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CALTECH-INTEL

Motivation

- **Problem:** At SiO2 thickness of ~15–20 Å leakage current, by direct tunneling through SiO2 device gate reaches unacceptable levels.
- **Solution:** Replace SiO2 with CVD or ALD of materials with higher dielectric constant, thereby allowing thicker films. E.g. TiO2, Ta2O5, SrTiO3, ZrO2, and Zn–Sn–Ti–O.

High-dielectric constant metal–oxide thin films have potential for replacing SiO_2 in MOSFETs and memory devices (gate oxide layers)

CVD/ALE/ADL TiO2 growth precursors

- Titanium chloride $TiCl_4$ (0.59A/cycle) and water [1]. $TiCl_4$ has smaller molecular size.
- Titanium isoproxide $Ti(OCH(CH_3)_2)_4)$ (0.30A/cycle) plus water (or hydrogen peroxide H_2O_2) [2].
- Titanium ethoxide $Ti(OCH_2CH_3)_4$. Reduced steric hindrance ethoxide groups are more effective as bridging ligands between metal cations than isoproxide groups.
- Titanium isopropoxide on Si [3].
- Tetrakis(diethylamino) titanium [4] (0.1nm/cycle) on Si.

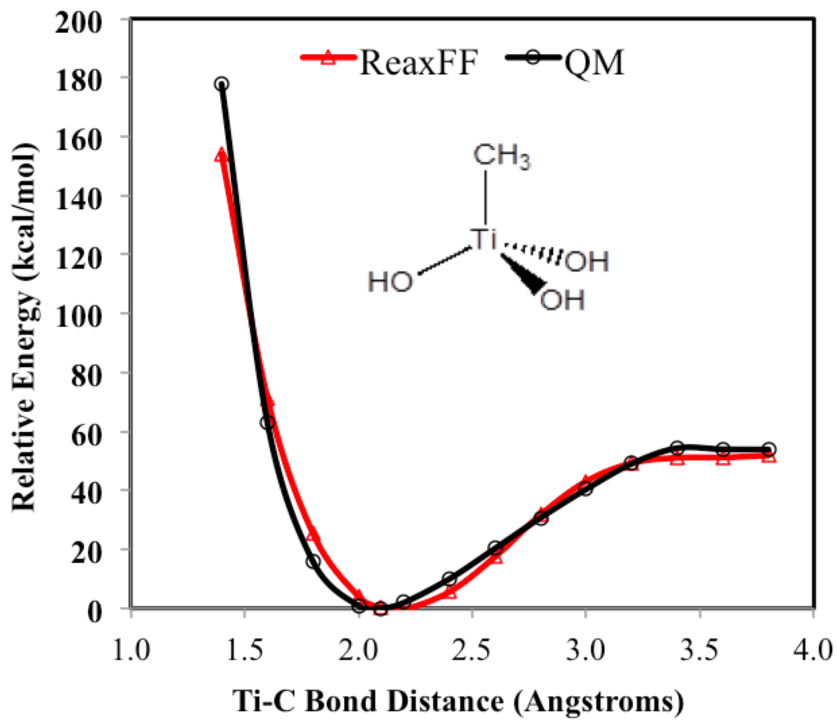
[1] Aarik et al, Applied Surface Science 172 (2001) 148-158
[2] Aarik et al, Applied Surface Science 161 (2000) 385–395
[3] Sandel et al J. Appl. Phys., Vol. 92 (2002), No. 6.
[4] Tao et al, Thin Solid Films 520 (2012) 6752–6756

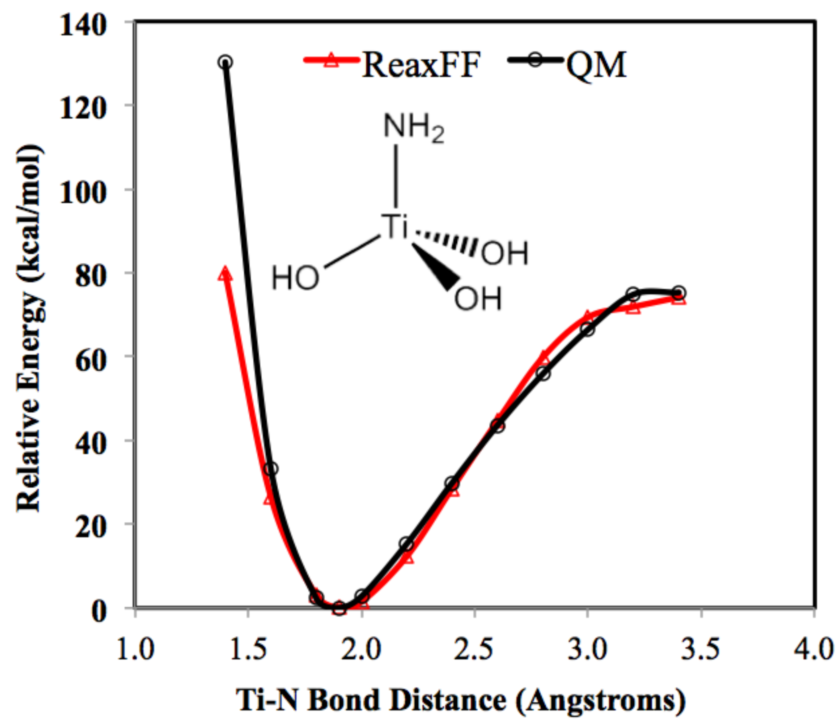
ReaxFF for Ti/O/C/H interactions training set

- Bulk phases: rutile, anatase, brookite, columbite, baddeleyite, fluorite, pyrite, and cotunnite structures,
- Cold compression EOS,
- Anatase and rutile water adsorption energy on slab,
- TiO_2 relative energies between phases,
- Anatase and rutile surface energies,
- Anatase water dissociation energies,
- General oxide heats of formation,
- Finite selected cluster isomers,
- Relative cluster stabilities with respect to most stable form,
- Water addition and rearrangement energies,
- Hydrated cluster growth,
- Rutile water dissociating energies,
- Rutile and anatase cell parameters and charge distribution.
- Titanium-carbon bond curves and cold compression EOS
- Carbon-titanium-oxygen angle energies.

Jaramillo-Botero et al, accepted PRL October 2012

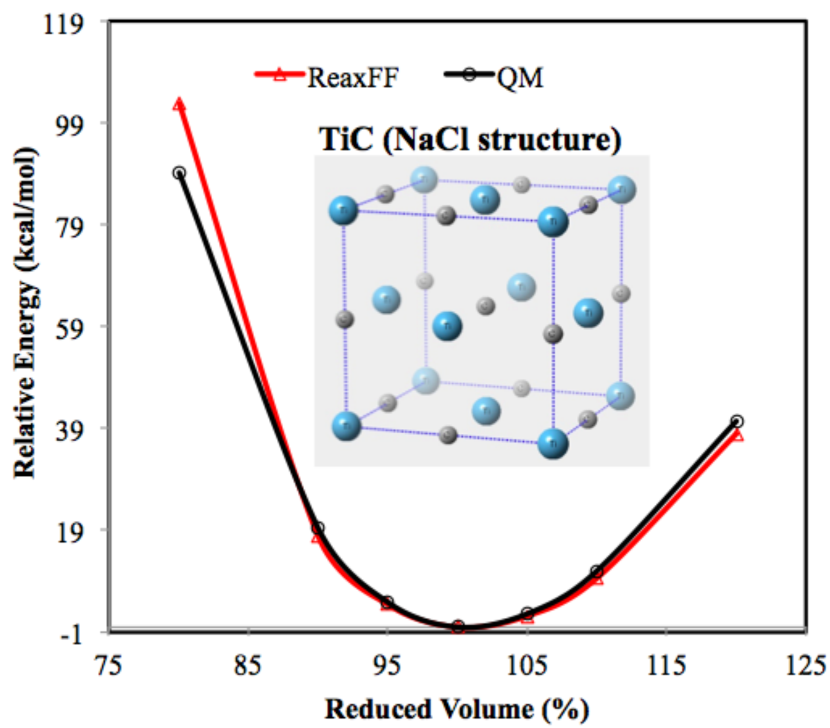
ReaxFF for TiO2 growth
T-C bond

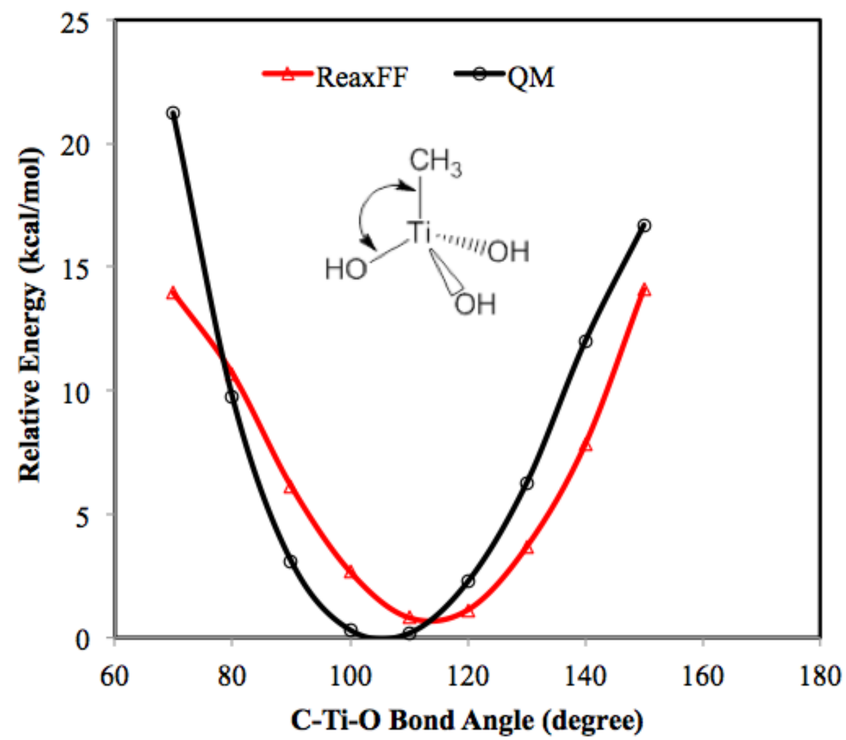




ReaxFF for TiO2 growth

T-C (NaCl EOS) and C-Ti-O Angle





Outline of proposed study

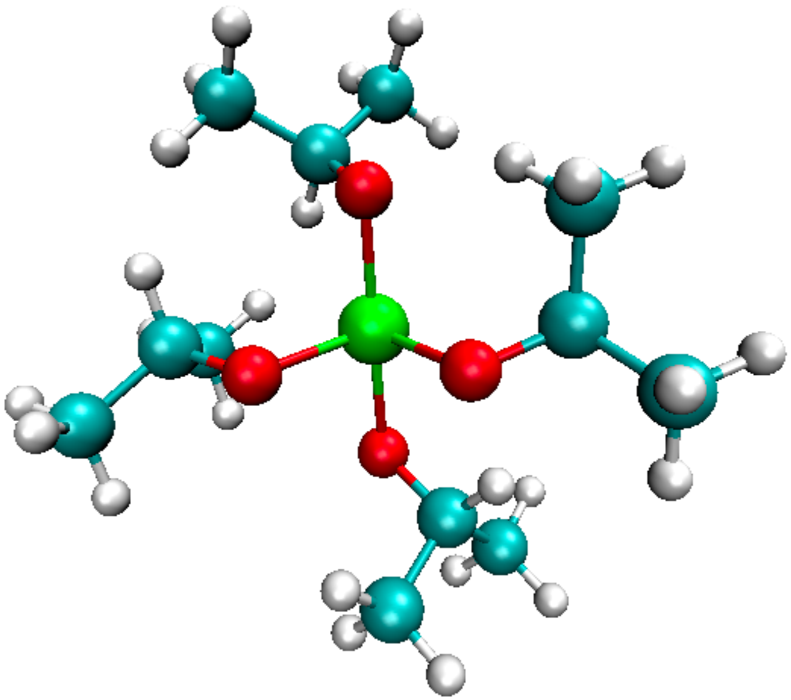
1. Isopropoxide reactions with water
   - Need to revise T-O on surface
2. TiO2 growth on pure Ti or TiO2 rutile
3. TiO2 growth rate on Si (100) surface or SiO2
   - Need to revise Ti-Si ffield interactions
4. SiO2 or Si (100) to TiO2 interfacial properties

Titanium isopropoxide + water reactions

- $Ti\{OCH(CH_3)_2\}_4 + 2\ H_2O \rightarrow TiO_2 + 4\ (CH_3)_2CHOH$

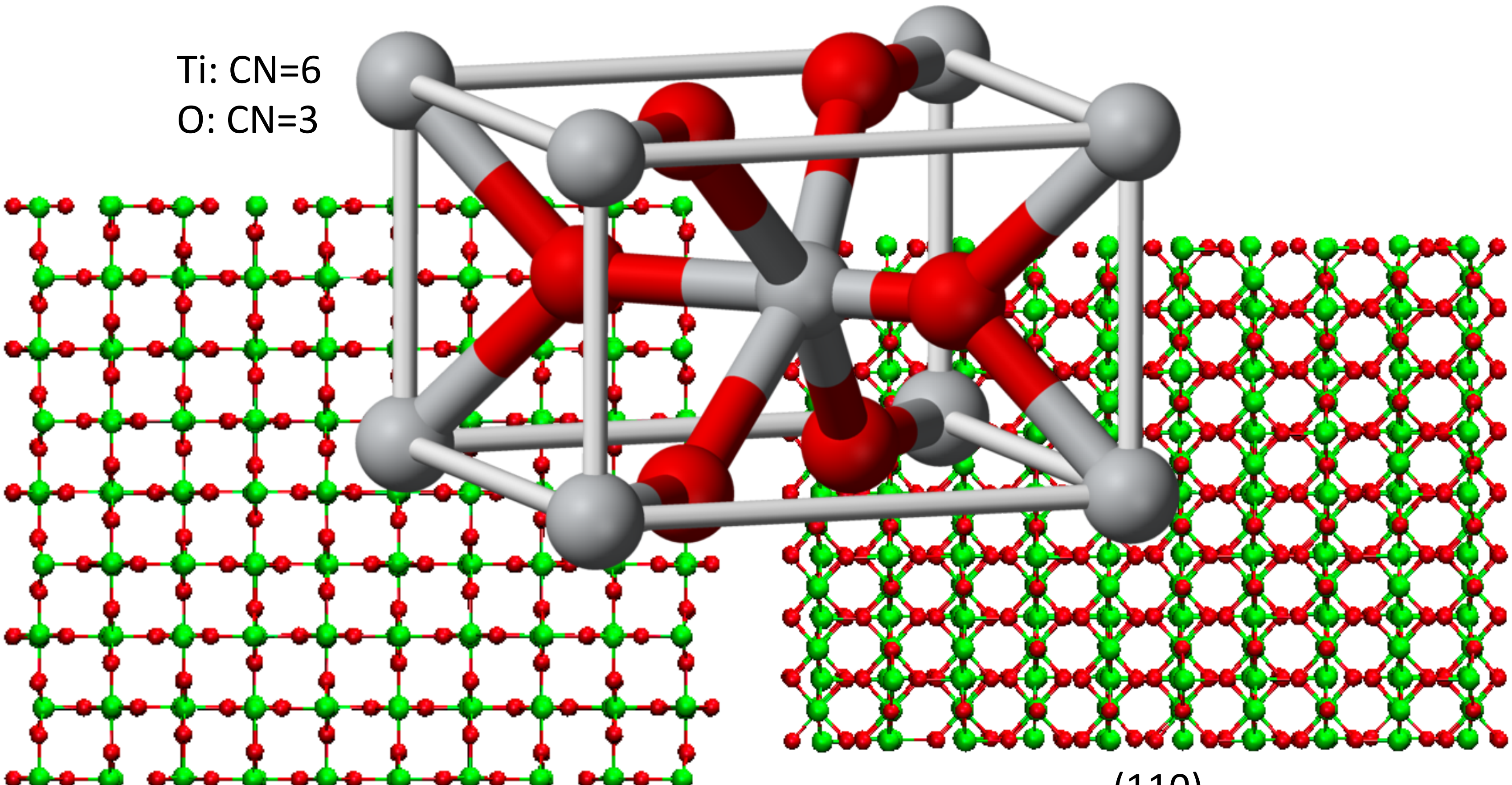
NVT @315.15K (42C) and 20Pa Pressure

Applied Surface Science 161 (2000). 385–395



Rutile

Ti: CN=6
O: CN=3



(110)

[1] Rutile primitive tetragonal unit cell, with unit cell parameters a=4.587Å, and c=2.953Å.

ReaxFF lattice parameters: a=4.62A, and c=2.84A

[1] Surface Science Reports, 48, pp 53-229 (2003)

Metal oxidation

See Slides from Patrick Theofanis (10-12-2012)

- How Ti bulk oxidates on amorphous SiO_2
- Goal: Pure metal oxidation (rates) in ambient conditions. Not growth process, but how fast do metals oxidise (Ti, Zr). Use ozone as O precursor (1eV binding).
- Confirmed B3PW91 and B3LYP do not get correct TiO_2 relative phase energies