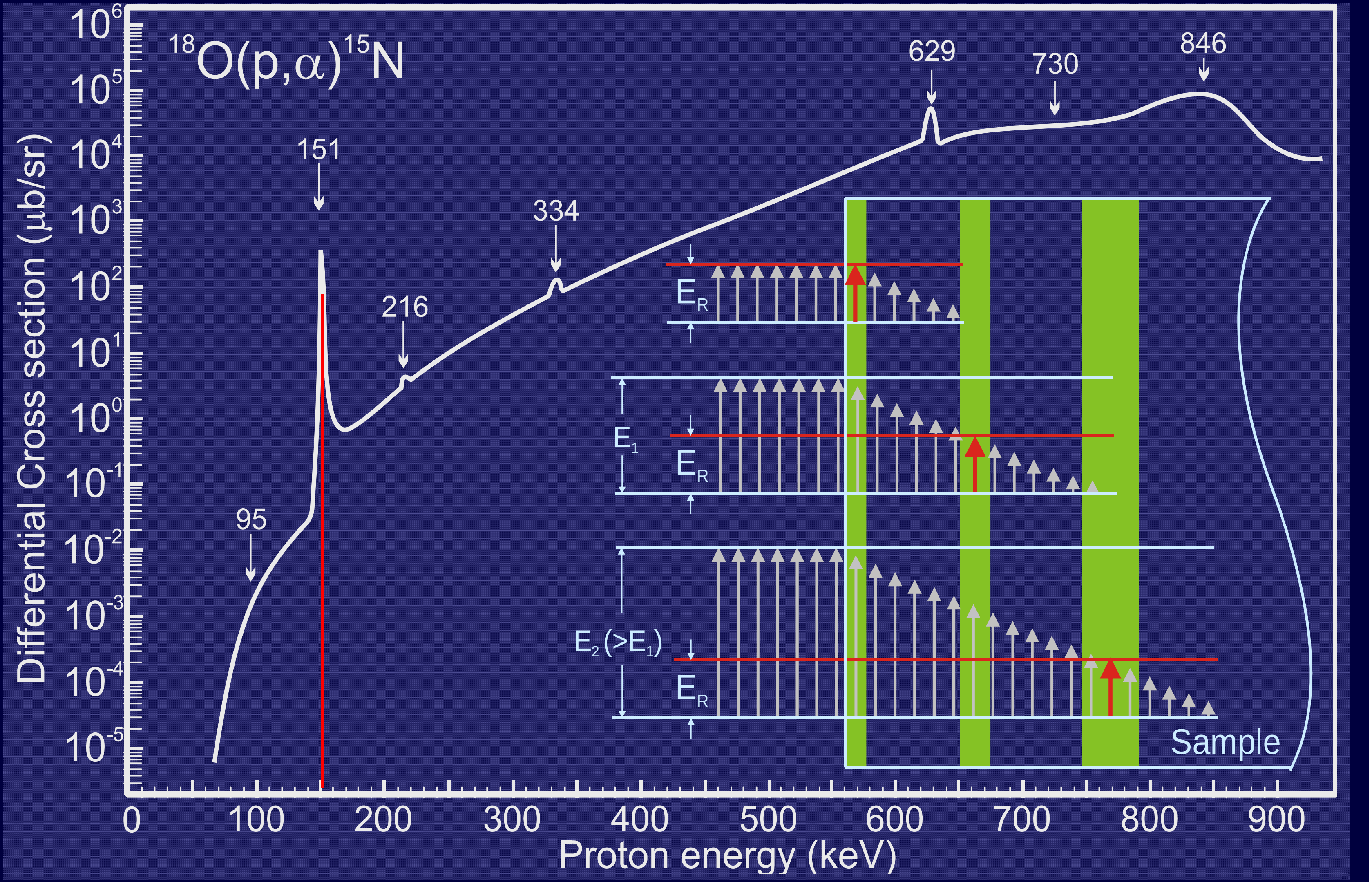
HVEE 3 MV Tandetron

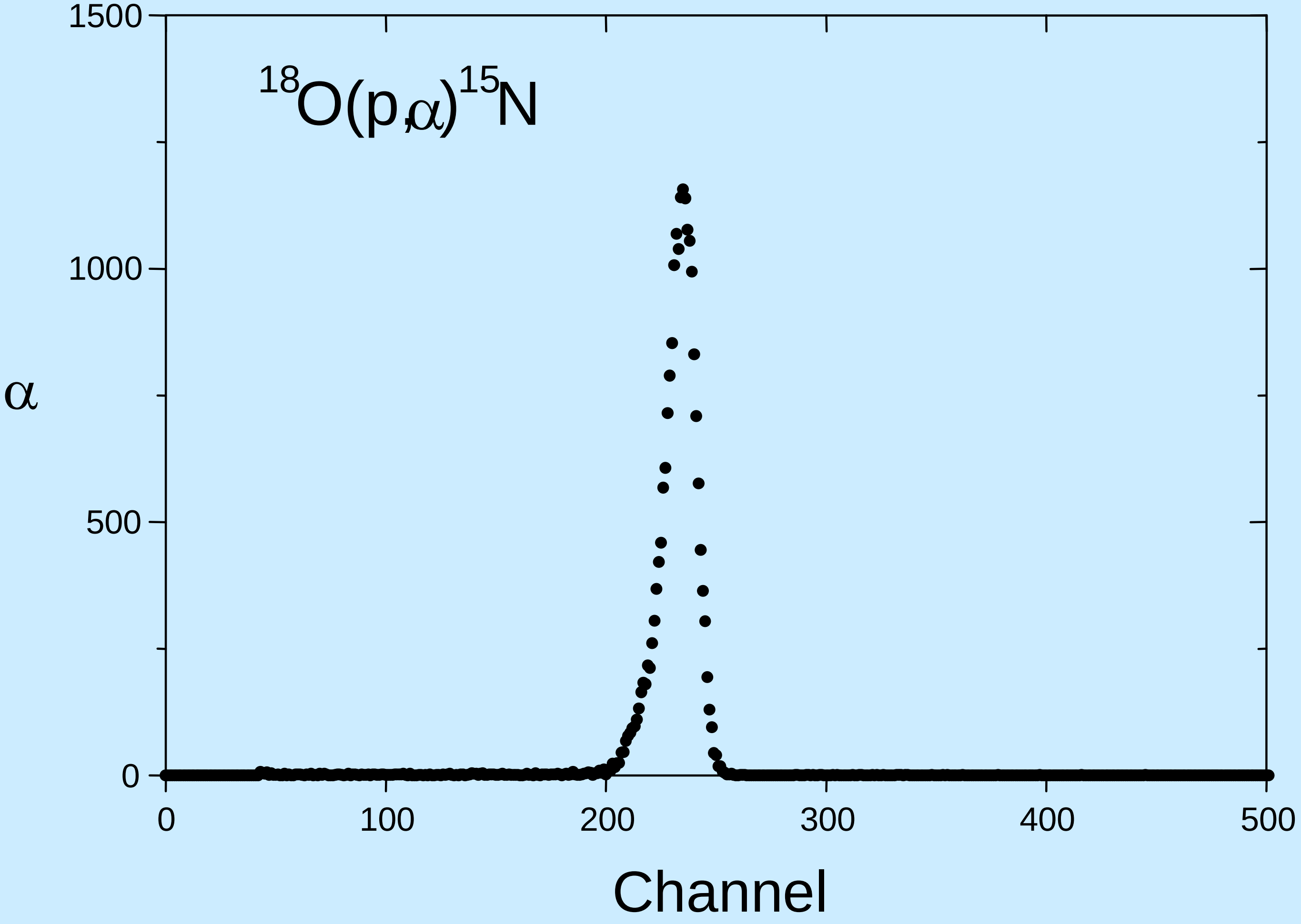
NRA and RBS chamber

HVEE 500 kV single-ended: NRP chamber



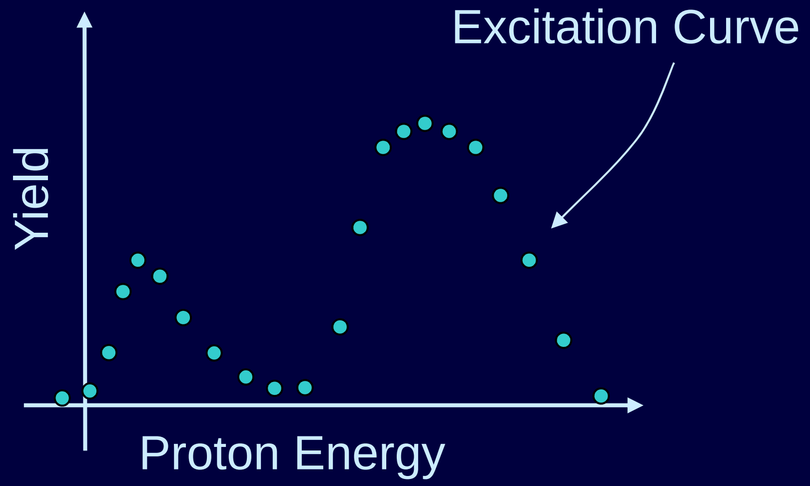
Resonant Nuclear Reaction - NRP

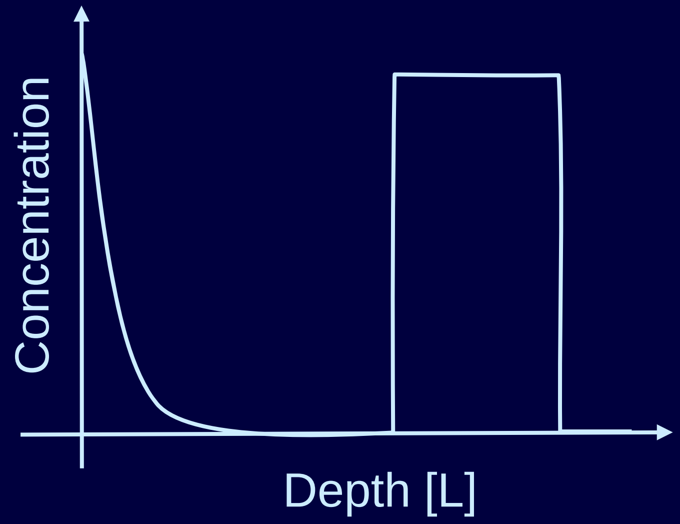


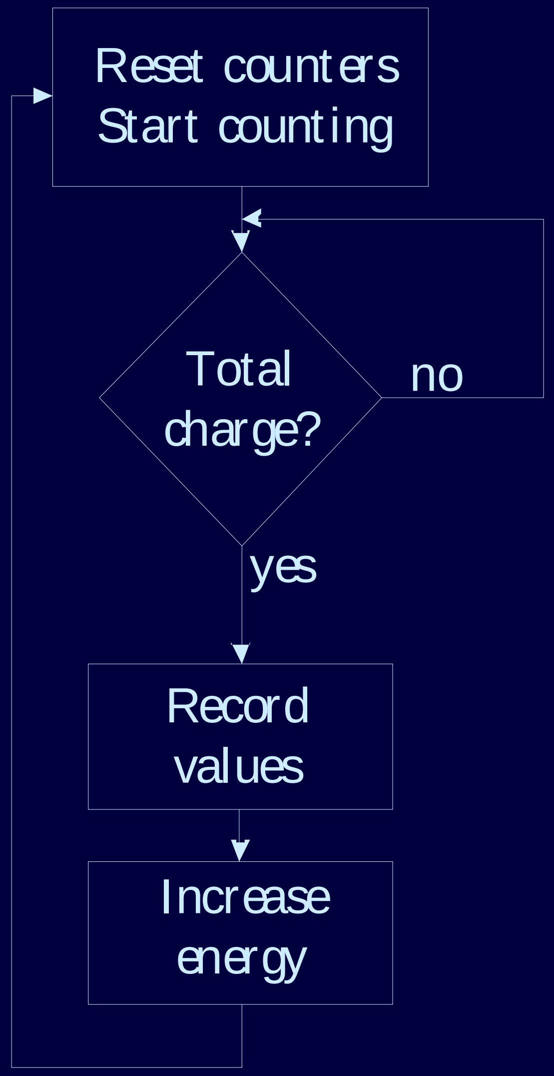


$^{18}O(p,\alpha)^{15}N$
α
Channel
1500
1000
500
0
0
100
200
300
400
500

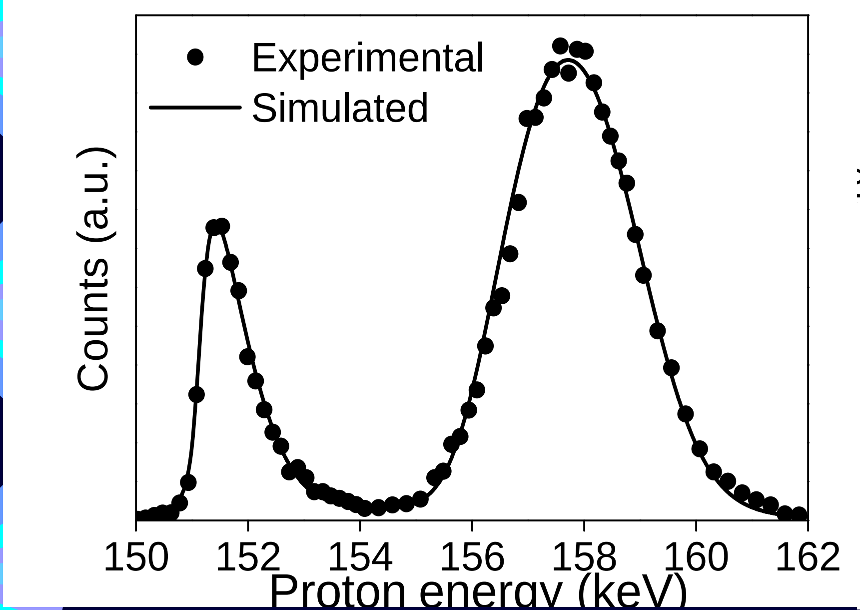
Profile

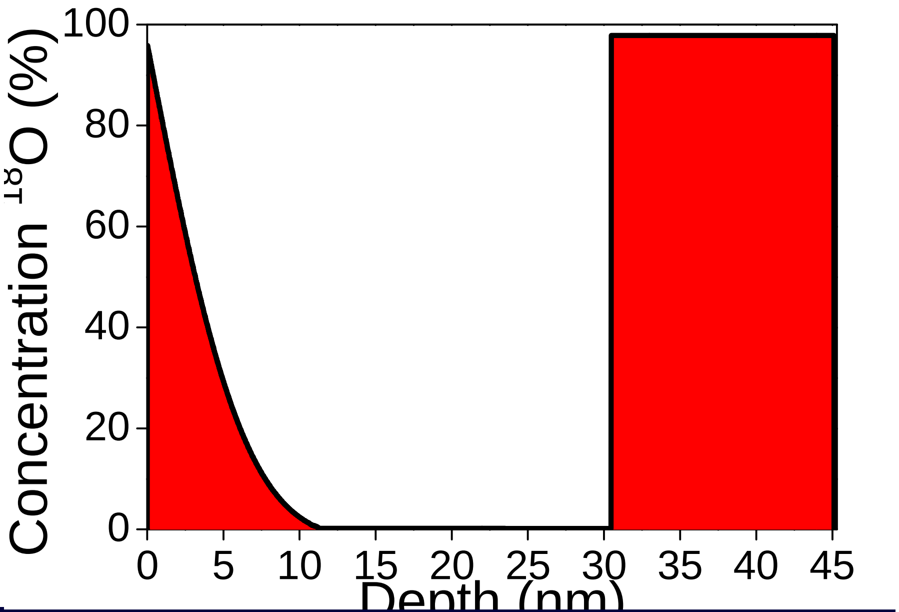

Excitation Curve
Yield
Proton Energy


Concentration
Depth [L]


Reset counters
Start counting
Total charge?
no
yes
Record values
Increase energy

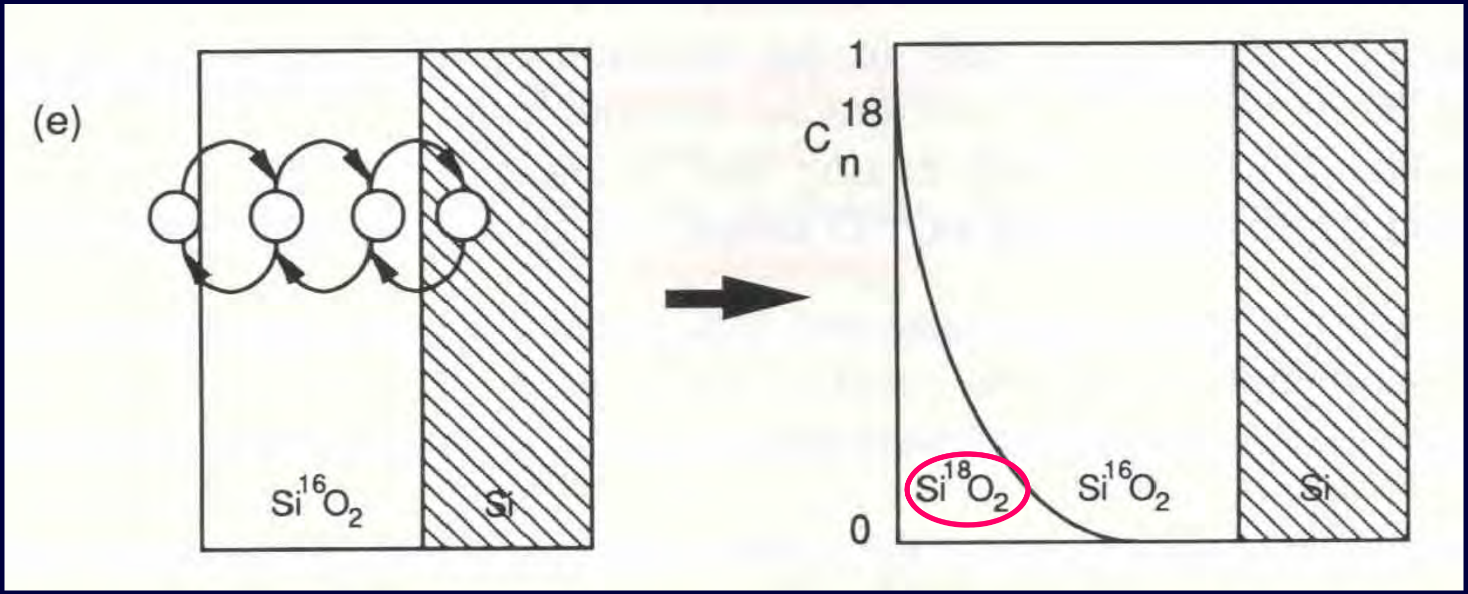
$^{16}O_2$ -$^{18}O_2$ @ 1000ºC

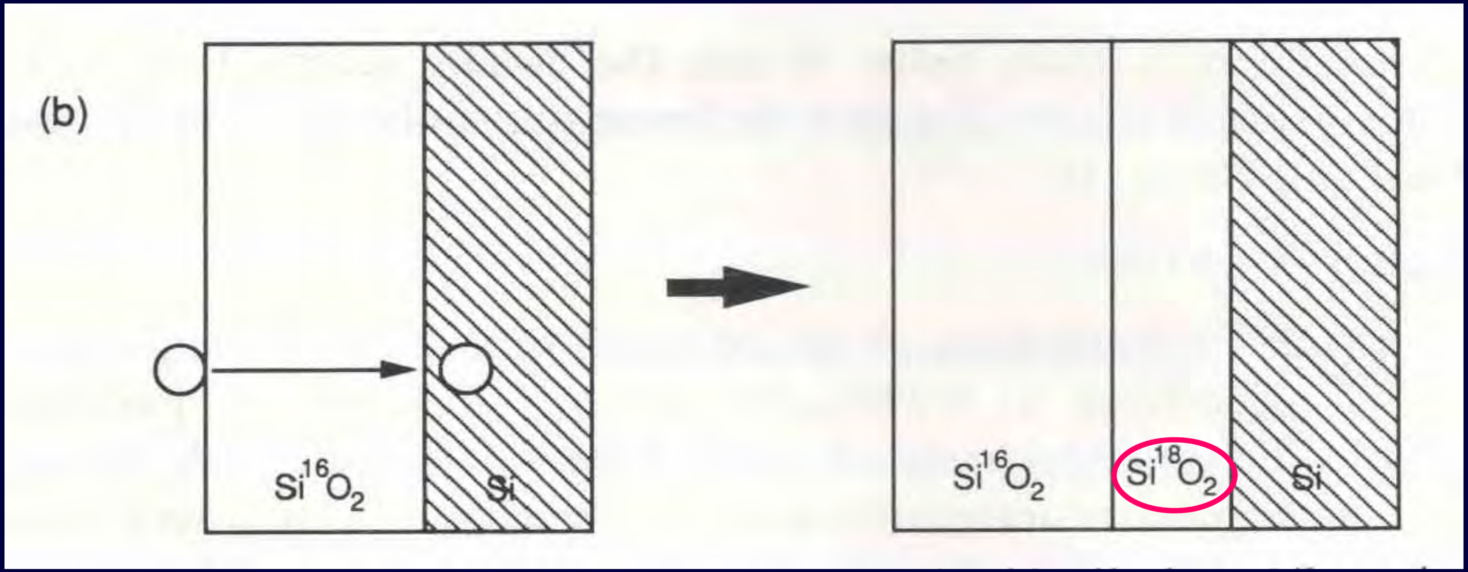




Oxygen is the mobile species and it is transported:

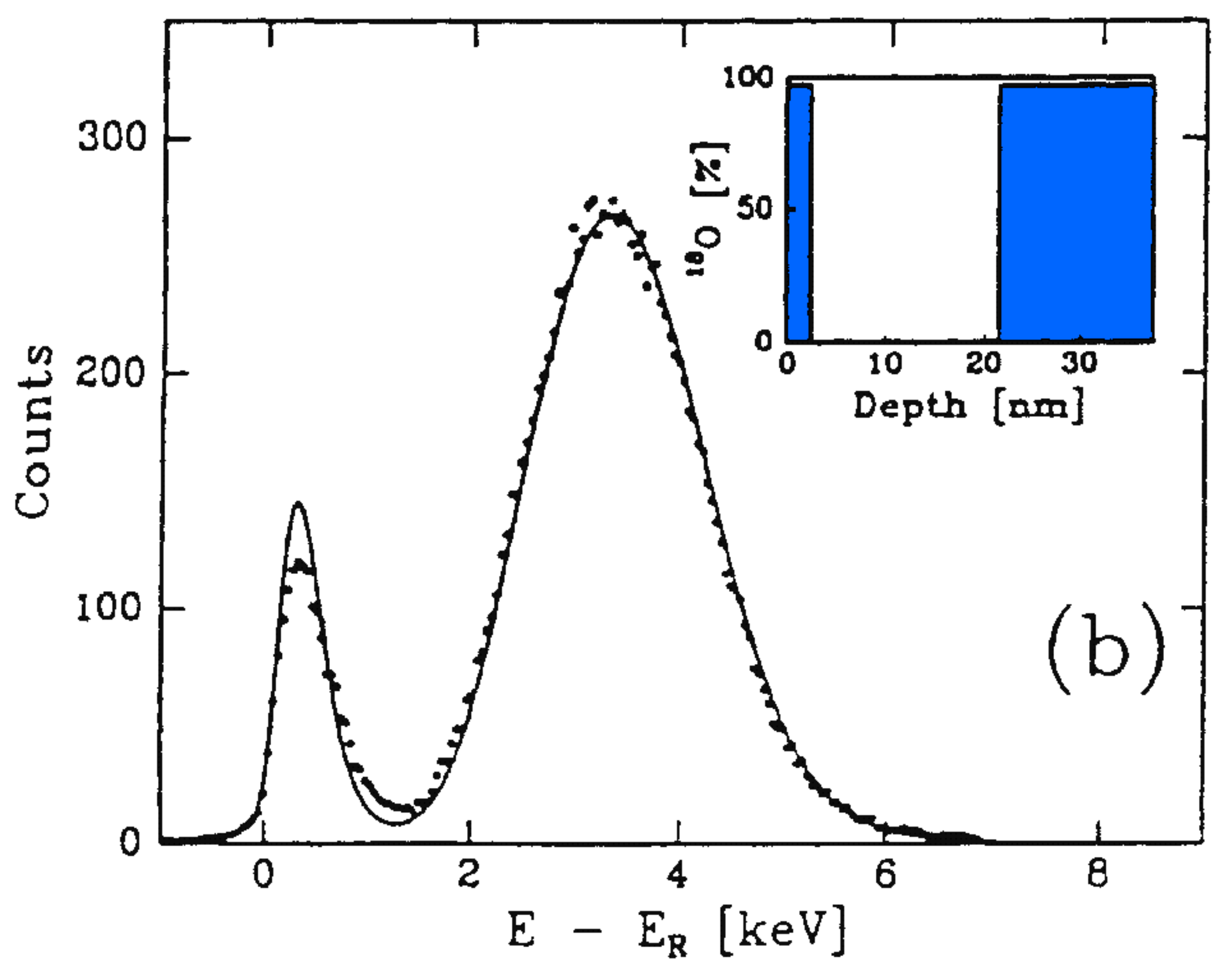
- By diffusion, interacting with network defects (surface region)
- Interstitially, without reacting with the oxide already formed, until reaching the semiconductor interface and there reacting forming SiO_2


(e)
Si16O2
Si
1
C18n
0
Si18O2
Si16O2
Si

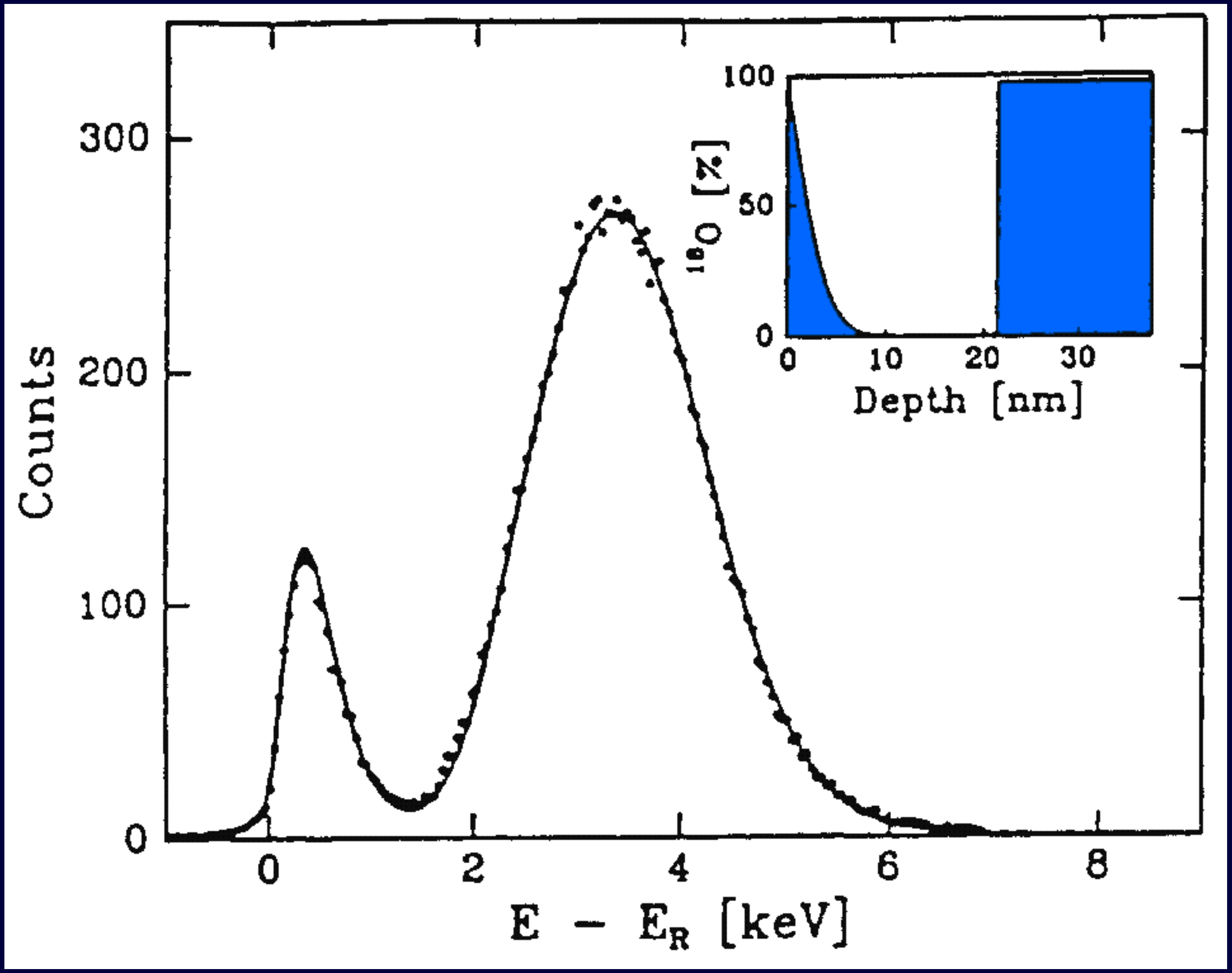

(b)
Si16O2
Si
Si16O2
Si18O2
Si

Profiles reliability

$^{16}O_2$ - $^{18}O_2$ @ 1000°C



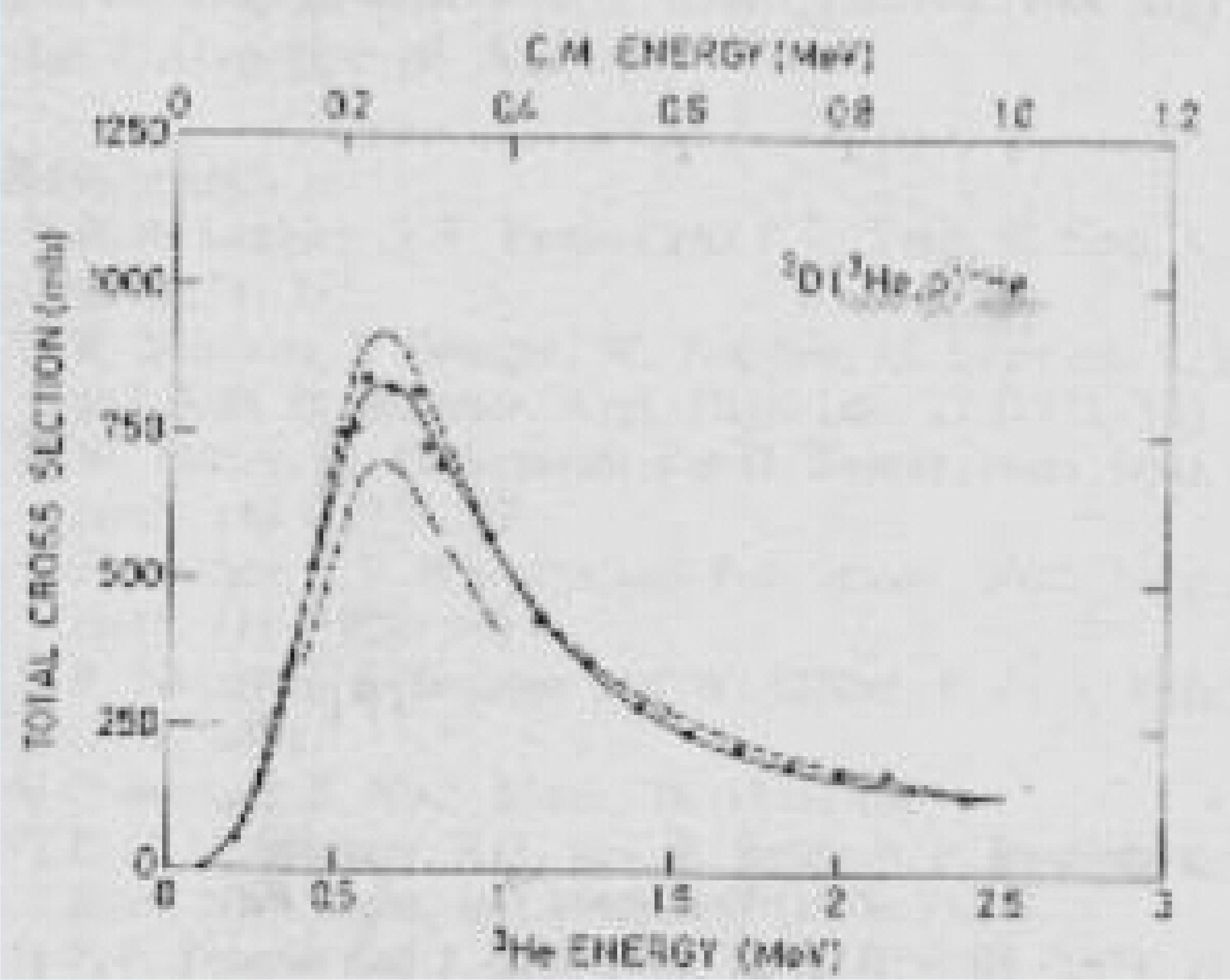
$^{16}O_2$ -$^{18}O_2$ @ 1000°C



Trimaille et al. The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface - 3, ed. H.Z. Massoud *et al.* (The Electrochemical Society, Pennington, 1996), vol.96-1, p. 59

NRA: D amounts

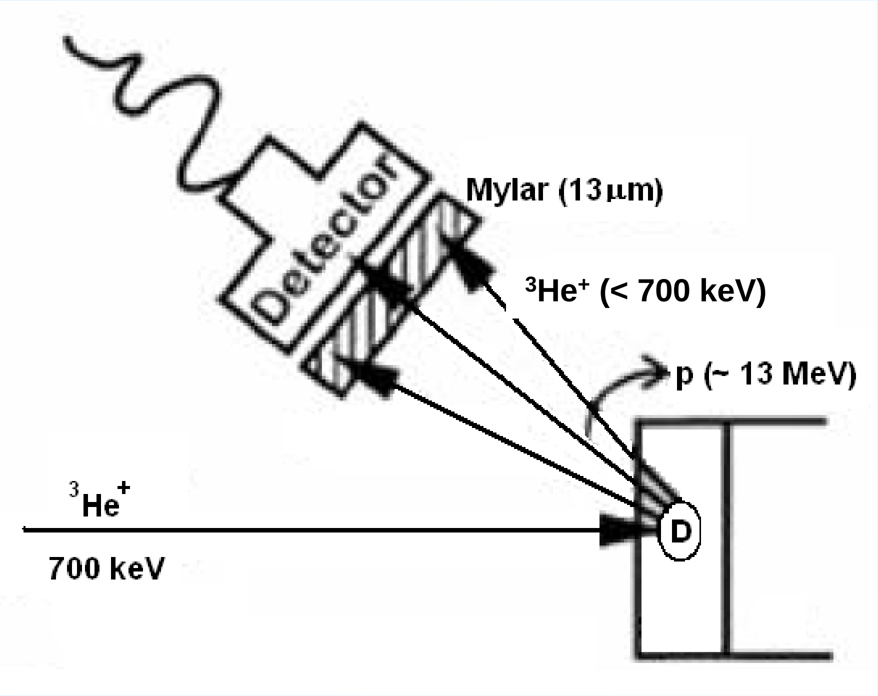
- Nuclear reaction **$D(^3He,p)^4He$**: plateau ~ 700 keV
- Total amounts of D (insensitive to H)

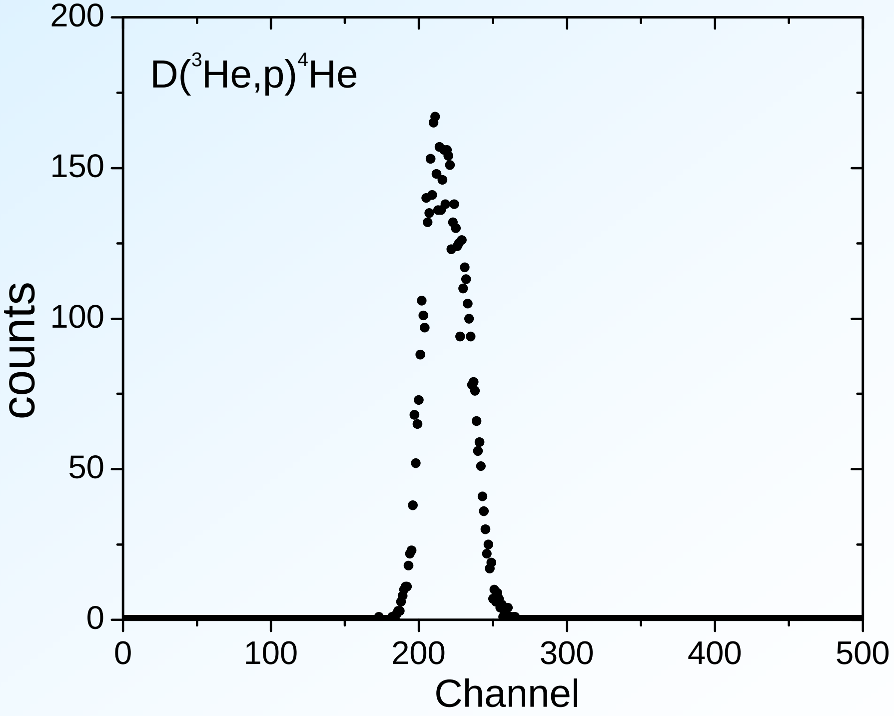


D. Dieumegard *et al.*
NIM 166 (1979) 431

D quantification

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

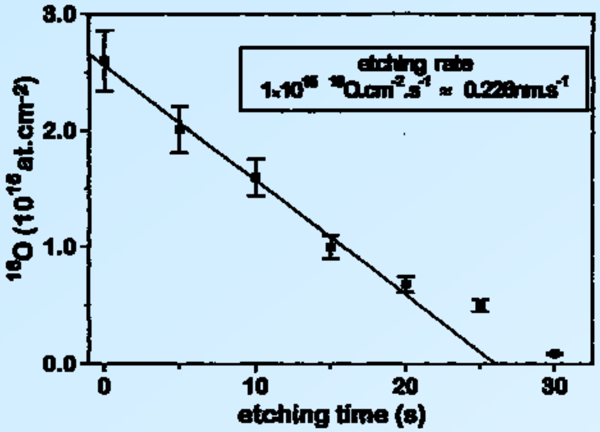




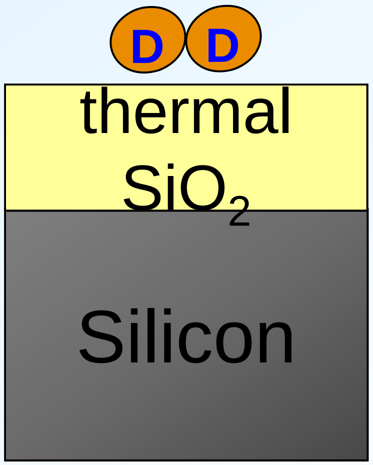
sensitivity ~ 4.0 x 10^{12} D.cm^{-2}

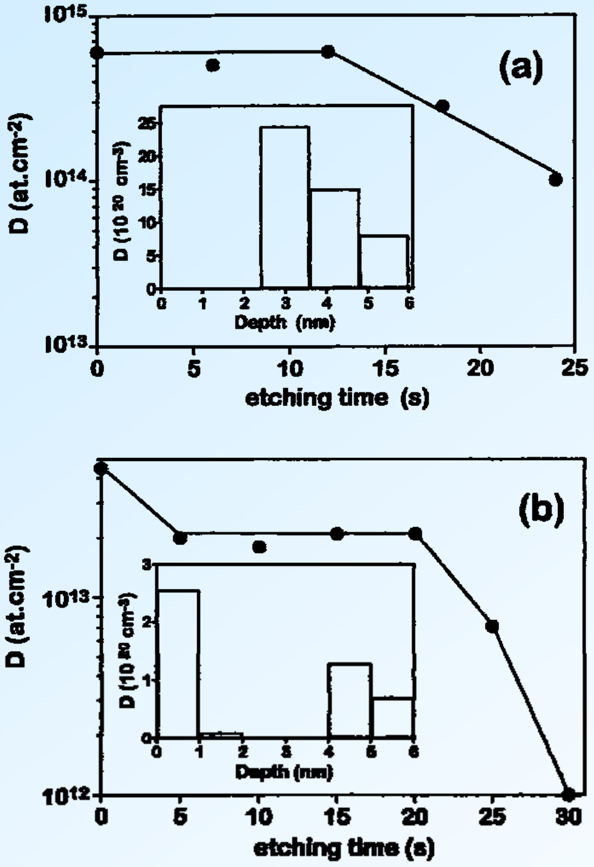
Accuracy: 10%

D profiling



Areal density of ^{16}O in oxide films versus time of chemical dissolution in dilute HF-solution



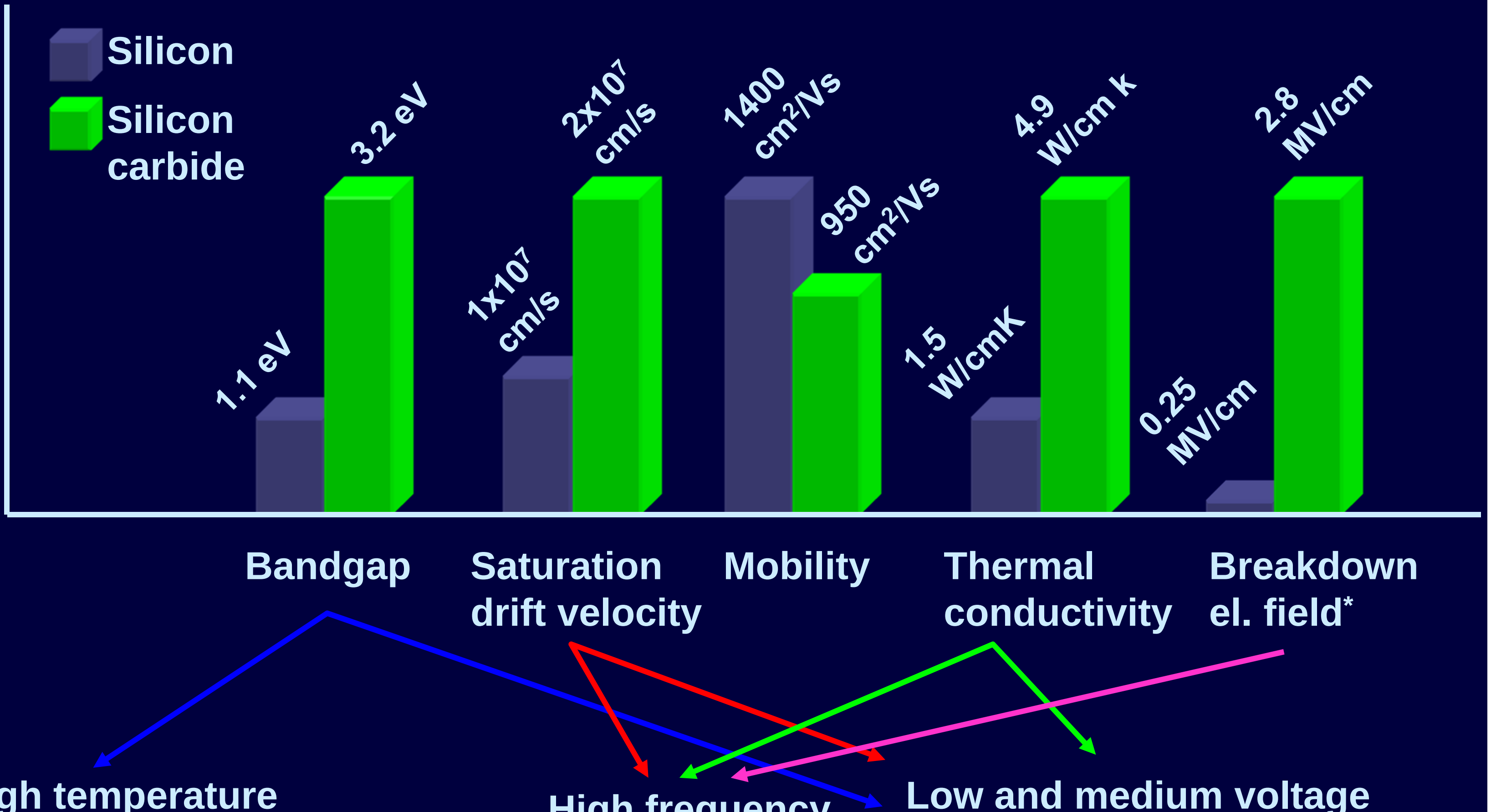


Areal densities of deuterium in oxide films versus time of chemical etching. The corresponding **D profiles** determined by differentiation are shown in the insets: **(a)** as-loaded with D_2; **(b)** loaded with D_2 and annealed in vacuum at 650ºC for 30 min

I.J.R. Baumvol, **F.C. Stedile**, C. Radtke, F.L. Freire, Jr., E.P. Gusev, M.L. Green, D. Brasen, Nucl. Instrum. Meth. B 204

I.J.R. Baumvol, E.P. Gusev, **F.C. Stedile**, F.L. Freire, Jr., M.L. Green, D. Brasen, Appl. Phys. Lett. 72 (1998) 450.

Motivation SiC



High temperature Electronics and sensors

High frequency power devices

Low and medium voltage high switching frequency power electronic devices with low losses

* for 1200 V blocking voltage

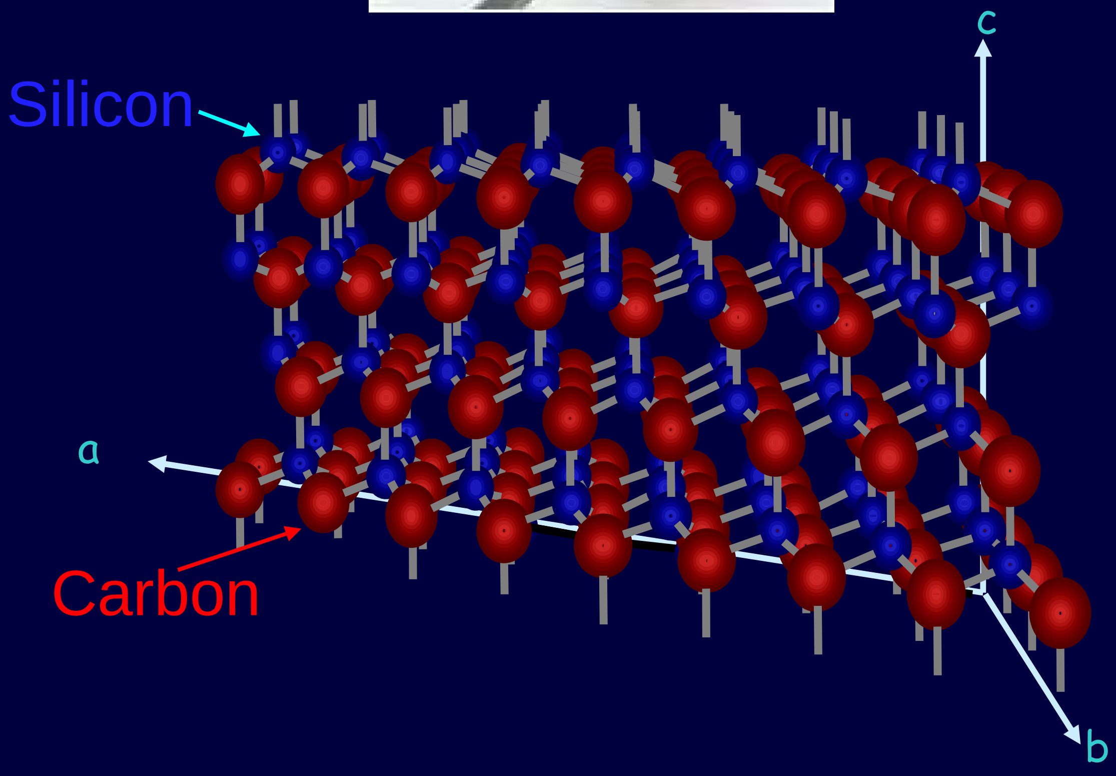
SiC < energy loss than Si

Si bipolar transistor → SiC MOSFET

85% less energy loss

Japan: 1% less energy loss

Energy save ~ 4 nuclear power plants



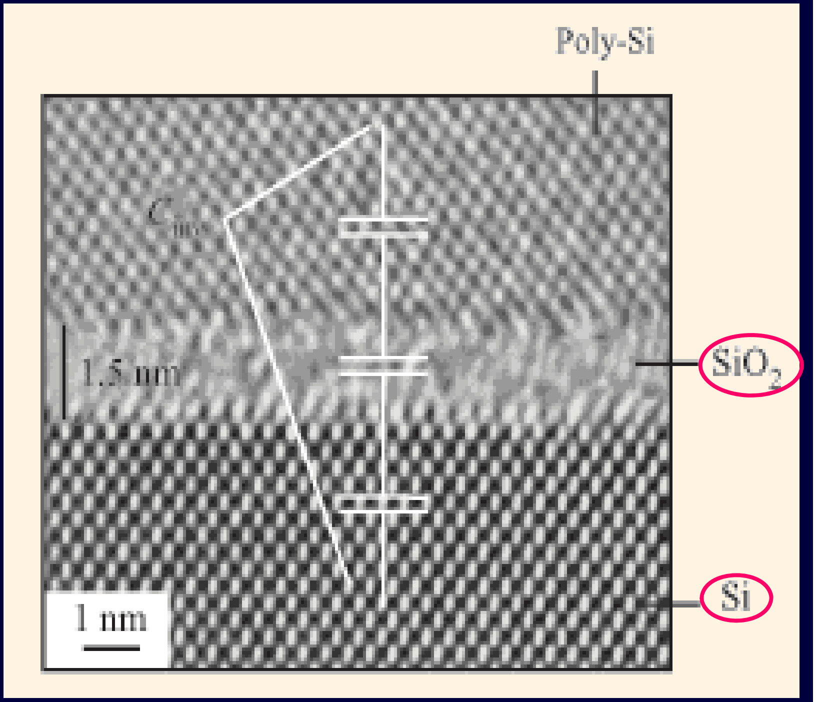
6H-SiC
Si-face
(0001)

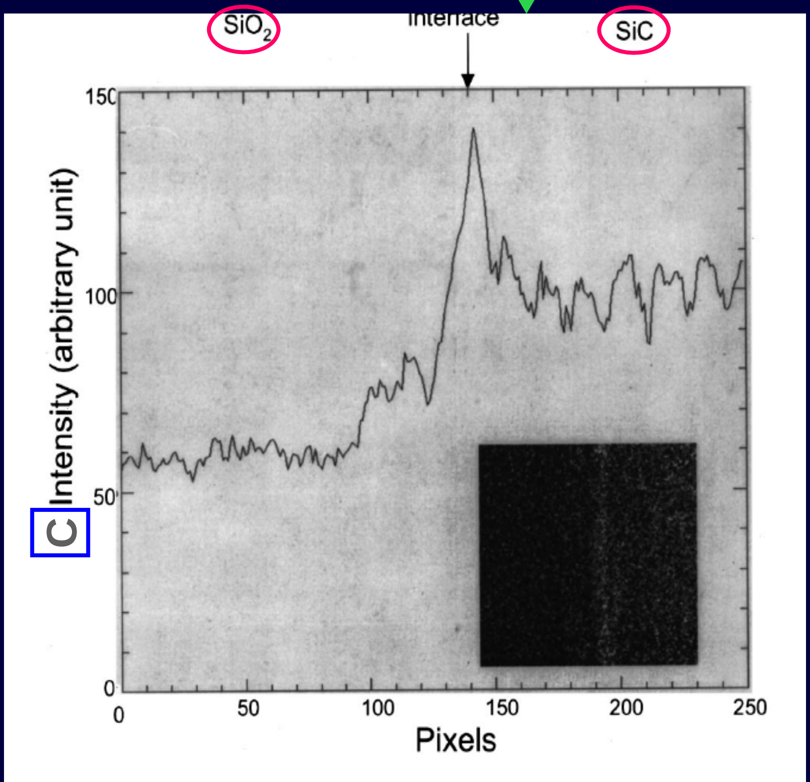
6H-SiC
C-face
($000\bar{1}$)

SiC : only compound semiconductor on which it is possible to thermally grow a SiO_2 film, as on Si

- ➢ Part of SiO_2/Si technology can be transfered or adapted to the SiO_2/SiC technology

Interfaces: SiO_2/Si x SiO_2/SiC





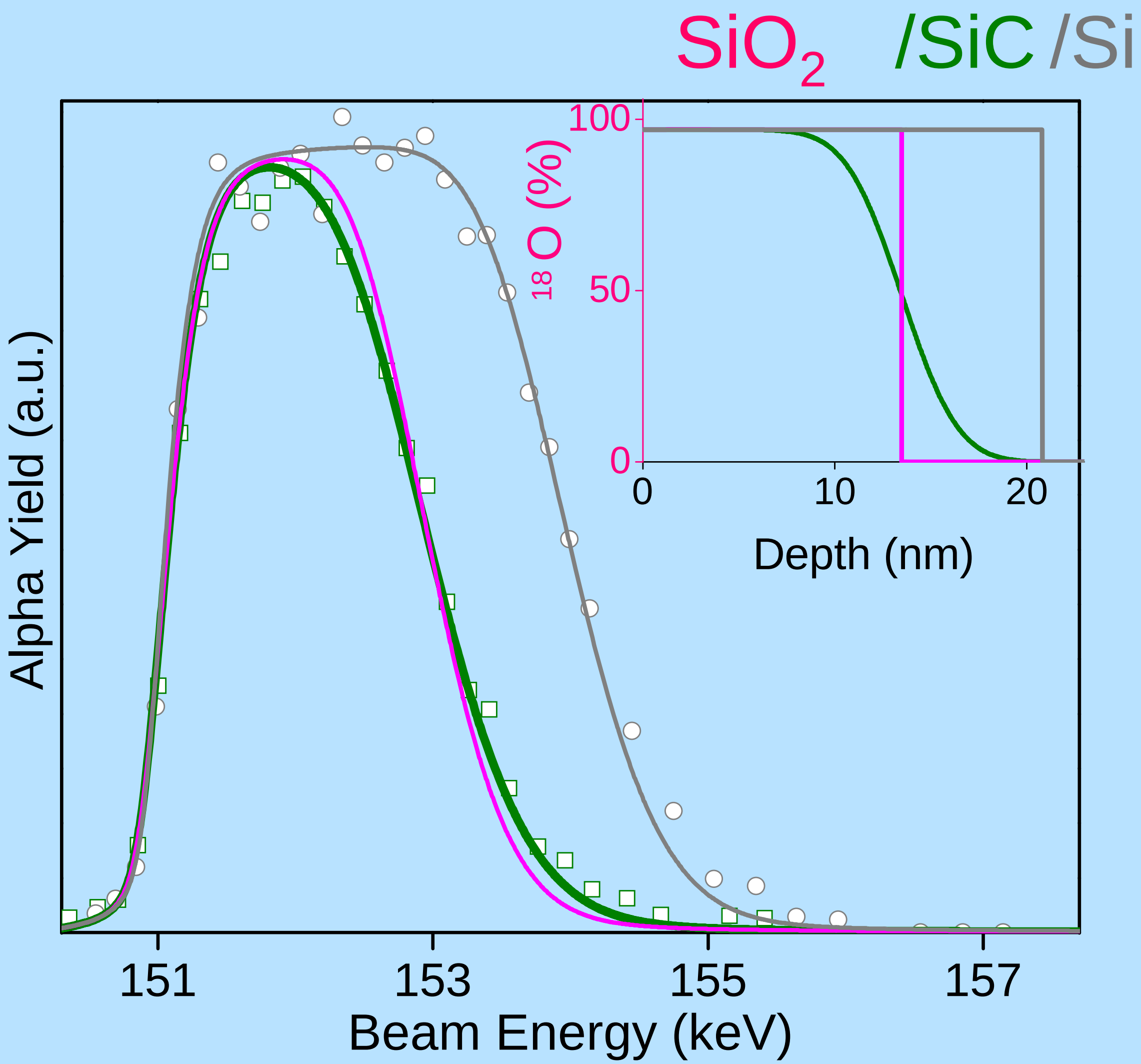
http://www.ibm.com

K.C. Chang *et al.* Appl. Phys. Lett. 77 (2000) 2186

Single step in $^{18}O_2$

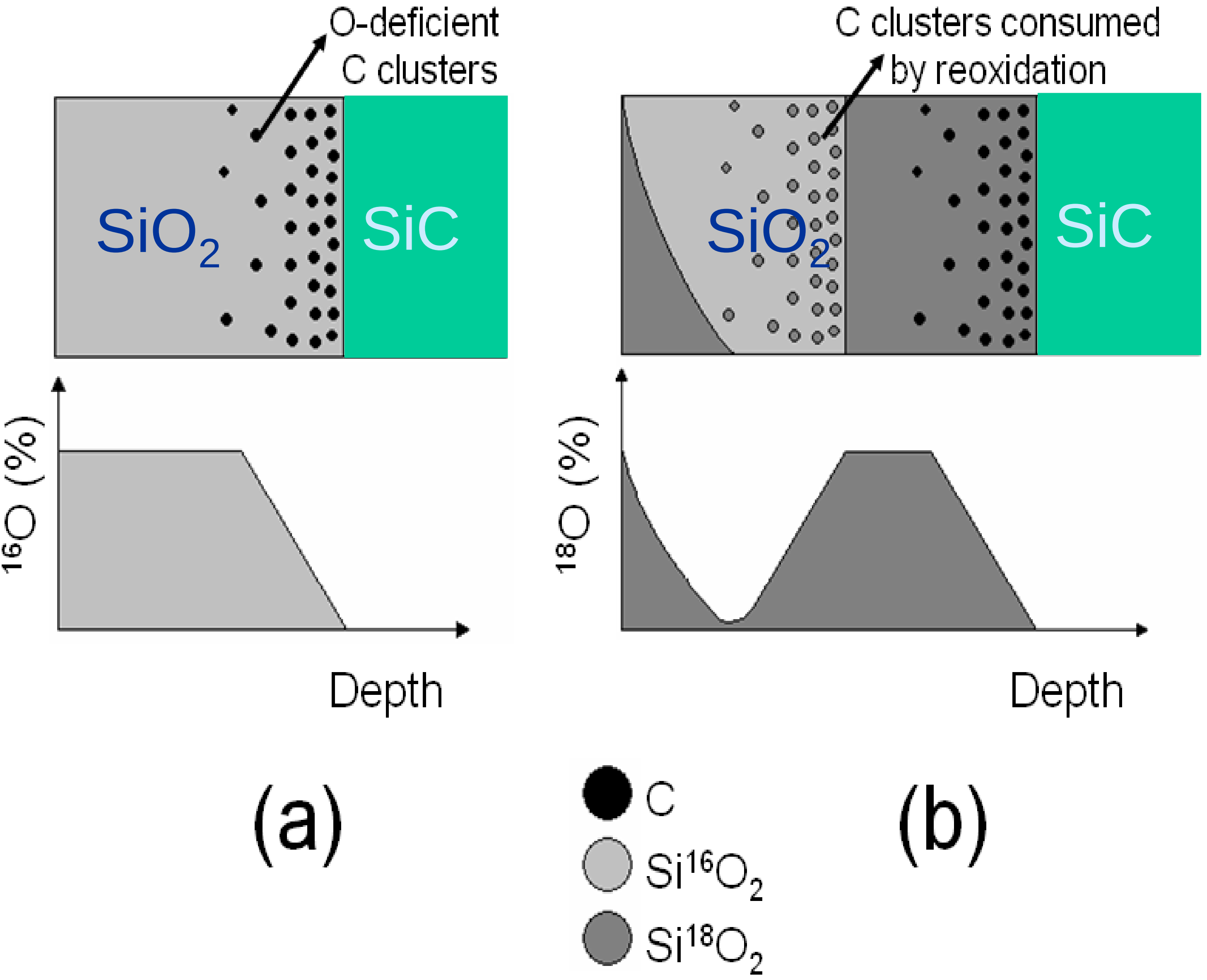
○ Si

□ SiC
Si-face

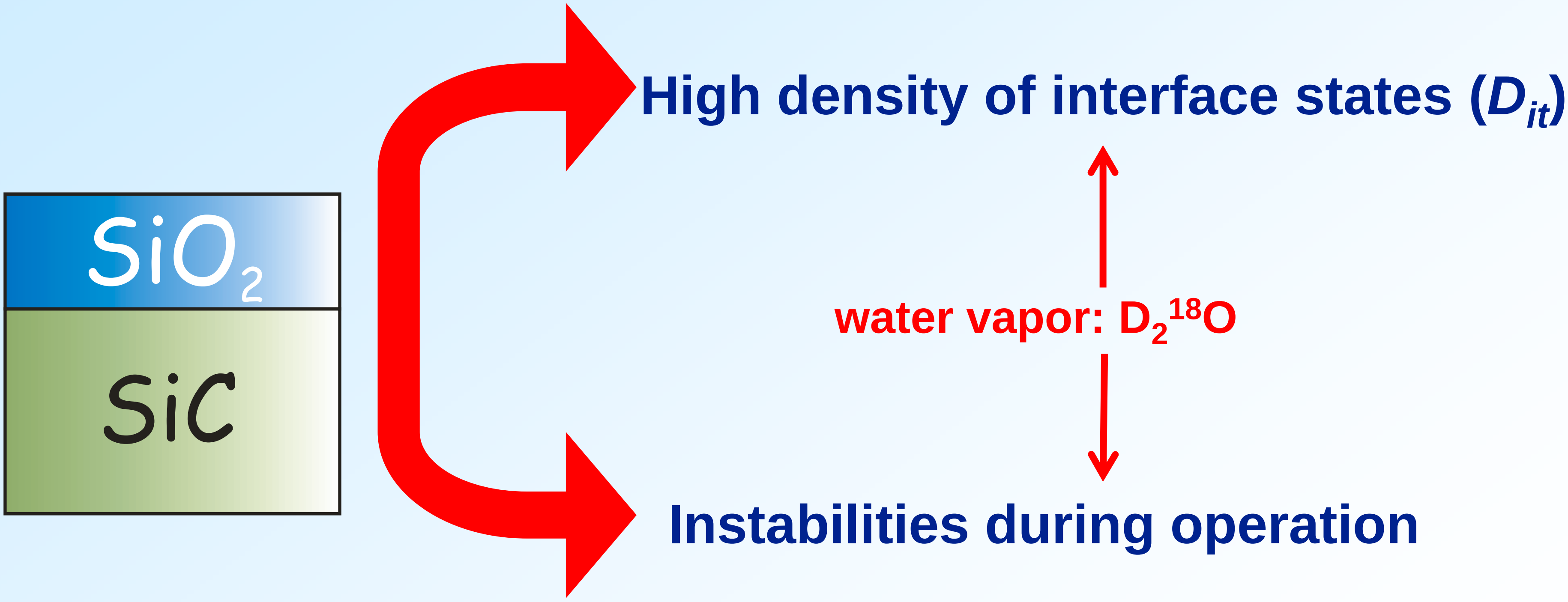


C. Radtke**,** I.J.R. Baumvol, B.C.Ferrera, **F.C. Stedile**
Appl. Phys.Lett. 85 (2004) 3402

oxidation in $^{16}O_2$ oxidation in $^{16}O_2+^{18}O_2$



Challenges in SiC technology



High density of interface states (D_{it})

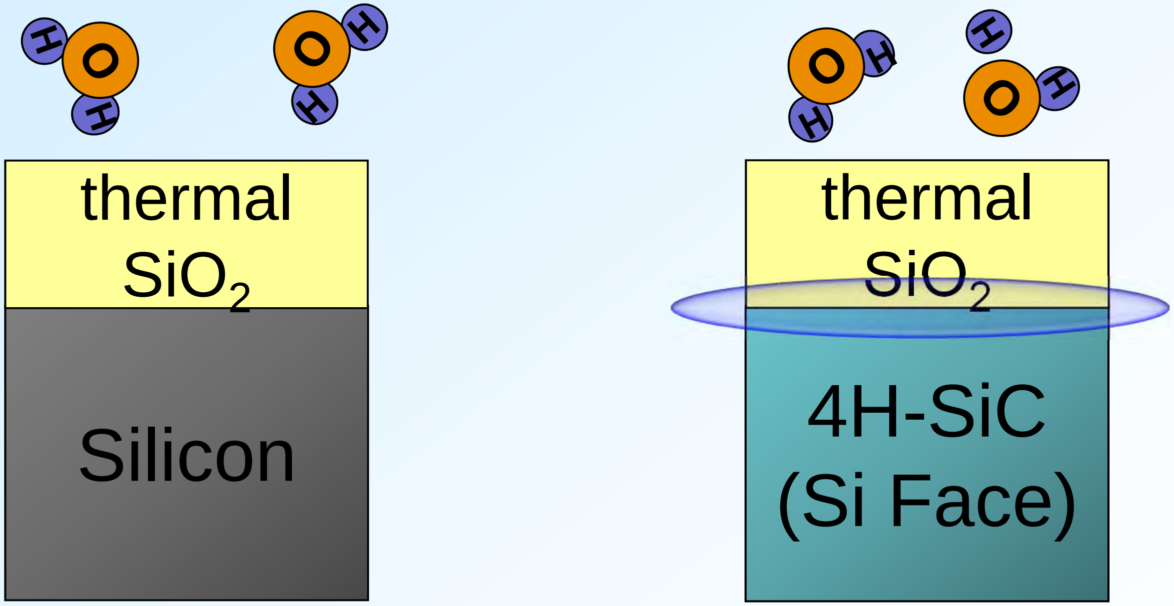
water vapor: $D_2{}^{18}O$

Instabilities during operation

Water related problems in SiO_2/Si

- 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

Water vapor incorporation in SiO_2/SiC and SiO_2/Si



G.V. Soares, I.J.R. Baumvol, S.A. Corrêa, C. Radtke**, F.C. Stedile**
Appl. Phys.Lett. 95 (2009) 191912

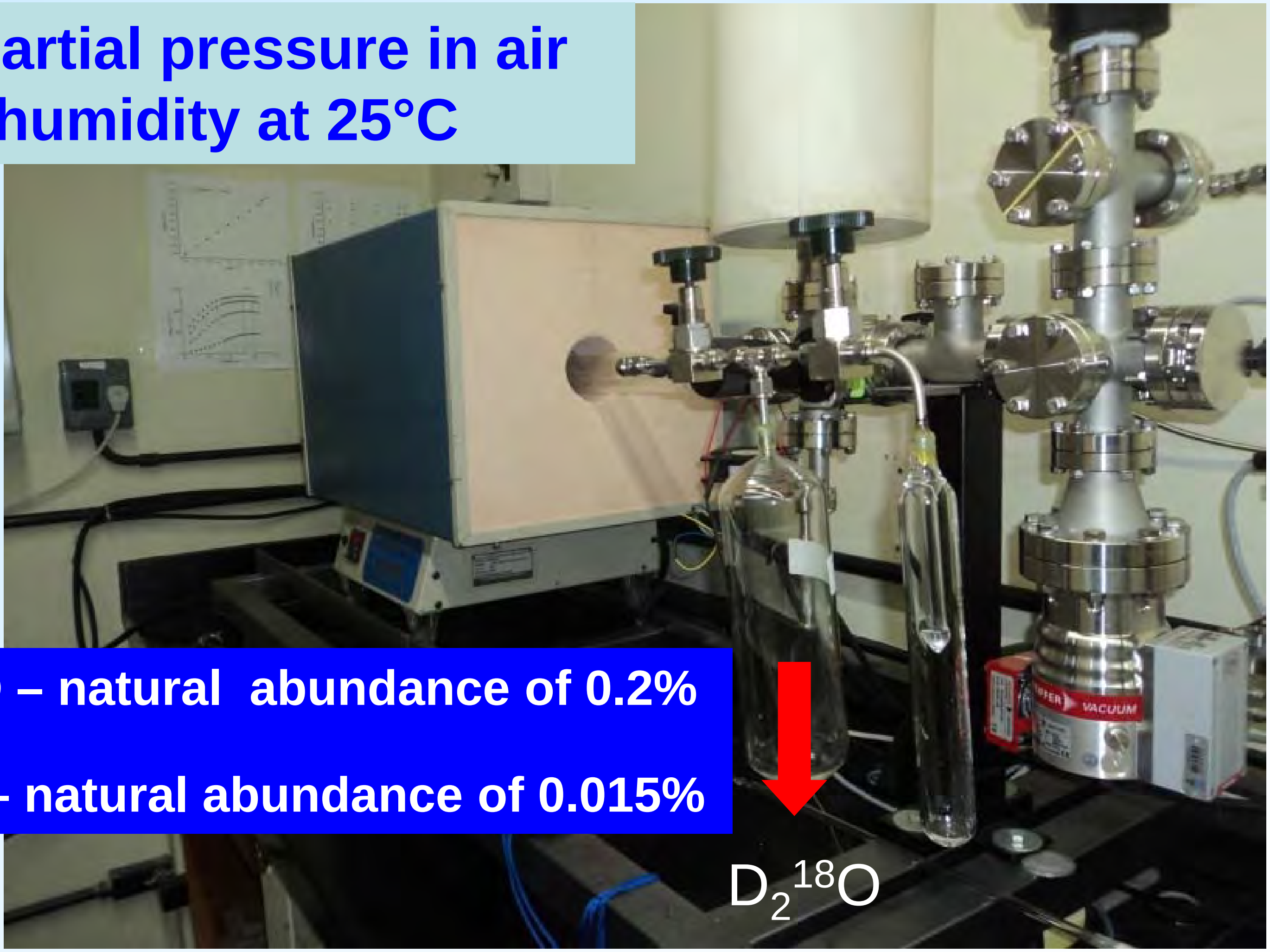
G.V. Soares, I.J.R. Baumvol, S.A. Corrêa, C. Radtke**, F.C. Stedile**
Electrochemical and Solid-State Letters 13 (2010) G95

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

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

Samples preparation

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



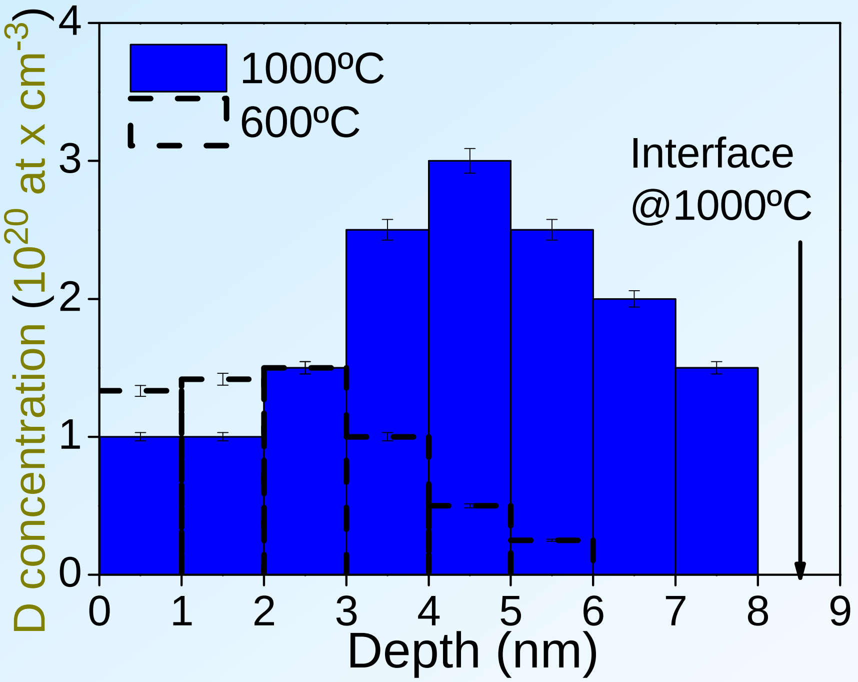
^{18}O – natural abundance of 0.2%

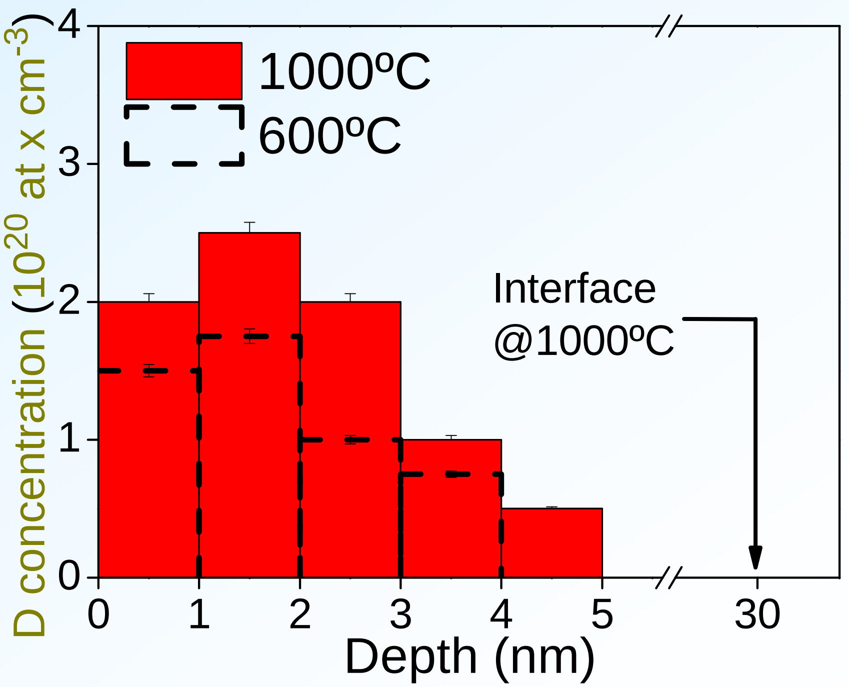
D – natural abundance of 0.015%

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

D profiles

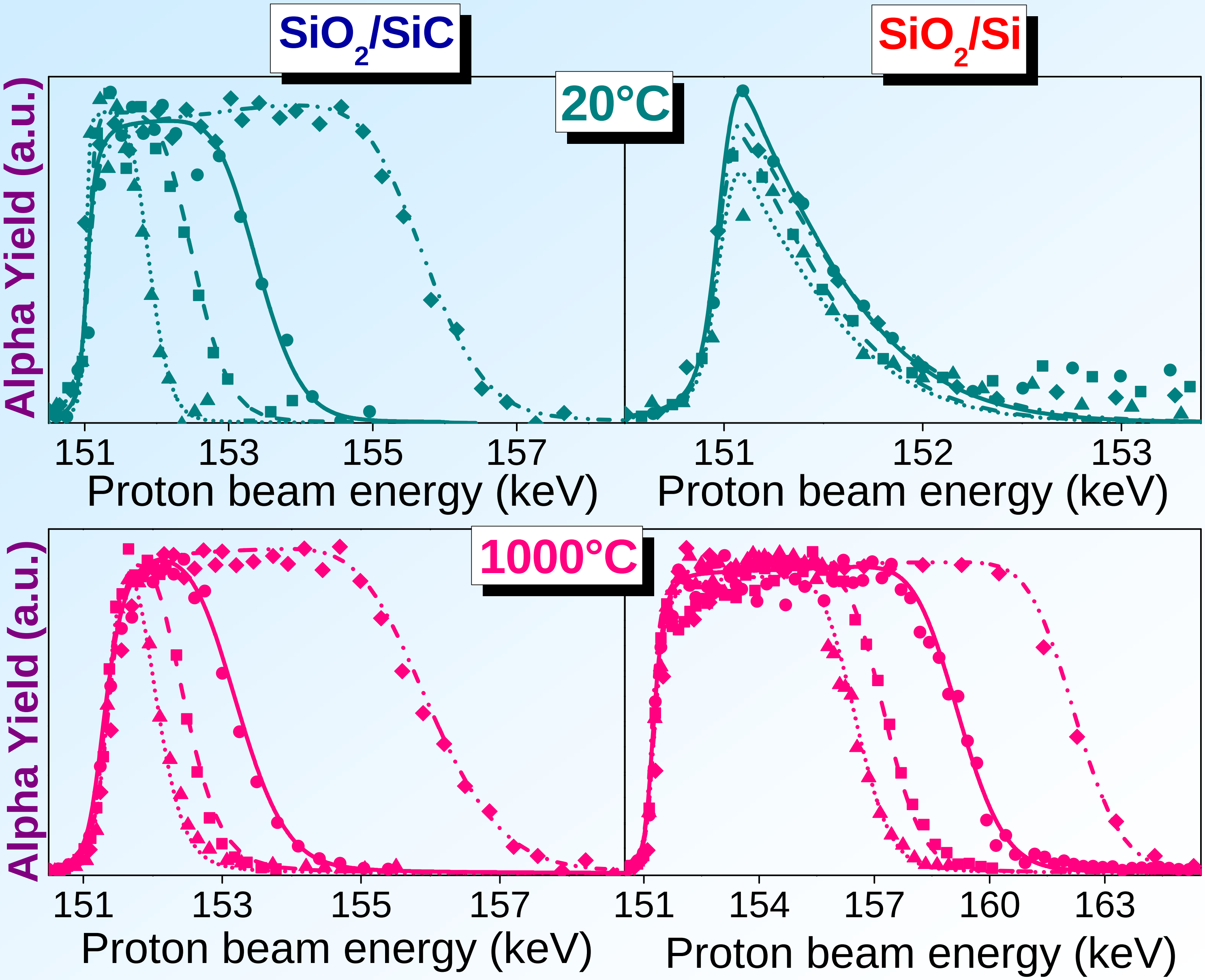
in $Si^{16}O_2/SiC$ and in $Si^{16}O_2/Si$



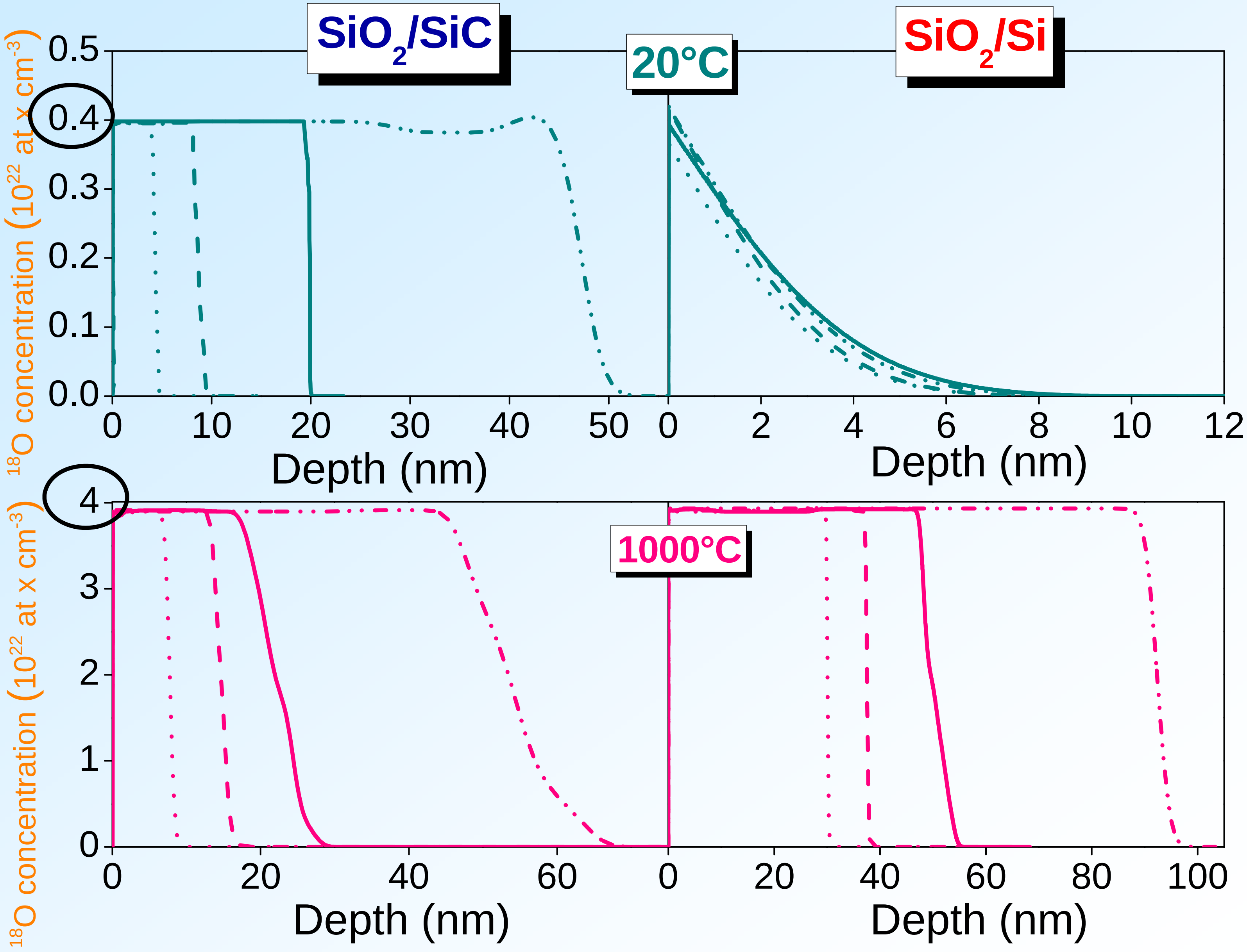


$D(^3He,p)^4He$ at 700 keV

^{18}O excitation curves



^{18}O profiles



Experimental

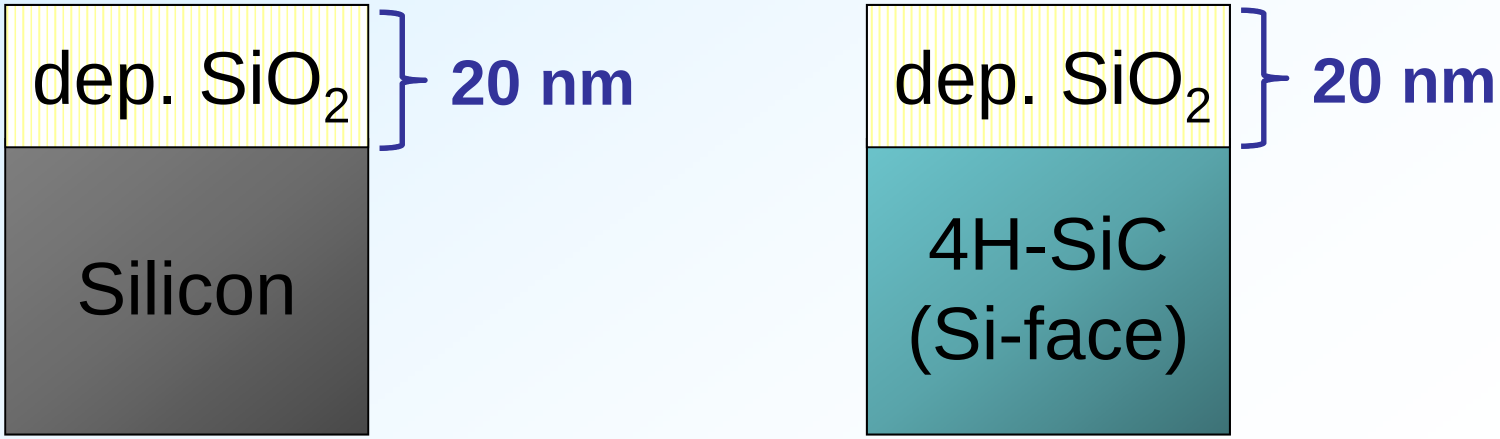
Deposition on Si and on 4H-SiC substrates

RF Sputtering conditions:

- Target: SiO_2, 90 W
- 2 mtorr of Ar, flux of 20 sccm

Deposition rate ~ 0.1 Å/s

t = 2,000 s



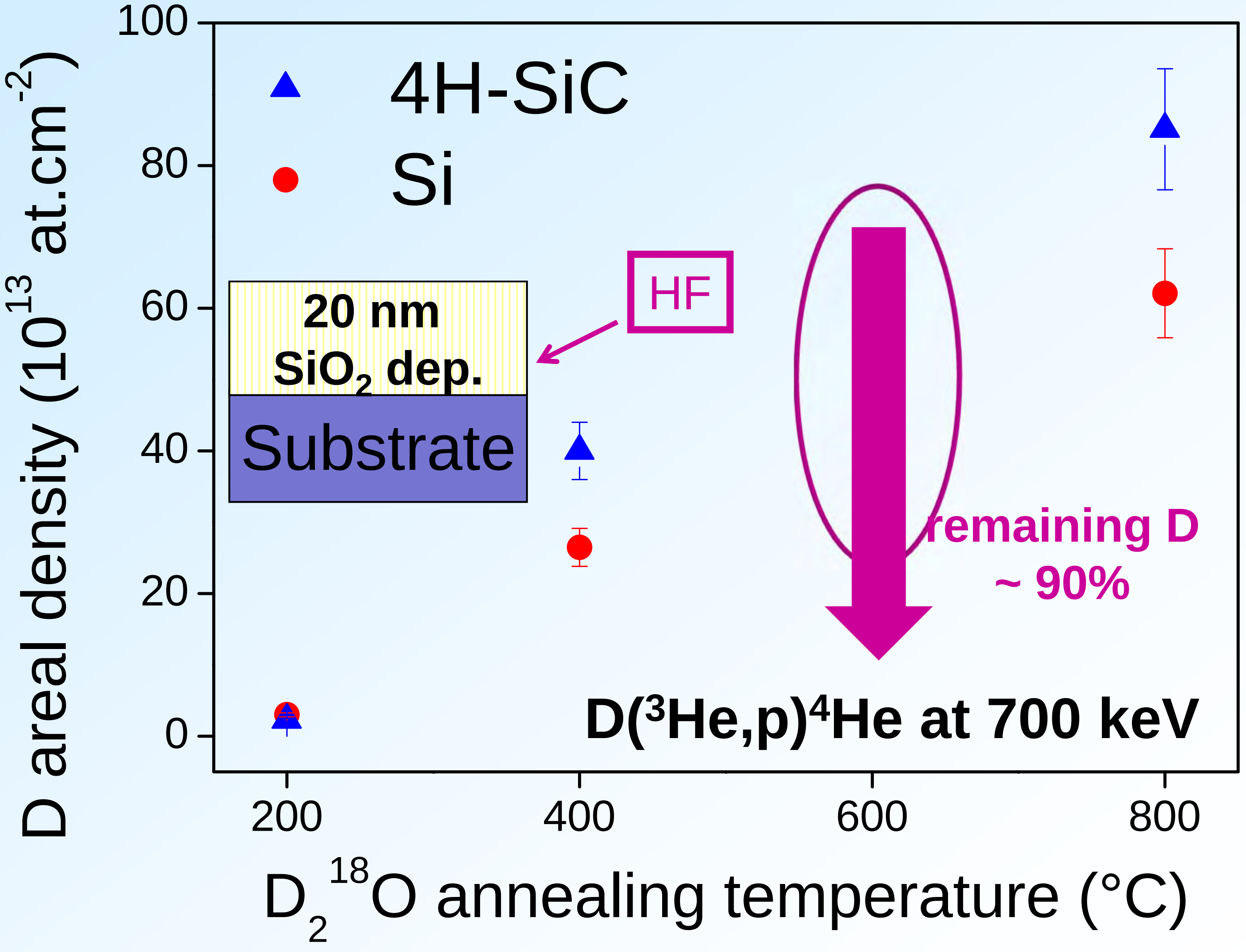
dep. SiO_2 **20 nm**

Silicon

dep. SiO_2 **20 nm**

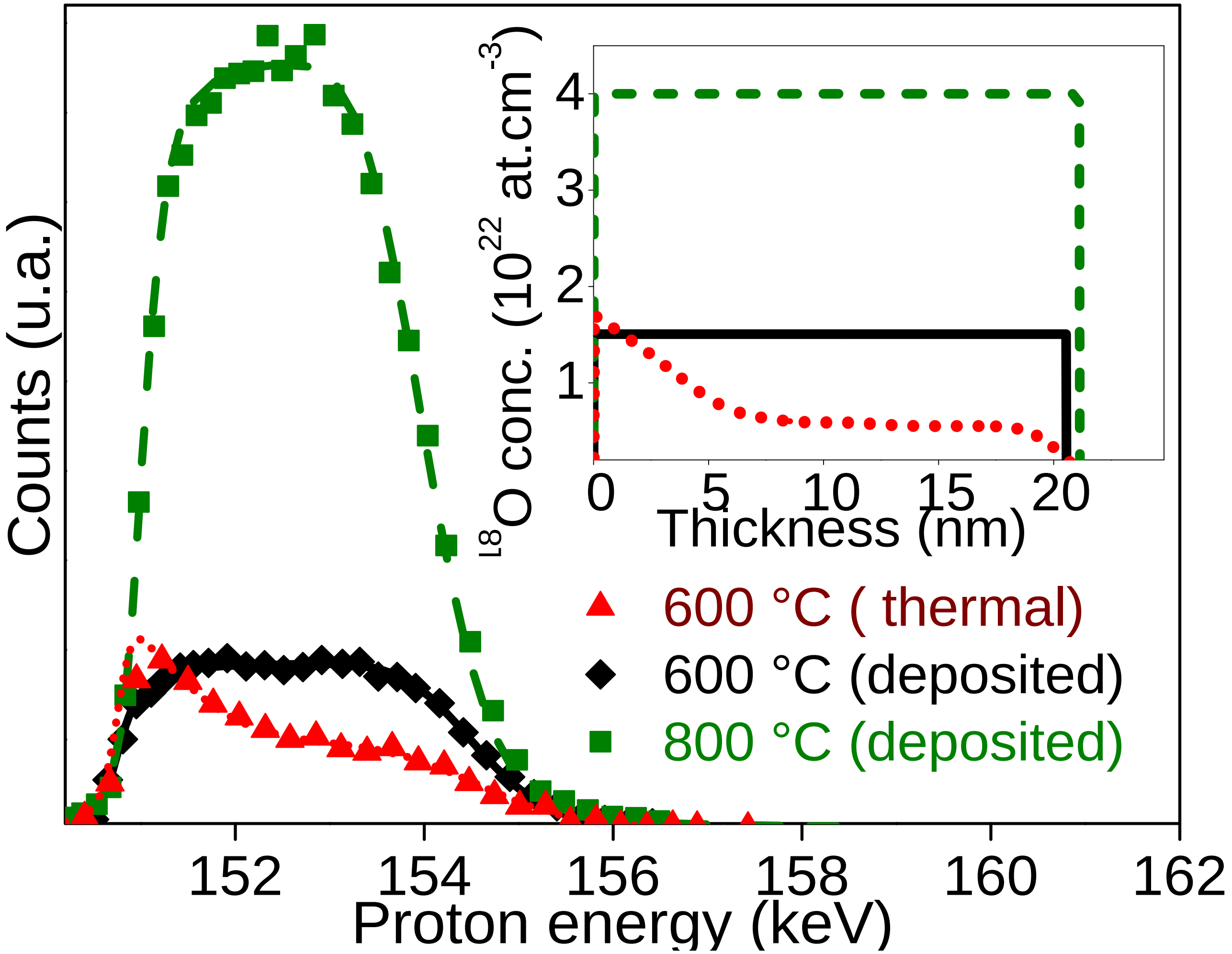
4H-SiC (Si-face)

Temperature and substrate influence in $D_2{}^{18}O$ vapor incorporation



^{18}O profiles

SiO$_2$/SiC + 10 mbar D$_2$^{18}O, 1h

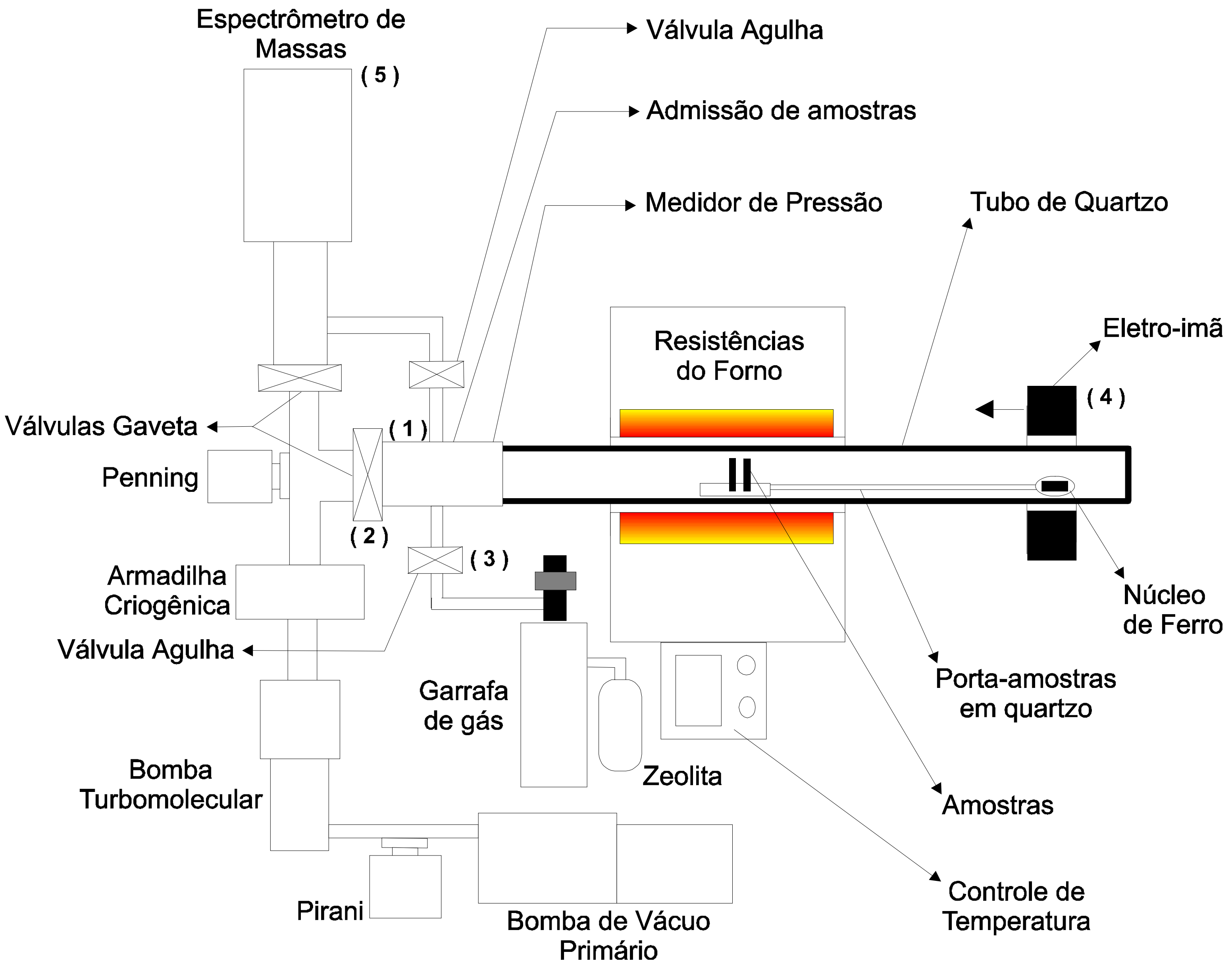


E. Pitthan *et al.* Appl. Phys. Lett. 104 (2014) 111904

Further research topics

- Mechanism and limiting step of thermal growth of SiO_2 on SiC
- Annealings in D_2 of SiO_2 / 4H-SiC and SiO_2 / 6H-SiC structures with and without Pt
- Annealings in NO of Pt / SiO_2 / SiC structures
- Reoxidations and sequencial annealings em H_2O_2
- Oxidations in $^{18}O_2$ of 6H and 4H-SiC (Si and C-faces) varying P, t and T
- Brief thermal growth followed by SiO_2 deposition
- Nitridation in $^{15}NH_3$ of SiC and of SiO_2 /SiC folllowed by SiO_2 deposition
- CO annealings of SiO_2 / SiC and SiO_2 / Si structures
- Incorporation and quantification of P in SiO_2 / SiC

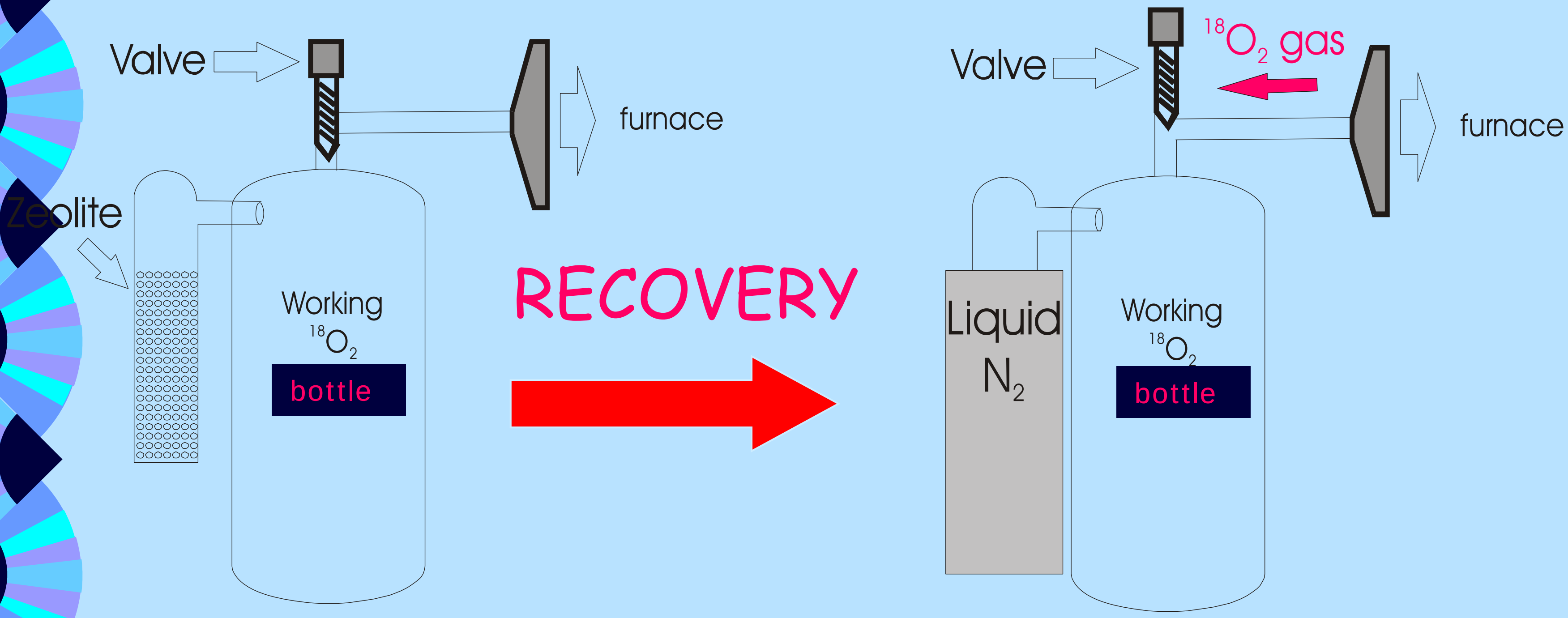
Thank you!


Espectrômetro de Massas
(5)
Válvula Agulha
Admissão de amostras
Medidor de Pressão
Tubo de Quartzo
Eletro-imã
(4)
Resistências do Forno
Válvulas Gaveta
(1)
Penning
(2)
(3)
Armadilha Criogênica
Válvula Agulha
Núcleo de Ferro
Porta-amostras em quartzo
Garrafa de gás
Zeolita
Amostras
Bomba Turbomolecular
Pirani
Bomba de Vácuo Primário
Controle de Temperatura

Manipulation and Recovering of $^{18}O_2$

- Expensive gas: about U$ 1,000/L

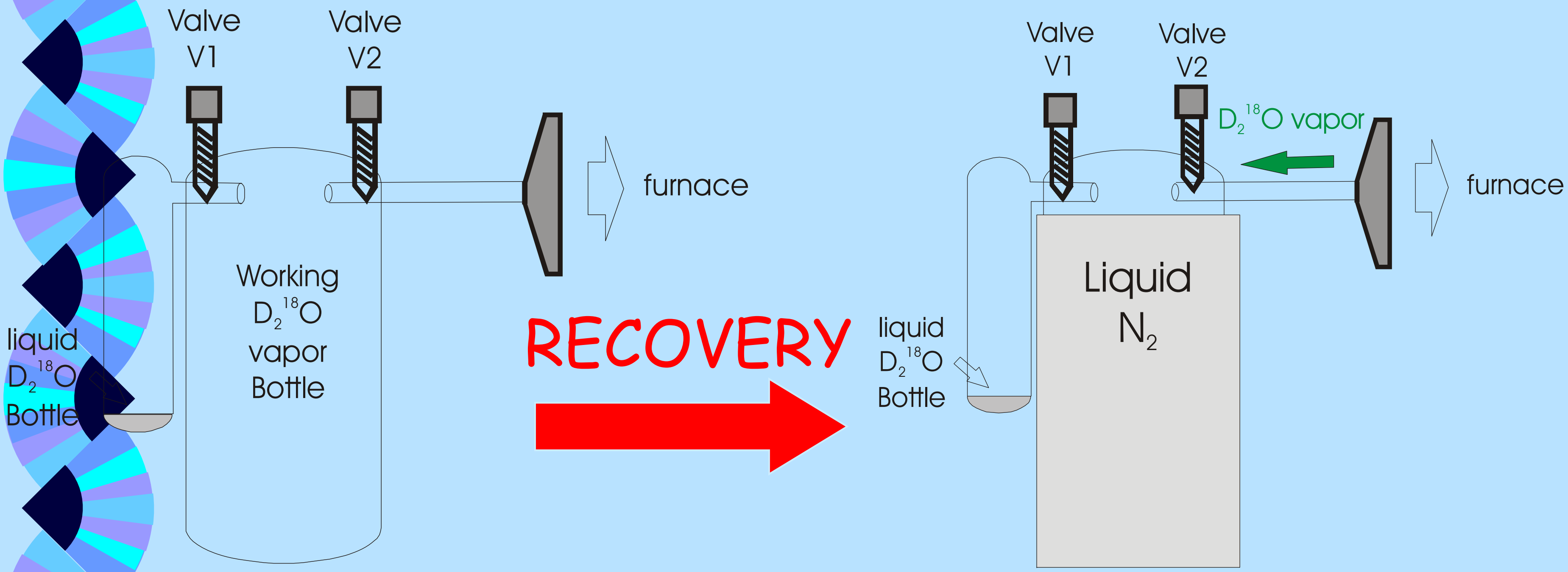
  (97% enriched in the ^{18}O isotope)

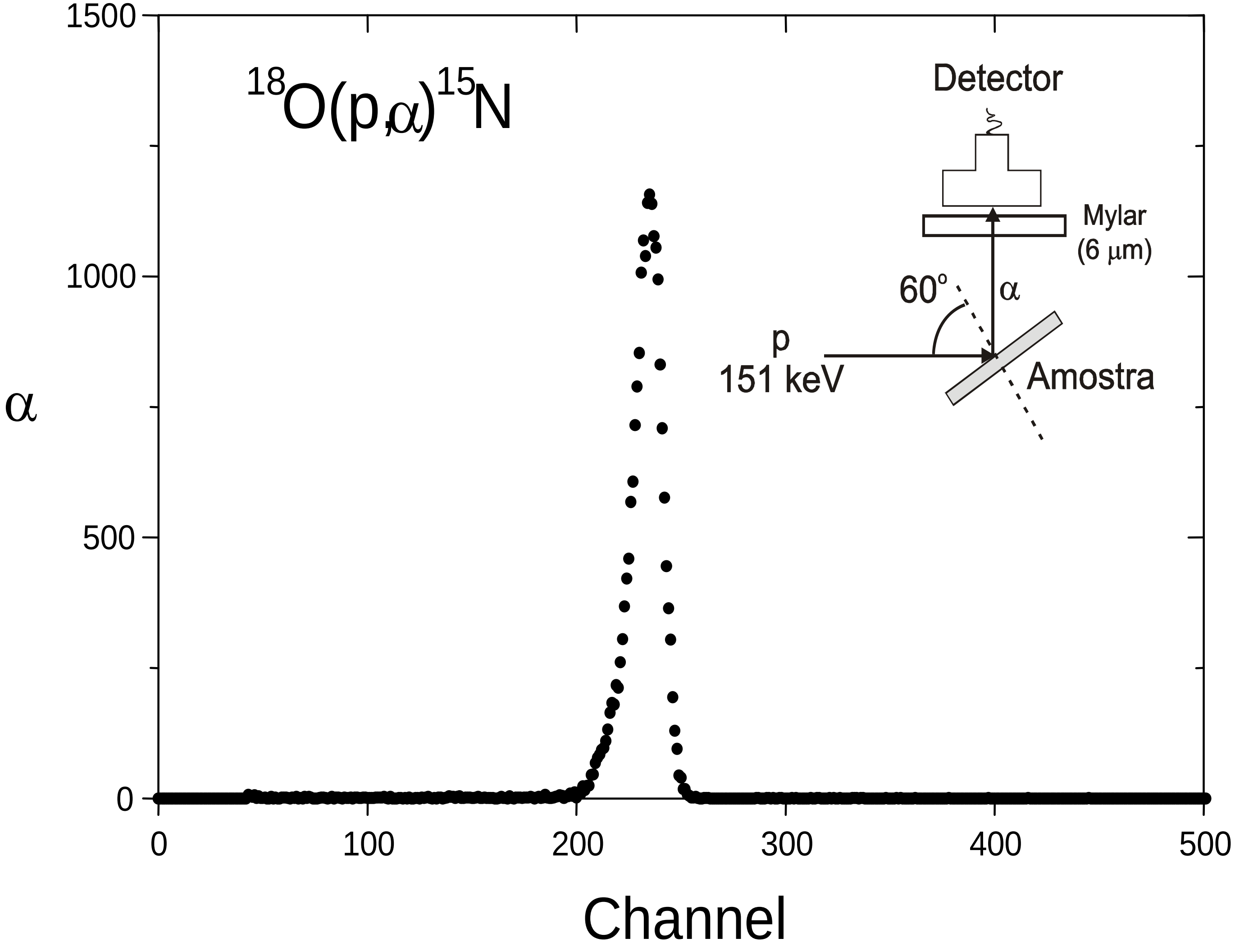


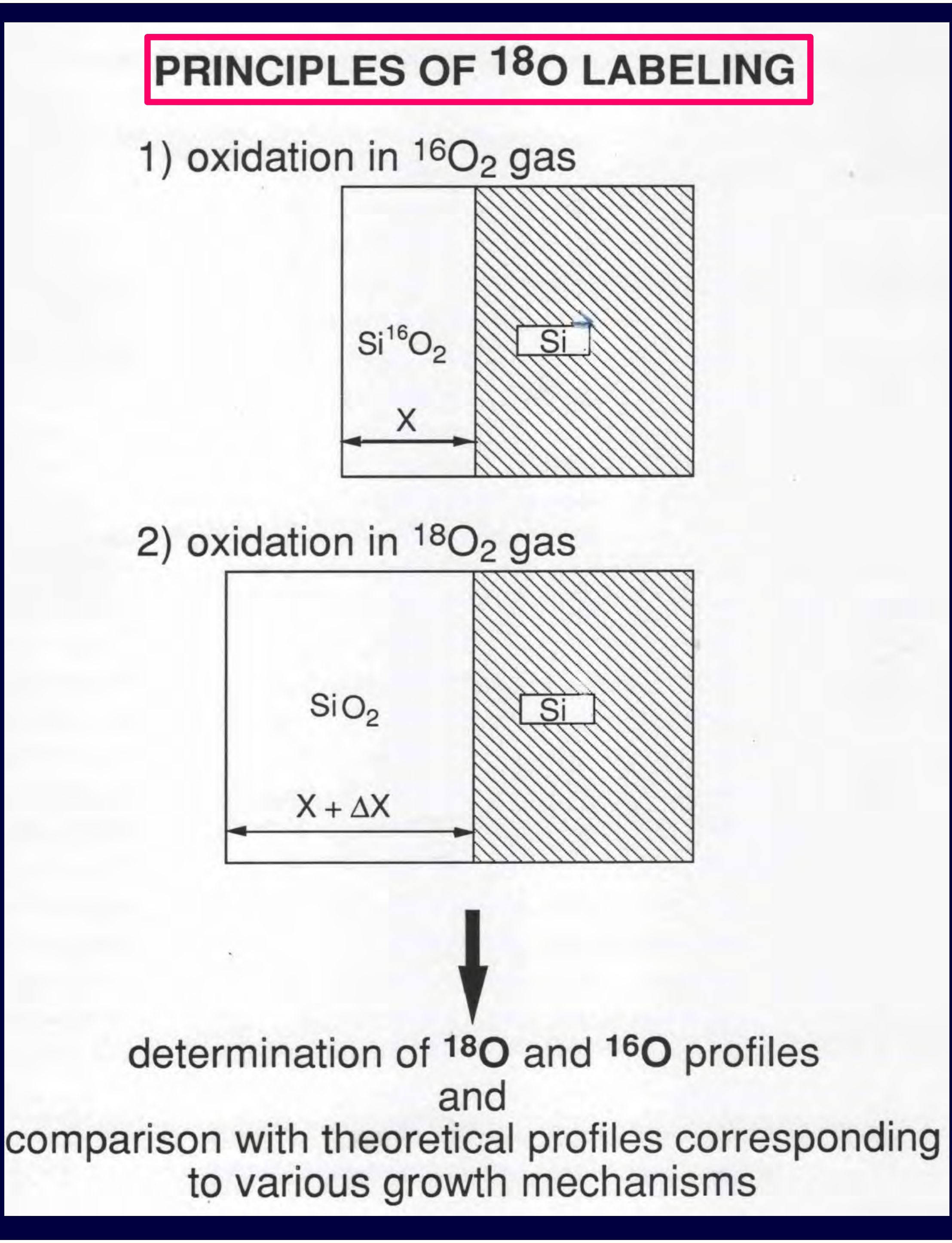
Natural Oxygen: 99.759% ^{16}O 0.204% ^{18}O 0.037% ^{17}O

Manipulation and Recovering of $D_2{}^{18}O$

- VERY expensive : about U$ 2,000/mL !!!




$^{18}O(p,\alpha)^{15}N$
Detector
Mylar
(6 μm)
60°
α
p
151 keV
Amostra
α
1500
1000
500
0
0
100
200
300
400
500
Channel



PRINCIPLES OF ^{18}O LABELING

1) oxidation in $^{16}O_2$ gas

2) oxidation in $^{18}O_2$ gas

determination of ^{18}O and ^{16}O profiles
and
comparison with theoretical profiles corresponding to various growth mechanisms

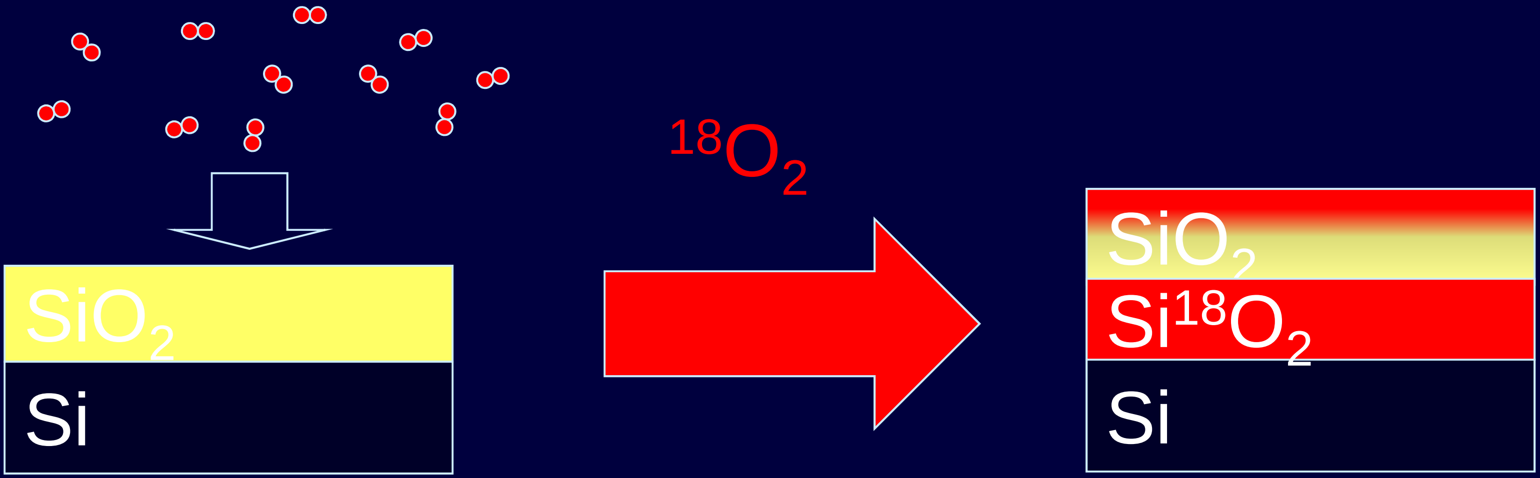
O_2 natural:
99,759% ^{16}O
0,204% ^{18}O
0,037% ^{17}O

$^{18}O_2$ 97%

Utilizando NRP para compreender o transporte atômico durante a oxidação do Si

Espécies móveis durante a oxidação?

Resultados:



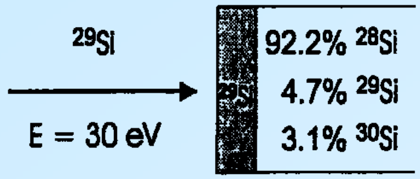
oxigênio é a espécie móvel, e que se desloca de duas maneiras:

-Por difusão, interagindo com os defeitos de rede(região superficial)

- Intersticialmente, sem reagir com o óxido já formado até chegar à interface com o semicondutor e reagir formando SiO_2

Isotopic tracing of Si in thermal growth of silicon oxide films on Si in dry O_2

Step 1: ^{29}Si deposition on Si (111)


^{29}Si

E = 30 eV

^{29}Si

92.2% ^{28}Si

4.7% ^{29}Si

3.1% ^{30}Si

Step 2: epitaxial recrystallization: 600 ºC , 30 min , UHV

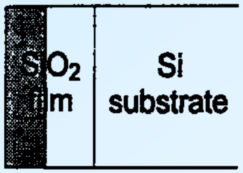
Step 3: ^{29}Si depth profiling

Step 4: thermal oxidation in O_2: 1000 ºC , 60 min , 50 mbar

Step 5: ^{29}Si depth profiling

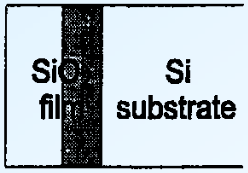
Step 6: comparison of ^{29}Si profile with predictions:

Si immobile and O mobile


SiO_2 film

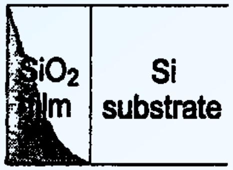
Si substrate

Si mobile and O immobile


SiO_2 film

Si substrate

or


SiO_2 film

Si substrate

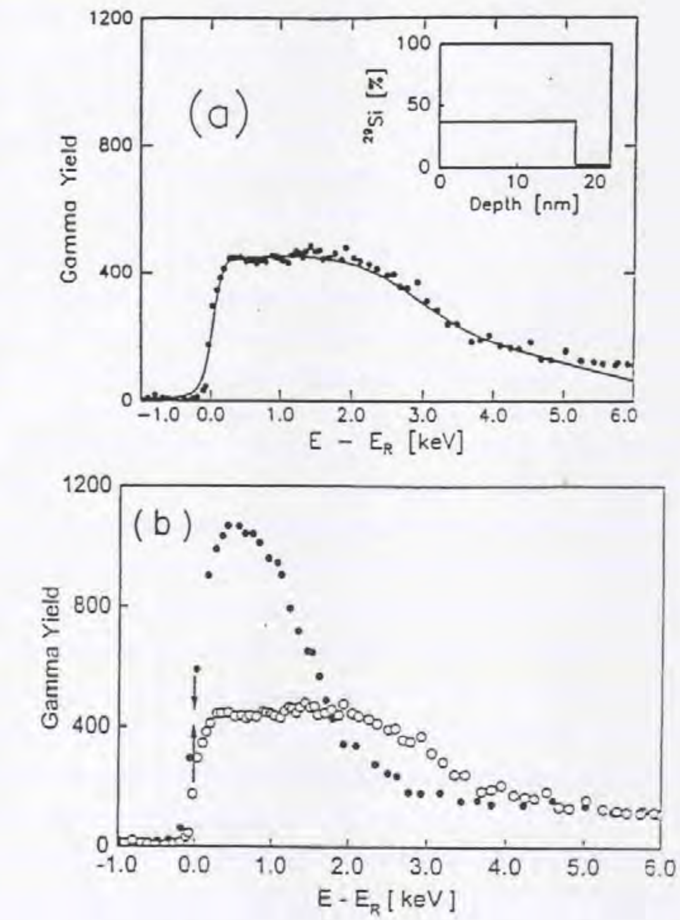
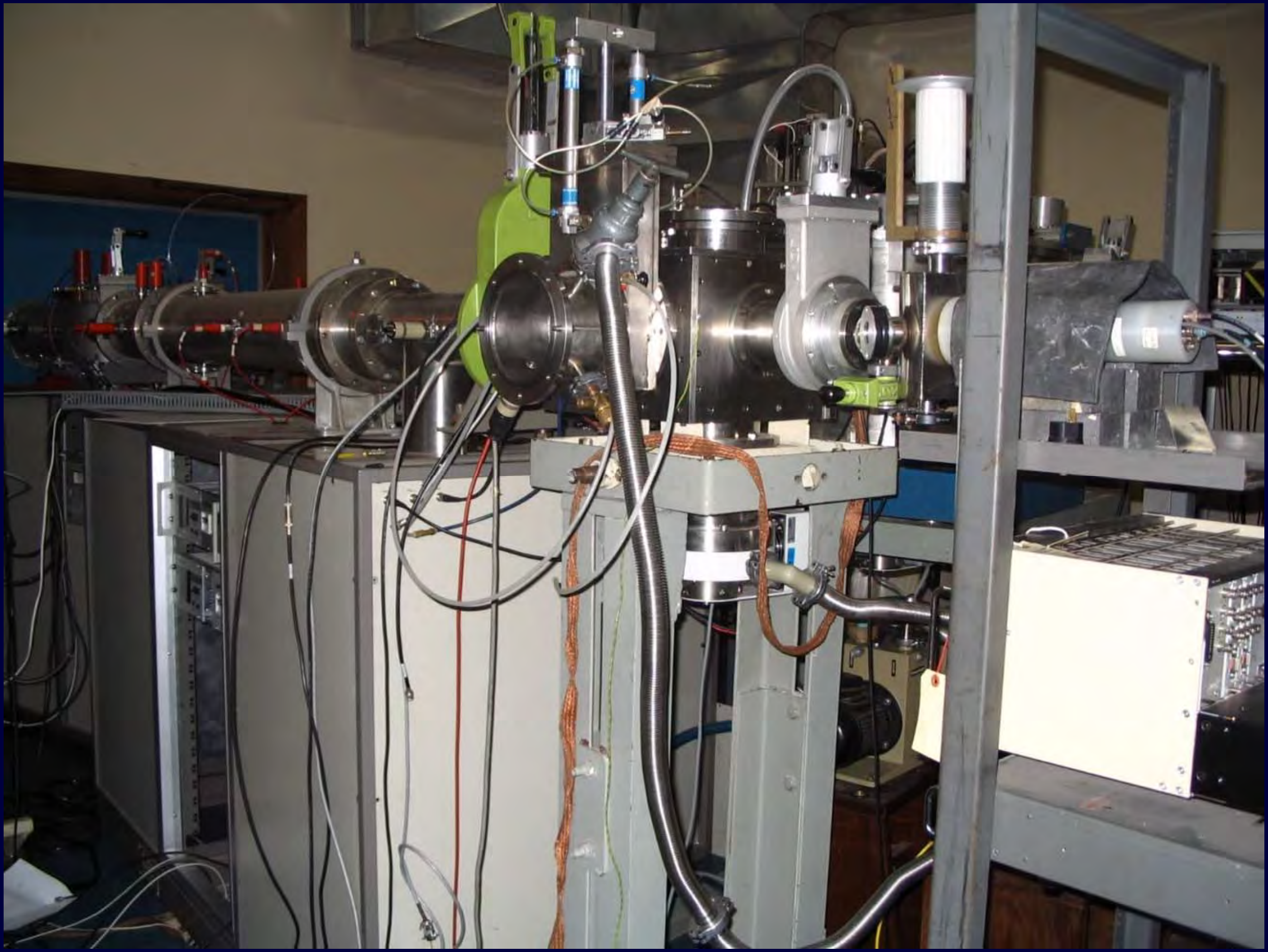


FIG. 4. (a) ^{29}Si excitation curve (solid circles), its simulation (solid line), and ^{29}Si profile in the inset for the oxidized sample. (b) ^{29}Si excitation curves in the pre-oxidation [solid circles, ^{29}Si epitaxial on Si(111)] and post-oxidation [empty circles, ^{29}Si in SiO_2/Si(111)] samples. The arrows indicate the energy positions of the half maxima in the leading edges for the pre-oxidation (arrow pointing downwards) and post-oxidation (arrow pointing upwards) samples.

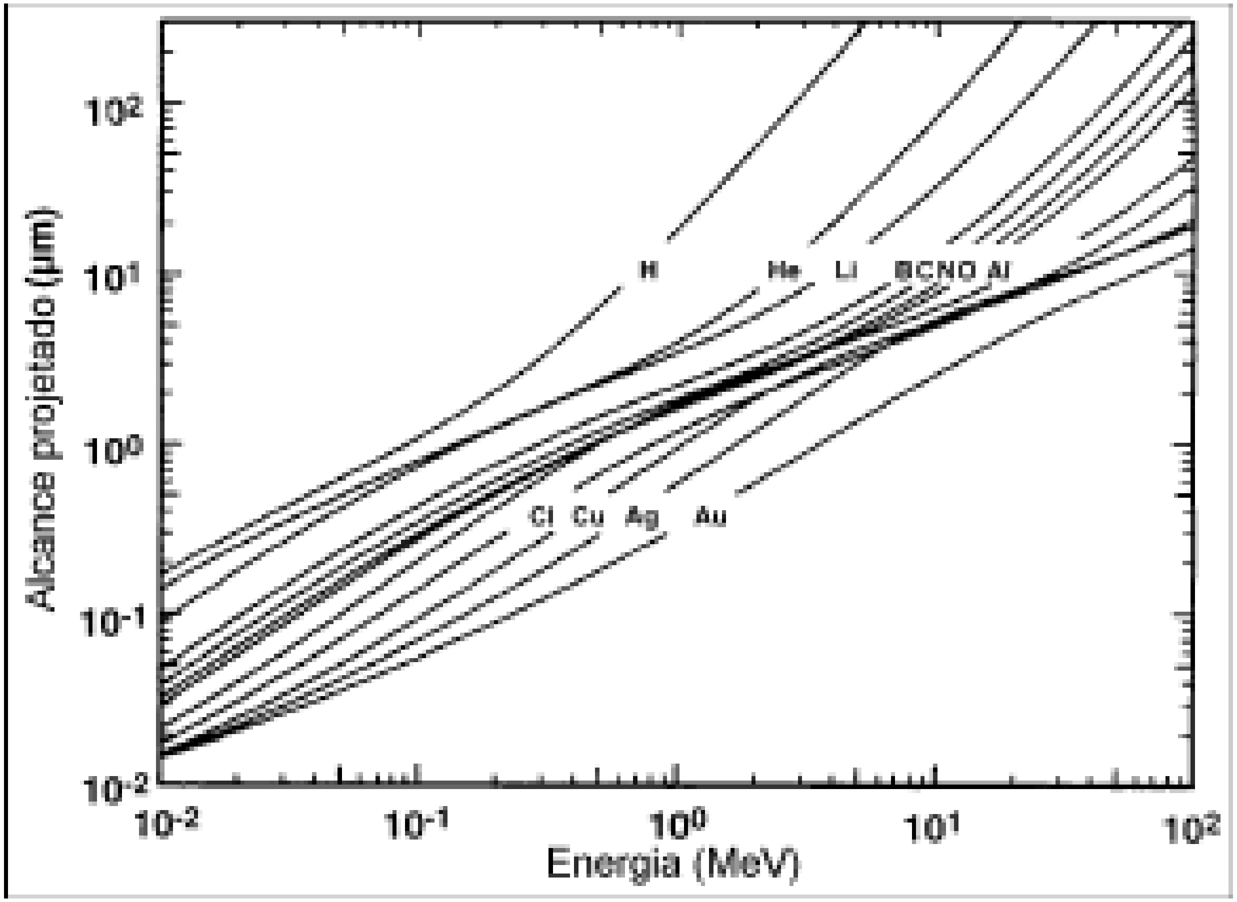
I.J.R. Baumvol, C. Krug, **F.C. Stedile**, F. Gorris, W.H. Schulte
Phys. Rev. B 60 (1999) 1492

Ions decelerator

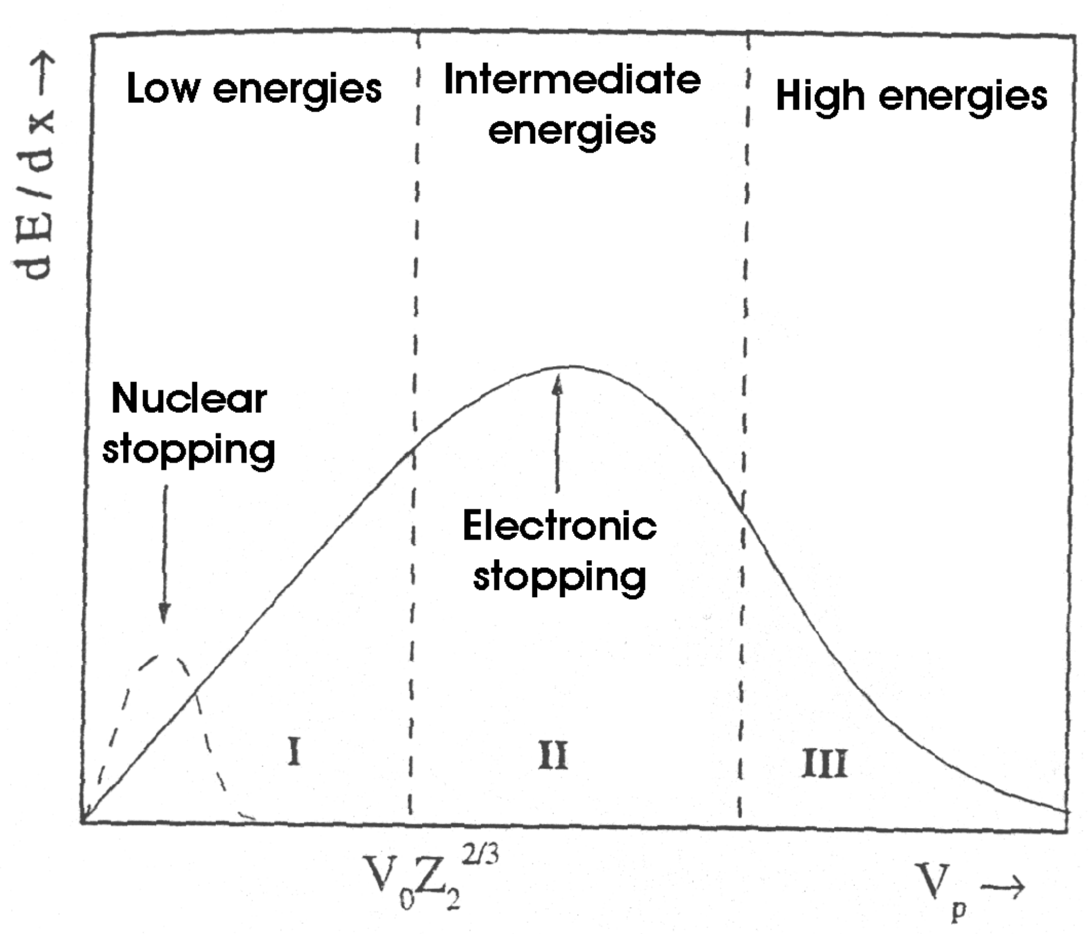
$^{29}Si(p,\gamma)^{30}P$ E_R = 417 keV; Γ=100 eV



Alcance das partículas no Mylar

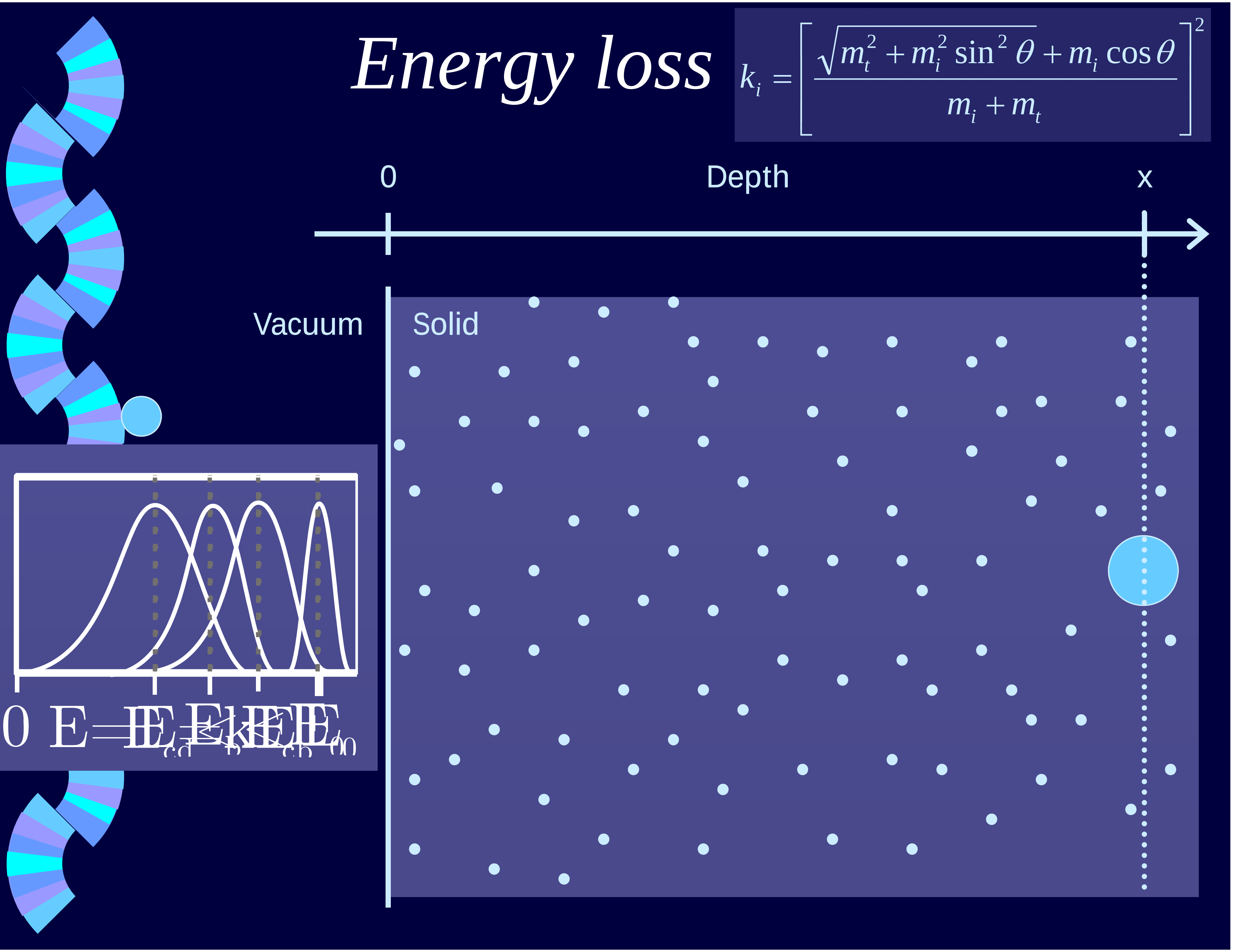


Electronic and nuclear dE/dx

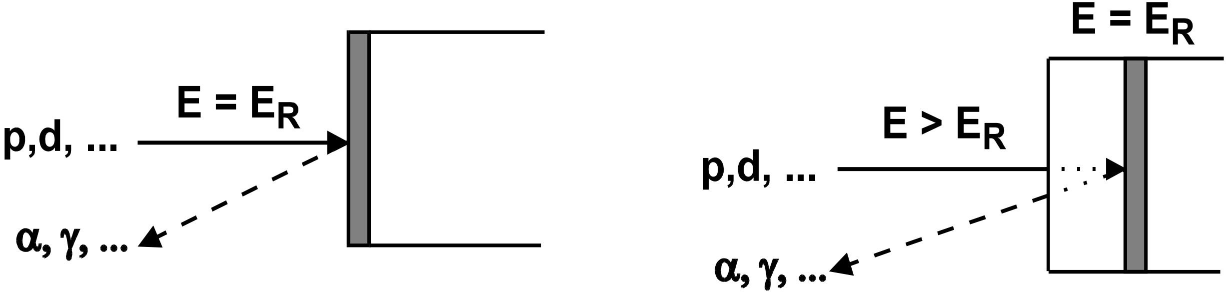


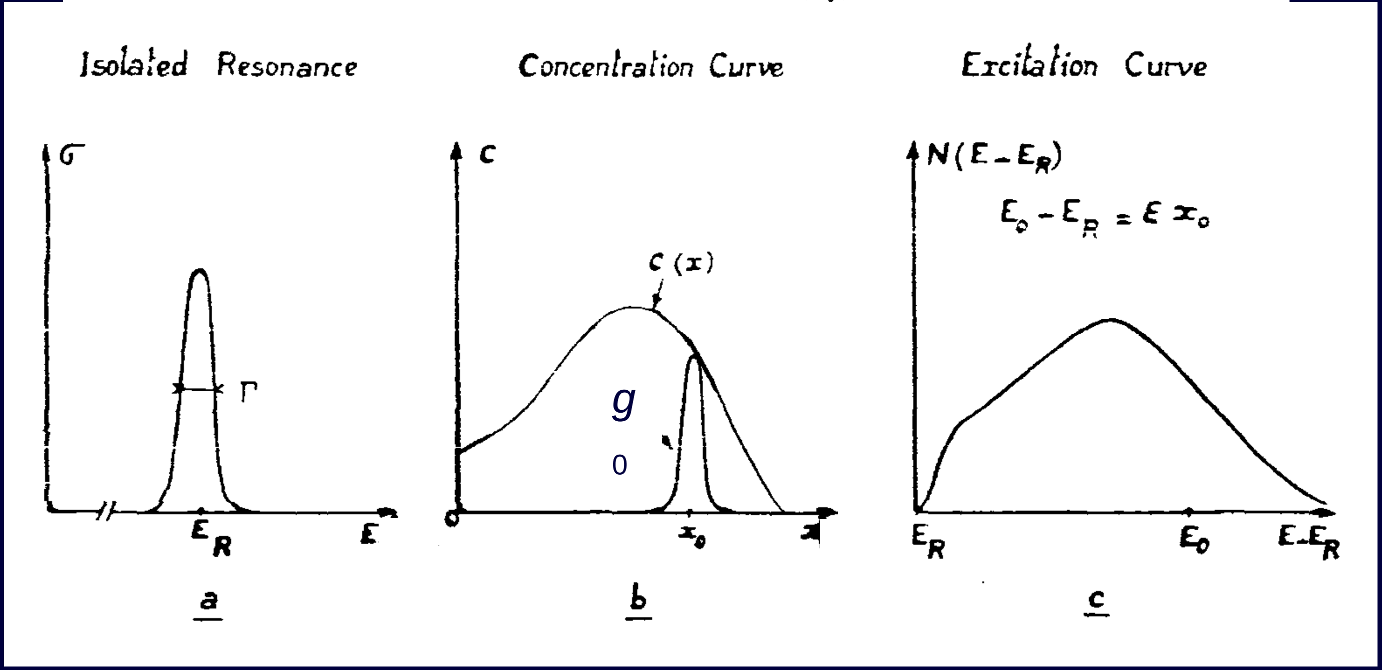
Energy loss

$$k_i = \left[\frac{\sqrt{m_t^2 + m_i^2 \sin^2\theta} + m_i \cos\theta}{m_i + m_t} \right]^2$$



Narrow Resonance Nuclear Reaction Profiling: NRP





Interpretation: SPACES code

I. Vickridge and G. Amsel, Nucl. Instr. and Meth. B 45 (1990) 6

FLATUS

beam particle energy, mass and atomic number; energy loss per unit length and energy straggling corresponding to the material and energy of interest

↓

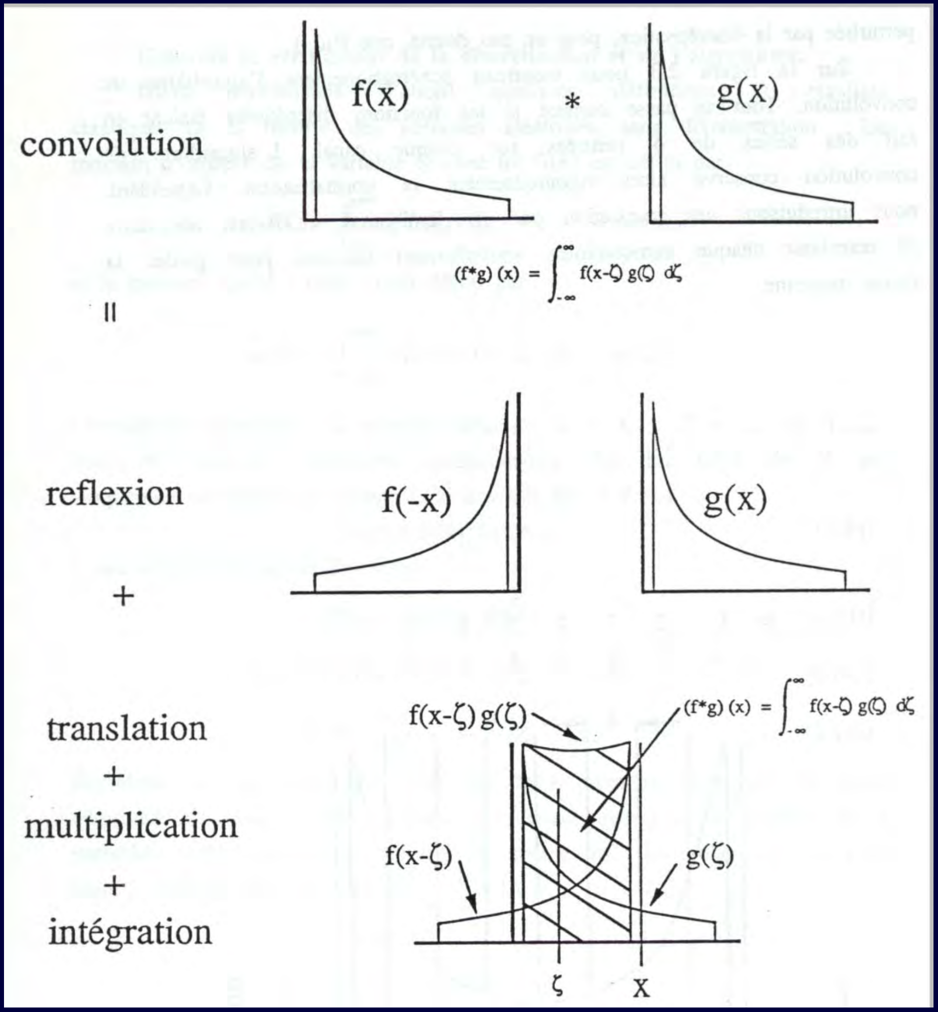
AUTOCONVOLUTION FILE

convolution with resonance line shape (assumed Lorentzian) and width, ion beam energy spread (assumed Gaussian) and its widening due to the Doppler effect at room temperature (assumed Gaussian), and concentration of the probed nuclide and thickness of each layer of a first temptative profile

↓

THEORETICAL EXCITATION CURVE

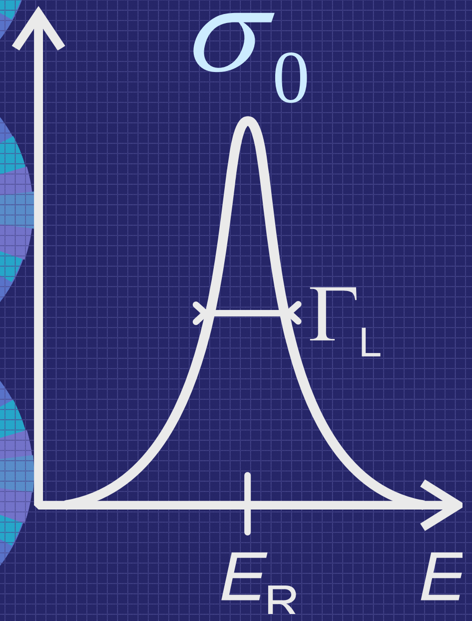
Convolution

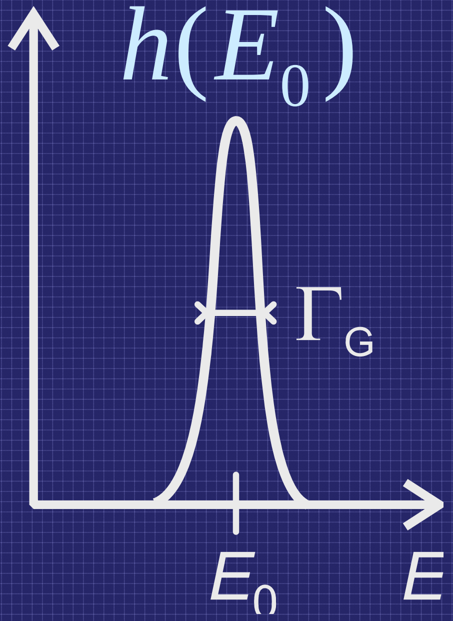


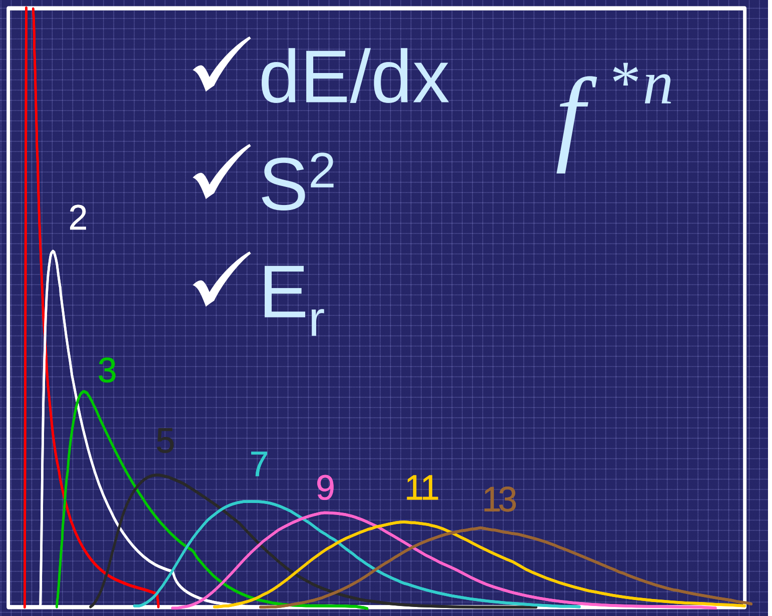
I. Vickridge, Thesis, University of Paris VII (1990)

Modeling

$$N(E_0) = c.\sigma_0(E) * h(E_0) * \sum_0^\infty K_n f^{*n}(E - E_0)$$







$$K_n = \int_0^\infty \frac{(mx)^n}{n!} e^{-mx} C(x)dx \qquad C(x) = ?$$

G. Amsel, et al., Nucl. Instr. Meth., v. **197, n.** 1, p. 1 (1990).

Exemplo de Aplicação: ^{18}O em Si

1965: modelo de Deal e Grove p/ oxidação térmica do silício

Deal and Grove, JAP **36**, 3770 (1965)

❖ Principais suposições:

- existência de uma camada de óxido inicial (~ 20 nm);

- regime estacionário;

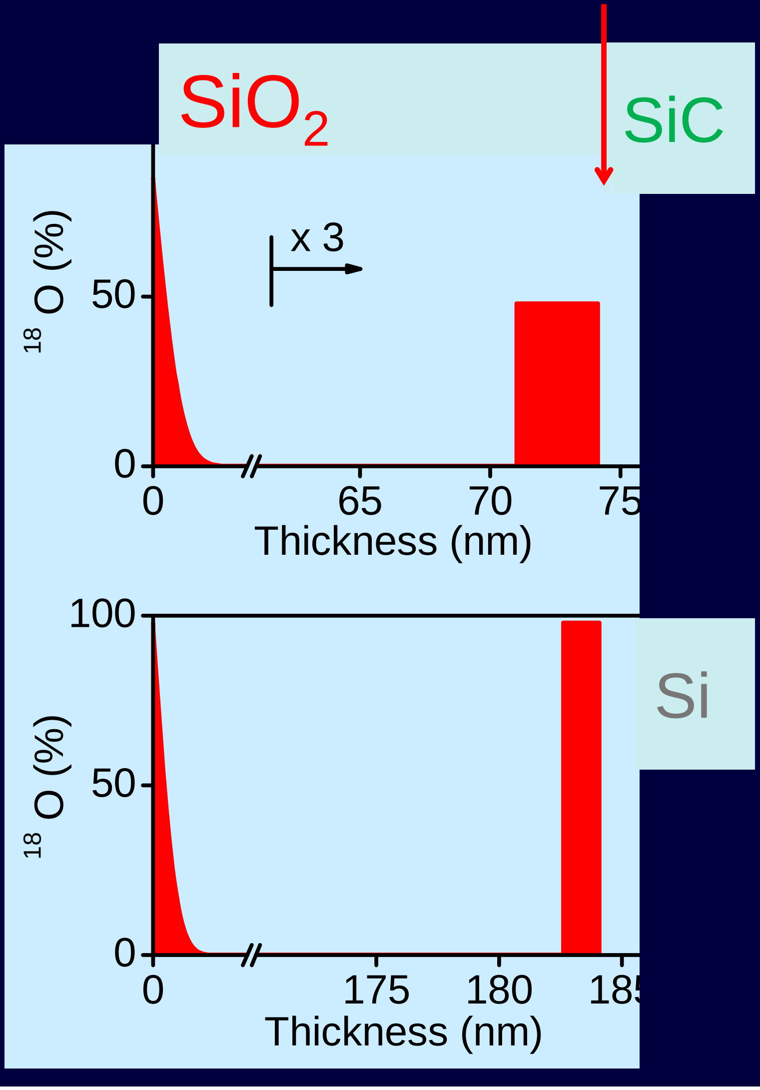
- difusão de O_2 através do filme de óxido de silício e reação na interface SiO_2/Si.

Osbourne Executive produzido nos anos 80 x iPhone em 2009:
28.75 pounds / 135g = 100 x + pesado
4MHz / 412 MHz = 100 x + lento
$2500 / $200-300 = 10 x + caro
(52cm x 23cm x 33cm)/(115mm x 61mm x 11.6mm) = 485 x maior

Mecanismo e Etapa Limitante do Crescimento Térmico de SiO_2 sobre SiC

I.C. Vickridge *et al.*, Phys. Rev. Lett. 89 (2002) 256102

- Traçagem Isotópica – ^{16}O / ^{18}O
- $^{18}O(p,\alpha)^{15}N$ E_p = 151 keV
- 6H-SiC tipo n polidas nas faces (0001) e (000$\underline{1}$) e Si (001)



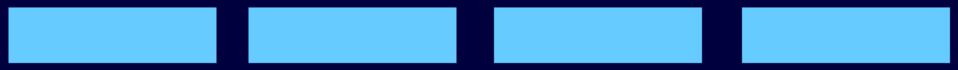
1º grupo de amostras

🟨 $Si^{16}O_2$

🟥 $Si^{18}O_2$

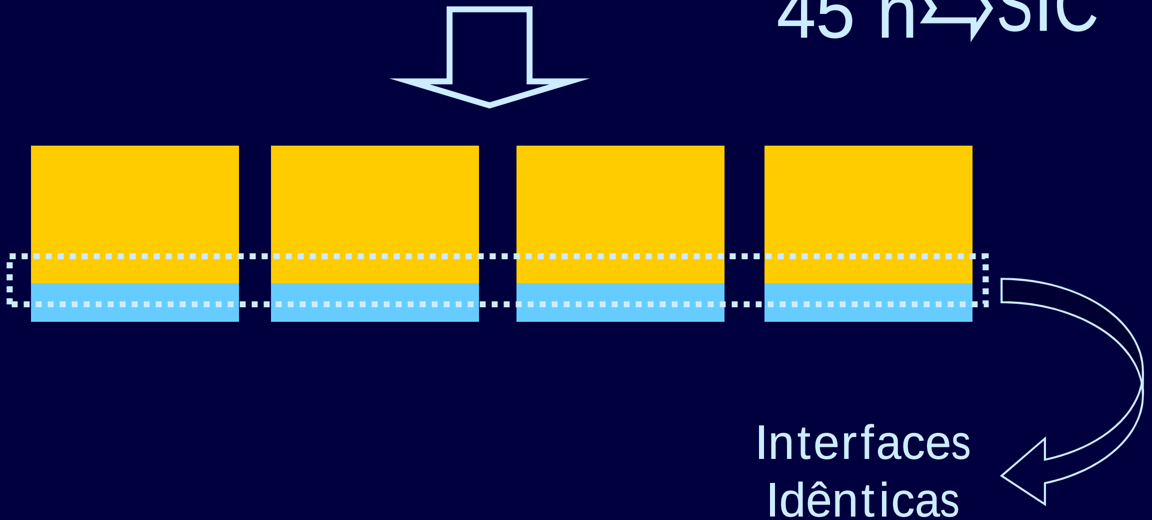
🟦 SiC ou Si

⇨ Limpeza das amostras



⇨ 1100 ºC 100mbar $^{16}O_2$ 8 h ⇨ Si

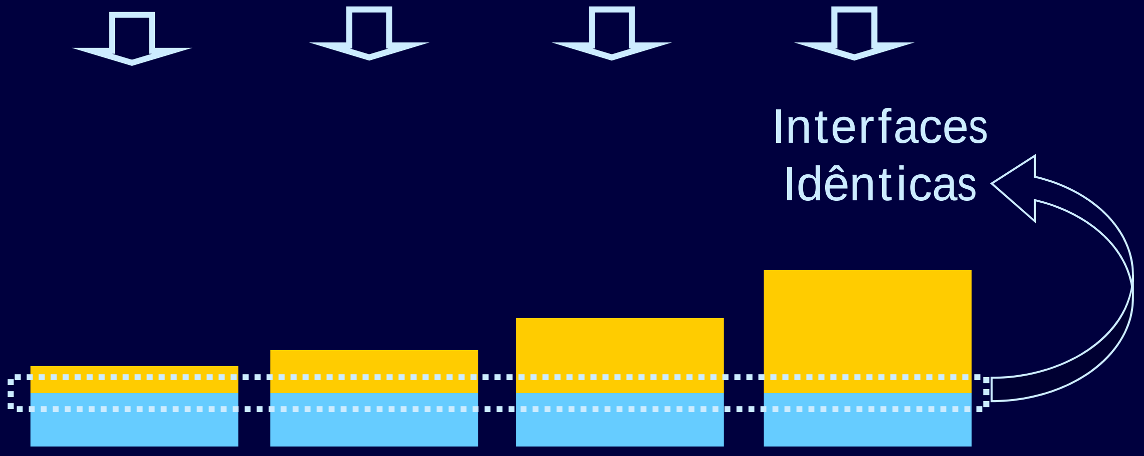
45 h ⇨ SiC



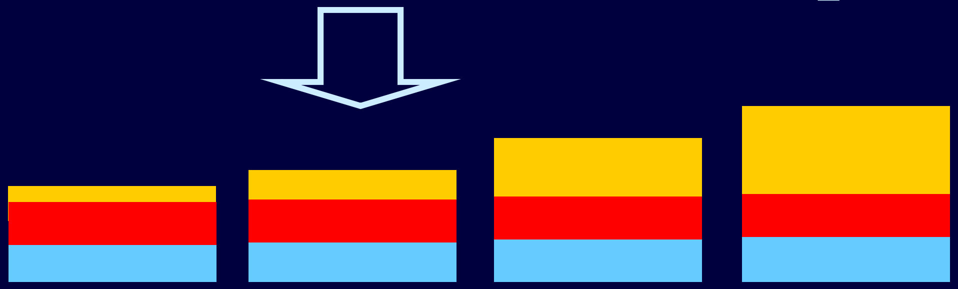
Interfaces
Idênticas

HF: taxa de ataque ~ 1 nm/s

70 s	40 s	30 s	1 s	⇨ Si
30 s	20 s	10 s	1 s	⇨ SiC


Interfaces Idênticas

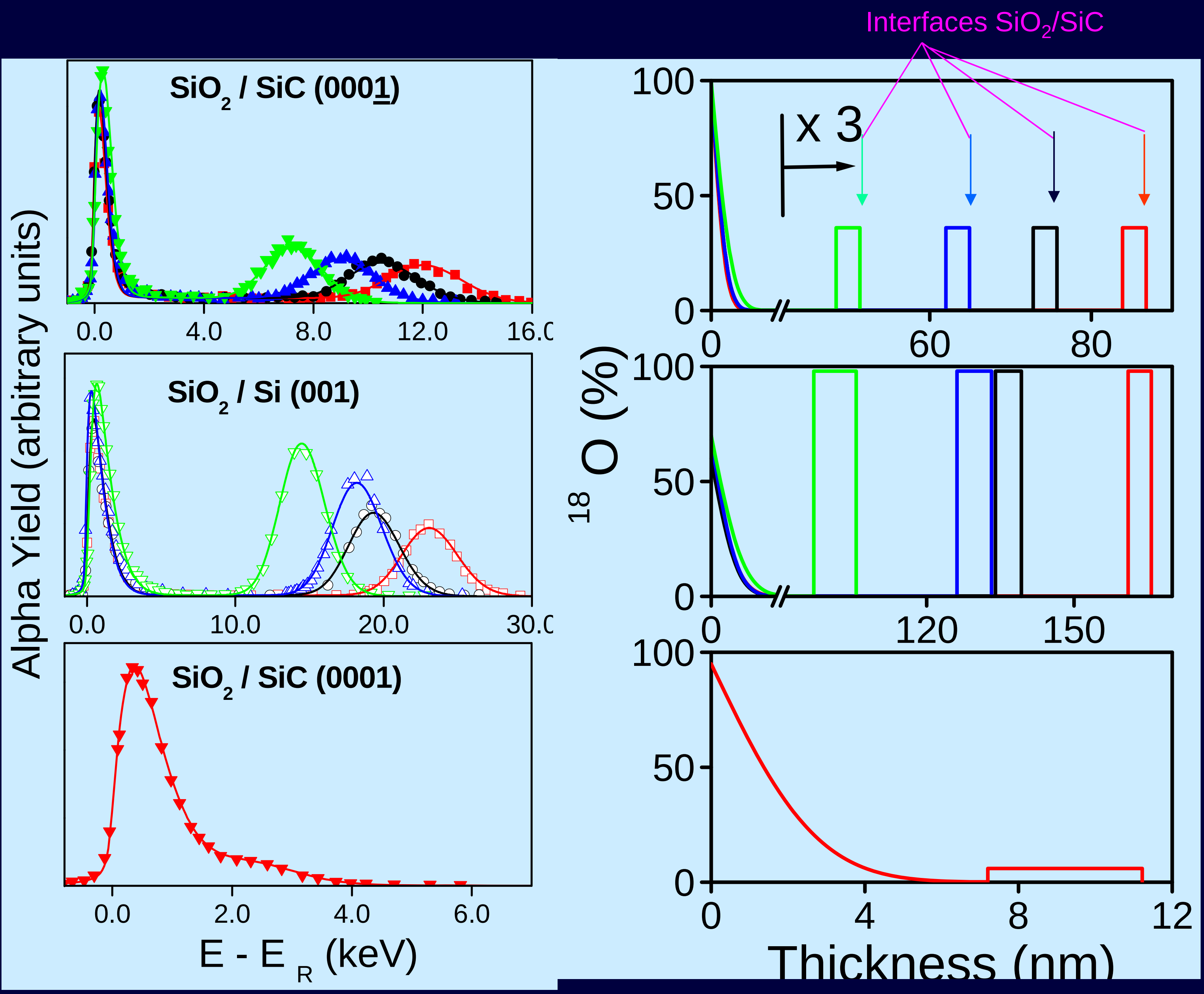
1100ºC 100 mbar 1h $^{18}O_2$



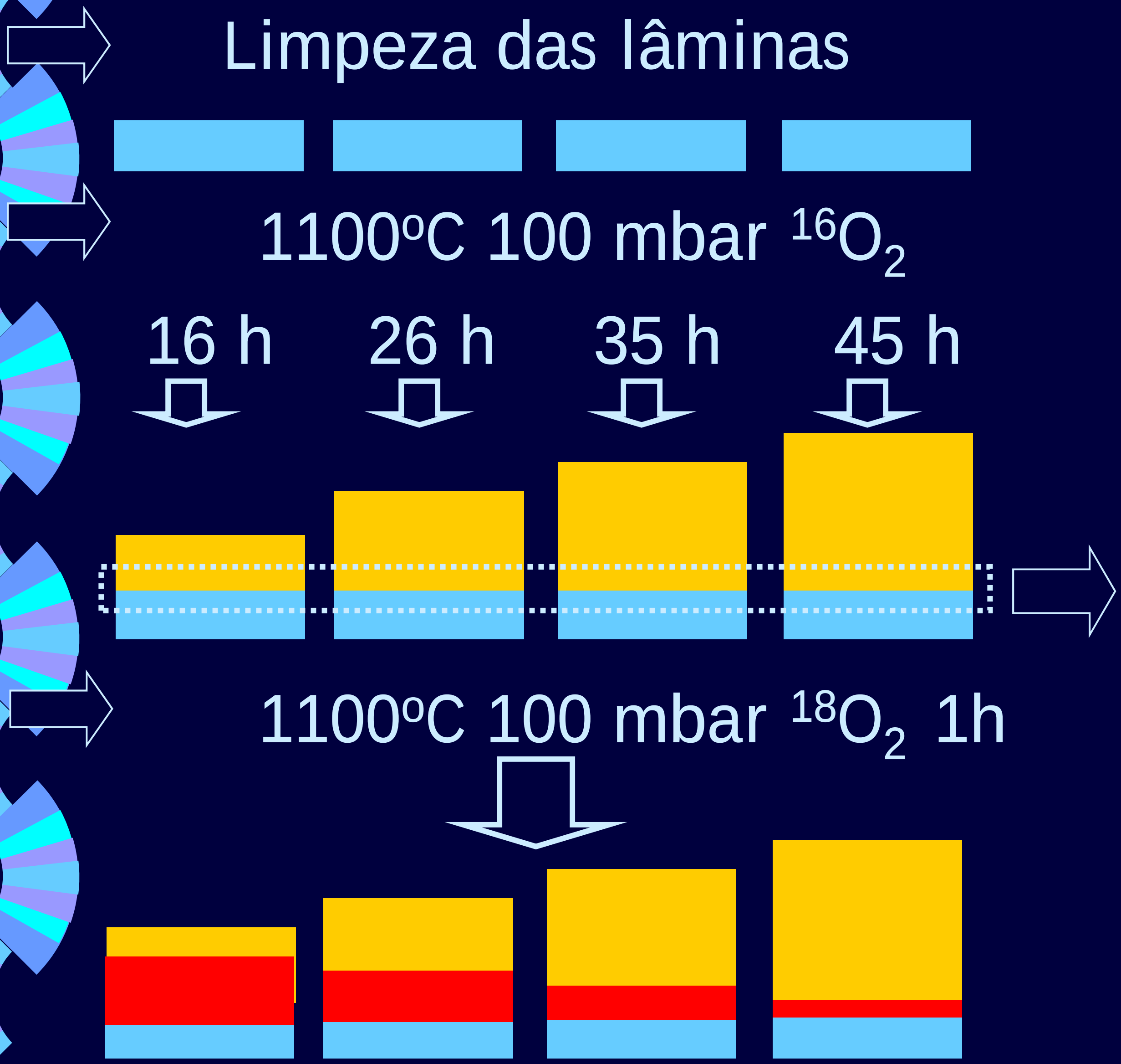
🟨 $Si^{16}O_2$

🟥 $Si^{18}O_2$

🟦 SiC or Si


SiO$_2$ / SiC (000$\underline{1}$)
SiO$_2$ / Si (001)
SiO$_2$ / SiC (0001)
Alpha Yield (arbitrary units)
0.0
4.0
8.0
12.0
16.0
0.0
10.0
20.0
30.0
0.0
2.0
4.0
6.0
E - E$_R$ (keV)
Interfaces SiO$_2$/SiC
x 3
100
50
0
0
60
80
120
150
4
8
12
^{18}O (%)
Thickness (nm)

2º grupo de amostras



Limpeza das lâminas

1100ºC 100 mbar $^{16}O_2$

16 h

26 h

35 h

45 h

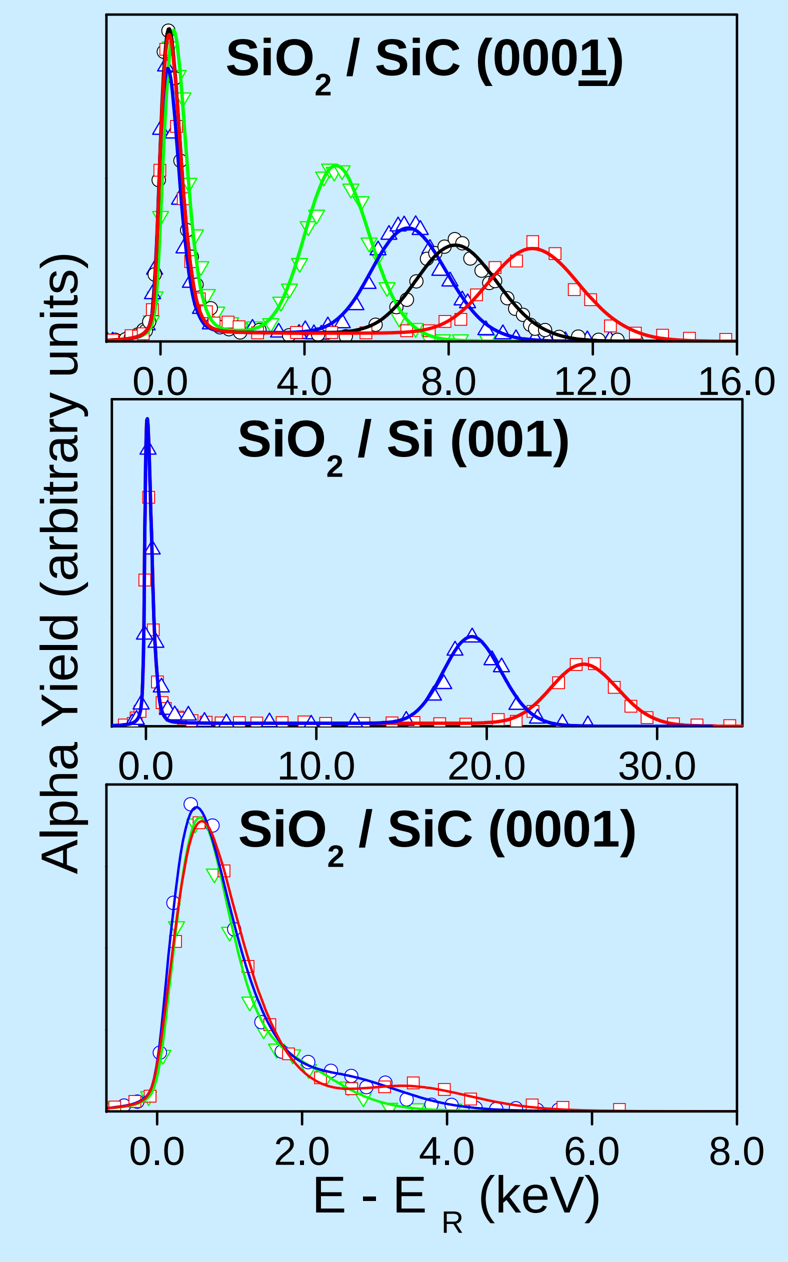
Interfaces distintas ?

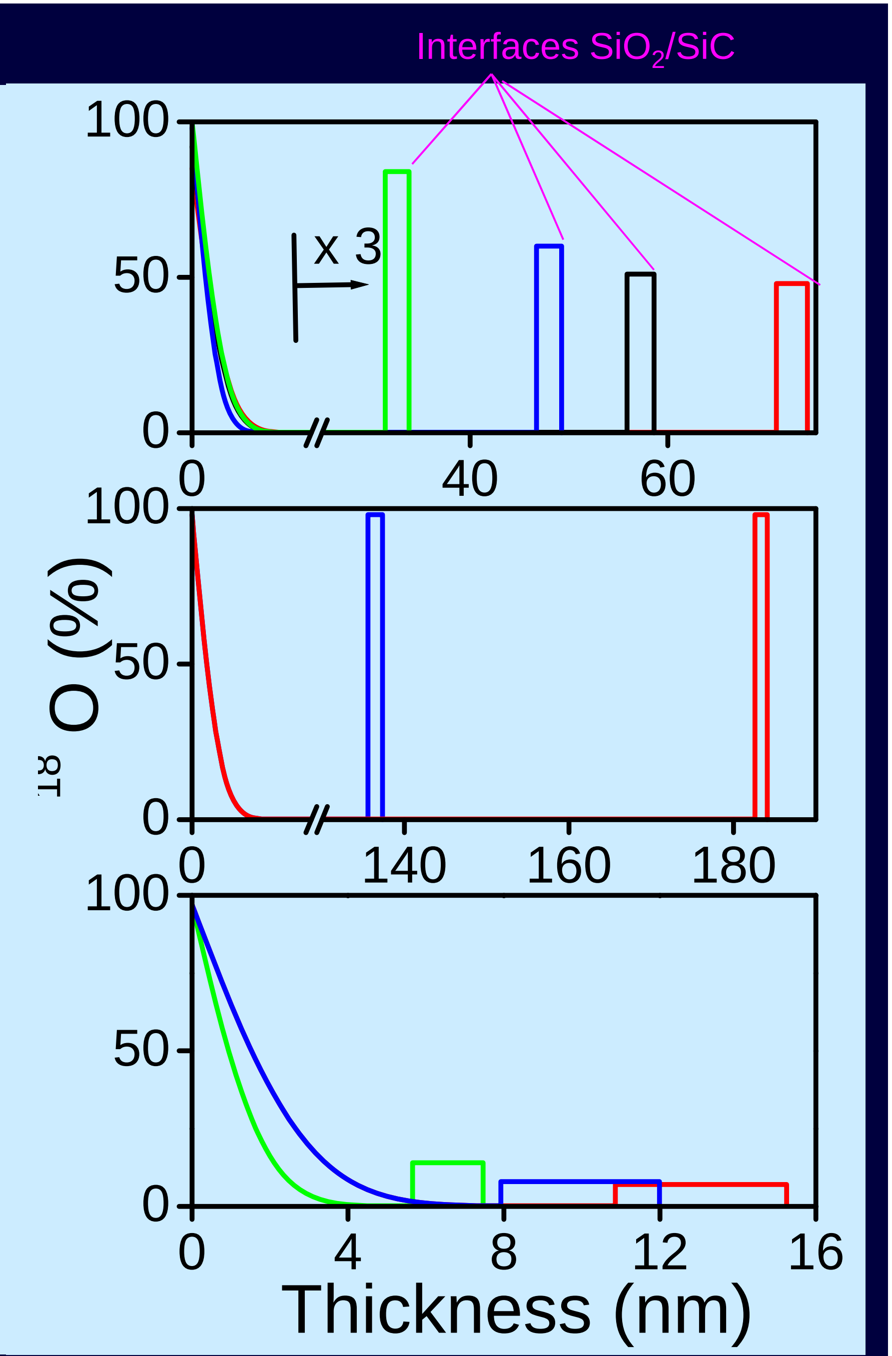
1100ºC 100 mbar $^{18}O_2$ 1h

🟦 SiC ou Si

🟨 $Si^{16}O_2$

🟥 $Si^{18}O_2$


SiO2 / SiC (0001)
SiO2 / Si (001)
SiO2 / SiC (0001)
Alpha Yield (arbitrary units)
0.0
4.0
8.0
12.0
16.0
0.0
10.0
20.0
30.0
0.0
2.0
4.0
6.0
8.0
E - E R (keV)


Interfaces SiO2/SiC
x 3
100
50
0
0
40
60
100
50
0
0
140
160
180
100
50
0
0
4
8
12
16
18O (%)
Thickness (nm)

Colaboradores atuais

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  IC: Gustavo Dartora
- Profs. Gabriel V. Soares, Henry Boudinov – IF UFRGS
- Profs. Cláudio Radtke – IQ UFRGS
- Prof. Rodrigo Prioli Meneses – DF PUC-RJ
- Prof. Sima Dimitrijev, Griffith University, Australia
- Prof. Leonard Feldman, Rutgers University, E.U.A.
- Dr. Aivars Lelys, Army Research Lab., E.U.A.
- Dr. Anant Agarwal, Cree Inc.→ DOE, E.U.A.