

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

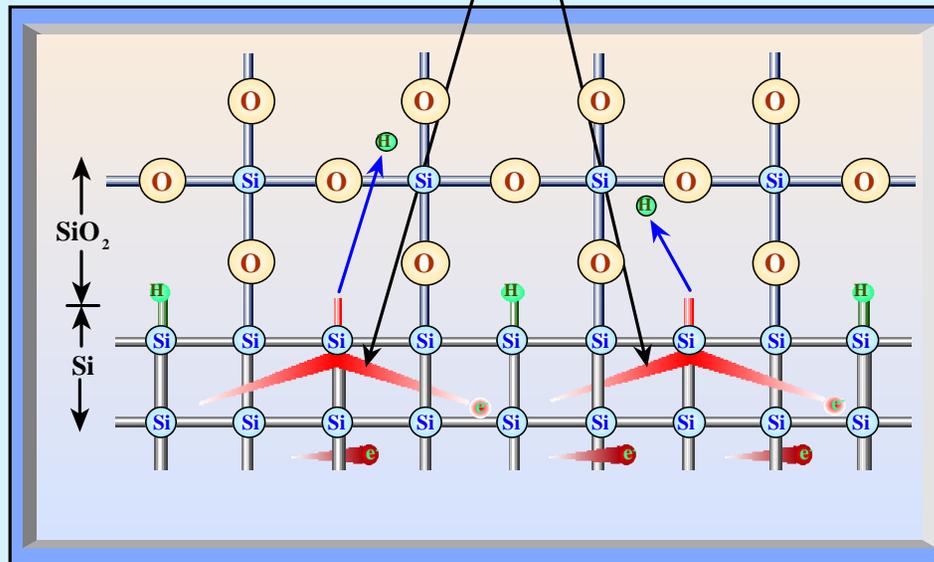
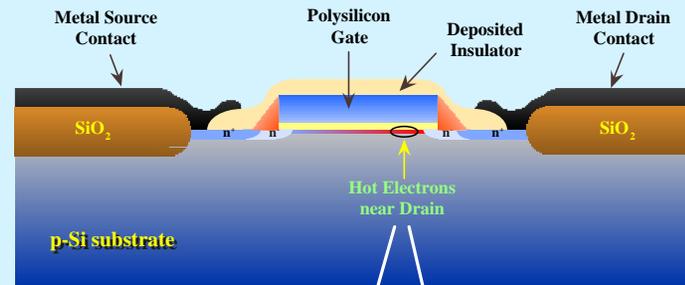
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Outline

- **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**

Hydrogen Passivated MOSFET



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 $\nu \sim 650 \text{ cm}^{-1}$.

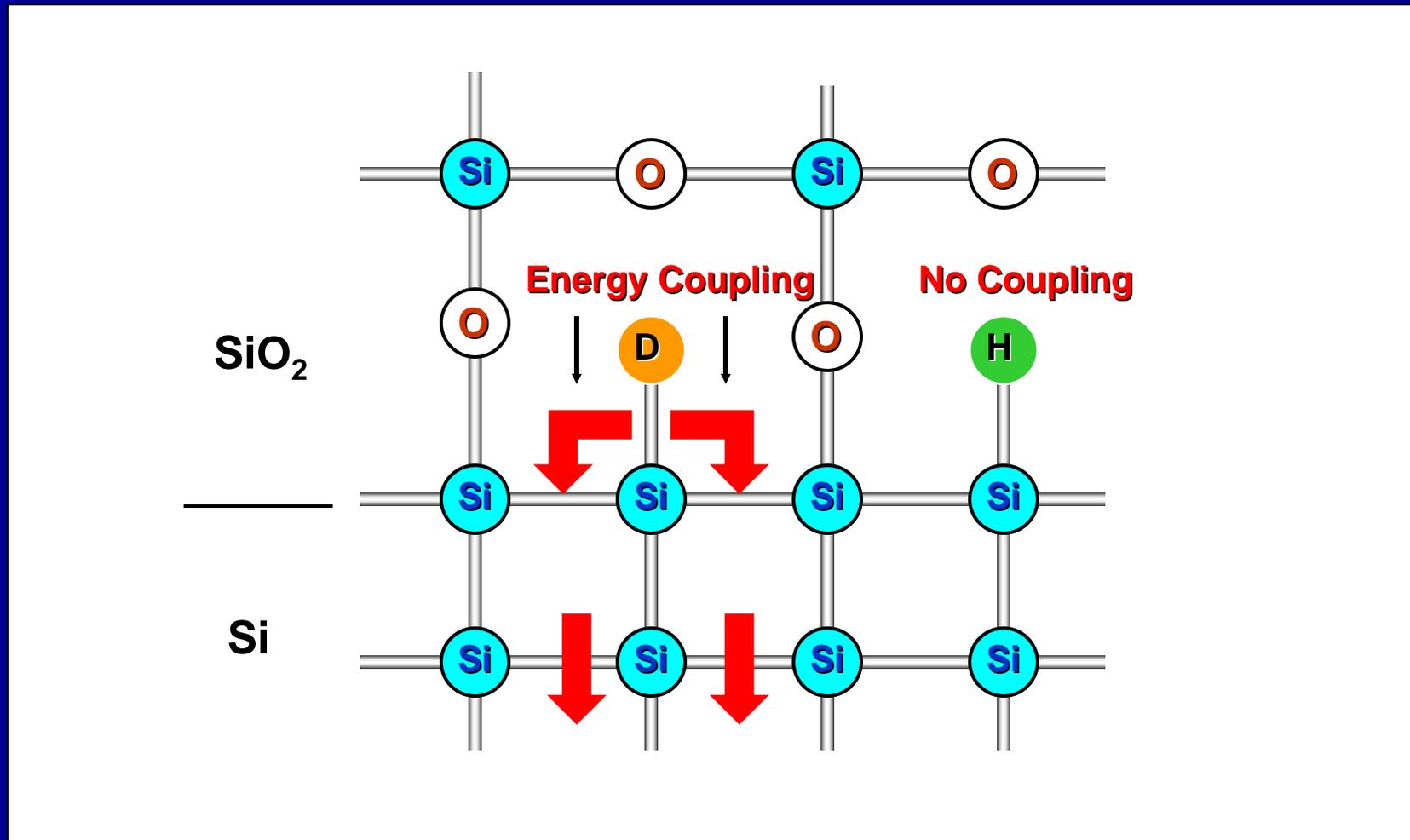
Si-D vibrational frequency $\approx 460 \text{ cm}^{-1}$ (Si-Si TO phonon mode)

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

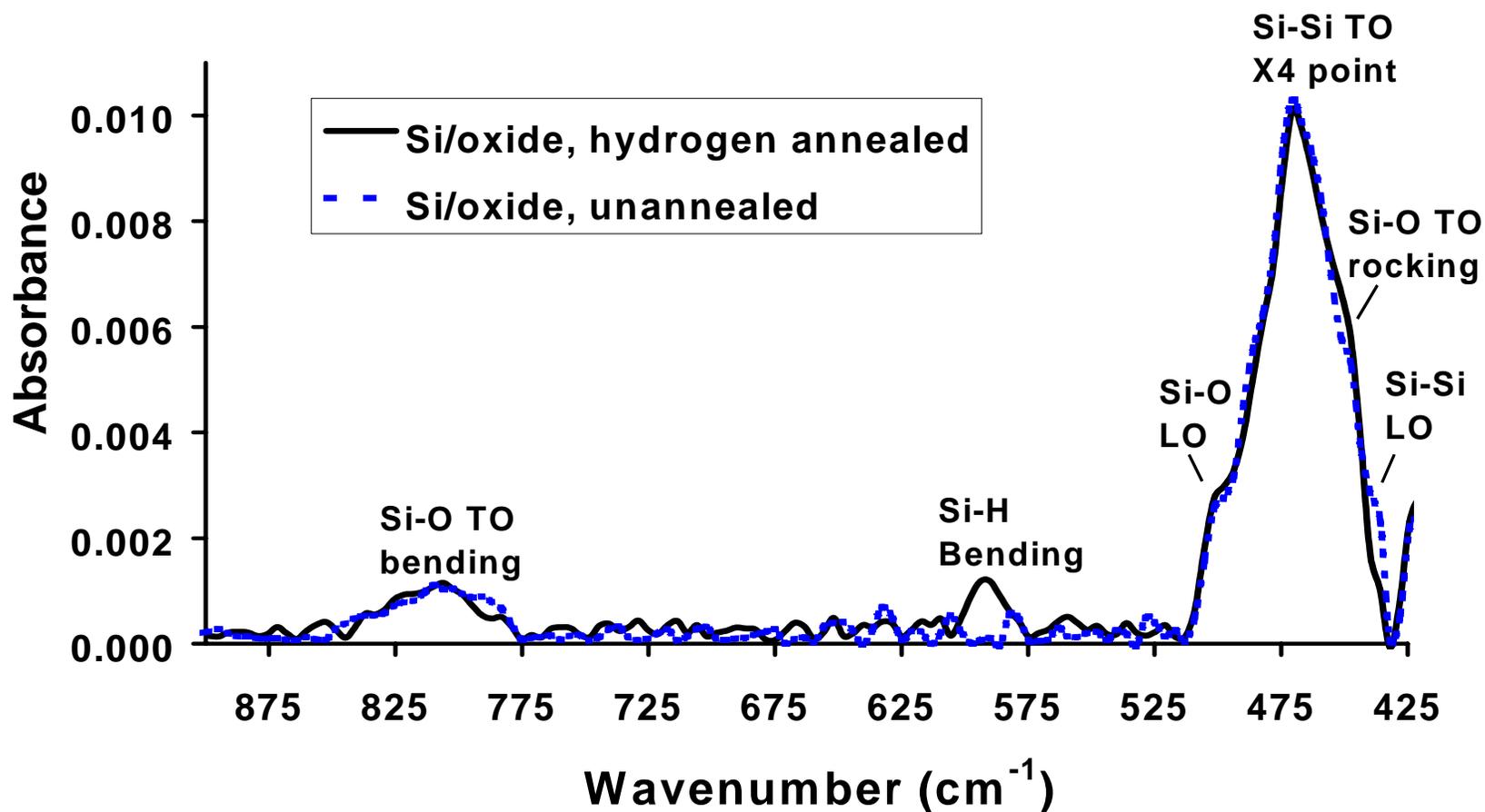
No experimental data available for Si-D vibrational frequency in the SiO₂/Si interface

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.

*J.-H. Wei, M.-S. Sun, and S.-C. Lee, Appl. Phys. Lett. 71, 1498 (1997).

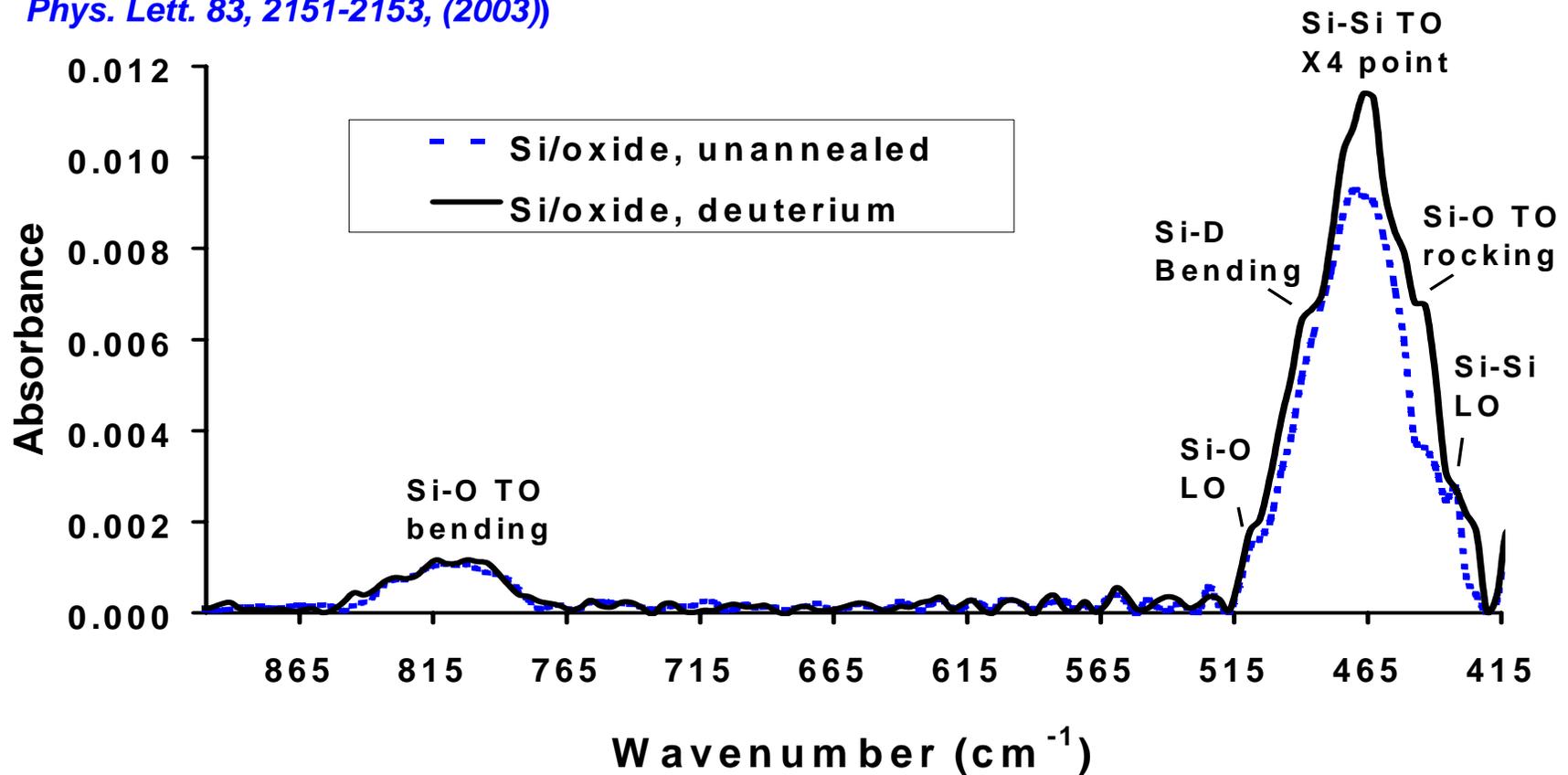
Origin of the Isotope Effect: No Energy Coupling from Si-H to Si-Si TO phonon

No difference between the H-annealed sample and the as-oxidized one, except for the Si-H bending vibration. (Chen et al. *Appl. Phys. Lett.* 83, 2151-2153, (2003))



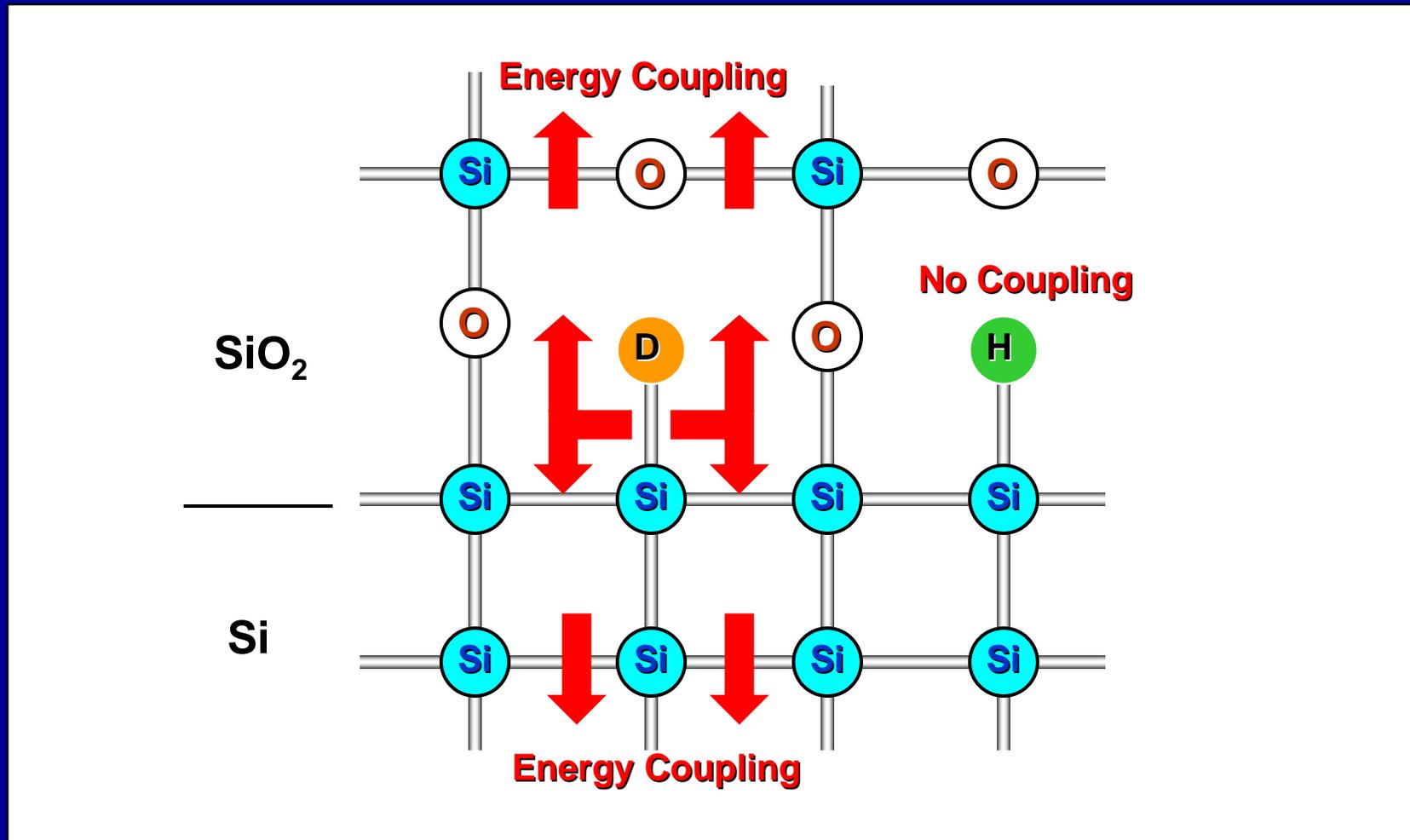
Origin of the Isotope Effect: Energy Coupling from Si-D to Si-Si TO phonon & Si-O TO rocking mode (Chen et al. Appl. Phys. Lett.)

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

(Chen et al. Appl. Phys. Lett. 83, 2151-2153, (2003))



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 ($\sim 6-8 \text{ cm}^{-1}$)

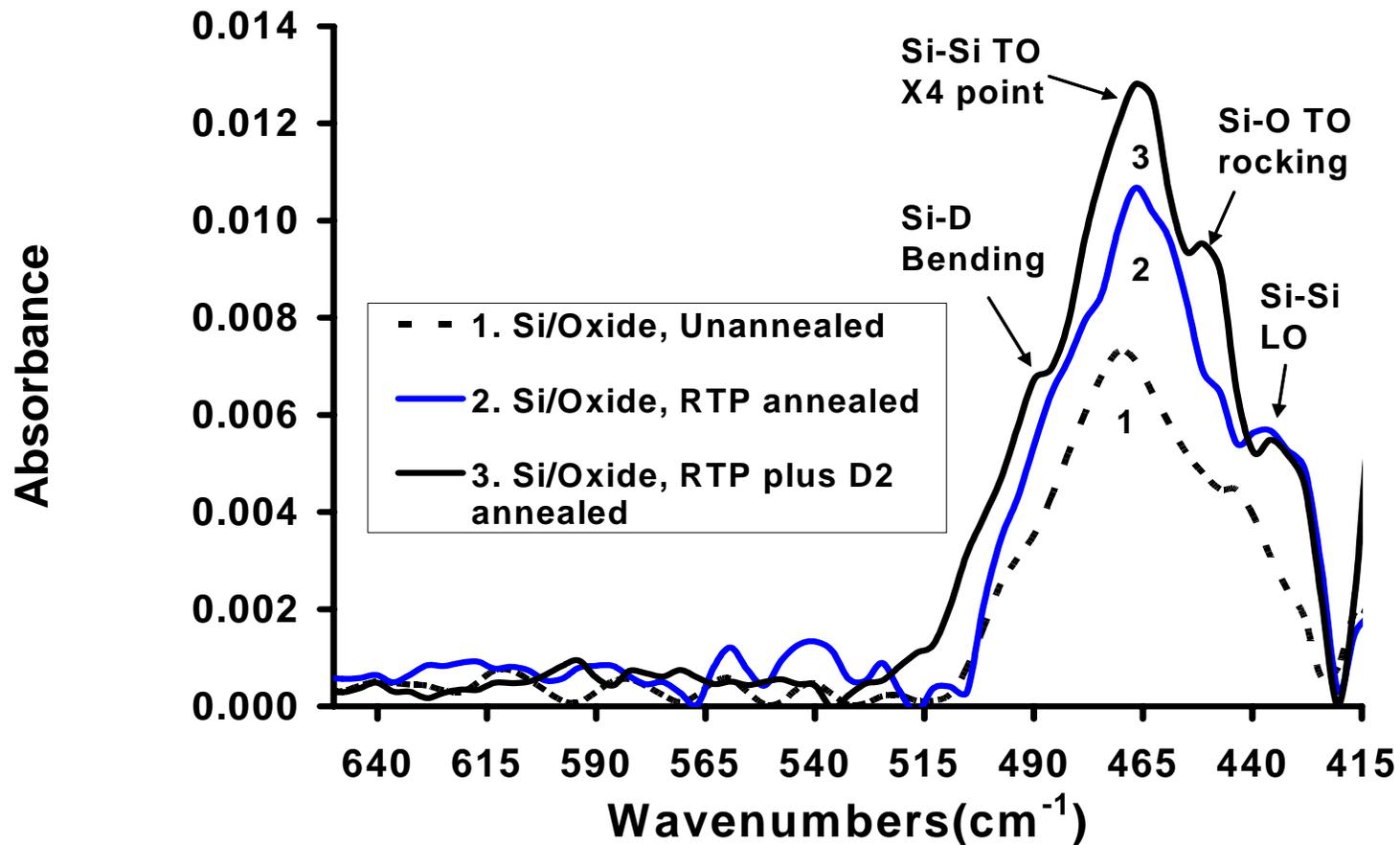
Method 2: Electrical stress

Method 3: Thermal stress

→ How?

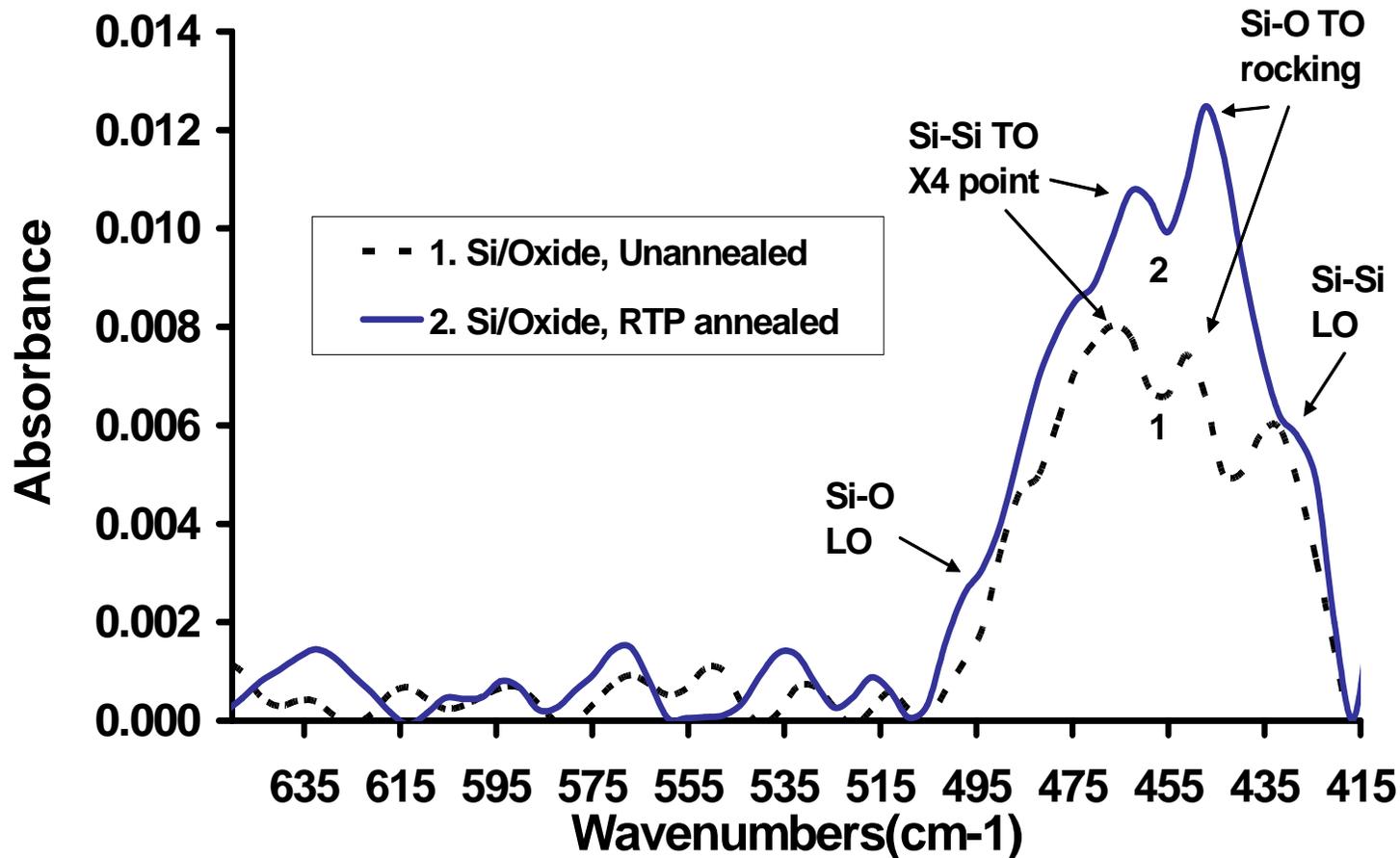
Surprising Discovery: Phonon Energy-Coupling Enhancement

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.



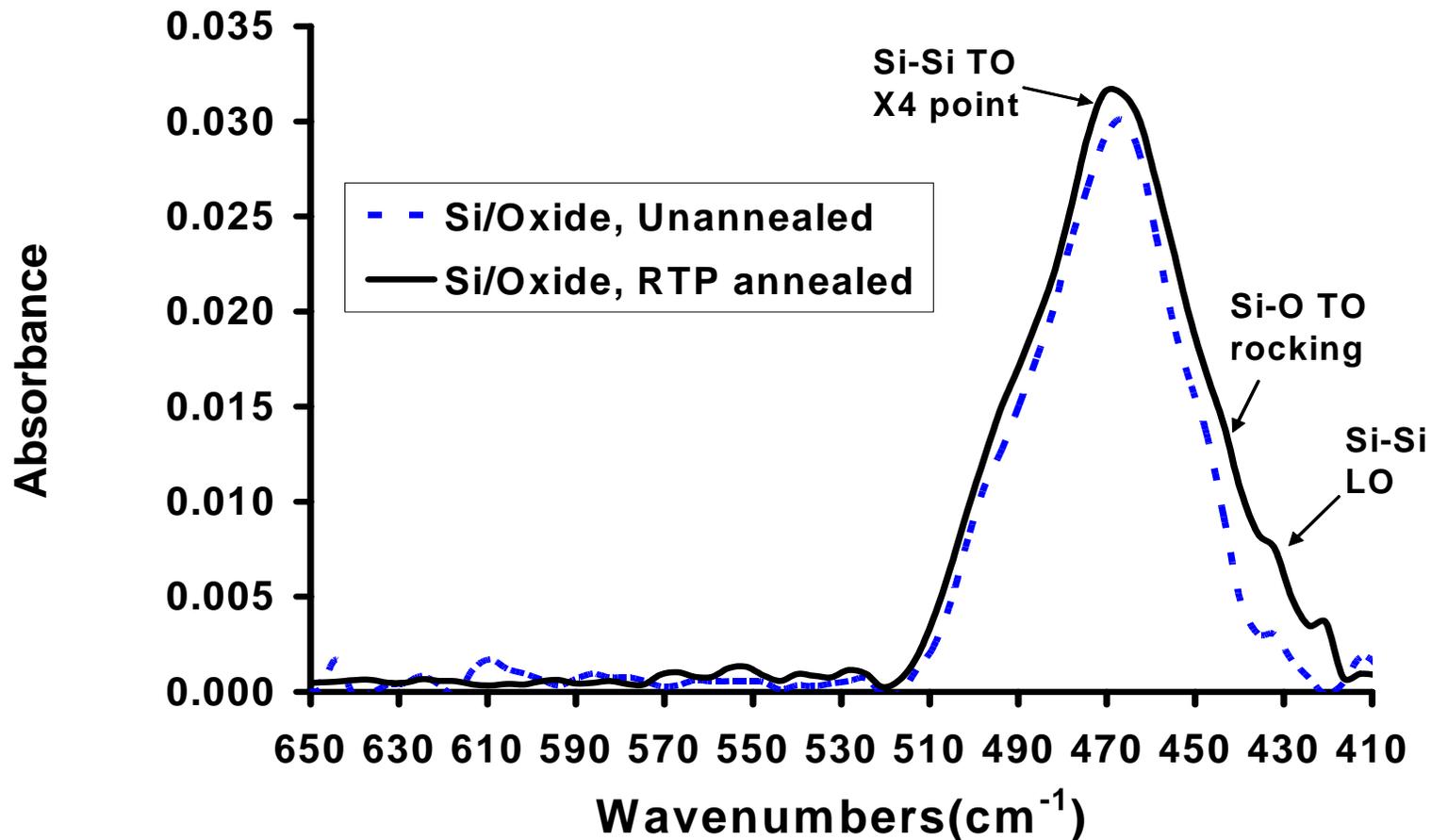
The Enhancement is not due to the Surface Plasmon.

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 ($n=2 \times 10^{14} \text{ cm}^{-3}$ and $\rho=20.8 \text{ } \Omega\text{-cm}$) for experiments.



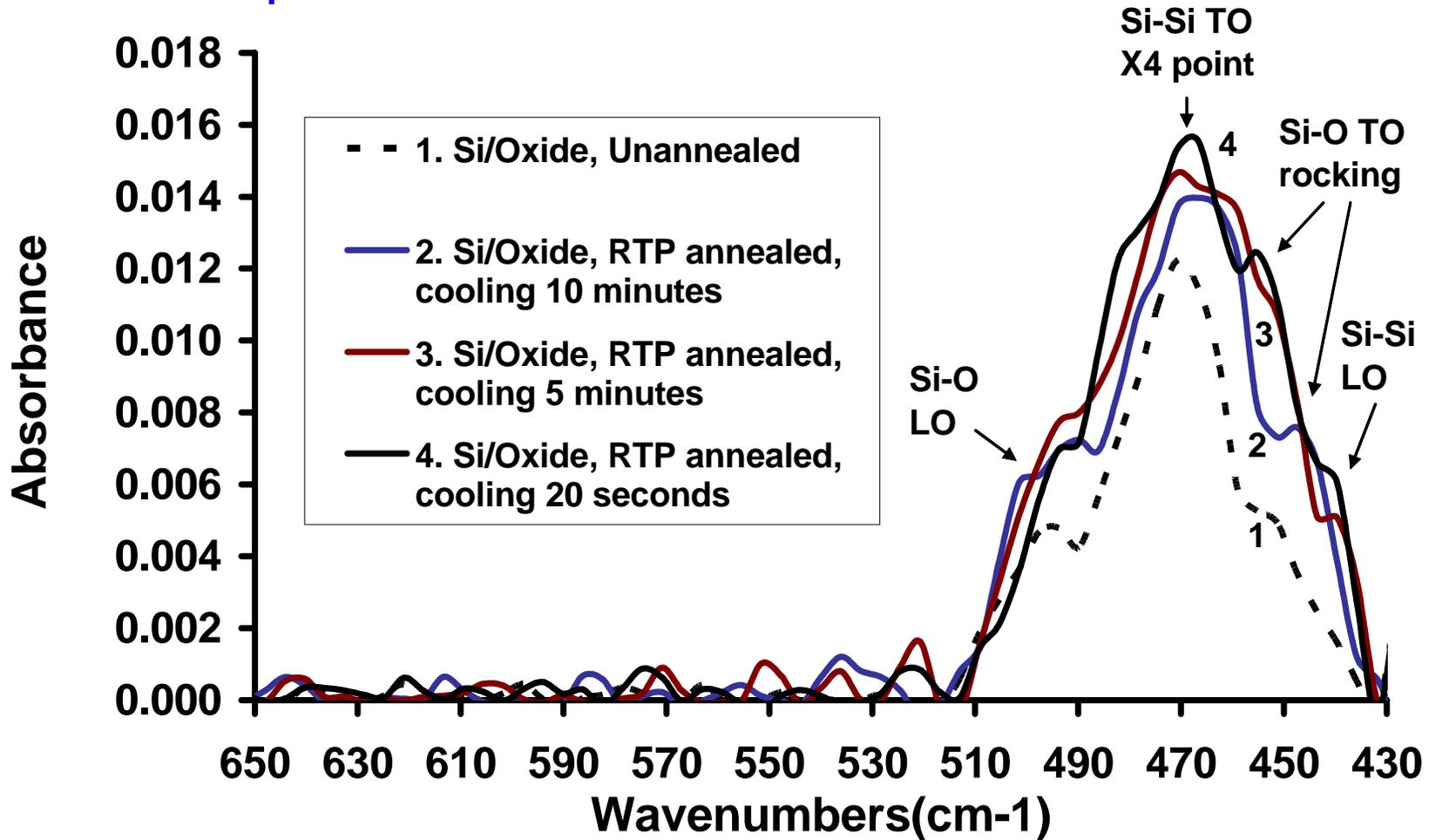
Dependence of Enhancement on the Oxide Thickness

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.



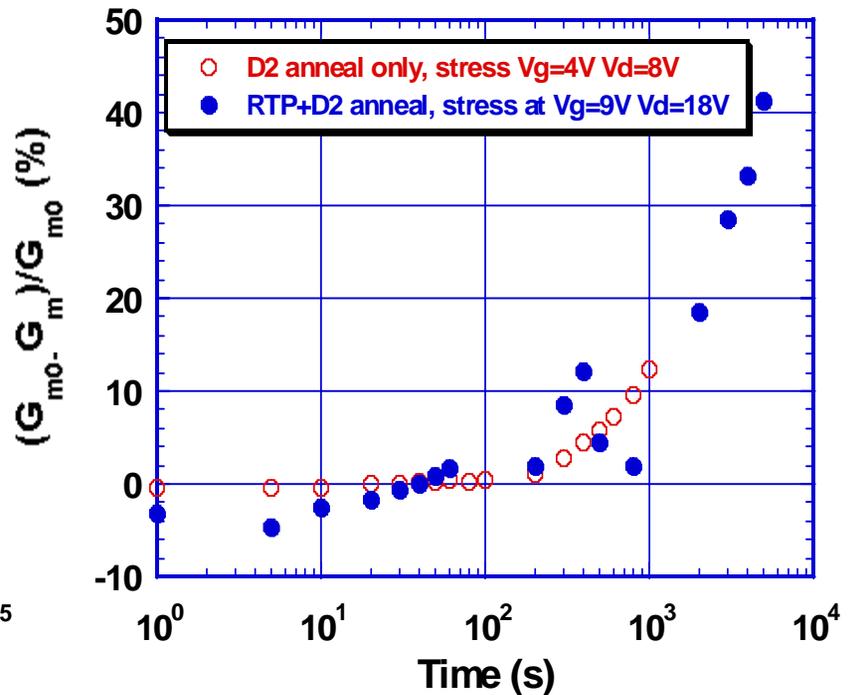
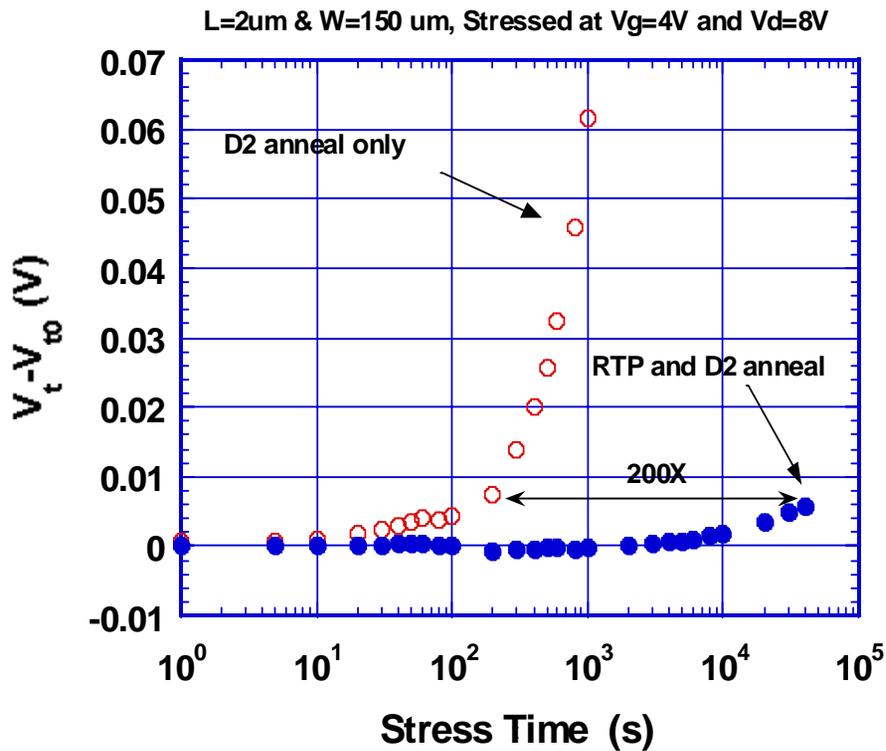
Dependence of Enhancement on the Cooling Time

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

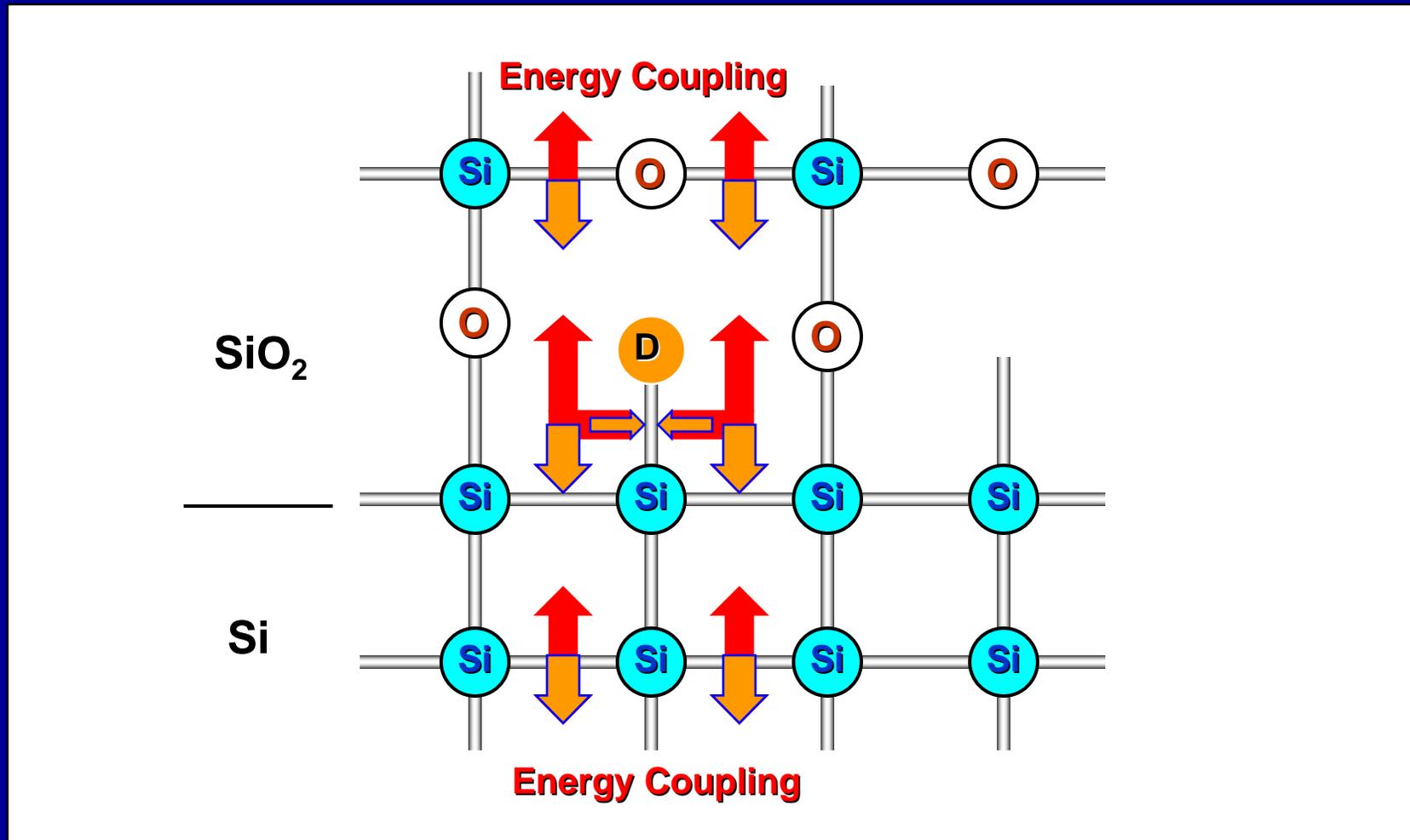


Phonon Energy-Coupling Enhancement: improvement of hot-electron degradation

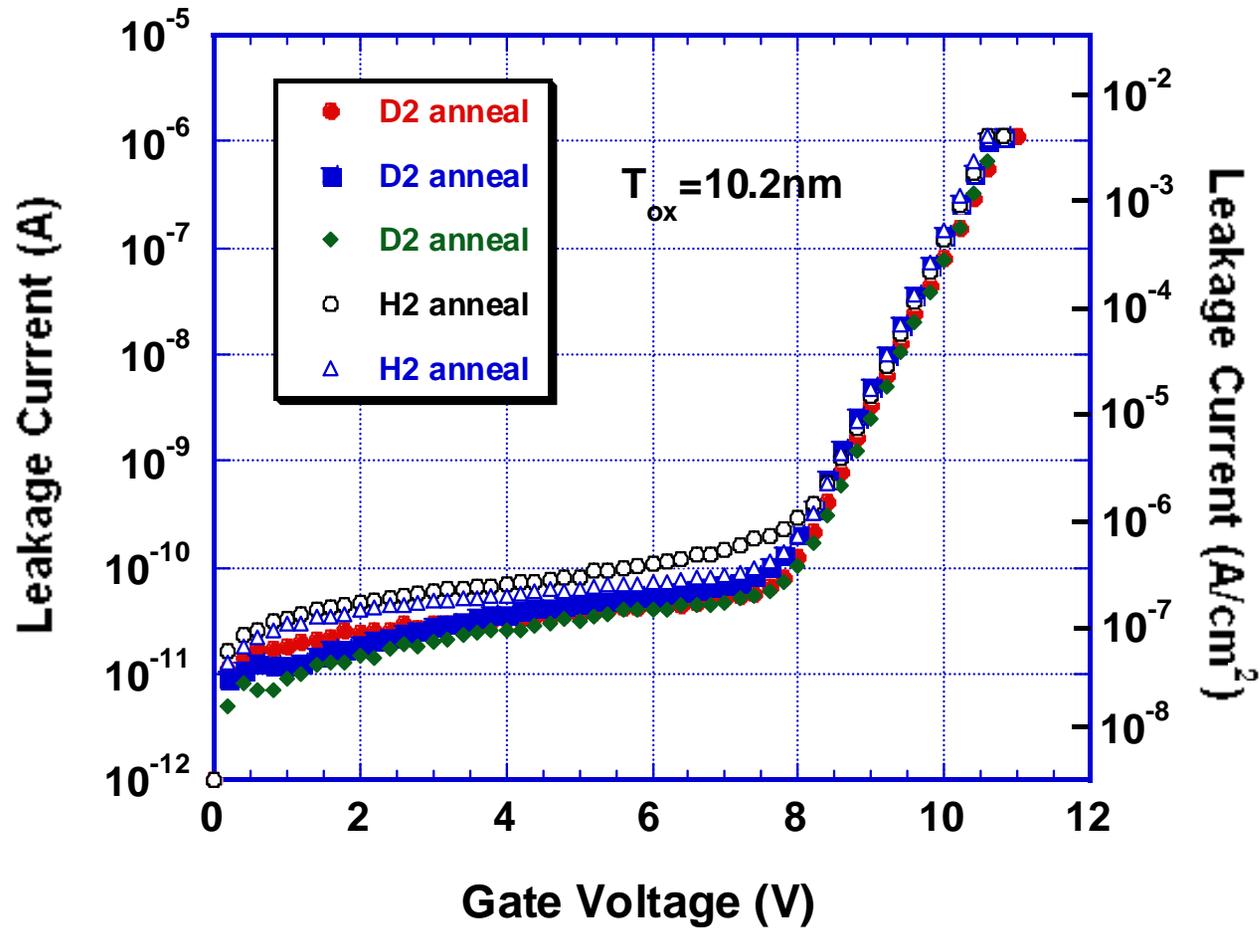
Z. Chen and J. Guo, presented at the 35th IEEE SISC, San Diego, CA, Dec. 9-11, 2004.



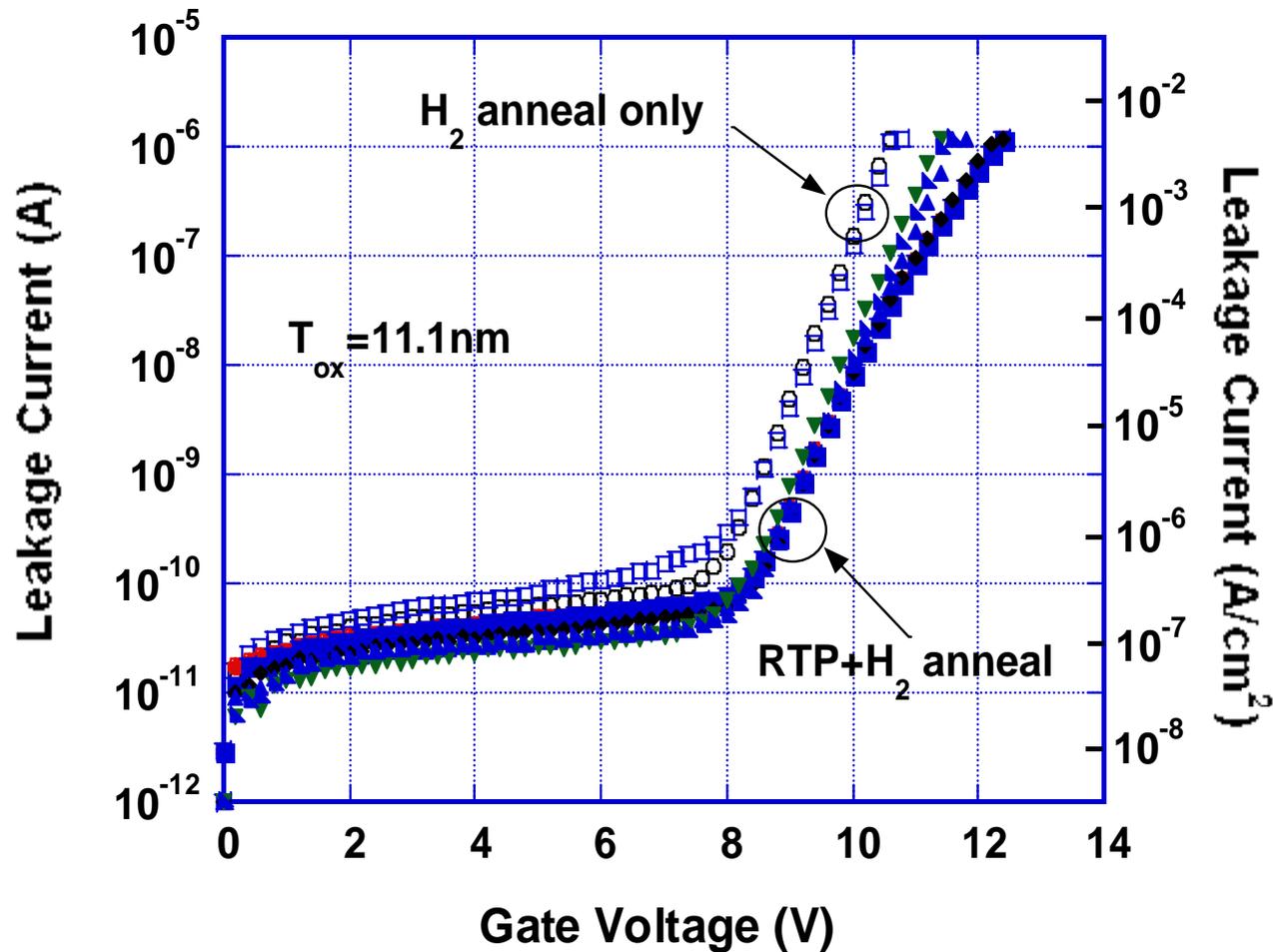
Hypothesis: Si-O bonds might be strengthened.
This is because energy is also coupled from Si-O rocking mode to Si-Si TO phonon mode and also to Si-D bending mode



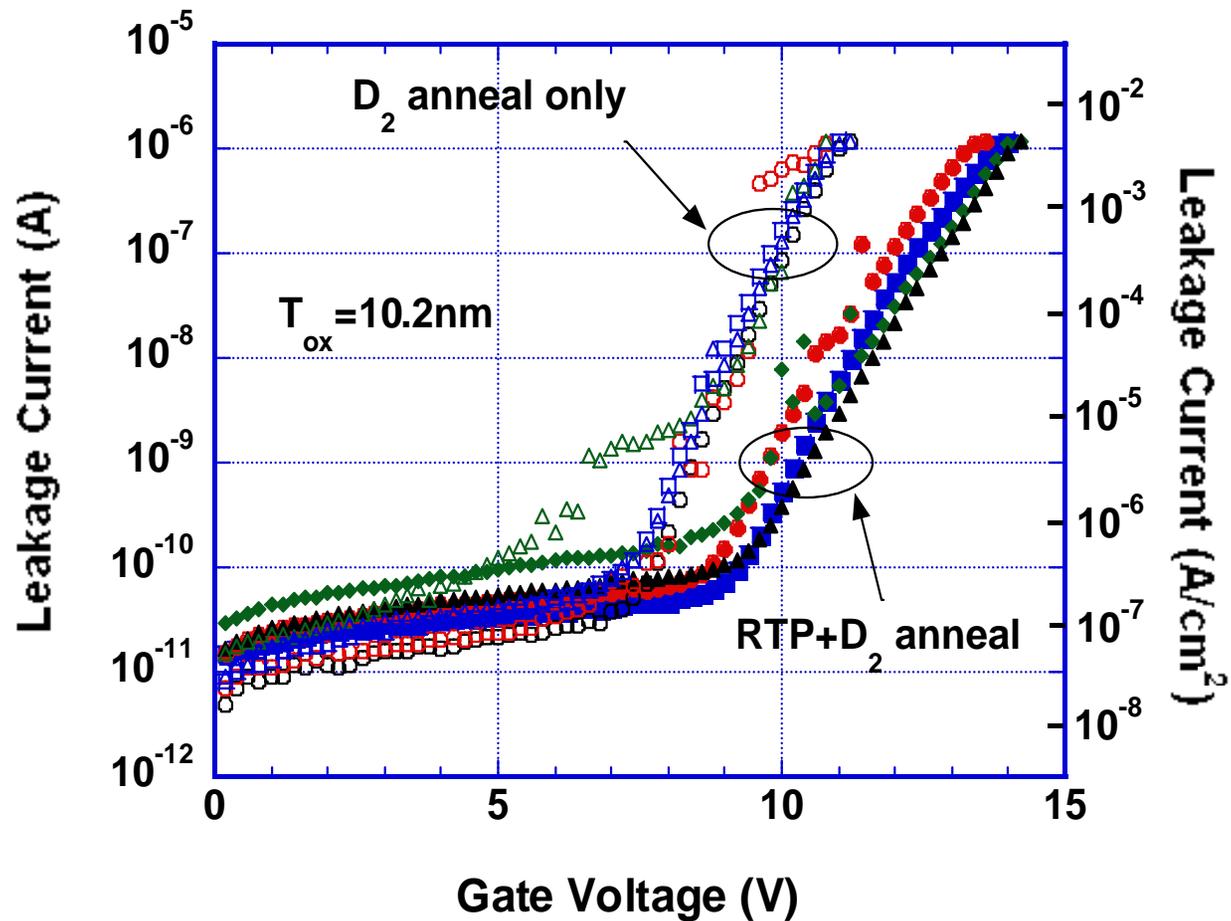
Hydrogen/Deuterium Effect on Gate Oxide: No Effect



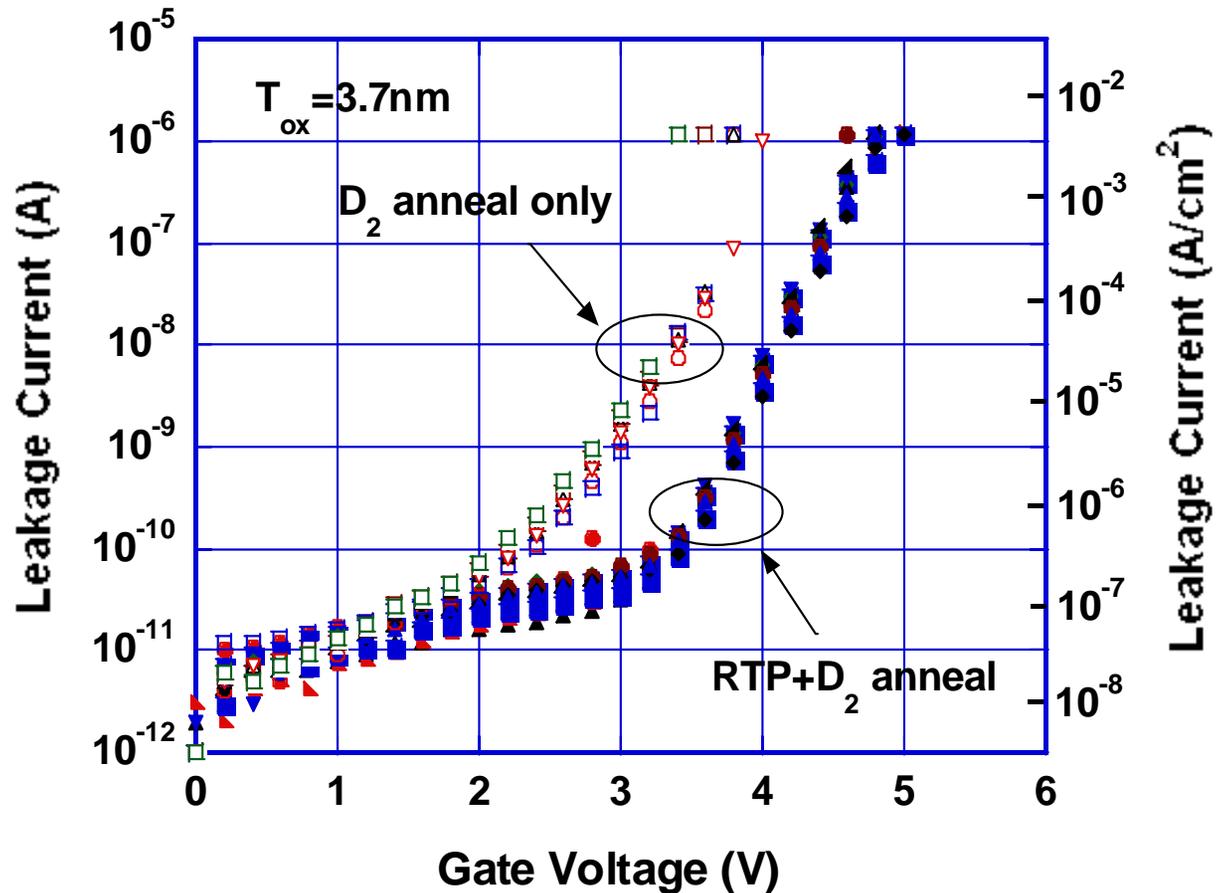
Direct Rapid Thermal Processing Only: Improvement of Breakdown Voltage (15%) and Reduction of Leakage Current (10X)



Direct Rapid Thermal Processing Plus D₂ Anneal: Improvement of Breakdown Voltage (30%) and Reduction of Leakage Current (100X)

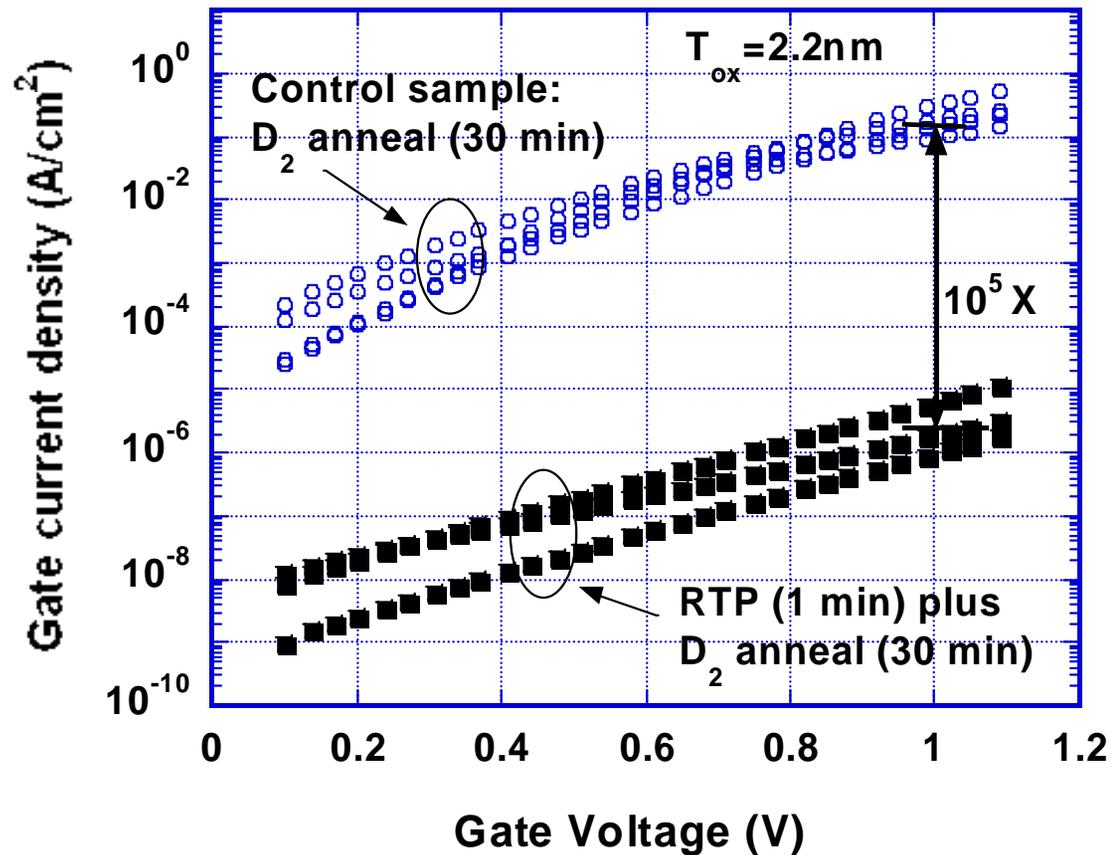


Direct Rapid Thermal Processing Plus D₂ Anneal: Improvement of Breakdown Voltage (30%) and Reduction of Leakage Current (100X)



Direct Rapid Thermal Processing Plus D₂ Anneal of Thin Oxides: Reduction of leakage current (10⁵X)

This is similar to that of HfSiON (*Gusev et al., IEDM Technical Digest, 451-454 (2001)*)



Capacitance-Voltage Curves and oxide thickness of oxide measured before and after RTP

There is only a slight flat-band voltage shift and thickness remains unchanged after RTP.

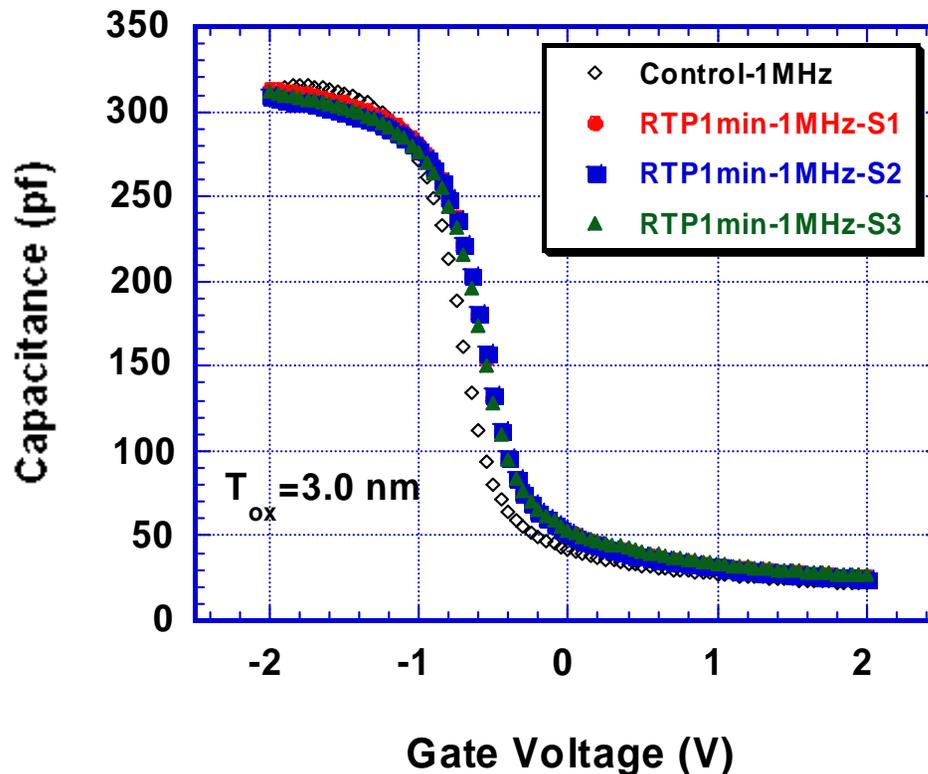


Table: Comparison of oxide thickness measured using ellipsometry before and after RTP

Sample No.	Oxidation Parameters	T_{ox} before RTP	T_{ox} after RTP
#1110051	N ₂ @1000sccm, O ₂ @20 sccm, 900°C for 20 s	22.4 Å	23.3 Å
#0628052	N ₂ @1000sccm, O ₂ @20 sccm, 900°C for 10 s	19.8 Å	20.9 Å
#1110052	N ₂ @2000sccm, O ₂ @20 sccm, 900°C for 20 s	19.5 Å	20.09 Å

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

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