Dramatic Reduction of Gate Leakage Current of Ultrathin Oxides through Oxide Structure Modification

Zhi Chen, Jun Guo, and Chandan B. Samantaray

Department of Electrical and Computer Engineering
University of Kentucky
Lexington, KY 40506
Outline

• Theory of Hydrogen/Deuterium Isotope Effect
• Experimental Evidence for Origin of Isotope Effect
• Discovery of Phonon Energy-Coupling Enhancement
• Dramatic Improvement of Quality of Gate Oxides
Hot electrons desorb hydrogen, creating interface states which degrade device performance.
Van de Walle & Jackson Theory
(Van de Walle et al., Appl. Phys. Lett. vol. 69, 2441 (1996))

Two competing processes:

• Hot electron excitation causes Si-H/D bond breaking.

• De-excitation is due to energy coupling from Si-D to phonon.

Reason: \( \nu \propto \sqrt{1/m} \) based on IR spectroscopy theory

Si-H vibrational frequency \( \nu \sim 650 \text{ cm}^{-1} \).
Si-D vibrational frequency \( \approx 460 \text{ cm}^{-1} \) (Si-Si TO phonon mode)

De-excitation is more efficient for Si-D bonds than for Si-H bonds
--- This is why Si-D bonds are stronger than Si-H ones.
Schematic of Hydrogen/Deuterium Effect:
Energy coupling from Si-D bending mode to Si-Si TO phonon mode
No coupling from Si-H bending mode to Si-Si TO phonon mode
Direct Measurement of the Vibrational Frequency of Si-H/D Bonds

No experimental data available for Si-D vibrational frequency in the SiO₂/Si interface.

Only in the deuterated amorphous Si (α-Si), the vibrational frequency (510 cm⁻¹) was measured*. However, the chemical environment of the amorphous Si is very different from that of crystal Si.

Origin of the Isotope Effect: Energy Coupling from Si-D to Si-Si TO phonon & Si-O TO rocking mode (Chen et al. Appl. Phys. Lett. 83, 2151-2153, 2003)

The absorbance of the Si-Si TO phonon mode and the Si-O TO rocking mode are all enhanced significantly (>25%) after deuterium anneal. (Chen et al. Appl. Phys. Lett. 83, 2151-2153, 2003)
New finding: Energy is coupled from Si-D bending mode to Si-Si TO phonon mode and also to Si-O TO rocking mode
Challenge: How to further enhance the energy coupling?

**Hypothesis:** Shift the Si-D vibrational mode toward Si-Si TO phonon mode.

**Method 1:** Mechanical stress  
just a little shift (~6-8 cm⁻¹)

**Method 2:** Electrical stress

**Method 3:** Thermal stress  
How?
The absorbance of the Si-Si TO phonon mode, the Si-O TO rocking mode, and Si-Si LO mode are all enhanced significantly (>50%) after rapid thermal processing (RTP). There is further enhancement after deuterium annealing. $T_{ox} = 23$ nm.
The Enhancement is not due to the Surface Plasmon.

It is well-known that the surface plasmon on the nanoscale metallic islands also produces strong surface-enhanced IR spectra. In order to avoid the metallic island-like surface, we used n⁻ wafer (n=2×10¹⁴ cm⁻³ and ρ=20.8 Ω-cm) for experiments.
For thick oxide ($T_{ox}=80$ nm), there is almost no enhancement except for the Si-Si LO mode after rapid thermal processing (RTP)--- implying stress-related phenomena. This also suggests that there should be no effect for the polysilicon/oxide stack.
Dependence of Enhancement on the Cooling Time

The enhancement is strongly dependent on the cooling time - implying the stress-related phenomena.

- 1. Si/Oxide, Unannealed
- 2. Si/Oxide, RTP annealed, cooling 10 minutes
- 3. Si/Oxide, RTP annealed, cooling 5 minutes
- 4. Si/Oxide, RTP annealed, cooling 20 seconds
Phonon Energy-Coupling Enhancement: improvement of hot-electron degradation

Hypothesis: Si-O bonds might be strengthened. This is because energy is also coupled from Si-O rocking mode to Si-Si TO phonon mode and also to Si-D bending mode.
Hydrogen/Deuterium Effect on Gate Oxide: No Effect

$T_{ox} = 10.2\text{nm}$
Direct Rapid Thermal Processing Only: Improvement of Breakdown Voltage (15%) and Reduction of Leakage Current (10X)

\[ T_{ox} = 11.1 \text{nm} \]

- H\textsubscript{2} anneal only
- RTP+H\textsubscript{2} anneal
Direct Rapid Thermal Processing Plus D₂ Annaeal: Improvement of Breakdown Voltage (30%) and Reduction of Leakage Current (100X)

\[ T_{ox} = 10.2 \text{nm} \]
Direct Rapid Thermal Processing Plus D$_2$ Anneal: Improvement of Breakdown Voltage (30%) and Reduction of Leakage Current (100X)

$T_{ox} = 3.7$nm

D$_2$ anneal only

RTP+$D_2$ anneal

Leakage Current (A)

Leakage Current (A/cm$^2$)

Gate Voltage (V)
Direct Rapid Thermal Processing Plus D₂ Anneal of Thin Oxides: Reduction of leakage current \(10^5 X\)

This is similar to that of HfSiON (Gusev et al., IEDM Technical Digest, 451-454 (2001))
There is only a slight flat-band voltage shift and thickness remains unchanged after RTP.

Table: Comparison of oxide thickness measured using ellipsometry before and after RTP

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Oxidation Parameters</th>
<th>$T_{ox}$ before RTP</th>
<th>$T_{ox}$ after RTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1110051</td>
<td>$N_2$ @1000sccm, $O_2$ @20 sccm, 900°C for 20 s</td>
<td>22.4 Å</td>
<td>23.3 Å</td>
</tr>
<tr>
<td>#0628052</td>
<td>$N_2$ @1000sccm, $O_2$ @20 sccm, 900°C for 10 s</td>
<td>19.8 Å</td>
<td>20.9 Å</td>
</tr>
<tr>
<td>#1110052</td>
<td>$N_2$ @2000sccm, $O_2$ @20 sccm, 900°C for 20 s</td>
<td>19.5 Å</td>
<td>20.09 Å</td>
</tr>
</tbody>
</table>
Summary

- We discovered a new effect, phonon energy-coupling enhancement, i.e. the energy coupling from the Si-D bond to the Si-Si TO mode and the Si-O rocking mode is dramatically enhanced after the RTP processing directly on the oxide.

- In addition to strengthening Si-D bonds, Si-O bonds are also strengthened. The breakdown voltage of oxides after RTP processing is improved by 30%.

- The leakage current of thin oxide (2.2 nm) after direct RTP processing is reduced by $10^5$ times, similar to that of high-k oxides.
Acknowledgements

• This research is supported by National Science Foundation ECS-0093156 and EPS-0447479.