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$_2$)
  Excellent electrical and thermodinamic characteristics
- SiO$_2$/Si interface
  Low density of electrically active states
Silicon: the most widely used semiconductor in the microelectronic industry

![Graph showing the decrease in volume (cm³) over time from 1970 to 2000 for different devices: Desktop PC, Notebook PC, H/PC, Calculator, Video camera, Mobile phone. The y-axis represents volume in cm³, and the x-axis represents years from 1970 to 2000. Performance is indicated on the right side of the graph.](image-url)
MOSFET

Gate oxide

Source

Gate Electrode

Drain

V^+_-

Metal

N Type

P Type

P Type

Dielectric/semiconductor 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% ~US$ 1,000/L  D$_2$$^{18}$O ~US$ 2,000/mL
Static atmosphere reactor
Using isotopes and nuclear reactions to understand the atomic transport during the Si thermal oxidation

Oxidation in \( O_2 \) (natural abundance):

\[ (T = \sim 1000 \, ^\circ C) \]
Oxidation in $^{18}\text{O}_2$

Who is the mobile species? O, Si, or both?
Mobile species during oxidation

1st possibility: Si is the mobile species

SiO$_2$  

$^{18}$O$_2$
Mobile species during oxidation

2nd possibility: $\text{O}$ is the mobile species
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.
Nuclear Reactions

\[ {}^{18}\text{O}(p,\alpha){}^{15}\text{N} \]

\[ \text{POW!} \]

\[ \text{NRP} \]

\[ \text{NRA} \]

Differential Cross section (\(\text{mb/sr}\))

Proton energy (keV)

\[ {}^{15}\text{N} \]

\[ \alpha \]

\[ 151 \]

\[ 216 \]

\[ 334 \]

\[ 629 \]

\[ 730 \]

\[ 846 \]
$^{18}\text{O}(p,\alpha)^{15}\text{N}$
Ion Implantation Laboratory
UFRGS
HVEE 3 MV Tandetron

NRA and RBS chamber
HVEE 500 kV single-ended: NRP chamber
Resonant Nuclear Reaction - NRP

18O(p,α)15N

Differential Cross section (μb/sr)

Proton energy (keV)

Sample
Profile

Excitation Curve

Yield

Concentration

Proton Energy

Depth [L]

Reset counters
Start counting

Total charge?

yes

Record values

Increase energy

no
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$_2$
Profiles reliability

$^{16}\text{O}_2 - ^{18}\text{O}_2 \ @ \ 1000^\circ\text{C}$
\[ ^{16}\text{O}_2 - ^{18}\text{O}_2 \@ 1000^\circ\text{C} \]

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 $D(^3\text{He},p)^4\text{He}$: plateau $\sim 700$ keV
- Total amounts of D (insensitive to H)

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

\[ D(^{3}\text{He},p)^{4}\text{He} \text{ at 700 keV} \]

- **sensitivity**: \(\sim 4.0 \times 10^{12} \text{ D.cm}^{-2}\)
- **Accuracy**: 10%
Areal density of $^{16}\text{O}$ 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 $\text{D}_2$; (b) loaded with $\text{D}_2$ and annealed in vacuum at $650^\circ\text{C}$ for 30 min.


D profiling
Motivation SiC

- Bandgap: 1.1 eV
- Saturation drift velocity: 3.2 eV
- Mobility: 2x10^7 cm/s
- Thermal conductivity: 1400 cm²/Vs
- Breakdown el. field*: 950 cm²/Vs
- 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

Japan: 1% less energy loss

Si bipolar transistor → SiC MOSFET
85% less energy loss

Energy save ~ 4 nuclear power plants
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 transferred or adapted to the SiO$_2$/SiC technology
Interfaces: SiO$_2$/Si x SiO$_2$/SiC

Single step in $^{18}$O$_2$

C. Radtke, I.J.R. Baumvol, B.C.Ferrera, F.C. Stedile
oxidation in $^{16}\text{O}_2$ oxidation in $^{16}\text{O}_2 + ^{18}\text{O}_2$

(a)  
(b)  

O-deficient C clusters

C clusters consumed by reoxidation

$\text{SiO}_2$  
$\text{SiC}$

$^{16}\text{O}_2$  
$^{18}\text{O}_2$

Depth

$16\%$  
$18\%$

C  
$\text{Si}^{16}\text{O}_2$  
$\text{Si}^{18}\text{O}_2$
Challenges in SiC technology

High density of interface states ($D_{it}$)

Instabilities during operation

water vapor: $D_2^{18}$O
Water related problems in $\text{SiO}_2/\text{Si}$

- humidity in a clean room fabrication facility is between 30 and 50%
- negative oxide charge buildup near the $\text{SiO}_2/\text{Si}$ interface
- increases in the interface state density already reported for $\text{SiO}_2/\text{Si}$
- negative-bias-temperature instabilities attributed to water related species at the $\text{SiO}_2/\text{Si}$ 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

$^{18}\text{O}$ – natural abundance of 0.2%
$D$ – natural abundance of 0.015%

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

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

$D(^{3}\text{He},p)^{4}\text{He}$ at 700 keV
$^{18}$O excitation curves

**SiO$_2$/SiC**

**SiO$_2$/Si**

**20°C**

**1000°C**

Alpha Yield (a.u.)

Proton beam energy (keV)
$^{18}$O profiles

$^{18}$O concentration (10$^{22}$ at cm$^{-3}$)

Depth (nm)

$^{18}$O concentration (10$^{22}$ at cm$^{-3}$)

Depth (nm)

SiO$_2$/Si

20°C

SiO$_2$/SiC

1000°C

SiO$_2$/SiC
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 $\sim$ 0.1 Å/s
$t = 2,000$ s

Silicon

dep. SiO$_2$

20 nm

4H-SiC (Si-face)

dep. SiO$_2$

20 nm
Temperature and substrate influence in $\text{D}_2^{18}\text{O}$ vapor incorporation

![Graph showing the influence of temperature and substrate on D areal density.](image)

- **4H-SiC**
- **Si**

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

- Remaining $\text{D}$ ~ 90%

Substrate:
- 20 nm SiO$_2$ dep.
$^{18}\text{O}$ profiles

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

Further research topics

- Mechanism and limiting step of thermal growth of SiO₂ on SiC
- Annealings in D₂ of SiO₂ / 4H-SiC and SiO₂ / 6H-SiC structures with and without Pt
- Annealings in NO of Pt / SiO₂ / SiC structures
- Reoxidations and sequential annealings em H₂O₂
- Oxidations in ¹⁸O₂ of 6H and 4H-SiC (Si and C-faces) varying P, t and T
- Brief thermal growth followed by SiO₂ deposition
- Nitridation in ¹⁵NH₃ of SiC and of SiO₂ /SiC followed by SiO₂ deposition
- CO annealings of SiO₂ / SiC and SiO₂ / Si structures
- Incorporation and quantification of P in SiO₂ / SiC
Thank you!
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 $\text{D}_2^{18}\text{O}$

- VERY expensive: about U$ 2,000/mL !!!
$^{18}\text{O}(p,\alpha)^{15}\text{N}$
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
Utilizando NRP para compreender o transporte atômico durante a oxidação do Si

Espécies móveis durante a oxidação?

**Resultados:**

O 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$_2$

![Diagrama de oxidação de Si com espécies móveis](imagens/diagrama.png)
Isotopic tracing of Si in thermal growth of silicon oxide films on Si in dry O₂

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

\[ \begin{align*}
29\text{Si} & \quad 92.2\% \quad 29\text{Si} \\
& \quad 4.7\% \quad 29\text{Si} \\
& \quad 3.1\% \quad 30\text{Si}
\end{align*} \]

\[ E = 30 \text{ eV} \]

Step 2: epitaxial recrystallization: 600 °C, 30 min, UHV

Step 3: $^{29}\text{Si}$ depth profiling

Step 4: thermal oxidation in O₂: 1000 °C, 60 min, 50 mbar

Step 5: $^{29}\text{Si}$ depth profiling

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

- Si immobile and O mobile

\[
\begin{array}{c|c}
\text{SiO}_2 \text{ film} & \text{Si substrate} \\
\end{array}
\]

- Si mobile and O immobile

\[
\begin{array}{c|c|c}
\text{SiO}_2 \text{ film} & \text{Si substrate} & \text{SiO}_2 \text{ film} & \text{Si substrate} \\
\end{array}
\]

FIG. 4. (a) $^{29}\text{Si}$ excitation curve (solid circles), its simulation (solid line), and $^{29}\text{Si}$ profile in the inset for the oxidized sample. (b) $^{29}\text{Si}$ excitation curves in the pre-oxidation (solid circles, $^{29}\text{Si}$ epitaxial on Si(111)) and post-oxidation (empty circles, $^{29}\text{Si}$ in SiO₂/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.

Ions decelerator
$^{29}\text{Si}(p,\gamma)^{30}\text{P}$

$E_R = 417$ keV; $\Gamma = 100$ eV
Alcance das partículas no Mylar
Electronic and nuclear $dE/dx$
Energy loss

\[ k_i = \left( \frac{\sqrt{m_i^2 + m_i^2 \sin^2 \theta + m_i \cos \theta}}{m_i + m_t} \right)^2 \]
Narrow Resonance Nuclear Reaction Profiling: NRP

Interpretation: SPACES code
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

Modeling

\[ N(E_0) = c \sigma_0(E) \ast h(E_0) \ast \sum_{n=0}^{\infty} K_n f^{*n}(E - E_0) \]

\[ K_n = \int_{0}^{\infty} \frac{(mx)^n}{n!} e^{-mx} C(x) dx \]

\[ C(x) = ? \]

Exemplo de Aplicação: $^{18}\text{O}$ em Si

1965: modelo de Deal e Grove p/ oxidação térmica do silício
Deal and Grove, JAP 36, 3770 (1965)

- existência de uma camada de óxido inicial (~ 20 nm);
- regime estacionário;
- difusão de $\text{O}_2$ 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 SiO₂ sobre SiC


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

1º grupo de amostras

زواج 1100 °C 100mbar 16O2 8 h \rightarrow Si 45 h \rightarrow SiC

Interfaces Idênticas
HF: taxa de ataque ~ 1 nm/s

<table>
<thead>
<tr>
<th>Duração (s)</th>
<th>Si</th>
<th>SiC</th>
</tr>
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<tbody>
<tr>
<td>70</td>
<td></td>
<td></td>
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<tr>
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<td>SiC</td>
</tr>
<tr>
<td>1</td>
<td>SiC</td>
<td></td>
</tr>
</tbody>
</table>

Interfaces Idênticas

1100°C 100 mbar 1h $^{18}\text{O}_2$

Diagrama de interações entre Si, $^{16}\text{O}_2$, $^{18}\text{O}_2$ e SiC.
Interfaces SiO$_2$/SiC
2º grupo de amostras

Limpeza das lâminas

1100°C 100 mbar $^{16}\text{O}_2$

16 h 26 h 35 h 45 h

1100°C 100 mbar $^{18}\text{O}_2$ 1h

SiC ou Si

$\text{Si}^{16}\text{O}_2$

$\text{Si}^{18}\text{O}_2$

Interfaces distintas?
Interfaces SiO$_2$/SiC

**SiO$_2$/SiC (0001)**

**SiO$_2$/Si (001)**

**SiO$_2$/SiC (0001)**

Alpha Yield (arbitrary units)

E - E$_R$ (keV)

Thickness (nm)

O (%)
Colaboradores atuais

- Doutorando: Eduardo Pitthan Fº
  IC: Gustavo Dartora
- Profs. Gabriel V. Soares, Henry Boudinov – IF UFRGS
- Profs. Cláudio Radtke – IQ UFRGS
- Prof. Rodrigo Prioli Meneses – DF PUC-RJ
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- Prof. Leonard Feldman, Rutgers University, E.U.A.
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- Dr. Anant Agarwal, Cree Inc.→ DOE, E.U.A.