Simulation of Oxidation and Dopant Redistribution Using SUPREM4

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Statement of the Problem

Simulate using Suprem4 on prime grade 100 mm Si wafer:

1. Dry oxidation at 1100°C, 5 min
2. Wet oxidation at 1100°C, 60 min
3. Dry oxidation again
4. Wafer preclean: acetone 1500 rpm (30s), IPA 1500 rpm (30s), spin dry 4000 rpm (60s)
5. HMDS at 4000 rpm for 30s
6. PR (AZ 5214-E): 4000 rpm, 30s
7. Prebake: 89°C for 20 min
8. Expose (active/gate area mask): 7.5s (g-line)
9. Develop (AZ 312 MIF): 75s
10. DI rinse: 180s

11. Postbake: 109°C (30 min)
12. Descum/ash: O_2/100W/30mTorr/30s
13. BHF etch: 7 min
14. DI quench: 1 min
15. Cascade rinse: 3 min
16. PR strip: PRS2000 at 100°C for 15 min, acetone rinse 3 min, IPA rinse 3 min, cascade rinse 5 min
17. Gate oxide growth: dry oxidation at 1000°C for 60 min

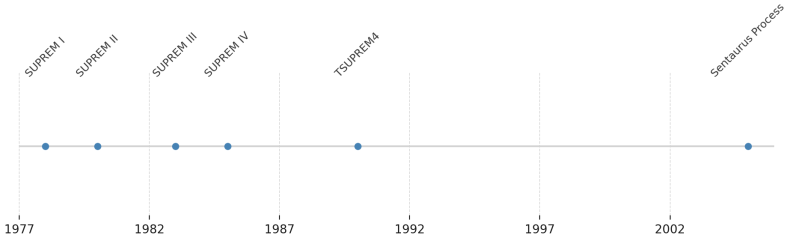
History of SUPREM Simulator

- The SUPREM (Stanford University Process Engineering Models) family of simulators has played a pivotal role in the evolution of process simulation for integrated circuit (IC) fabrication. Developed originally at Stanford University in the late 1970s, SUPREM was intended to model semiconductor fabrication steps such as oxidation, diffusion, ion implantation, and annealing — all essential for predicting dopant profiles and layer thicknesses in ICs.
- The development of SUPREM began as a response to the growing need for accurate modeling tools during the MOSFET scaling era. As device geometries shrank, process variability became increasingly critical, and empirical design methods proved insufficient. The SUPREM series, starting from SUPREM I, gradually incorporated more physics-based models and robust numerical solvers.

- SUPREM III was among the first versions to gain wide adoption in academia and industry due to its capability to simulate one-dimensional vertical cross-sections. It could predict dopant redistribution during high-temperature steps with reasonable accuracy. This version relied on finite-difference techniques to solve the diffusion equations.
- SUPREM IV, the version most commonly referenced and used in process modeling studies, introduced more advanced features. These included:
  - Two-dimensional (2D) process simulation capabilities.
  - More accurate modeling of oxidation kinetics using the Deal-Grove and Massoud models.
  - Support for a wider range of dopants and material systems.
  - Integration with graphical user interfaces and support tools (like TSUPREM4 and DECKBUILD).

- Eventually, SUPREM technology was integrated into commercial TCAD (Technology Computer-Aided Design) frameworks, notably those offered by Synopsys, such as Sentaurus Process. While SUPREM IV itself is no longer actively developed, it laid the foundation for modern process simulators and remains a key reference in semiconductor education and research.
- In this project, SUPREM IV is used to simulate oxidation processes and dopant redistribution in a boron-doped silicon wafer, offering insight into how real-world fabrication steps influence final device structures.

Evolution of SUPREM



Process Flow

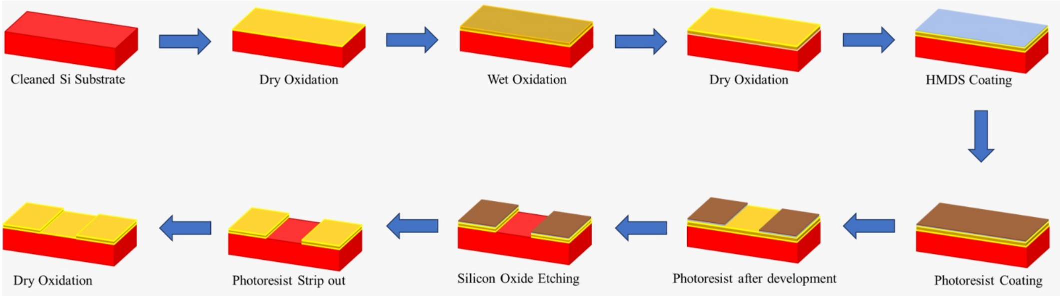


Figure: Overall Process Flow

Oxide Thickness Measurements

- After Step 1: 0.0280 μm oxide
- After Step 2: 0.6931 μm oxide
- After Step 3: 0.6944 μm oxide
- After Gate Oxide: 0.7008 μm oxide

Oxide Thickness Calculation

The Deal–Grove equation is:

$$X^2 + AX = B(t + \tau) \tag{1}$$

where,

$$A = 2D\left(\frac{1}{k_s} + \frac{1}{h_g}\right) \tag{2}$$

$$B = \frac{2DHP_g}{N_1} \tag{3}$$

$$\tau = \frac{t_o^2 + At_o}{B} \tag{4}$$

Step 1: Dry Oxidation starting initially for 5 mins

$$X_1^2 + A_{\text{dry}} X_1 = B_{\text{dry}} t_1 \tag{1}$$

Step 2: Wet Oxidation Starting from X_1 for 60 mins

$$X_2^2 + A_{\text{wet}} X_2 = B_{\text{wet}} t_2 + X_1^2 + A_{\text{wet}} X_1 \tag{3}$$

Step 3: Dry Oxidation starting from X_2 for 5 mins

$$X_3^2 + A_{\text{dry}} X_3 = B_{\text{dry}} t_3 + X_2^2 + A_{\text{dry}} X_2 \tag{3}$$

Dry and Wet Oxidation Coefficients for Silicon

Temp (°C)	Dry		τ (hr)	Wet (640 torr)	
	A (μm)	B (μm^2/hr)		A (μm)	B (μm^2/hr)
800	0.370	0.0011	9.0	0.50	0.203
920	0.235	0.0049	1.4	0.226	0.287
1000	0.165	0.0117	0.37	0.226	0.287
1100	0.090	0.027	0.076	0.110	0.510
1200	0.040	0.045	0.027	0.050	0.720

Table: Dry and Wet oxidation coefficients for silicon

The τ parameter is used to compensate for the rapid growth regime for thin oxides.

- Step 1: (Dry oxidation) X1 $= 0.02035\mu m$
- Step 2: (Wet oxidation) X2 $= 0.6631\mu m$
- Step 3: (Dry oxidation) X3 $= 0.6644\mu m$

Conductivity

$$\sigma = q * \mu_p * N_A \tag{5}$$

At $4.34 \times 10^{16}\,\mathrm{cm}^{-3}$, a good typical value for $\mu_p \approx 410\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$.

Now plug into the formula:

$$\sigma = (1.6 \times 10^{-19}) \times (410) \times (4.34 \times 10^{16})$$

Let's calculate:

$$\sigma = 1.6 \times 410 \times 4.34 \times 10^{-3}$$

$$\sigma = 2.85\,\mathrm{S/cm}$$

Step 0

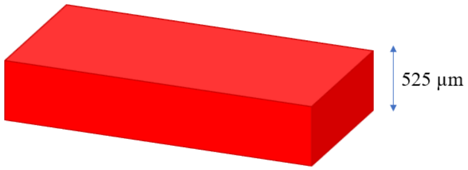
```
set echo
option quiet
mode one.dim

#the vertical definition
line x loc = 0      spacing = 0.02 tag = top
line x loc = 25.0  spacing = 0.02
line x loc = 525.0   spacing = 0.25 tag=bottom


#the silicon wafer
region silicon xlo = top xhi = bottom

#set up the exposed surfaces
boundary exposed  xlo = top  xhi = top

#set up the backside surfaces
boundary backside xlo=bottom xhi=bottom
```



Step 1

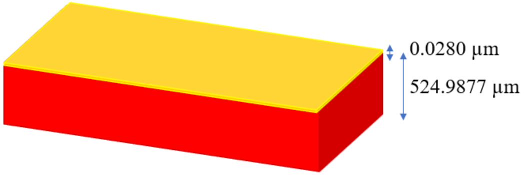
```
#automatic grid generation for the initial substrate
initialize boron conc=4.34e16 ori=100


#dry oxidation
diffuse time=5 temp=1100 dryo2

#Print layer information
select z=x label="Depth(A)"
print.1d y.v=0
form=8.0f

#plot results
select z=log10(boron) label=log(concentration)
plot.1d x.min=-0.5 x.max=1.5 y.min=14 y.max=20
```

SiO_2 = 0.0280 µm
Si Consumed = 0.01228 µm
(43.84% of total SiO_2)



- Thickness of oxide = 0.02802896 micron
- Thickness of Si consumed = 0.01228589 micron

```
select z=x label="Depth(A)"
SUPREM4 print.1d y.v=0
print.1d y.v=0
x coordinate in um              Depth(A)         Material
       -0.01574307        -1.574307e-06        oxide
        0.01228589         1.228589e-06        oxide
        0.01228589         1.228589e-06        silicon
        0.02000000         2.000000e-06        silicon
        0.04000000         4.000000e-06        silicon
        0.06000000         6.000000e-06        silicon
        0.08000000         8.000000e-06        silicon
        0.10000000         1.000000e-05        silicon
        0.12000000         1.200000e-05        silicon
        0.13999999         1.400000e-05        silicon
```

Figure: Dry oxidation for 5 mins

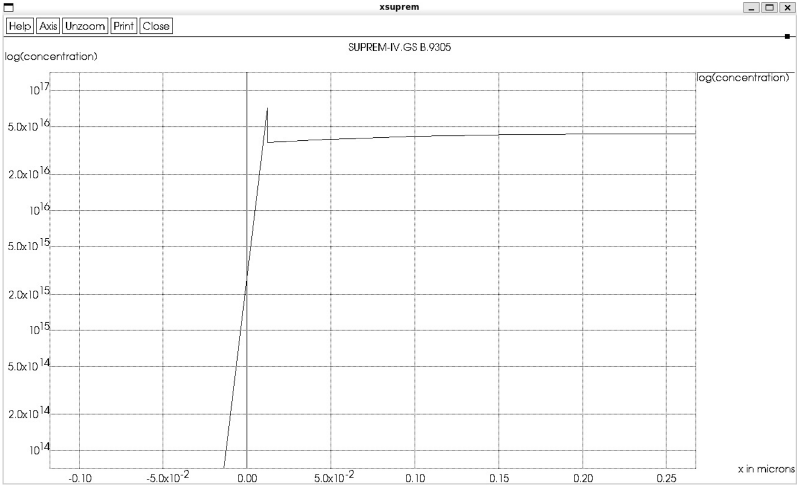


Figure: Dry Oxidation for 5 minutes at 1100 °C

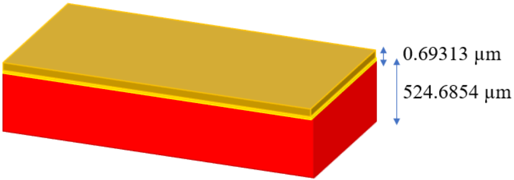
Step 2

```
#wet oxidation
diffuse time=60 temp=1100 weto2

#Print layer information
select z=x label="Depth(A)"
print.1d y.v=0
form=8.0f

#plot results
#select z=log10(boron) label=log(concentration)
#plot.1d x.min=-0.5 x.max=1.5 y.min=14 y.max=20
```

SiO_2 = 0.69313 µm
Si Consumed = 0.31460 µm
(45.38% of total SiO_2)



- Thickness of oxide = 0.69313916 micron
- Thickness of Si consumed = 0.31460870 micron

```
SUPREM4 select z=x label="Depth(A)"
select z=x label="Depth(A)"
SUPREM4 print.1d y.v=0
print.1d y.v=0
x coordinate in um                Depth(A)        Material
      -0.37853046       -3.785305e-05       oxide
      -0.25726906       -2.572691e-05       oxide
      -0.11638631       -1.163863e-05       oxide
       0.00656929        6.569289e-07       oxide
       0.13294462        1.329446e-05       oxide
       0.26135403        2.613540e-05       oxide
       0.31460870        3.146087e-05       oxide
       0.31460870        3.146087e-05       silicon
       0.34000001        3.400000e-05       silicon
       0.35999998        3.600000e-05       silicon
       0.37999998        3.800000e-05       silicon
       0.39999999        4.000000e-05       silicon
       0.42000000        4.200000e-05       silicon
```

Figure: Wet oxidation for 60 mins

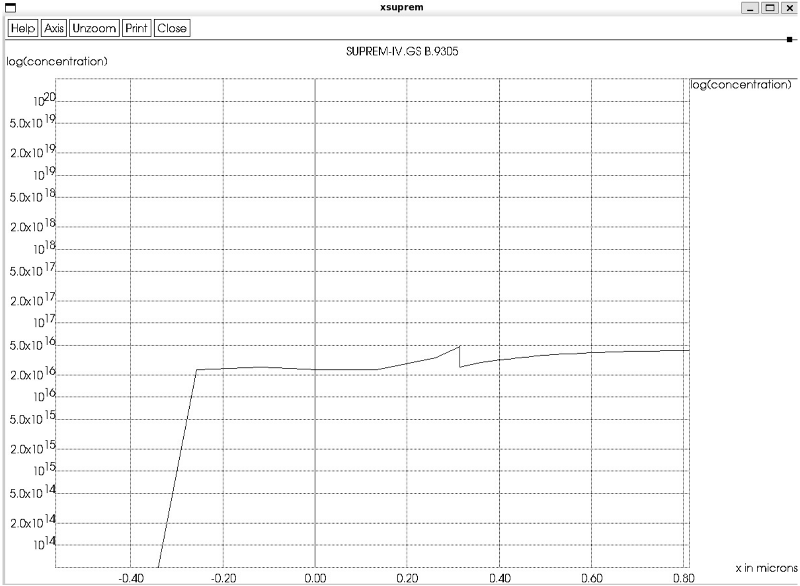


Figure: Wet Oxidation for 60 minutes at 1100 °C

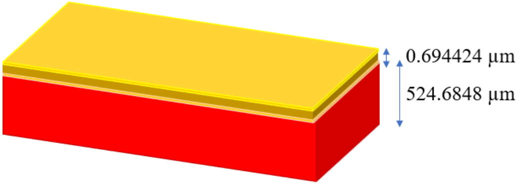
Step 3

#dry oxidation
diffuse time=5 temp=1100 dryo2

#Print layer information
select z=x label="Depth(A)"
print.1d y.v=0
form=8.0f

#plot results
select z=log10(boron) label=log(concentration)
plot.1d x.min=-0.5 x.max=1.5 y.min=14 y.max=20

SiO_2 = 0.694424 µm
Si Consumed = 0.315194 µm
(45.38% of total SiO_2)



- Thickness of oxide = 0.69442751 micron
- Thickness of Si consumed = 0.31519427 micron

```
SUPREM4 select z=x label="Depth(A)"
select z=x label="Depth(A)"
SUPREM4 print.1d y.v=0
print.1d y.v=0
x coordinate in um              Depth(A)         Material
       -0.37923324      -3.792332e-05          oxide
       -0.25797179      -2.579718e-05          oxide
       -0.11708905      -1.170890e-05          oxide
        0.00586655       5.866555e-07          oxide
        0.13224188       1.322419e-05          oxide
        0.26065130       2.606513e-05          oxide
        0.31519427       3.151943e-05          oxide
        0.31519427       3.151943e-05          silicon
        0.34000001       3.400000e-05          silicon
        0.35999998       3.600000e-05          silicon
        0.37999998       3.800000e-05          silicon
        0.39999999       4.000000e-05          silicon
        0.42000000       4.200000e-05          silicon
        0.44000000       4.400000e-05          silicon
        0.45999997       4.600000e-05          silicon
        0.47999998       4.800000e-05          silicon
```

Figure: Dry oxidation for 5 mins

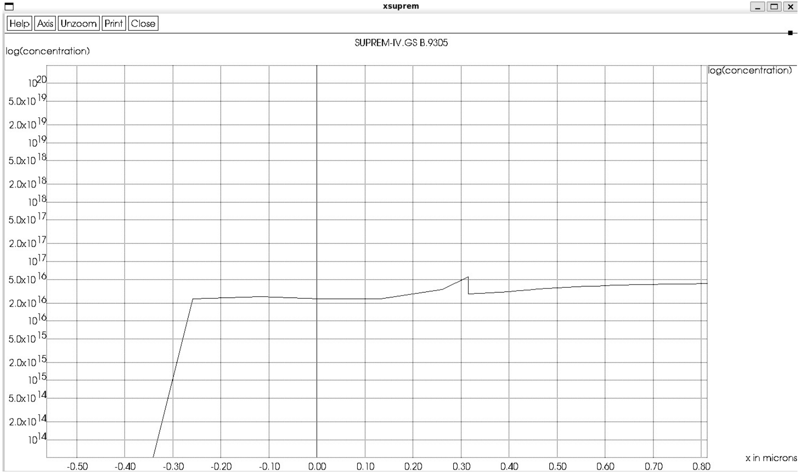


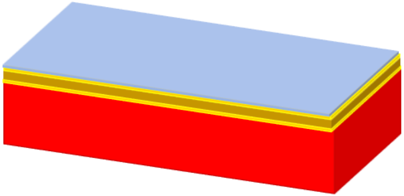
Figure: Dry Oxidation for 5 minutes at 1100 °C

Step 4 and 5

#Acetone Cleaning is not supported by SUPREM-IV
#We use an alternate method to acheive a clean surface
#Etch away a thin layer of surface (oxide)
etch dry thick=0.01

Deposit a thin layer of oxide again
deposit oxide thick=0.01
structure out=preclean.str

#HMDS Coating

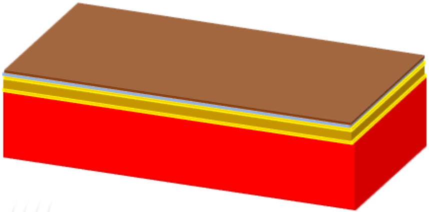


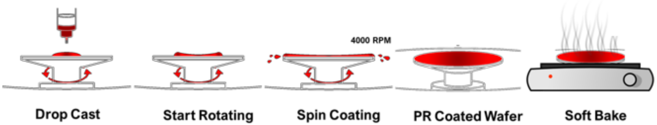
Step 6

Deposit the photoresist
From the datasheet of AZ-5214E, the thickness at 4000rpm is 1.4 µm

deposit nitride thick=1.4

structure out=photoresist.str





Datasheet of AZ-5214E

PHYSICAL and CHEMICAL PROPERTIES

		AZ 5214E	
Solids content [%]		28.3	
Viscosity [cSt at 25°C]		24.0	
Absorptivity [l/g*cm] at 377nm		0.76	
Solvent	methoxy-propyl acetate (PGMEA)		
Max. water content [%]	0.50		
Spectral sensitivity	310 - 420 nm		
Coating characteristic	striation free		
Filtration [µm absolute]	0.1		

FILM THICKNESS [µm] as FUNCTION of SPIN SPEED (characteristically)

spin speed [rpm]	2000	3000	**4000**	5000	6000
AZ 5214E	1.98	1.62	**1.40**	1.25	1.14

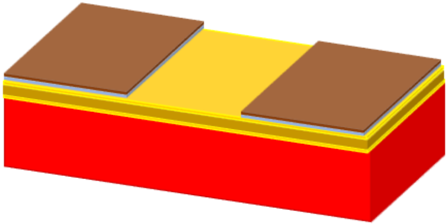
Step 7 to 9

```
# Pre-Bake
# The order is slightly confusing, as deposition of AZ-5214E requires
# The Si Wafer to be pre-baked

diffuse time=20 temp=89

# Expose and Develop the Photoresist

etch nitride left p1.x=0.5
etch nitride right p1.x=3.5
structure out=mask.str
```



Step 10 to 12

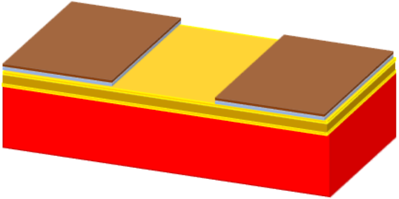
DI rinse: 180 s
Postbake: 109 ◦C (30min)
Descum/ash: O2/100W/30mTorr/30 s

Post-Bake
#Strenghtens the resist

diffuse time=30 temp=109

Descum - Simulated by etching away all exposed photores by a small amount

etch nitride dry thick=0.01
structure out=descum.str

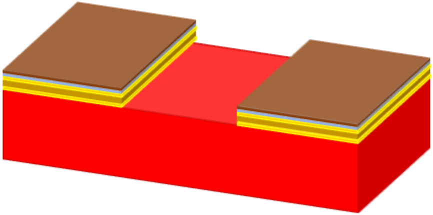


Step 13 to 15

```
# BHF Etch - Removes all oxide

etch oxide all


etch dry oxide thick=0.05
structure out=oxide_etch.str
```

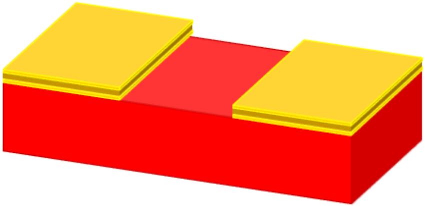


Step 16

```
# BHF Etch - Removes all photoresist

etch nitride all


structure out=bhf.str
```

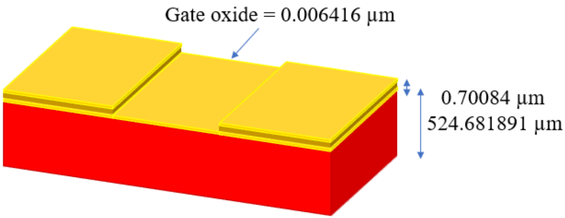


Step 17

```
# Gate Oxide Growth
diffuse time=60 temp=1000 dryo2
structure out=gate.str


#Print layer information
select z=x label="Depth(A)"
print.1d y.v=0
form=8.0f

#plot results
select z=log10(boron) label=log(concentration)
plot.1d x.min=-0.5 x.max=1.5 y.min=14 y.max=20
end
```



SiO_2 = 0.70084 µm
Si Consumed = 0.318109 µm
(45.38% of total SiO_2)

- Thickness of oxide = 0.70084137 micron
- Thickness of Si consumed = 0.31810963 micron

```
SUPREM4 select z=x label="Depth(A)"
select z=x label="Depth(A)"
SUPREM4 print.1d y.v=0
print.1d y.v=0
x coordinate in um                 Depth(A)         Material
       -0.38273174        -3.827317e-05        oxide
       -0.26147020        -2.614702e-05        oxide
       -0.12058746        -1.205875e-05        oxide
        0.00236813         2.368128e-07        oxide
        0.12874348         1.287435e-05        oxide
        0.25715290         2.571529e-05        oxide
        0.31810963         3.181096e-05        oxide
        0.31810963         3.181096e-05        silicon
        0.34000001         3.400000e-05        silicon
        0.35999998         3.600000e-05        silicon
        0.37999998         3.800000e-05        silicon
        0.39999999         4.000000e-05        silicon
        0.42000000         4.200000e-05        silicon
        0.44000000         4.400000e-05        silicon
        0.45999997         4.600000e-05        silicon
        0.47999998         4.800000e-05        silicon
        0.49999999         5.000000e-05        silicon
```

Figure: Dry oxidation for 60 mins

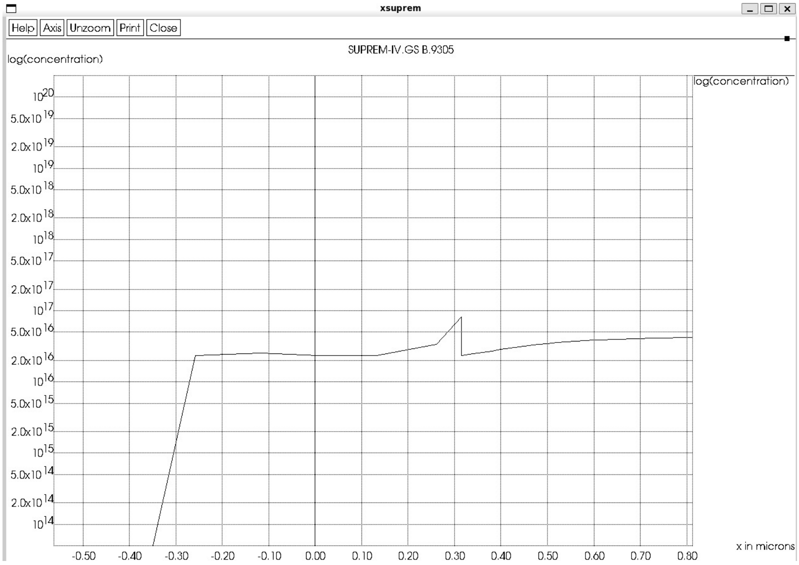
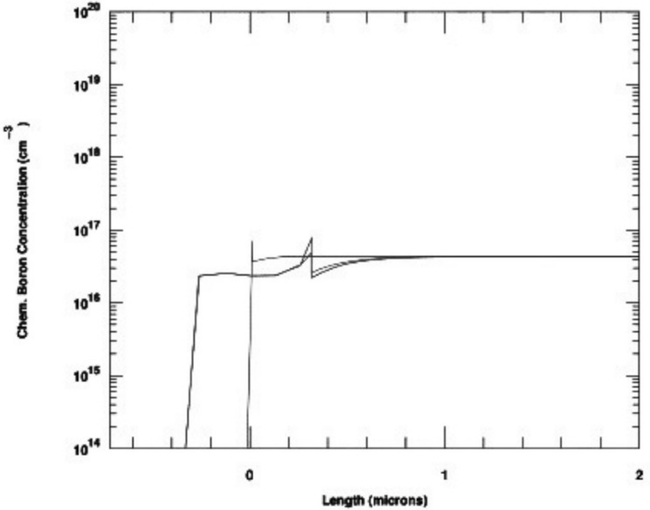


Figure: Dry Oxidation for 60 minutes at 1100 °C

Comparision of Steps 1, 2, 3 and 17



Mismatch Analysis between Simulation and Theory

Aspect	Analytical Model	SUPREM Simulation
Initial Oxide Thickness	Assumes $t_0 = 0$ (bare wafer)	Considers native oxide (~ 2–$5\,\text{nm}$) before oxidation
Oxide Accumulation	Stepwise addition: $x_{\text{total}} = x_1 + x_2 + x_3$	Dynamic accumulation, non-linear effects during growth
Dopant Redistribution (Boron)	Ignores dopant motion and segregation	Models boron segregation ($k \approx 0.3$) and diffusion into SiO_2
Temperature and Pressure Dependence	Fixed A, B at nominal T from tables	Temperature-dependent diffusivity, reaction rates, and ambient effects
Interface Modeling	Sharp, ideal Si/SiO_2 boundary	Finite-width reaction zones and gradual transitions
Mathematical Solution	Solves simple ODE: $x^2 + Ax = Bt$	Solves full PDEs with discretization and moving boundaries
Oxidant Species Consideration	Average constants for dry/wet oxidation	Real gas fractions (O_2, H_2O, etc.) affect diffusivity and kinetics

Table: Reasons for mismatch between theory and SUPREM simulation.

CV Curve After Gate Oxide Growth

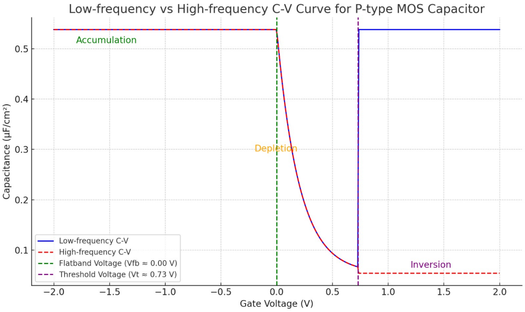


Figure: CV Curve After Gate Oxide Growth

$$C_{ox} = \frac{\epsilon_{ox} * \epsilon_o}{t_{ox}} \tag{6}$$

[2]
Here,

- $\epsilon_{ox} = 3.9$
- $\epsilon_o = 8.854 * 10^{-14}$
- $t_{ox} = 0.006416\mu m = 6.416 * 10^{-7} cm$

Thus,

$$C_{ox} = \frac{3.9 * 8.854 * 10^{-14}}{6.416 * 10^{-7}} = 5.383 * 10^{-7} F/cm^2 = 0.5383 \mu F/cm^2 \tag{7}$$

Boron Doping Profile : Three Regions

1. Linear increase in boron concentration (Region I)
2. Plateau with constant boron levels (Region II)
3. Unchanged profile in thin top oxide (Region III)

Region I: Linear Rise During Initial Dry Oxidation

- Thin, dense oxide forms in first 5 minutes of dry oxidation.
- Steady-state flux quickly achieved.
- **Fick's First Law:**

$$J = -D\frac{dC}{dz} \quad \Rightarrow \quad \frac{dC}{dz} = \text{constant} \quad \Rightarrow \quad C(z) \text{ is linear}$$

- **Distance dependence:** Boron diffusion rate depends on proximity to Si/SiO_2 interface.
- **Concentration dependence:** SiO generation affects boron diffusion.
- **Time dependence:** Profile evolves over time initially. [1]

Region II: Flat Profile During Wet Oxidation

- Wet oxidation grows thick oxide, minimal boron redistribution.
- Surface boron depleted during earlier dry oxidation.
- Very low boron diffusivity even in wet oxide:

$$D_{\text{wet}} \sim 10^{-15} \text{ to } 10^{-16} \, \text{cm}^2/\text{s}$$

- Small diffusion length:

$$\sqrt{Dt} \sim 0.02 \, \mu\text{m}$$

- No new boron flux or driving gradient.

Conclusion: The boron profile stays nearly flat across the wet-grown oxide.

Region III: Constant Profile During Final Dry Oxidation

- Final dry oxidation adds ∼8 nm oxide thickness.
- Boron diffusivity is extremely low in dry SiO_2.
- No new boron source is available.
- Short oxidation time (5 minutes) limits redistribution.

Result: The boron profile remains unchanged from Region II.

Team Contributions

- Aditya Gupta: Mathematical and theoretical analysis of oxidation thicknesses during successive dry oxidation followed by wet oxidation followed by dry oxidation again and comparison with obtained results. Worked on the C-V characteristics.
- Suryadeep Ghosh: Analytical reasoning of the various plots explaining each region of the obtained simulations. Generating the expressions of oxide thickness for successive dry oxidation followed by wet oxidation followed by dry oxidation again. Doing literature review on the history of Suprem 4 application. Mismatch analysis between theory and simulation. Made the report using LaTeX.
- Arpit Mahoday: Simulating dry oxidation followed by wet oxidation and again followed by dry oxidation. Simulating the final Gate oxide growth.
- Mohd Saqib: Suprem Code Implementation of each step and generating the simulations. Analyzing the C-V characteristics using MATLAB and calculating the value of C_{ox}. Diagrams of the process flow.

References

[1] James R. Patel. *Measurement of boron segregation at the SiO_2/Si interface*. 1984. DOI: 10.1116/1.572998. URL: https://pubs.aip.org/avs/jva/article/2/3/1266/242773/Measurement-of-boron-segregation-at-the-SiO2-Si.

[2] Dieter K. Schroder. *Semiconductor Material and Device Characterization*. 3rd ed. Wiley-Interscience, 2006. ISBN: 9780471739067. URL: https://books.google.co.in/books?id=J-YwRJx7ZQoC.