SiGe/Ge Surface Passivation by ALD

Ching-Ying Lu, Muyu Xue
Mentor advisor: Michelle Rincon & J Provine
Research advisor: James Harris
Why is Ge Passivation so Hard?

• There is no stable Ge oxide like SiO$_2$ to Si.

• Surface recombination provides a non-radiative pathway.

• Degradation of photoluminescence (PL) signal -> undesired for light emitting applications (LEDs / lasers).
Ge Oxidation

• 4 different oxidation states (1+, 2+, 3+, 4+)
• Affected by temperature, pressure, and methods
• GeO$_2$ passivates the surface and gives low Dit
• Unfortunately, it can be easily etched away by water (not stable!)
• How do we protect GeO$_2$ and relate low D$_{it}$ to higher PL signal?
Process Flow

1. Si wafer.
2. Epi growth.
3. HCl clean.
4. Thin ALD.
5. Oxidation
6. Thicker ALD for protection.
7. PL.
Oxidation Methods

• Ozone oxidation
  • Ozone is more reactive than $O_2$.
  • 400 °C is required to achieve high oxidation state ($GeO_2$ instead of $GeO_x$).
  • Higher temperature causes transformation of oxide.

• Forming gas anneal
  • Transient formation of water.
  • Water reoxidize the substrate surface.

Both methods can be done in the ALD system!
Design Parameters

- What ALD layer?
  - $\text{Al}_2\text{O}_3$ or HfO$_2$

- Precursors of ALD?
  - $\text{H}_2\text{O}$ (thermal) or $\text{O}_2$ plasma

- First layer thickness?
  - 1 nm or 2 nm.

- Oxidation methods?
  - Forming gas anneal or ozone

- Optimize the recipe (oxidation time, pressure...) for two different oxidation methods before varying the parameters above.
DOE (Al$_2$O$_3$)

<table>
<thead>
<tr>
<th>#</th>
<th>Precursors (O2 plasma/H2O)</th>
<th>Oxidation Methods (O3/FG)</th>
<th>1$^{st}$ layer thickness (1 nm/2 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O2 plasma</td>
<td>O3</td>
<td>1 nm</td>
</tr>
<tr>
<td>2</td>
<td>O2 plasma</td>
<td>FG</td>
<td>1 nm</td>
</tr>
<tr>
<td>3</td>
<td>O2 plasma</td>
<td>O3</td>
<td>2 nm</td>
</tr>
<tr>
<td>4</td>
<td>O2 plasma</td>
<td>FG</td>
<td>2 nm</td>
</tr>
<tr>
<td>5</td>
<td>H2O</td>
<td>O3</td>
<td>1 nm</td>
</tr>
<tr>
<td>6</td>
<td>H2O</td>
<td>FG</td>
<td>1 nm</td>
</tr>
<tr>
<td>7</td>
<td>H2O</td>
<td>O3</td>
<td>2 nm</td>
</tr>
<tr>
<td>8</td>
<td>H2O</td>
<td>FG</td>
<td>2 nm</td>
</tr>
</tbody>
</table>

For #9~#18, repeat the same runs for HfO$_2$
Heating & Cooling

- ALD growth at 200 °C but oxidation at 350 °C or 400 °C.
- 4 heaters: Reactor heater 1&2, Chuck & Cone
- ~30 min for all heaters to go from 200 °C to 300 °C.
- Chuck heats up the fastest and cools down the slowest (3.8 hrs for 350 °C to 200 °C).

Chuck Temperature (Cooling)

![Graph showing the temperature of the Chuck during cooling.]
Plasma Samples w/ FG

- Degradation of PL signals.
- Plasma strikes the surface and causes damages. Matches with past results where plasma ALD results in a higher $D_{it}$. 
Thermal Al$_2$O$_3$ w/ Ozone

- Not a constant flow of ozone: pulse ozone into the chamber, close the valve, wait for it to react, and open the valve.
- Half of ozone decompose to oxygen at 250 °C in one second. Decompose even faster at 400 °C!
Thermal Al$_2$O$_3$ w/ FG

- We obtained a clear improvement of PL signal after ALD treatment.
  - 30 min: 15% stronger
  - 1 hr: 56% stronger
Not able to repeat 56%..

1\textsuperscript{st} try: 56% stronger

2\textsuperscript{nd} try: 10% stronger
What makes the difference?

- Shorter heating time (sample exposed to remaining water vapor) gives better results?
- Higher pressure gives better results?
• Shorten heating time by setting ambience at a lower temp: 12%. 
• Shorten heating time by setting ambience at a lower temp: 12%.
• Double the flow rate of forming gas: 15%.
• Shorten heating time by setting ambience at a lower temp: 12%.
• Double the flow rate of forming gas: 15%.
• Increase water pulse during ALD growth: 0%.
• Shorten heating time by setting ambience at a lower temp: 12%.
• Double the flow rate of forming gas: 15%.
• Increase water pulse during ALD growth: 0%.
• Increase annealing time: 15%.
Key Observations

- Doubling flow rate increases pressure from 0.14 to 0.20 Torr. It has little effect on passivation.
  - Adjust the valve opening to have a larger change in pressure.
- Increasing the annealing time from 1 hour to 1.5 hour improves the signal by a negligible amount.
- Increasing water pulse may etch away GeO$_2$ formed during FGA and degrades the improvement.
Conclusions

• Demonstrated a repeatable 15% improvement on PL signal by forming gas anneal.
• Ozone capability of Fiji3 was first brought up.
Future Work

• Finish the DOE with the best recipe we have to understand how different ALD material and different 1st layer thickness affect the passivation.

• Study the degradation of signal over time with different cap layer thickness.

• Try O₃ as the precursor for ALD layer. This might prevent water to etch away the grown GeO₂ during the 2nd ALD layer growth.

• Apply the passivation method to microdisk resonator.
Questions?