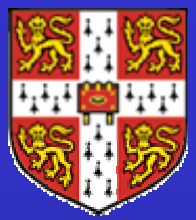
Materials for nuclear waste immobilization:

The effect of point defects in zircon

Miguel Pruneda

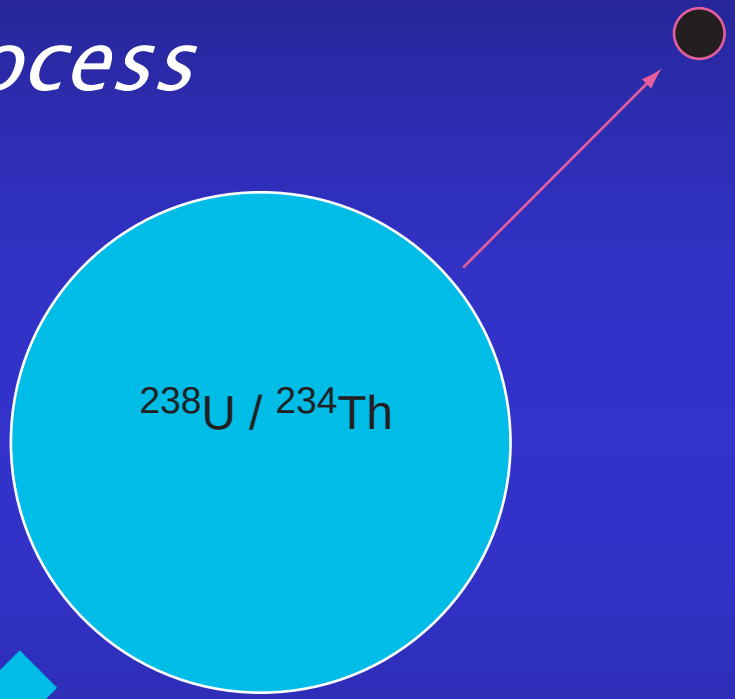


Department of Earth Sciences
University of Cambridge

Cambridge Centre for Ceramic Immobilisation

Radiation damage

α-decay process



α-particle

~ 5 MeV

Recoil

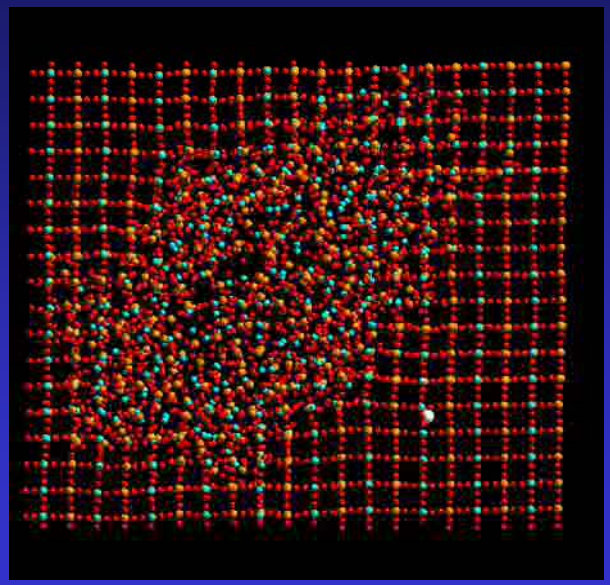
~ 100 keV

It causes:

- Amorphisation (metamict)
- Swelling
- Cracks
- Leaching

Zircon: model study: old natural samples

Why first principles?



- Atomistic description

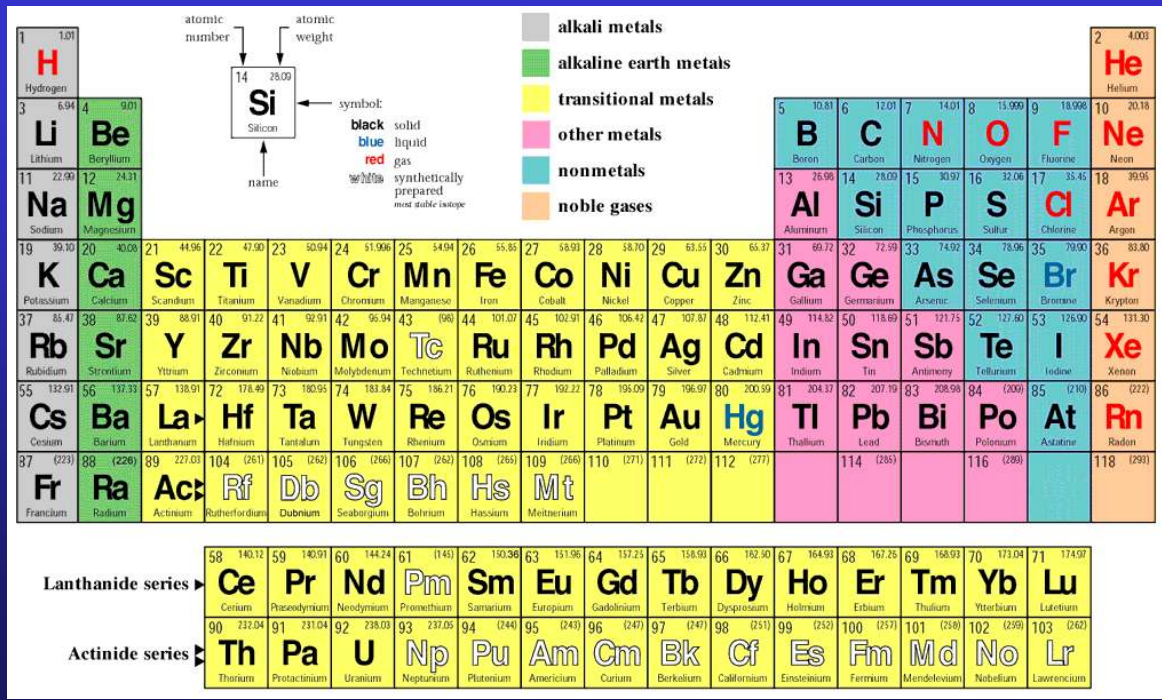
MD simulations

- Complex structures

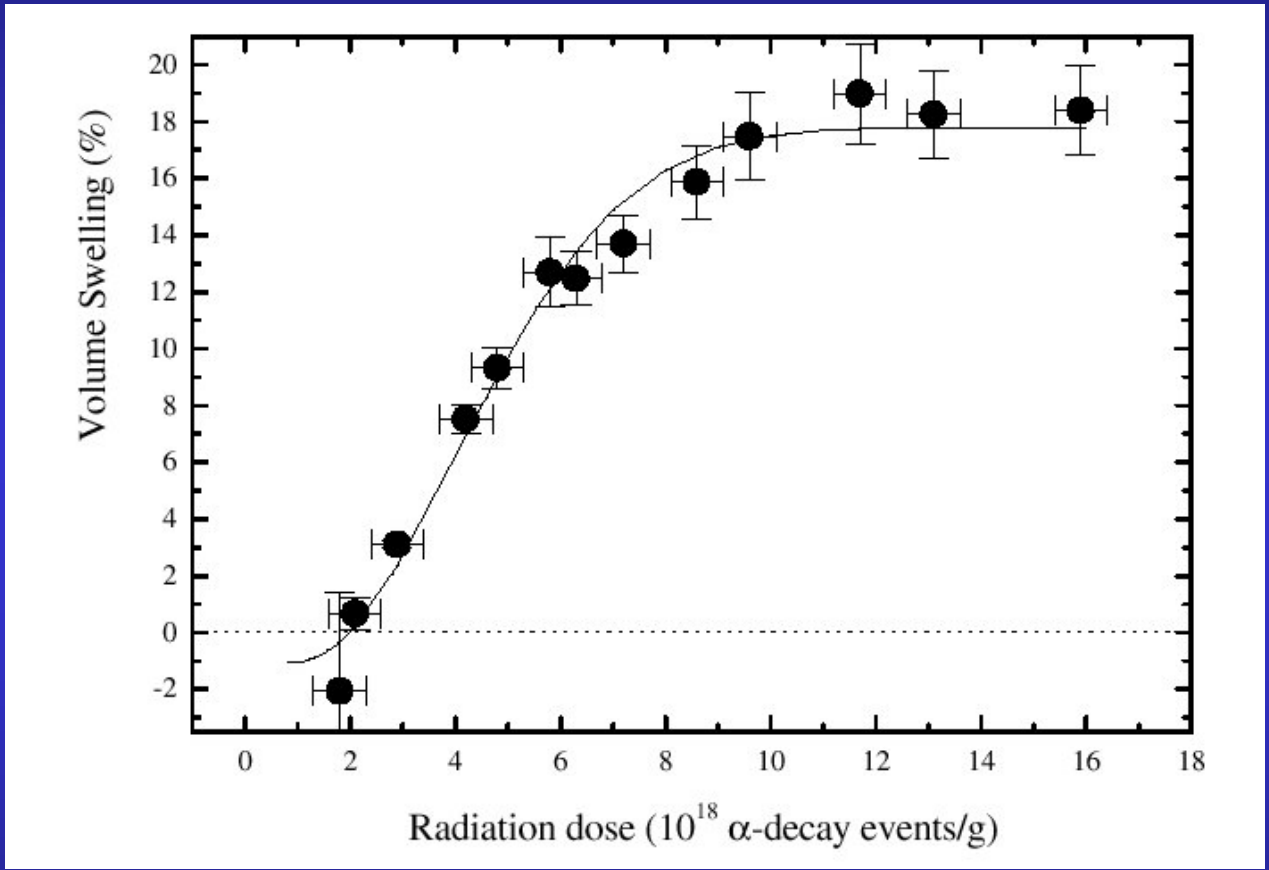
Empirical potentials

- Complex chemistry

Zr, Ti, Sn, Ca, La, Gd,…

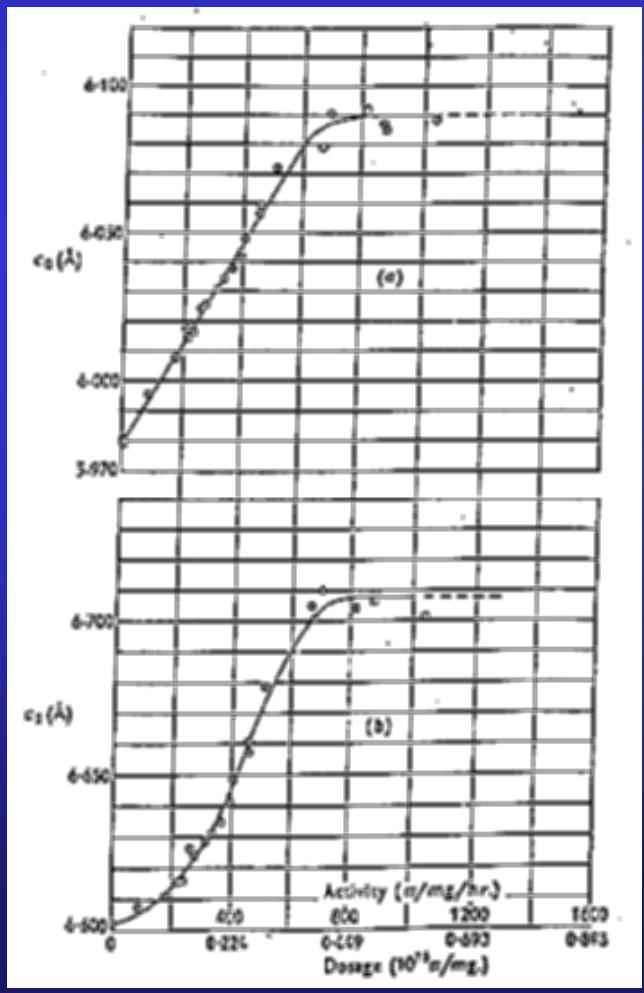


Swelling in zircon ($ZrSiO_4$)



X-Rays…

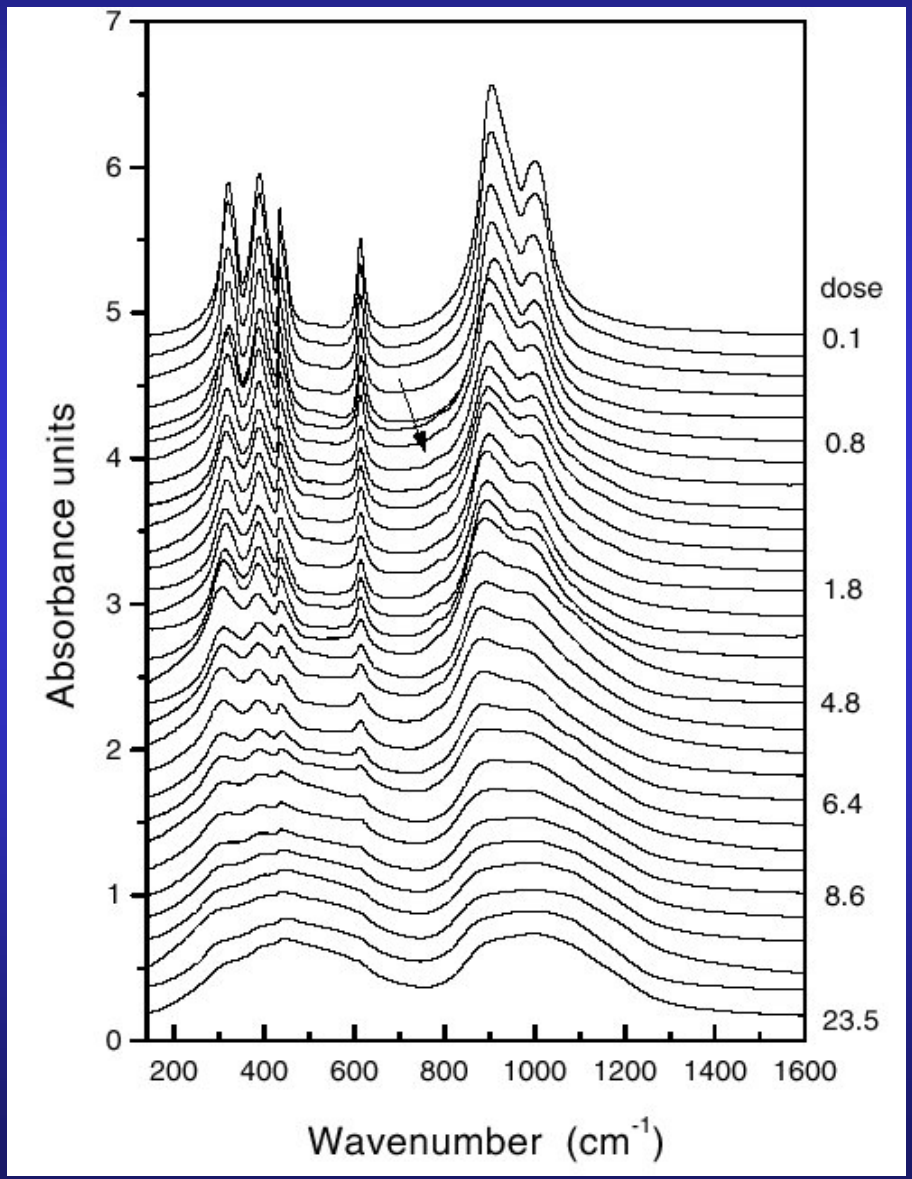
Crystalline swelling: lattice parameters vs dose



Total: ~20%

Crystalline: ~5% anisotropic

IR, Raman and NMR spectroscopies



IR

NMR

I. Farnan & E.K.H Salje, JAP **89**, 2084 (2001)

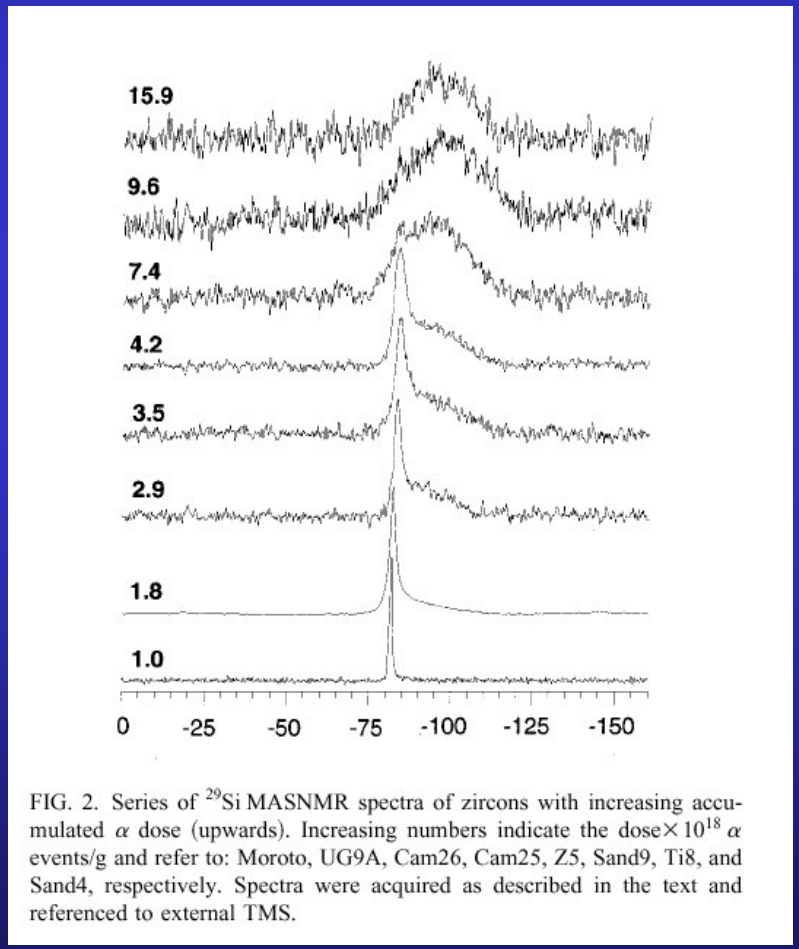


FIG. 2. Series of ^{29}Si MASNMR spectra of zircons with increasing accumulated α dose (upwards). Increasing numbers indicate the dose$\times 10^{18}$ α events/g and refer to: Moroto, UG9A, Cam26, Cam25, Z5, Sand9, Ti8, and Sand4, respectively. Spectra were acquired as described in the text and referenced to external TMS.

M. Zhang & E. K. H Salje, J. Phys. Condens. Matter **13**, 3057 (2001)

Localized defects in radiation-damaged zircon (Rios et. al. *Acta Cryst.* (2000) B**56**, 947)

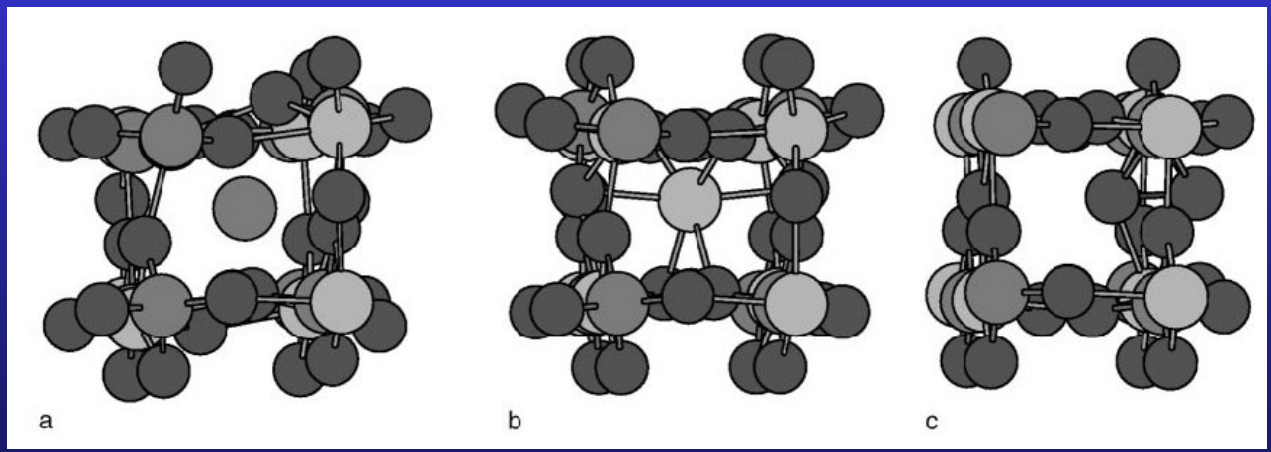
X-ray diffraction experiments in natural samples. (1.8×10^{18} α-decay/g)

- SiO_4 tetrahedra remain essentially undistorted
- Larger anisotropic displacement parameters found for Zr and O atoms

DFT calculations:

Formation energies for a choice of chemical potentials

High values of the formation energies for all defects, except oxygen interstitial



J.-P. Crocombette, *Phys. Chem. Minerals* **27**, 138 (1999)

Our method

Linear-scaling DFT based on NAOs (Numerical Atomic Orbitals)

P. Ordejon, E. Artacho & J. M. Soler , Phys. Rev. B 53, R10441 (1996)

- *Born-Oppenheimer (relaxations, mol. dynamics)*
- *DFT (LDA, GGA)*
- *Pseudopotentials (norm conserving, factorised)*
- *Numerical atomic orbitals as basis (finite range)*
- *Numerical evaluation of matrix elements (3D grid)*

Implemented in the SIESTA program

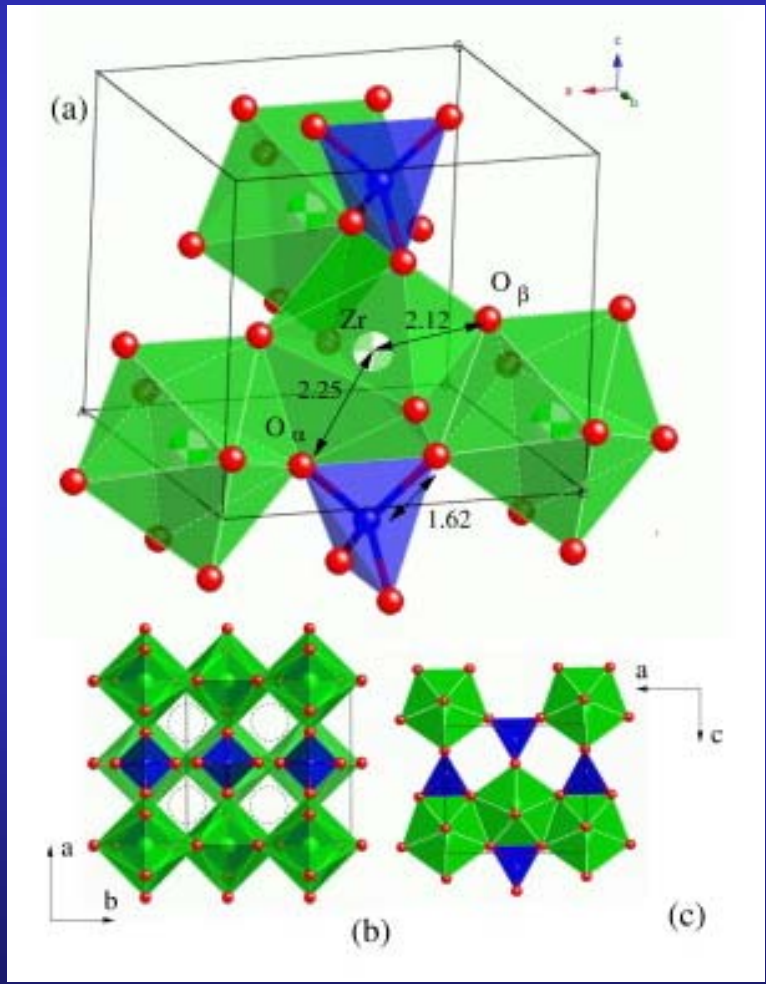
D. Sanchez-Portal, P. Ordejon, E. Artacho & J. M. Soler
Int. J. Quantum Chem. 65, 453 (1997)

Intrinsic point defects and volume swelling in $ZrSiO_4$

- Radiation cascades & defect accumulation

$\sim 10^{21}$ defects/cm^3

Si …0.2% swelling!!



- Tetragonal $I4_1/amd$ space group
- BCC unit cell with four formula units.
- Structural parameters: *a*, *c*, *u*, *v*

Alternating SiO_4 tetrahedra & ZrO_8 dodecadeltahedra

Playing with the "concentration of defects"

Supercell approach:

$n_x \times n_y \times n_z$ Repetitions of the unit cell

(Periodic super-structure of defects)

1x1x1 (24 atoms)
1x1x2 (48 atoms)
2x2x1 (96 atoms)
2x2x2 (192 atoms)

} Lattice relaxation

Low-concentration limit

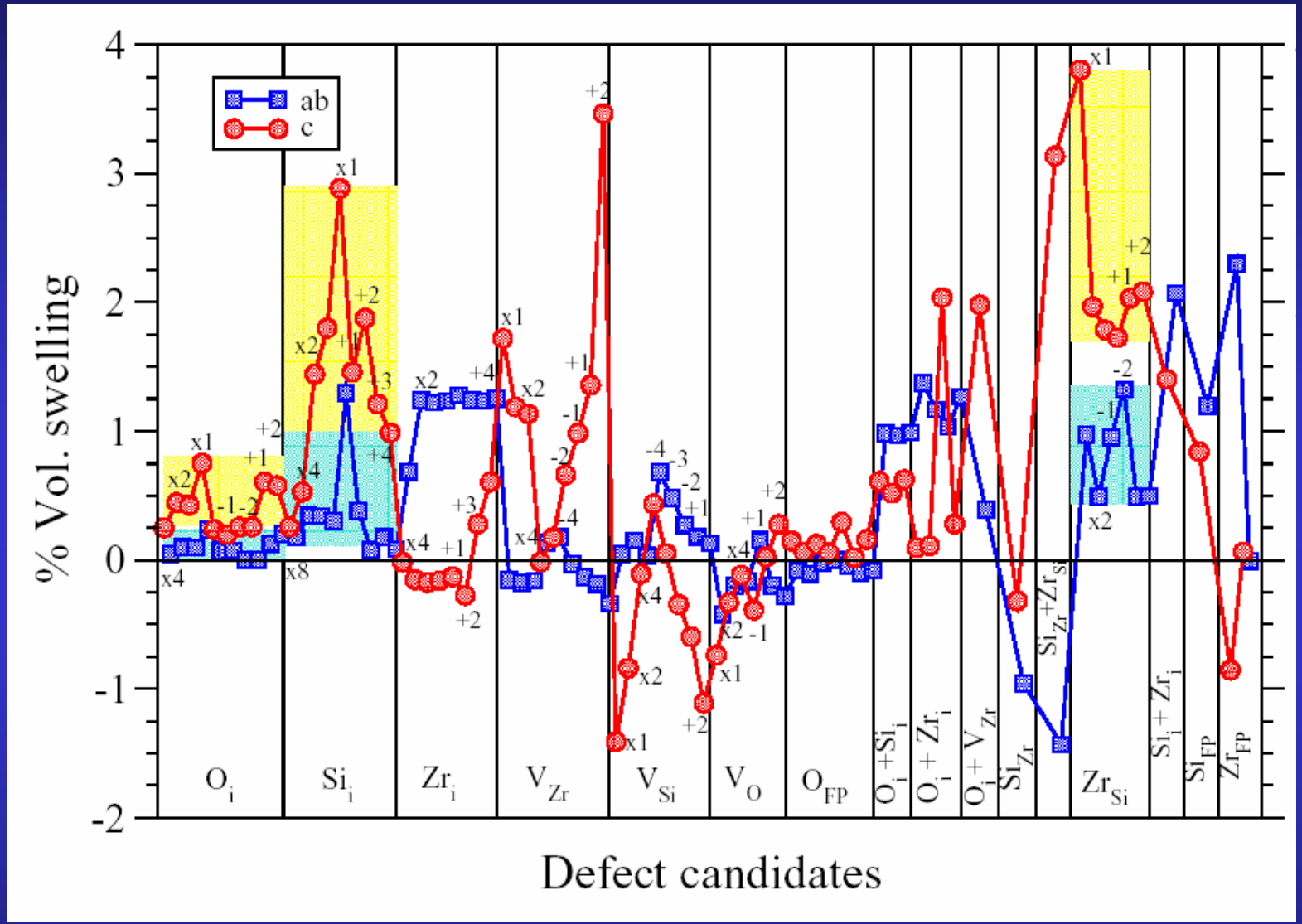
atomic relaxation only!

The catalogue of defects

- Interstitials: O_i , Si_i , Zr_i
- Vacancies: V_O , V_{si} , V_{Zr}
- Antisite defects: Zr_{Si} & Si_{Zr}
- Frenkel pairs: O_{FP} , Si_{FP} & Zr_{FP}

Different charge-states:

$-4,-3,-2,-1$ 0 $+1,+2,+3,+4$



J. M. Pruneda, T. Archer, and E. Artacho *to be published in* PRB

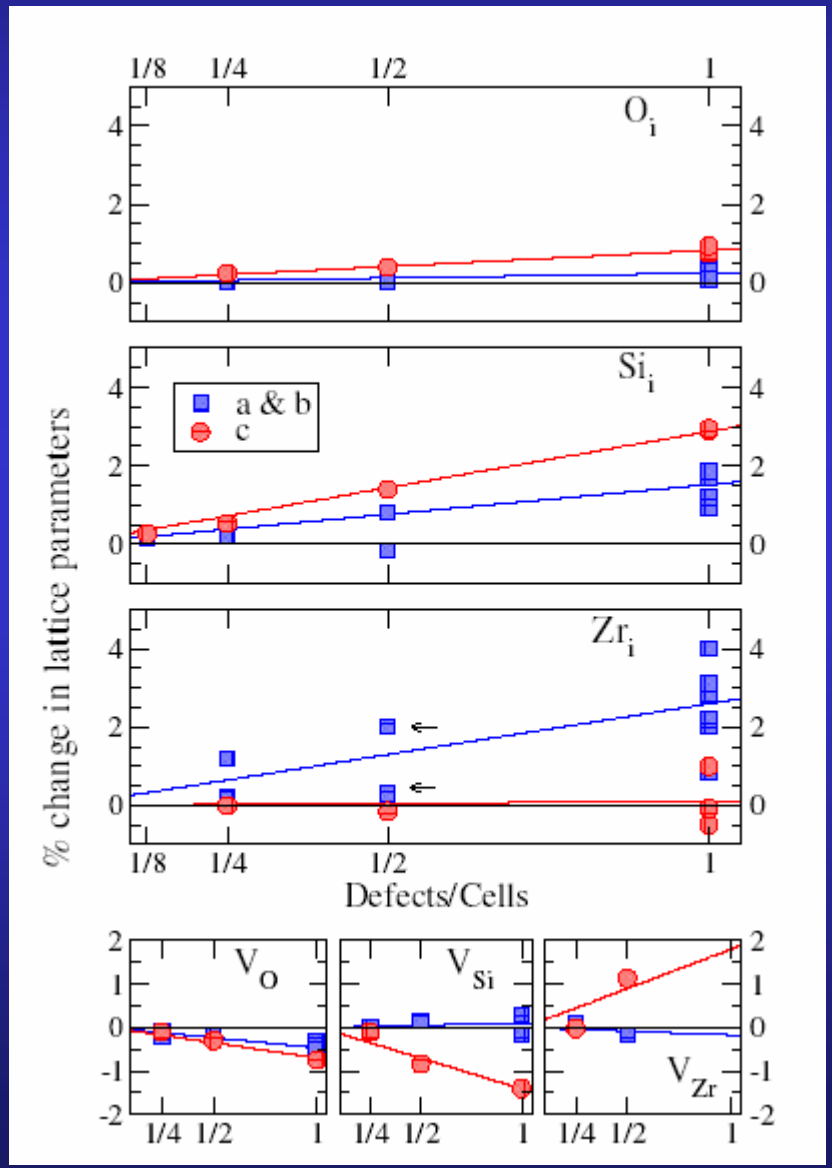
Possible defects:

O & Si interstitials

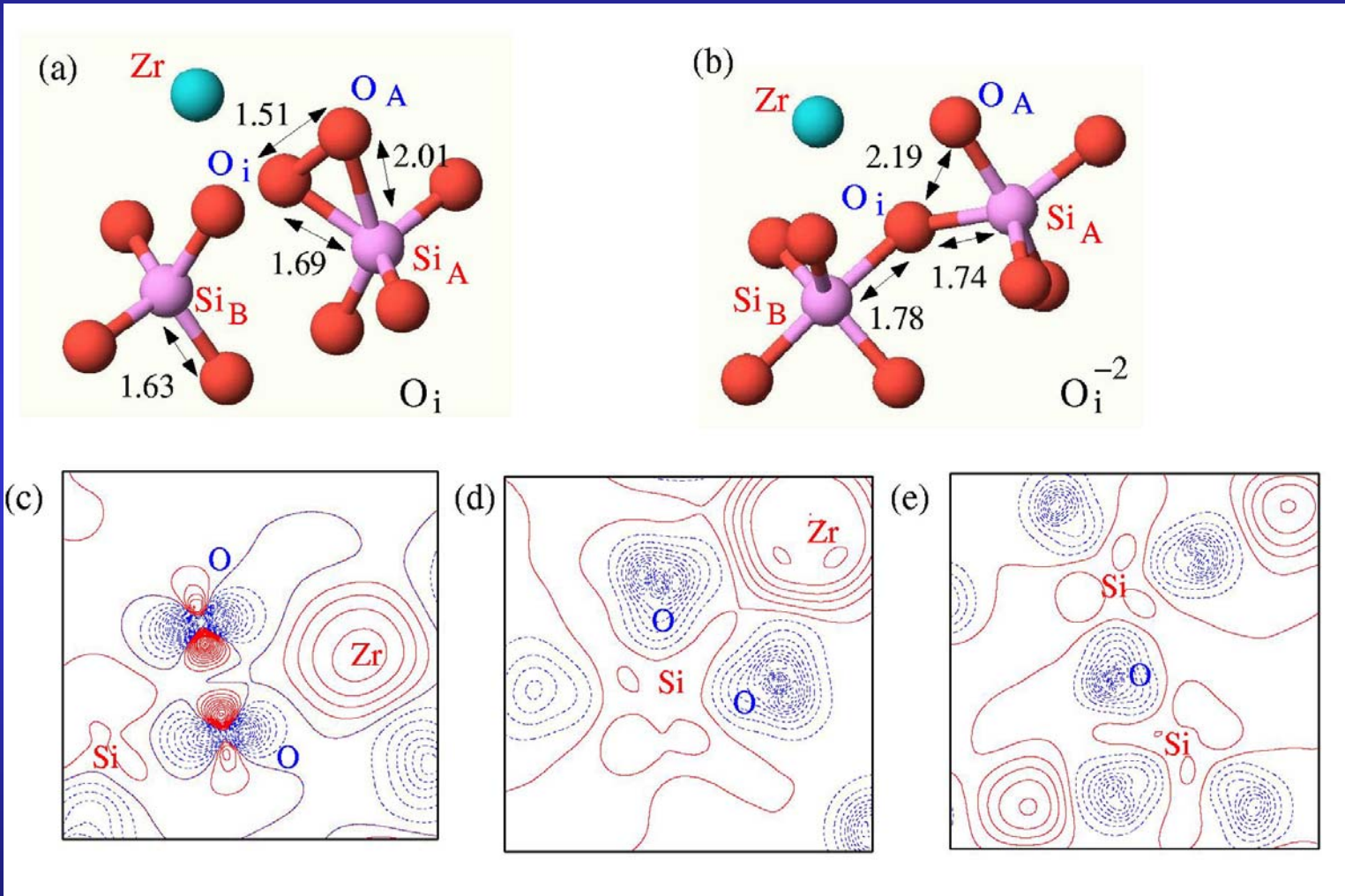
Zr_{Si} anti-site

Swelling as a function of the concentration

- Almost linear behavior
- Considerable anisotropy
- Effect of disorder

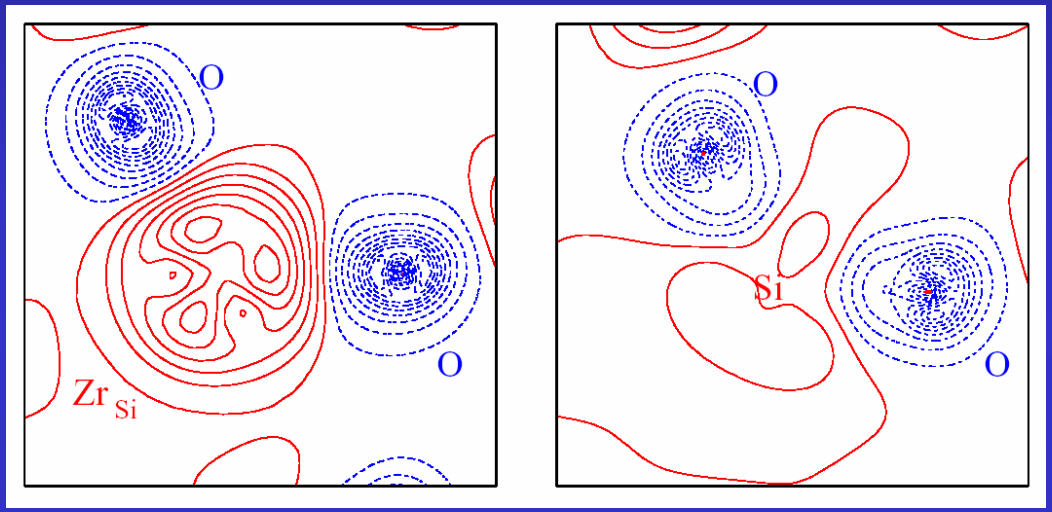


Oxygen interstitial

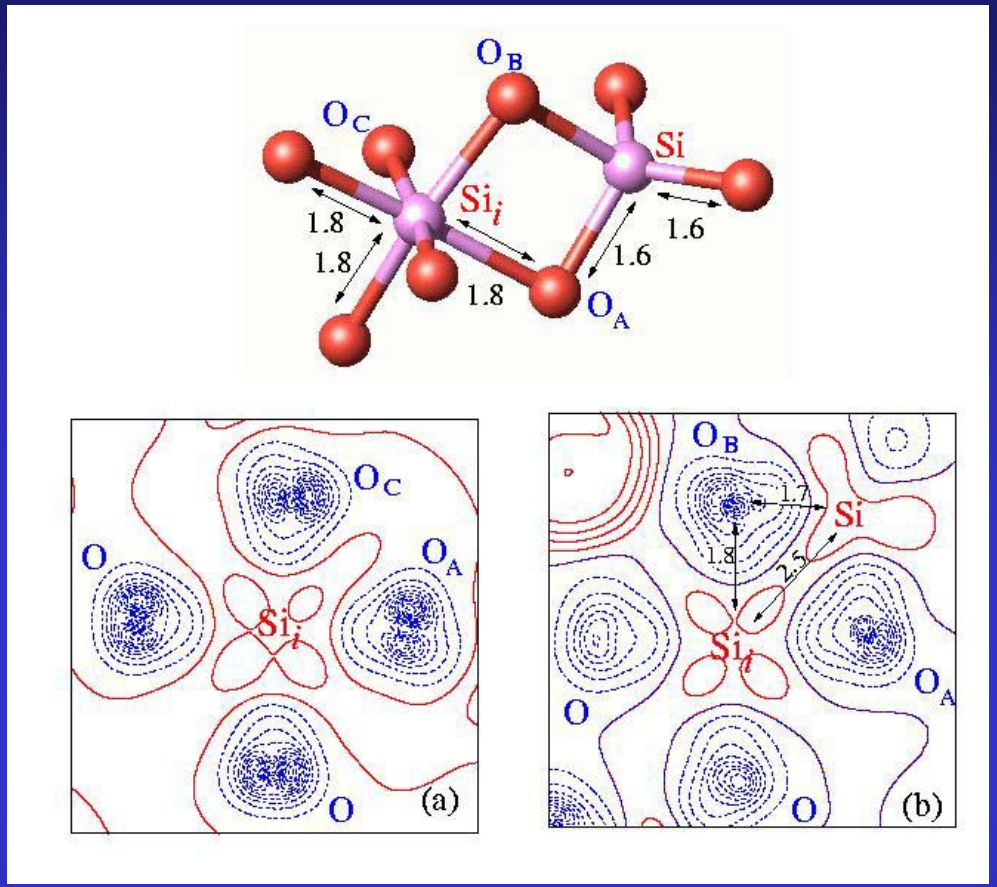


Neutral defect has a dumbbell structure similar to ZrO2.

Silicon interstitial



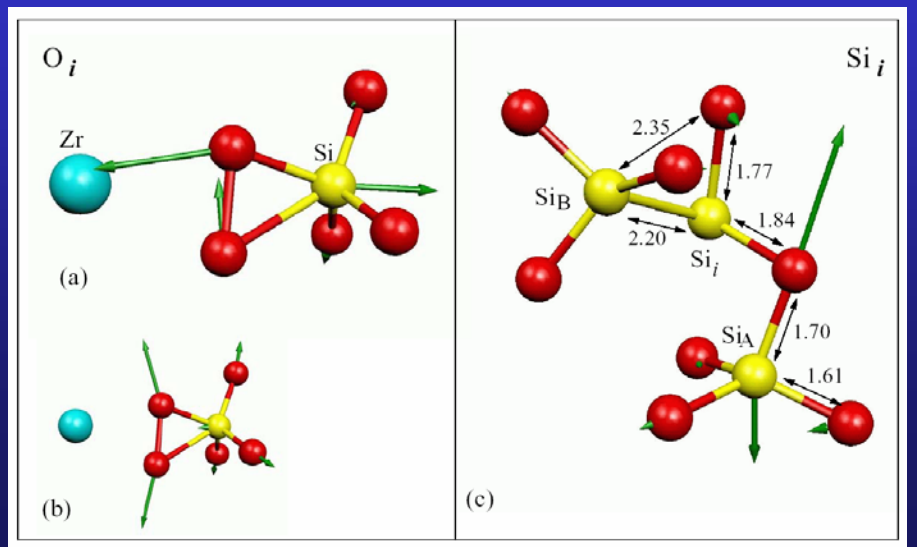
Zr_{Si} anti-site



Local Vibrational Modes

IR active at 729 cm^{-1} (O_i)

743 cm^{-1} (Si_i)



Simulation of NMR spectra

Combining methods: SIESTA+PARATEC

Experiments in damaged samples

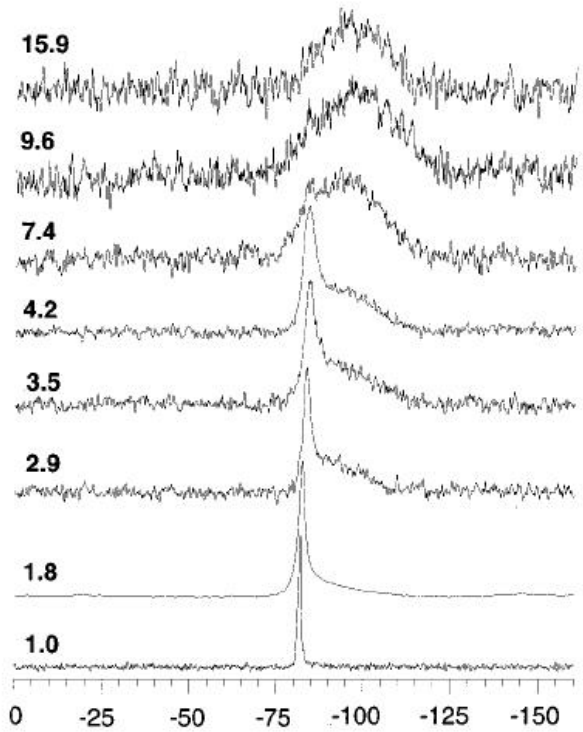
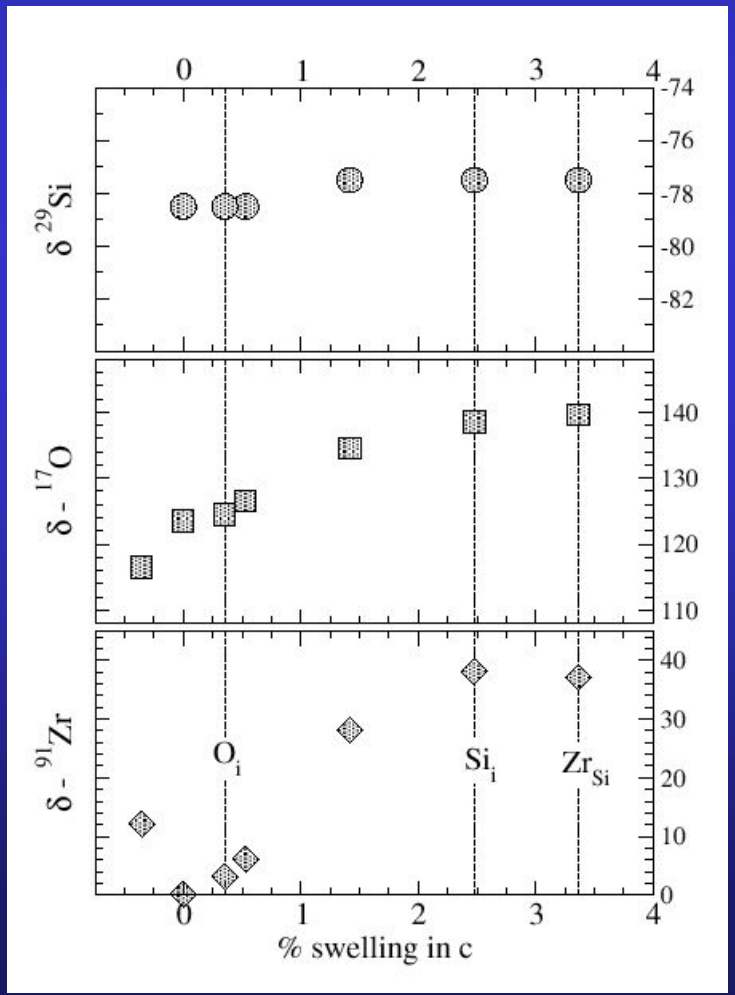


FIG. 2. Series of ^{29}Si MASNMR spectra of zircons with increasing accumulated α dose (upwards). Increasing numbers indicate the dose$\times 10^{18}$ α events/g and refer to: Moroto, UG9A, Cam26, Cam25, Z5, Sand9, Ti8, and Sand4, respectively. Spectra were acquired as described in the text and referenced to external TMS.

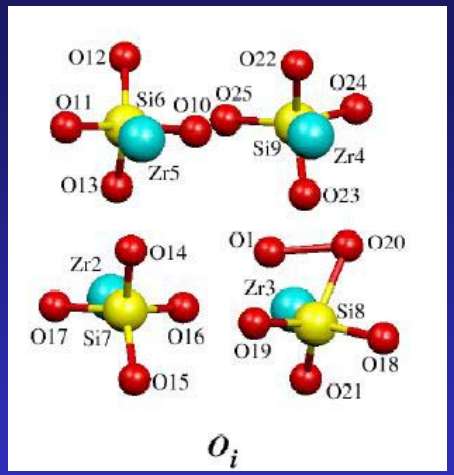
Chemical shifts due to swelling?



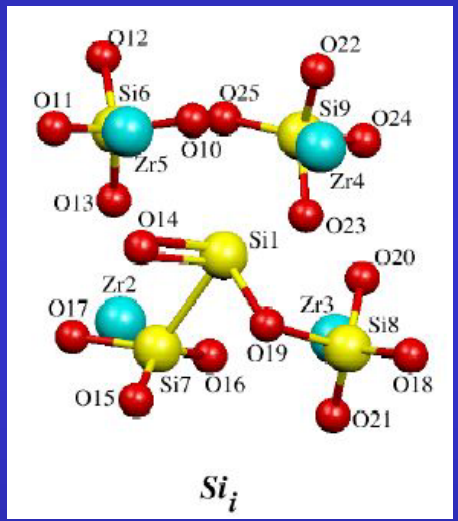
O: -170.1 (-170)
Si: -78.6 (-81.5)

	O_i	Si_i	Zr_{Si}
Si1		-7.5	
Si5			-82
Si6	-84	-76	
Si7	-81	-47	-82
Si8	-112	-75	-81
Si9	-86	-86	

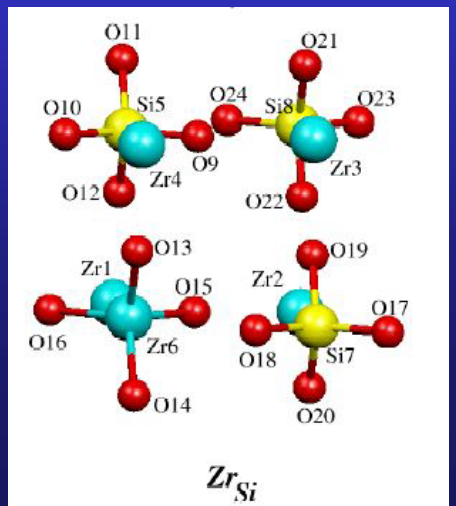
	O_i	Si_i	Zr_{Si}
Zr1	-24		49
Zr2	-38	-54	-39
Zr3	65	-180	-65
Zr4	-30	-404	-39
Zr5		-121	
Zr6			-432



O_i



Si_i

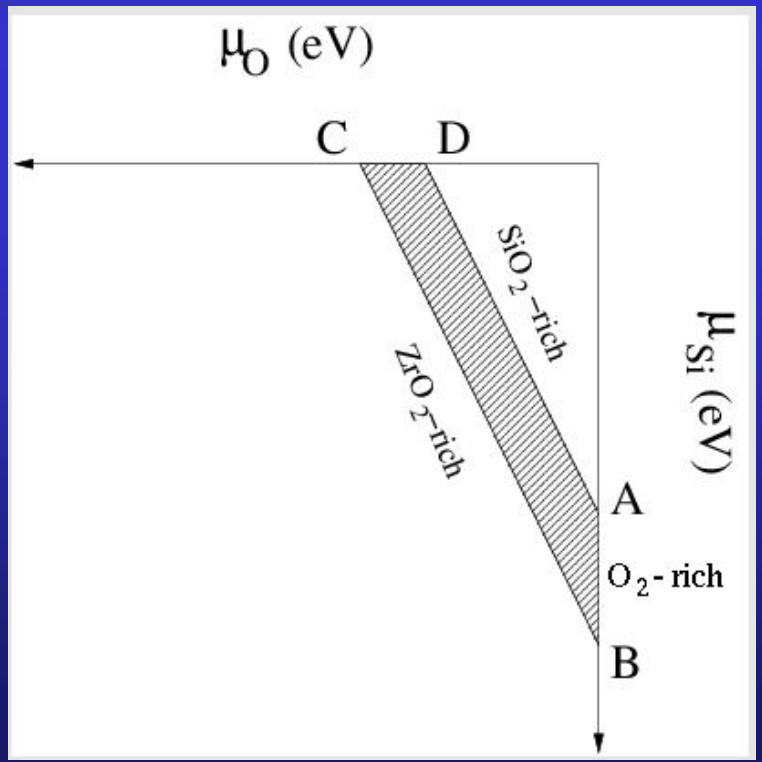


Zr_{Si}

	O_i	Si_i	Zr_{Si}
O1	282		
O9			148
O10	196	117	148
O11	154	167	158
O12	199	224	158
O13	158	149	464
O14	164	244	464
O15	162	201	464
O16	169	322	464
O17	168	212	158
O18	183	178	158
O19	165	95	148
O20	178	203	148
O21	177	172	166
O22	176	161	166
O23	144	166	166
O24	166	188	166
O25	169	114	

Formation Energies

$$E_f(\alpha,q) = E(\alpha,q) - \sum_i \mu_i \cdot n_i + q(\mu_e + E_V)$$



$$\mu_{Zr} + \mu_{Si} + 4\mu_O = \Delta G_f(ZrSiO_4)$$

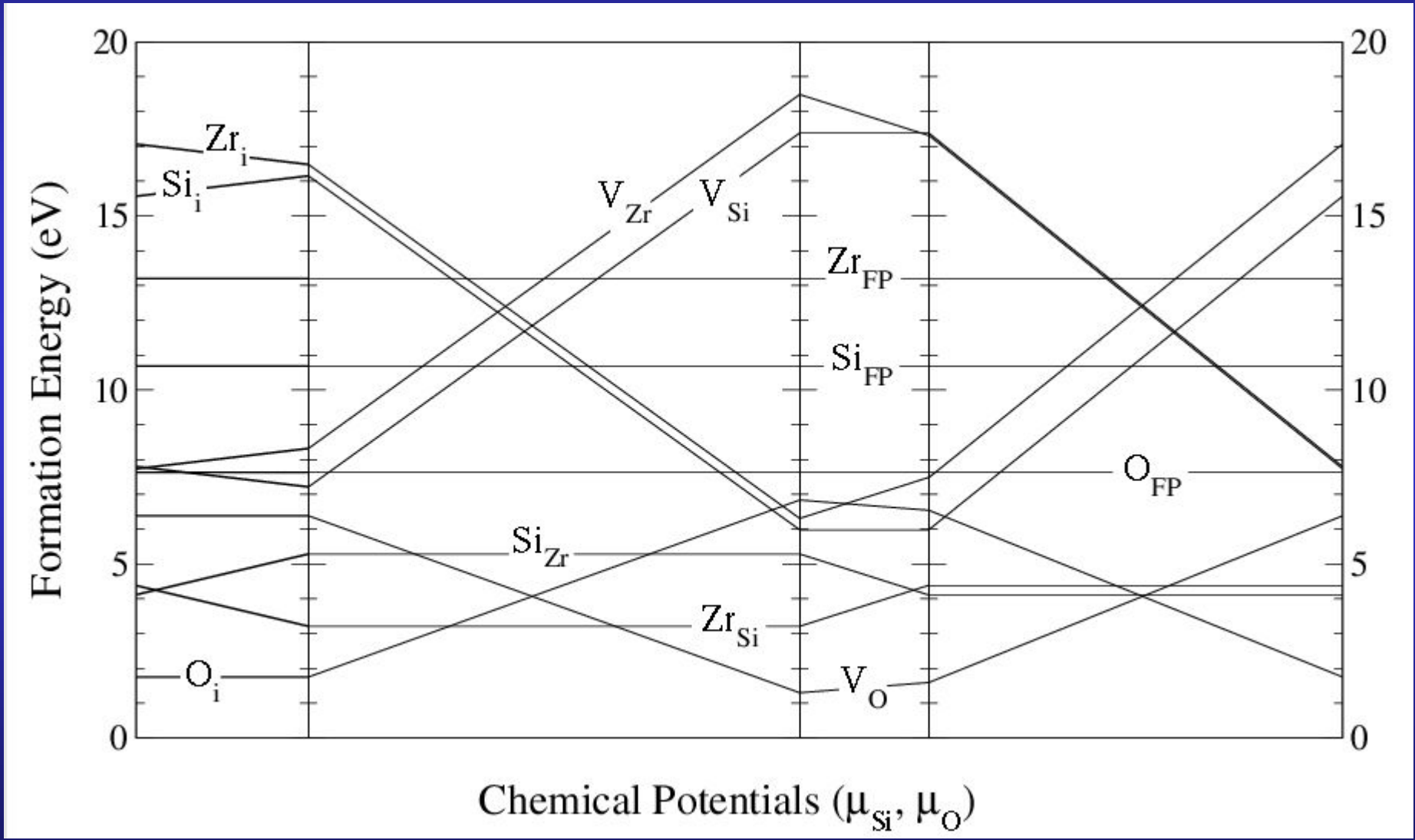
$$\mu_{Zr} + 2\mu_O \le \Delta G_f(ZrO_2)$$

$$\mu_{Si} + 2\mu_O \le \Delta G_f(SiO_2)$$

TABLE II: Calculated formation free energies (in eV) for $ZrSiO_4$, ZrO_2, and SiO_2.

Constituents	This work	Expt.
$Zr + O_2 \longrightarrow ZrO_2$	-12.1	-11.5[19]
$Si + O_2 \longrightarrow SiO_2$	-9.6	-9.8[20]
$Zr + Si + 2\times O_2 \longrightarrow ZrSiO_4$	-22.3	-20.9[20]

The stability triangle

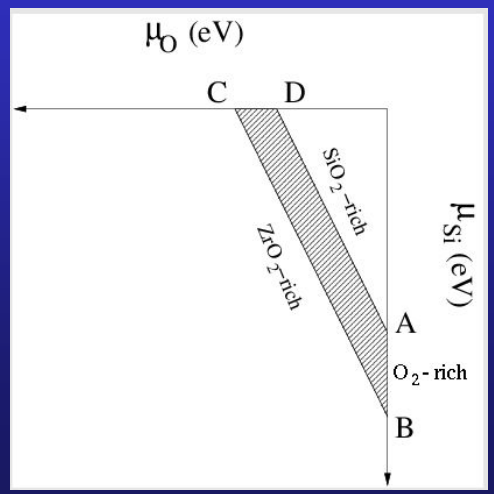


Formation energies for neutral defects

Defect α	24	48	96	192	Ref. [6]
O_i	1.7	1.7	2.0	1.1	1.7
Si_i	14.5	15.6	15.5	16.4	17.0
Zr_i		17.1	17.6	15.9	18.0
V_O	6.3	6.4	6.5	6.9	5.6
V_{Si}	3.6	7.8	8.5		5.8
V_{Zr}	7.4	7.7	7.9		5.9
O_{FP}		7.6			7.3
Si_{FP}		10.7			22.9
Zr_{FP}		13.2			24.0
Si_{Zr}		4.1			
Zr_{Si}	4.1	4.4		3.0	

Converged in size

Values given at the point "A"…



More stable defects:

- Vacancies and interstitials of O
- Antisites.

Properties of charged defects

Negative-U behavior

- Gain in energy when a second electron/hole is captured.

$$2O_i^- \rightarrow O_i^0 + O_i^{2-}$$

$$2V_O^+ \rightarrow V_O^0 + V_O^{2+}$$

- Strong ionic interaction for cation-defects (& charged FP)

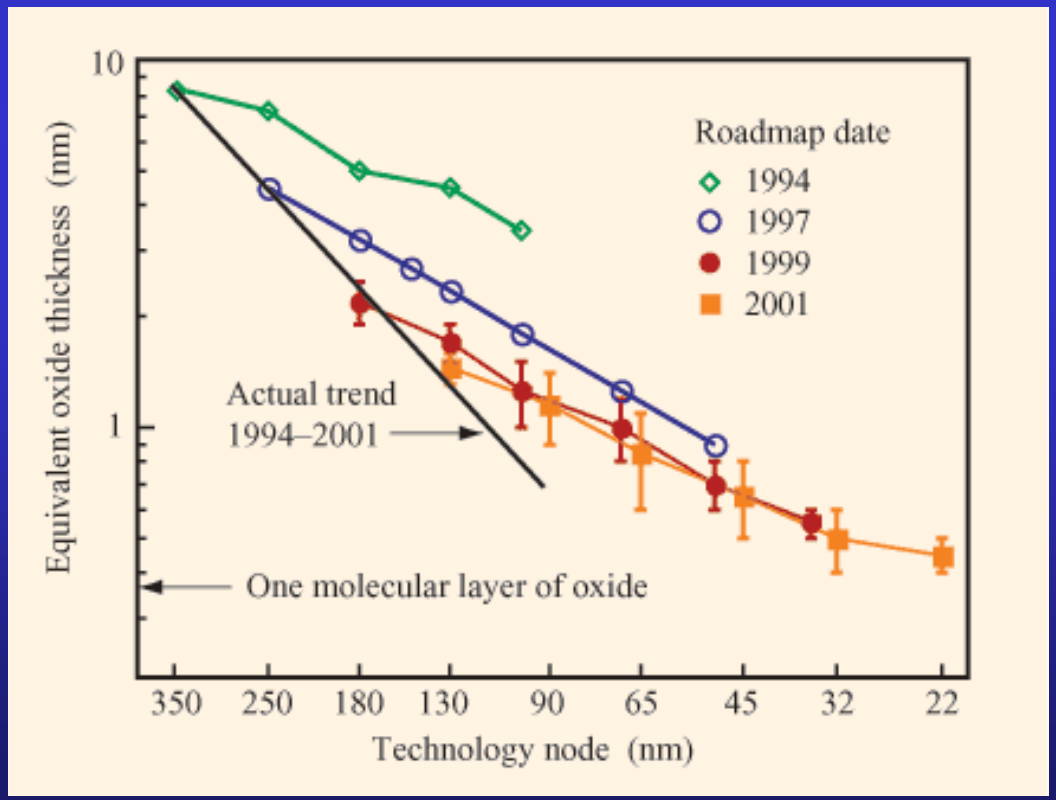
$$X_i^0 + V_X^0 \rightarrow X_i^{n-} + V_X^{n+}$$

TABLE IV: Energies for defect reactions, obtained from the formation energies of isolated defects.

Reaction	Energy (eV) high-C	Energy (eV) low-C
$O_i^0 + O_i^{2-} \longrightarrow 2O_i^-$	−0.4	−1.1
$V_O^0 + V_O^{2+} \longrightarrow 2V_O^+$	−1.7	−1.0
$O_i^0 + V_O^0 \longrightarrow O_i^- + V_O^+$	−0.5	−0.7
$O_i^- + V_O^+ \longrightarrow O_i^{2-} + V_O^{2+}$	1.6	1.4
$O_i^0 + V_O^0 \longrightarrow O_i^{2-} + V_O^{2+}$	1.1	0.7
$Si_i^0 + Si_i^{+2} \longrightarrow 2Si_i^+$	−1.5	−1.0
$Si_i^0 + Si_i^{+4} \longrightarrow 2Si_i^{2+}$	0.6	0.8
$Si_i^{+2} + Si_i^{+4} \longrightarrow 2Si_i^{3+}$	−2.8	−2.6
$V_{Si}^0 + V_{Si}^{2-} \longrightarrow 2V_{Si}^-$	0.3	
$V_{Si}^0 + V_{Si}^{4-} \longrightarrow 2V_{Si}^{2-}$	1.7	
$Si_i^0 + V_{Si}^0 \longrightarrow Si_i^- + V_{Si}^+$	3.0	
$Si_i^0 + V_{Si}^0 \longrightarrow Si_i^{2-} + V_{Si}^{2+}$	7.2	
$Si_i^0 + V_{Si}^0 \longrightarrow Si_i^{3-} + V_{Si}^{3+}$	8.3	
$Si_i^0 + V_{Si}^0 \longrightarrow Si_i^{3-} + V_{Si}^{3+}$	12.0	
$Zr_i^0 + Zr_i^{+2} \longrightarrow 2Zr_i^+$	−0.6	0.02
$Zr_i^0 + Zr_i^{+4} \longrightarrow 2Zr_i^{2+}$	2.4	2.3
$Zr_i^{+2} + Zr_i^{+4} \longrightarrow 2Zr_i^{3+}$	−0.2	0.1
$V_{Zr}^0 + V_{Zr}^{2-} \longrightarrow 2V_{Zr}^-$	0.2	
$V_{Zr}^0 + V_{Zr}^{4-} \longrightarrow 2V_{Zr}^{2-}$	1.3	
$Zr_i^0 + V_{Zr}^0 \longrightarrow Zr_i^- + V_{Zr}^+$	4.3	
$Zr_i^0 + V_{Zr}^0 \longrightarrow Zr_i^{2-} + V_{Zr}^{2+}$	9.0	
$Zr_i^0 + V_{Zr}^0 \longrightarrow Zr_i^{3-} + V_{Zr}^{3+}$	11.7	
$Zr_i^0 + V_{Zr}^0 \longrightarrow Zr_i^{4-} + V_{Zr}^{4+}$	14.3	

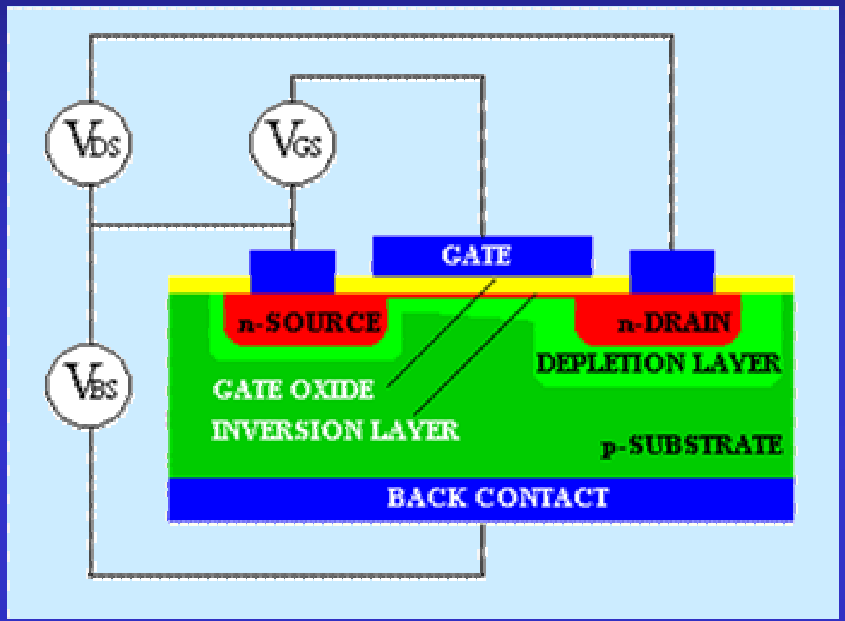
Alternative gate dielectrics

Device current drive is proportional to the oxide capacitance per unit area; thus, the best way to increase the drive current and thereby achieve high performance is to reduce the equivalent oxide thickness (EOT)



Scaling of the gate-oxide thickness: Roadmaps vs. actual trends.

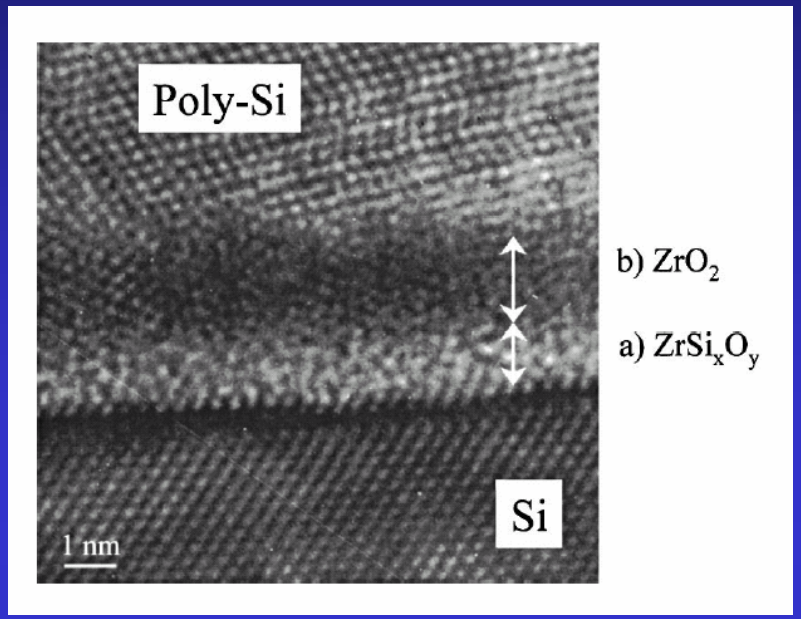
MOSFET

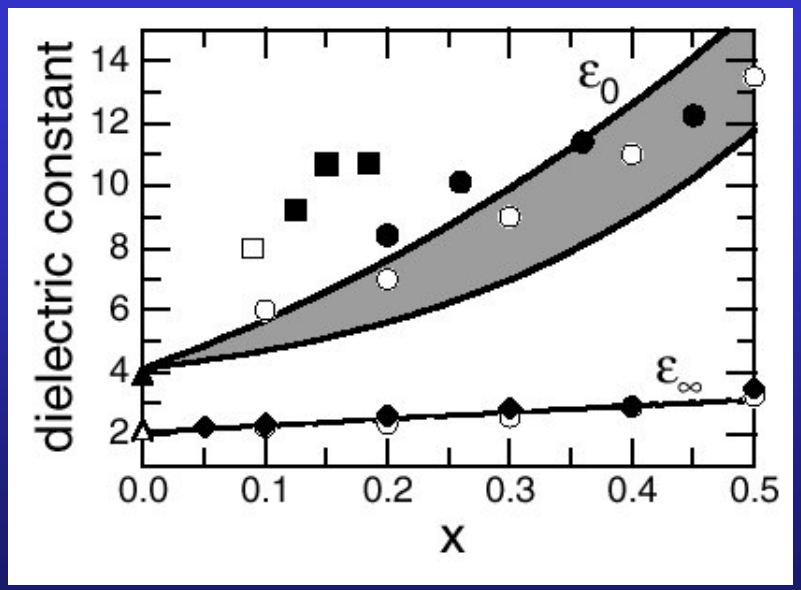


To reduce the gate leakage current:

1. the dielectric must be physically thick
2. it must have reasonably large band offsets to Si

Dielectric Constants of Zr Silicates





IBM Journal of Research and Development Vol. 46, **2/3**, 2002

Vertically scaled MOSFET gate stacks and junctions: How far are we likely to go?

"Materials such as HfO_2 and ZrO_2, having dielectric constants of about 15 and offsets of about 1.5 eV, have the potential of meeting the long-term leakage requirements. Their silicates have almost the same barrier height, nearly as high a dielectric constant, potentially lower charge levels, and much better thermal stability; thus, *they may be even better candidates.*"

G. –M. Rignanese, *et. al.* PRL **89**,117601 (2002)

Band-Offsets

In the interface, it is required a high tunneling barrier to both electrons and holes.

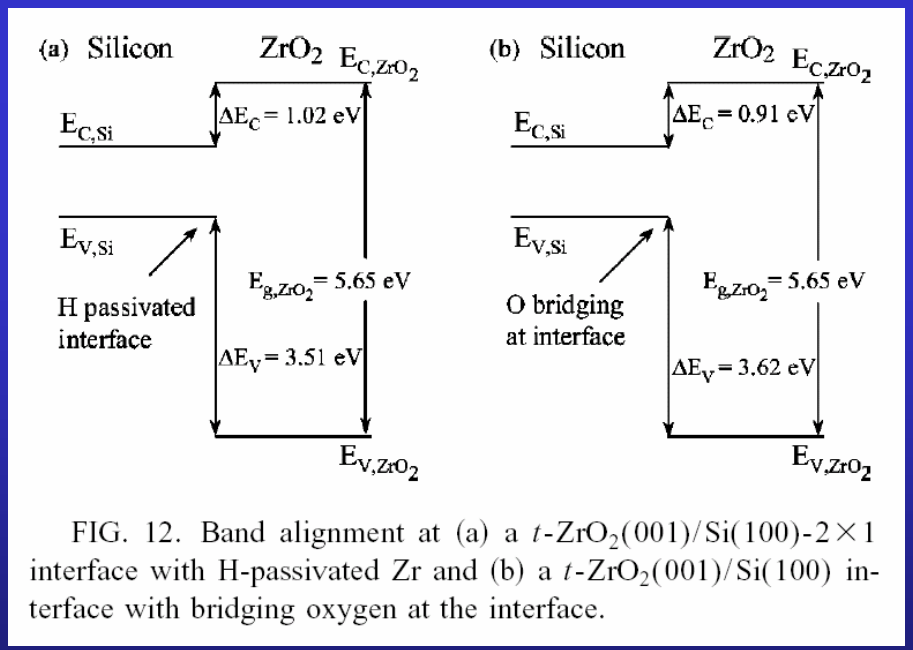
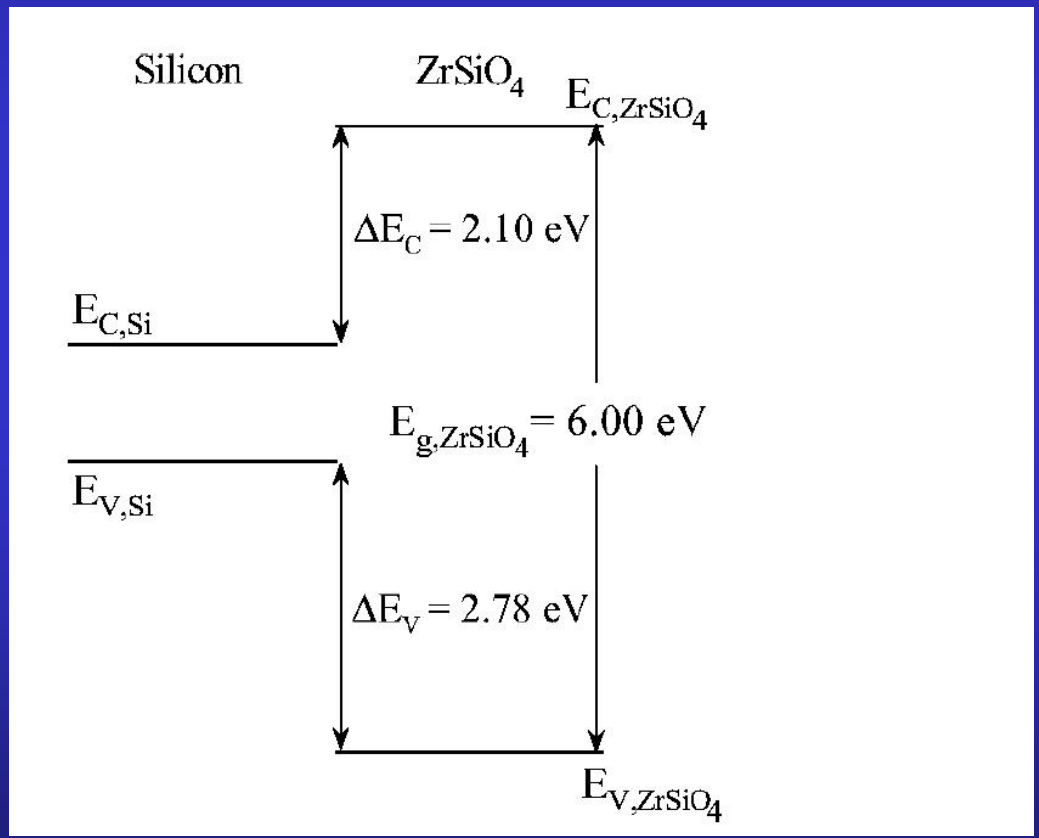


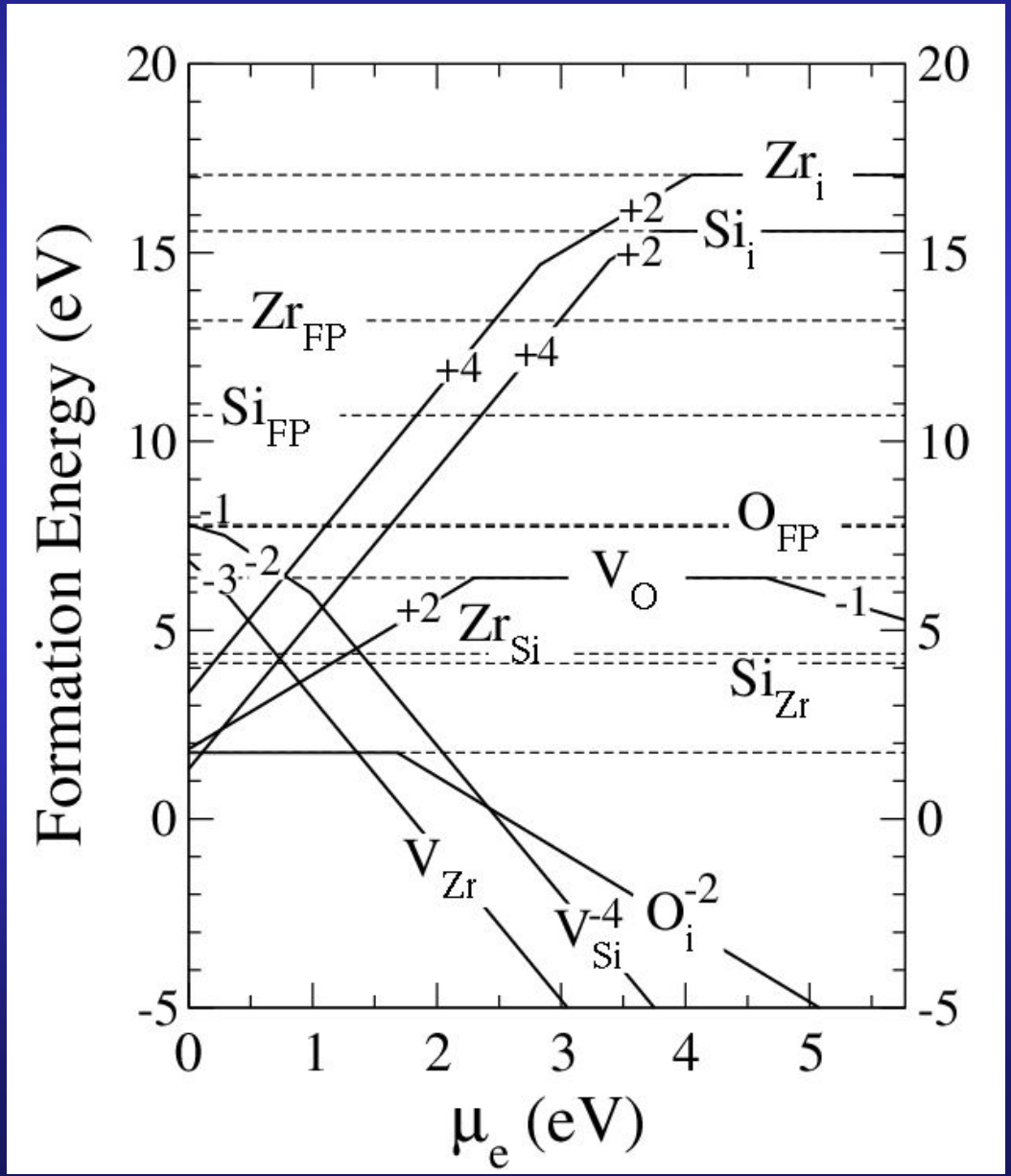
FIG. 12. Band alignment at (a) a t-$ZrO_2(001)/Si(100)$-2×1 interface with H-passivated Zr and (b) a t-$ZrO_2(001)/Si(100)$ interface with bridging oxygen at the interface.

R. Puthenkovilakam *et. al*. PRB 69 155329 (2004)



Band alignment at ZrSiO4(001)/Si(100) interface.
(No Zr d states in the gap)

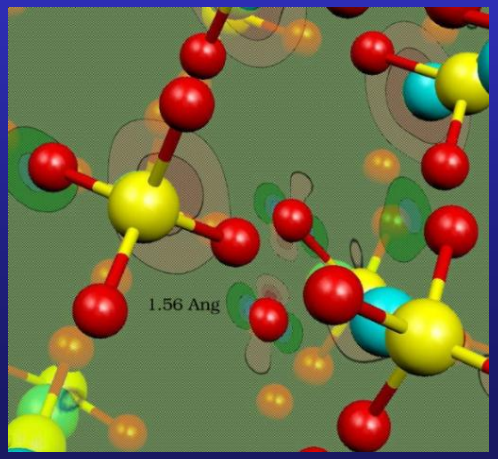
Charged defects!!

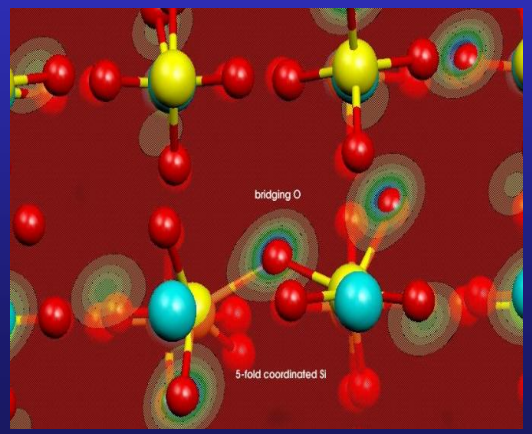


The dielectric cannot contain traps that would promote trap-assisted tunneling or locally uncompensated charges that would degrade channel mobility.

The conduction in the dielectric must be purely electronic, not ionic, and preferably by electrons only.

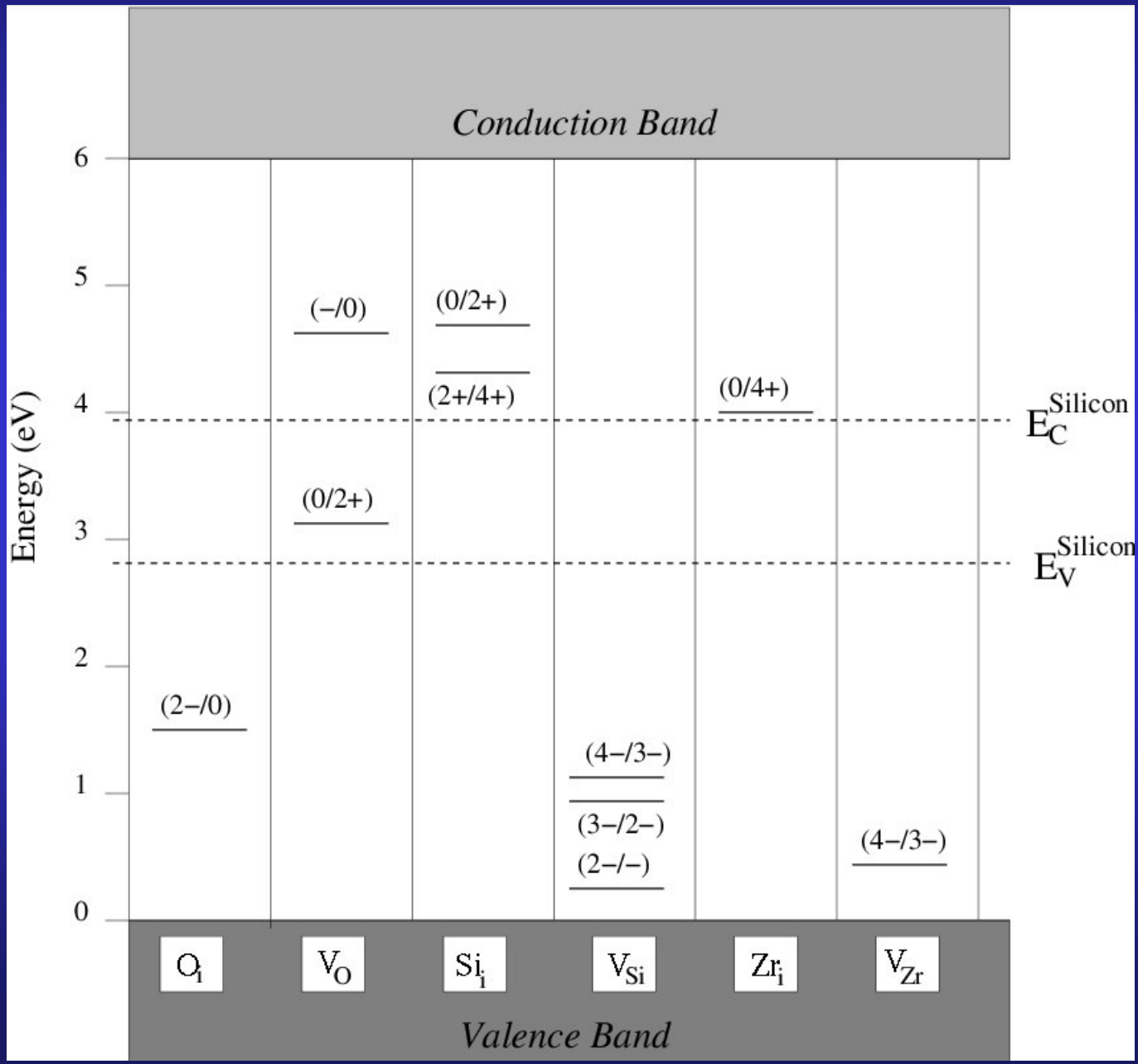
O_i O_i^{-2}





Transition Energies $E_\alpha(q/q') = [E_f(\alpha,q) - E_f(\alpha,q')]/(q'-q)$

- Acceptor levels for O_i, V_{Si} and V_{Zr} that can trap electrons from the bottom of the silicon valence band.
- Donor level of V_O can trap holes injected from silicon.



Conclusions

- We have studied the effect of high concentration of point defects in ZrSiO4.
- A roughly linear dependence between swelling and the defect concentration of periodically repeated defects was obtained.
- Based on experimental evidence of anisotropic lattice expansion, we have selected a set of defects as good candidates to be responsible of the swelling: O_i, Si_i, and Zr_{Si}.
- Interstitials and vacancies of oxygen, and the antisite Zr_{Si} are the most stable defects.
- There is a strong tendency towards ionization, and a negative-U behavior is observed.

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