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ECE695A: Reliability Physics of Nano-Transistors

Lecture 6: Defects in the Bulk and at Interfaces

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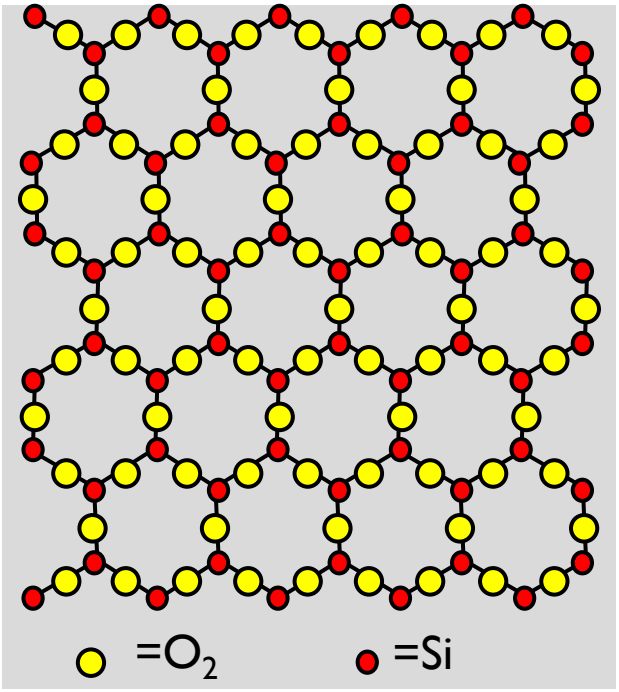
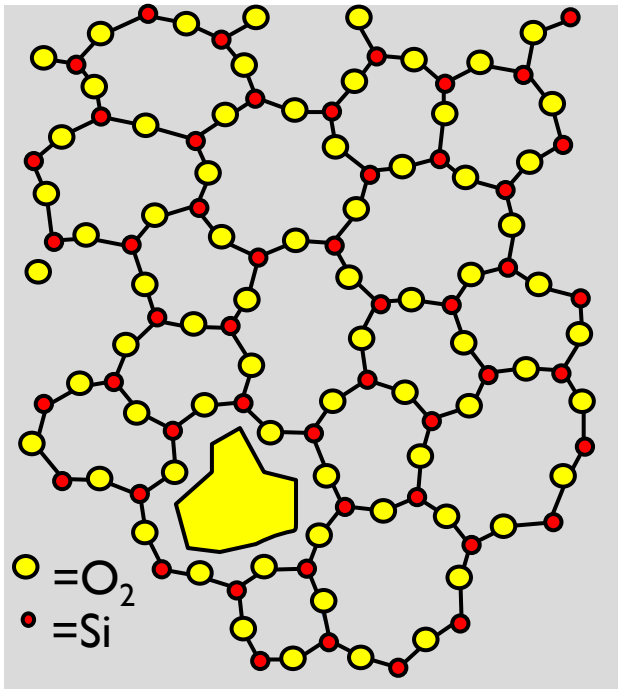
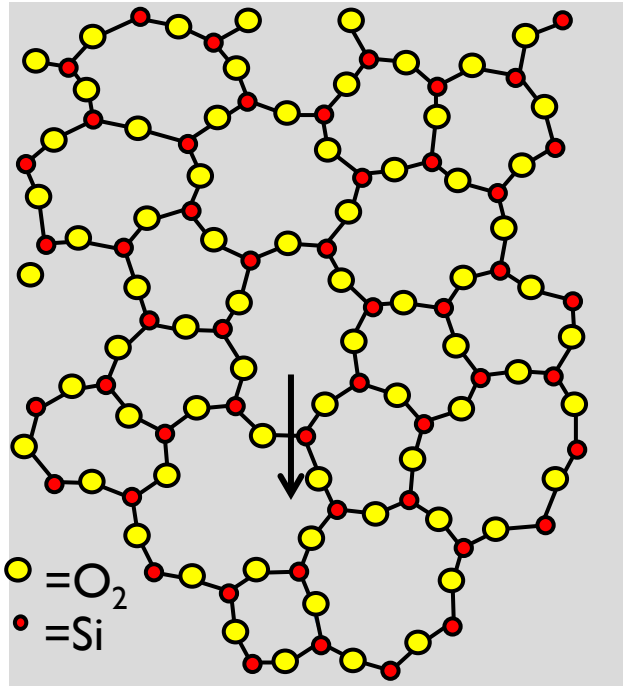
Outline of lecture 6

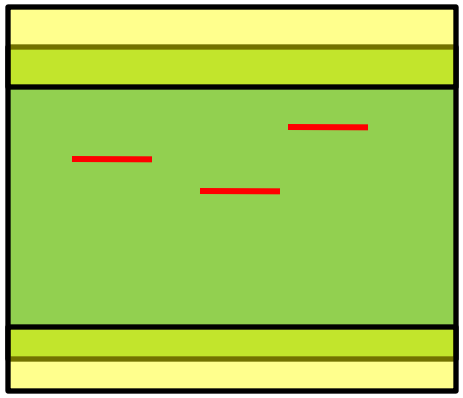
1. Strain in materials/origin of defects
2. Examples: bulk defects
3. Examples: interface defects
4. Measurements
5. Conclusions

Meaning of an oxide/nitride defect









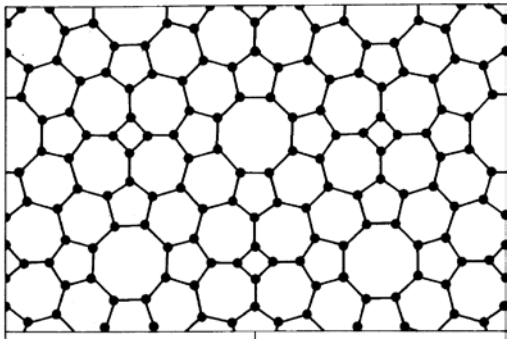
Origin of defects and Maxwell constraints

Dimensionality

Points to be stabilized

Constraints

$$M_0 = DN - N_c - (D + \alpha)$$



$$N \equiv \sum_{r=1}^{k} n_r$$

Types of atoms with different coordination

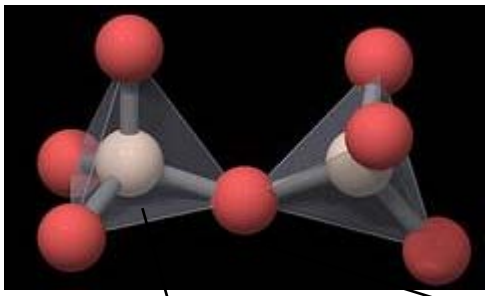
Number of atoms with coordination r

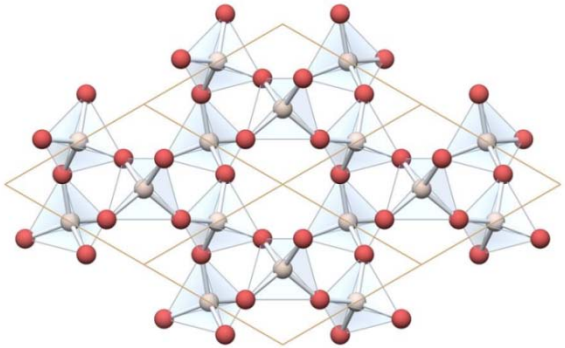
$$N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}(2r - D)\right]_{angle}$$

$M_0 > 0$ unstable, $M_0 < 0$ stable

Example 4: 3D constraints for binary solids

$$N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}(2r-D)\right]_{angle}$$





J.C. Phillips, 1979.
Thorpe, 1982.

$$N_c(Si) = \left[\frac{\langle N_{c,1}\rangle}{2}\right]_{r_{ij}} + \left[\left(2\langle N_{c,1}\rangle - 3\right)\right]_{\theta_{ijk}} \qquad N_c(O) = \left[\frac{\langle N_{c,2}\rangle}{2}\right] + 0$$

Average Si coordination … $\langle N_{c,1}\rangle$ Average O coordination … $\langle N_{c,2}\rangle$

Average coordination … $\left\langle N_c^{A_x B_{1-x}}\right\rangle = x\left\langle N_c^{A}\right\rangle + (1-x)\left\langle N_c^{B}\right\rangle$

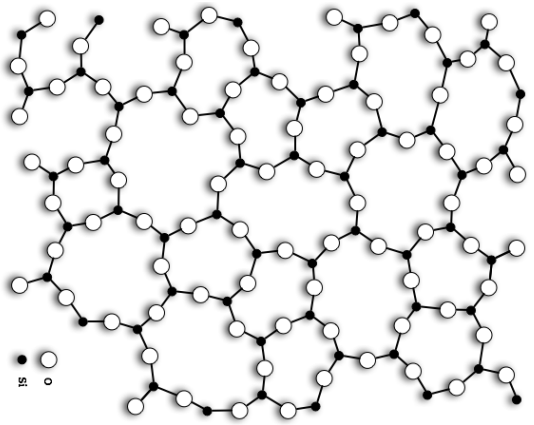
Example 4: at what value of x is SiO strain-free?

$$\frac{M_0}{N} \approx 3 - x\left[\frac{\langle N_c^{Si}\rangle}{2} + (2\langle N_c^{Si}\rangle - 3)\right] - (1-x)\left[\frac{\langle N_c^{O}\rangle}{2} + 0\right]$$

$$= 3 - x\left[\frac{4}{2} + (2\times 4 - 3)\right] - (1-x)\times\frac{2}{2}$$

$$0 \Rightarrow 7x + (1-x) = 3 \quad x = \frac{1}{3}$$

$Si_{1/3}O_{1-1/3} = SiO_2$ stress - free optimally coordianted!



$$\langle N_c^{SiO_2}\rangle = 0.33 * \langle N_c^{Si}\rangle + 0.66 * \langle N_c^{O}\rangle$$

$$= 2.64$$

A very important number that arises in all good 3D 'glass formers'

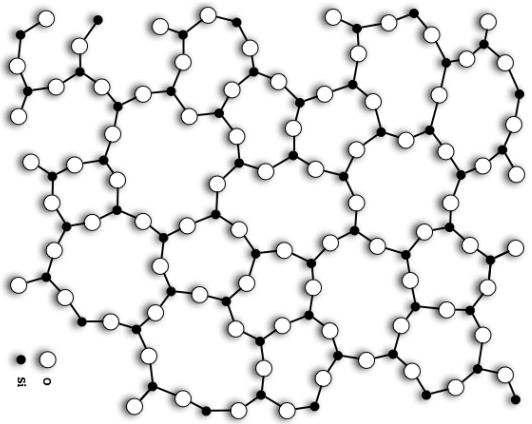
Example 2: Is Si_3N_4 optimally coordinated?

$$\frac{M_0}{N} \approx 3 - x\left[\frac{\langle N_c^{Si}\rangle}{2} + (2\langle N_c^{Si}\rangle - 3)\right] - (1-x)\left[\frac{\langle N_c^{O}\rangle}{2} + 0\right]$$

$$= 3 - \left\{\frac{3}{(3+4)}\left[\frac{4}{2} + (2\times 4 - 3)\right] + \frac{4}{(4+3)} \times \frac{3}{2}\right\}$$

$$= -0.8571$$

J.C. Phillips, 1979.
Thorpe, 1982.



Silicon nitride is over coordinated, therefore prone to defect formation

Average coordination ..... $\langle N_c^{Si_3N_4}\rangle = \frac{3}{7}\langle N_c^{Si}\rangle + \frac{4}{7}\langle N_c^{N}\rangle = \frac{24}{7} = 3.42$

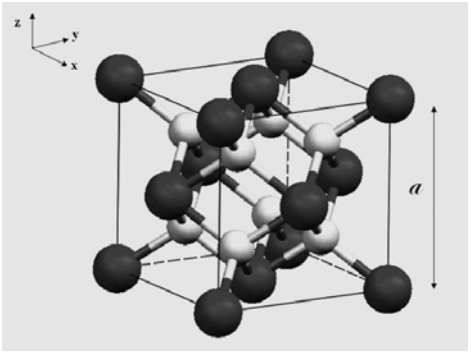
Probability of defect formation: $D \propto (\Delta\theta)^2 \sim (N_c - N_c^*)^2$

Example: what about HfO_2?

$$\frac{M_0}{N} \approx 3 - x\left[\frac{\langle N_c^{Hf}\rangle}{2} + (2\langle N_c^{Hf}\rangle - 3)\right] - (1-x)\left[\frac{\langle N_c^{O}\rangle}{2} + 0\right]$$

$$= 3 - \left\{\frac{1}{(1+2)}\left[\frac{8}{2} + (2\times 8 - 3)\right] + \frac{2}{(1+2)} \times \frac{4}{2}\right\}$$

$$= -4$$



HfO2 is over coordinated, therefore prone to defect formation

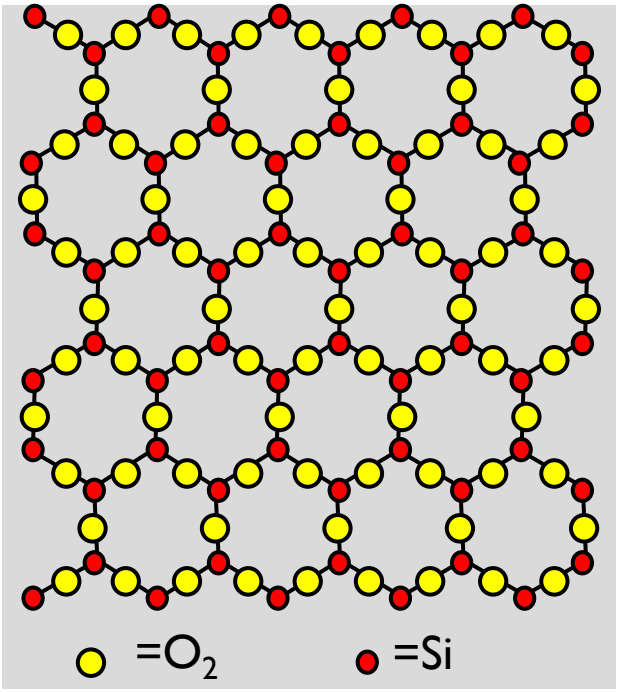
Average coordination ..... $\langle N_c^{HfO_2}\rangle = \frac{1}{3}\langle N_c^{Hf}\rangle + \frac{2}{3}\langle N_c^{O}\rangle = \frac{16}{3} = 5.33$

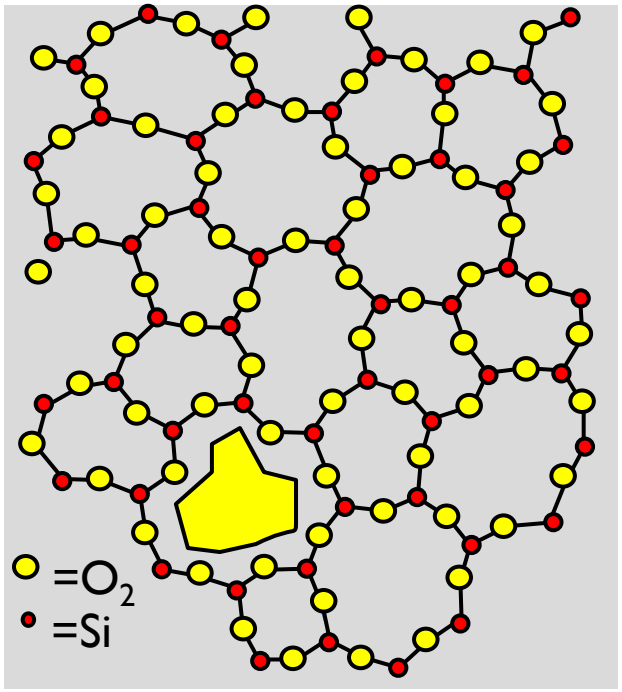
Probability of defect formation: $N_{Defects} \sim (N_c - N_c^*)^2$

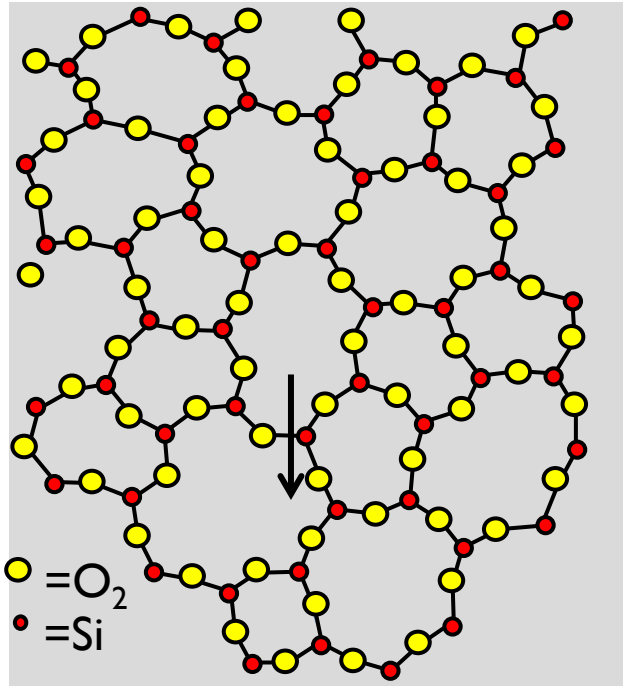
Outline

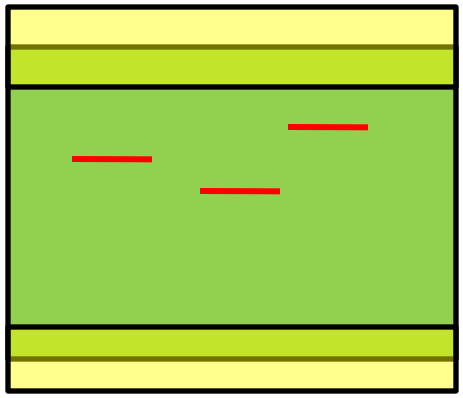
1. Strain in materials/origin of defects
2. Examples: bulk defects
3. Examples: interface defects
4. Measurements
5. Conclusions

Meaning of an oxide/nitride defect

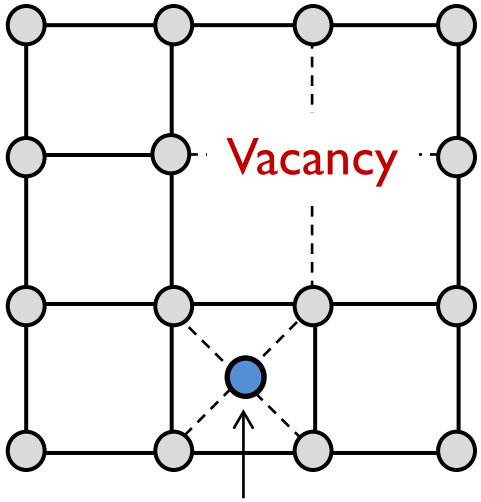


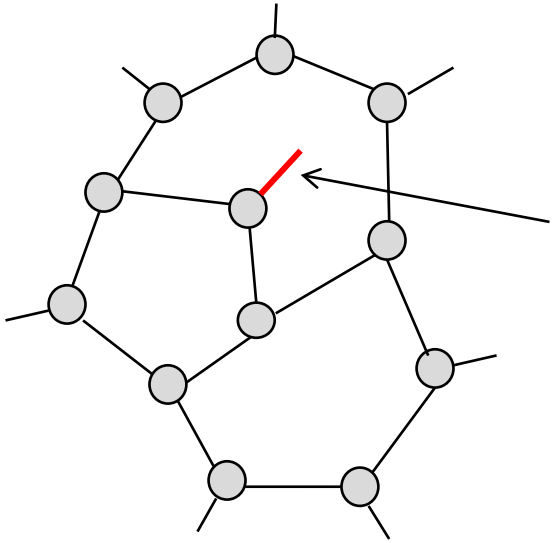


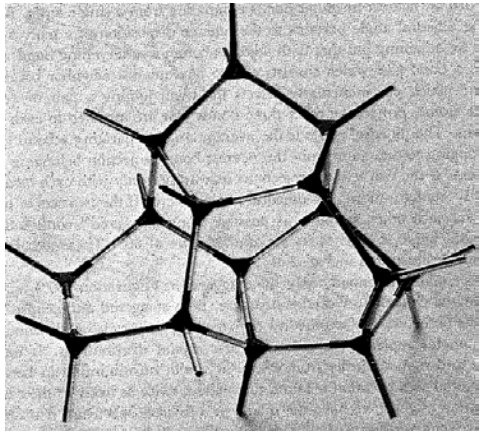


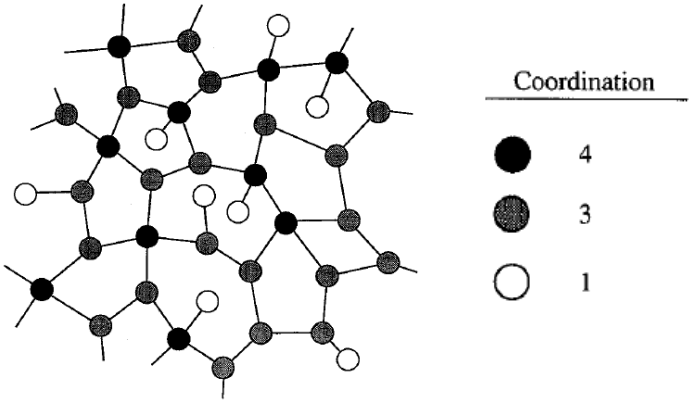


Defects in a-Si (coordination defects)









Far fewer **types** of defects compared to crystalline materials …

Examples: a-Si vs. a-Si:H

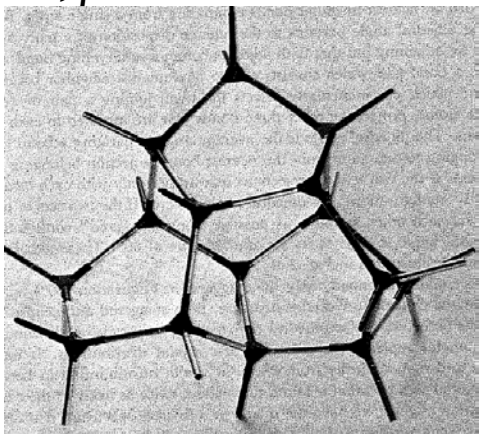
Ex. Is a-Si optimally coordinated?

$$\frac{M_0}{N} \approx 3 - \left[\frac{\langle N_c^{Si} \rangle}{2} + (2\langle N_c^{Si} \rangle - 3) \right]$$

$$= 3 - \left\{ \frac{4}{2} + (2 \times 4 - 3) \right\} = -4.$$

A-Si is highly overcoordinated , prone to defect formation

R.C. Street, Hydrogenated a-Si, p. 39.



Ex. At what value of x, is $Si_x H_{1-x}$ optimally coordinated?

$$\frac{M_0}{N} \approx 3 - x\left[\frac{\langle N_c^{Si} \rangle}{2} + (2\langle N_c^{Si} \rangle - 3) \right] + (1-x)\frac{\langle N_c^{H} \rangle}{2}$$

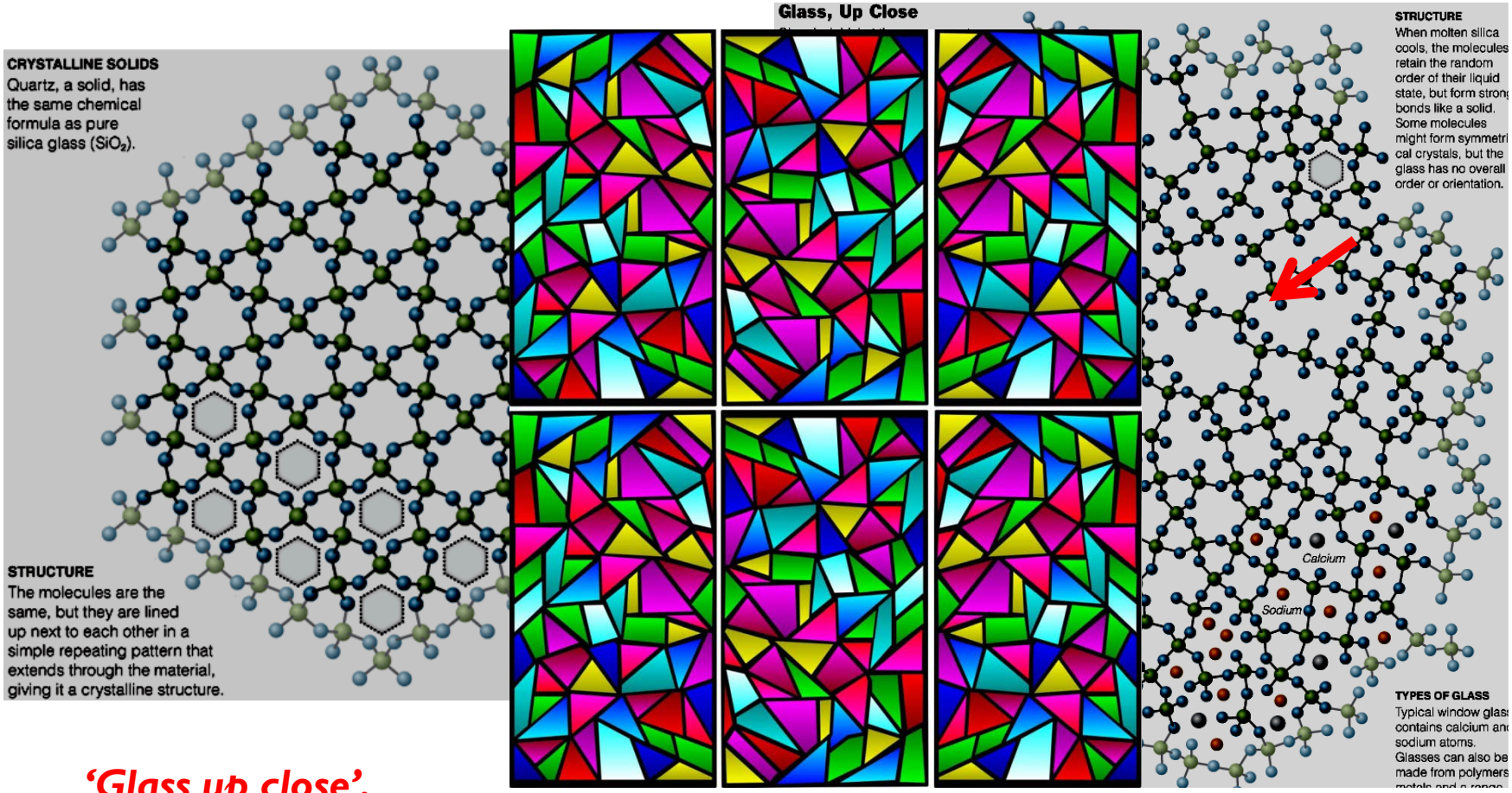
$$= 3 - x\left[\frac{4}{2} + (2 \times 4 - 3) \right] + (1-x)\frac{1}{2}$$

$$0 \Rightarrow 7x + (1-x)/2 = 3 \quad x = \frac{2.5}{6.5} = 40\%$$

Typically 10% H

$$\langle N_c^{SiH} \rangle = 0.9\langle N_c^{Si} \rangle + 0.1\langle N_c^{H} \rangle = 3.7$$

Crystalline vs. amorphous oxides

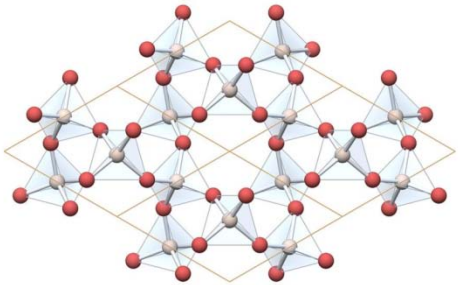


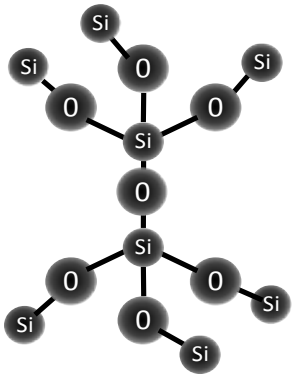
'Glass up close',
NY Times, July 29, 2008.

Purple: Nickel oxide
Blue: Cobalt oxide
Yellow/blue-green: Iron oxide
Cherry Red: Gold oxide

Bulk defects E' center

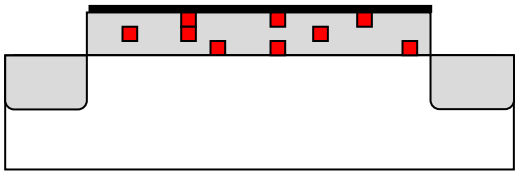
Courtesy:
Prof. Lenahan





(a) Vacancy free SiO_2

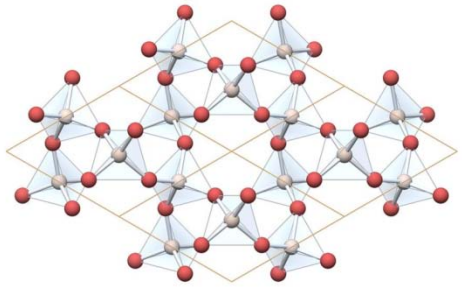
er

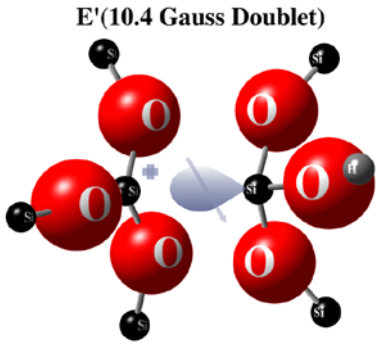


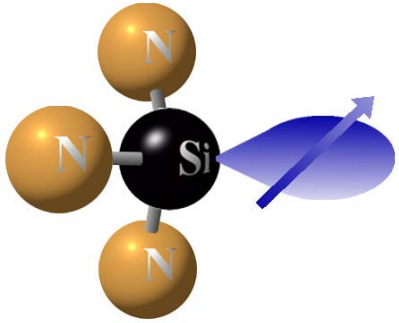
Responsible for gate dielectric breakdown as well as trapped charges

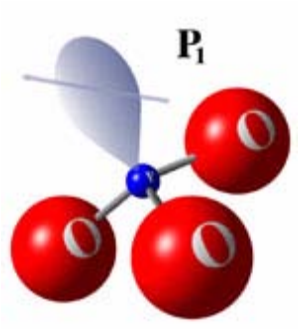
Bulk defects of missing Oxygen: E', K, and P defects

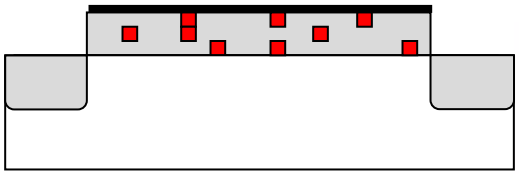
Courtesy: Prof. Lenahan

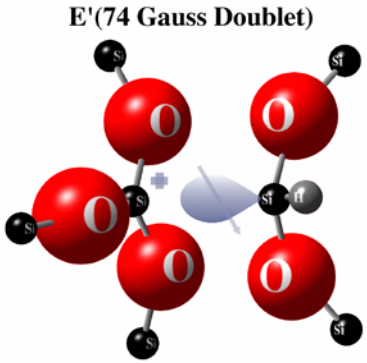


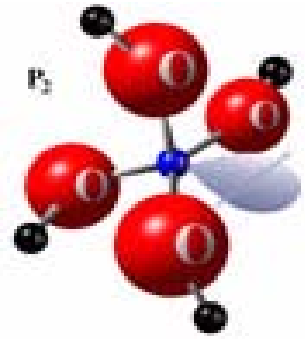


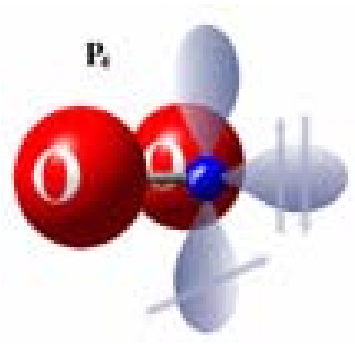












Responsible for gate dielectric breakdown

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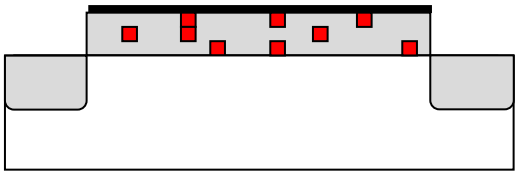
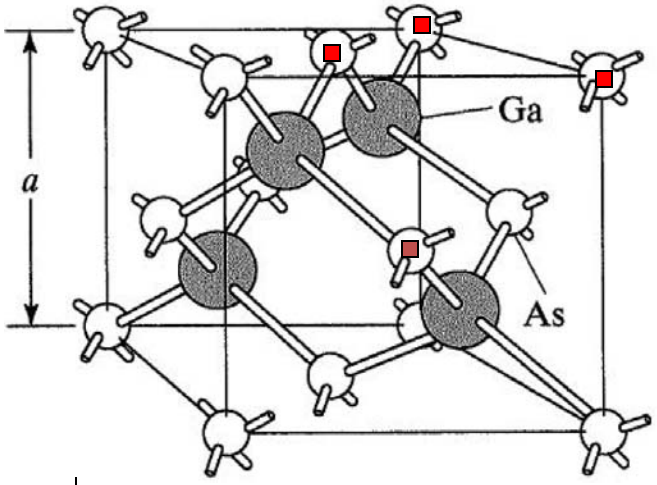
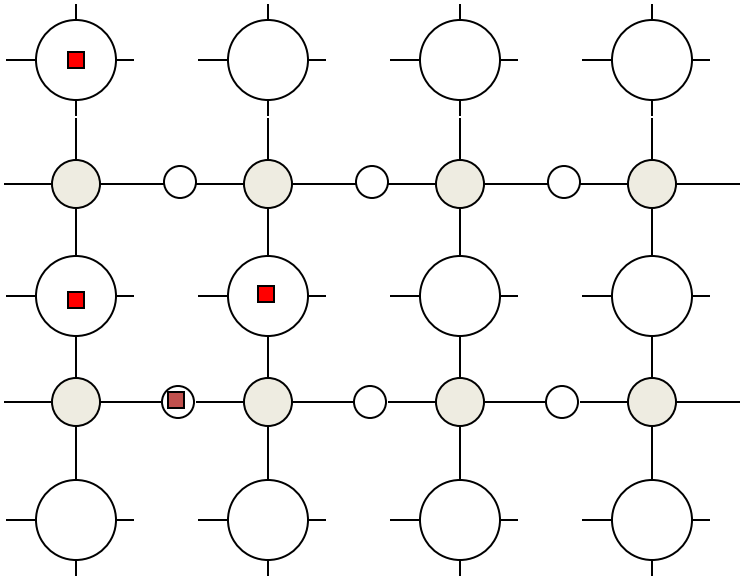
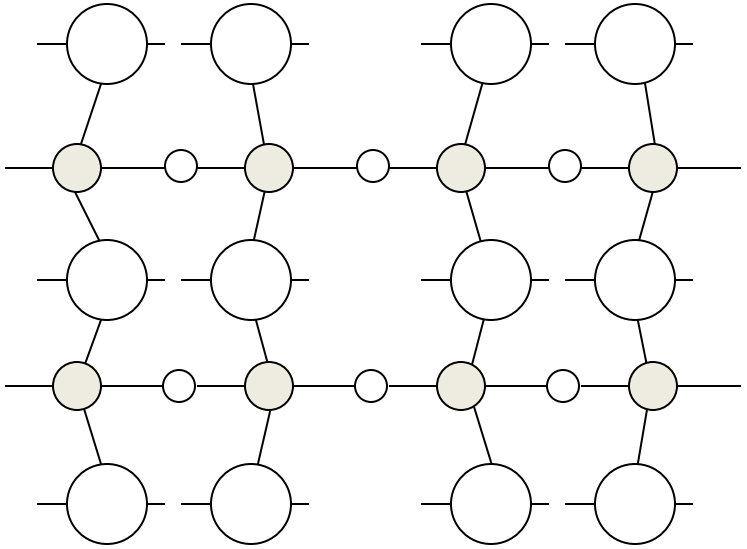
Surface reconstruction





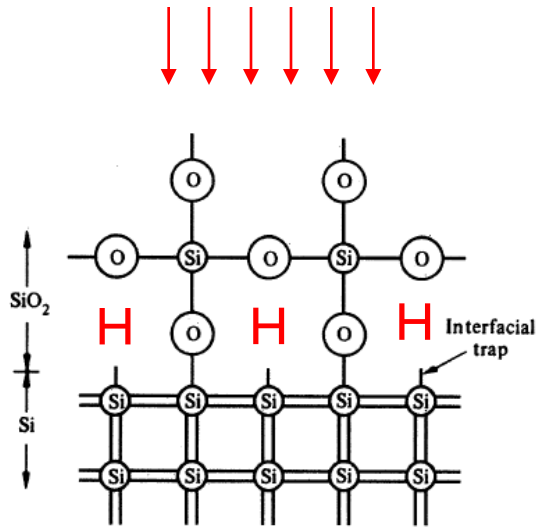
High defect density

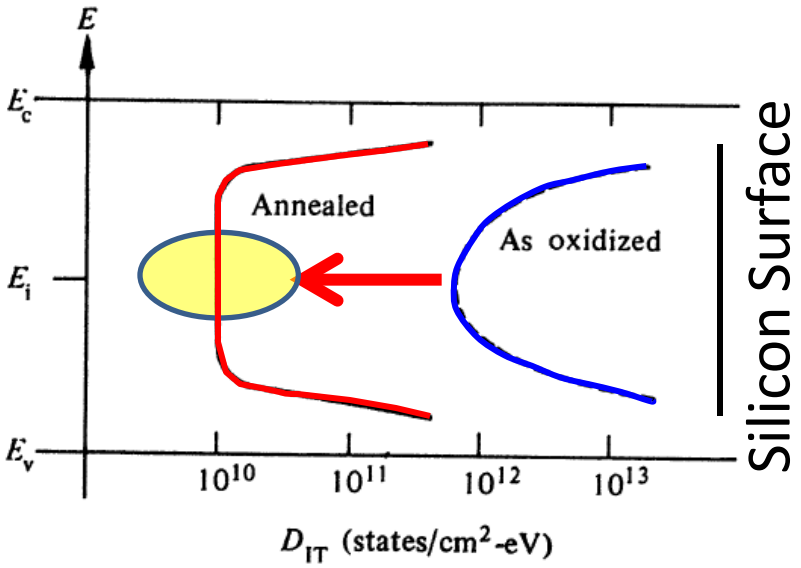


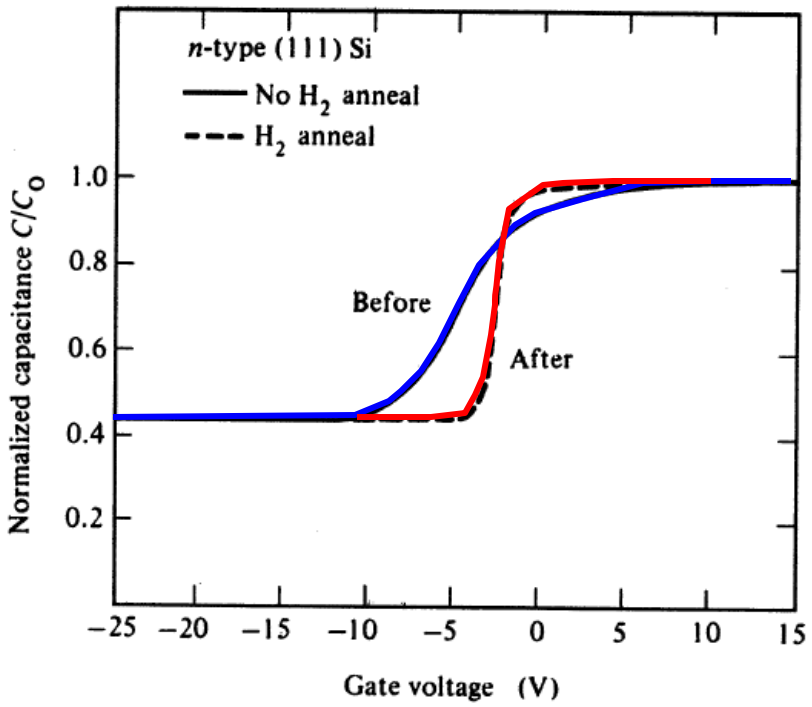


C-V Stretchout, interface defects, and Andy Grove

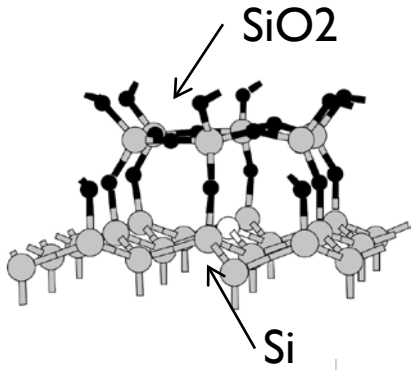
Forming gas anneal







Example: Si/SiO2 interface is strained



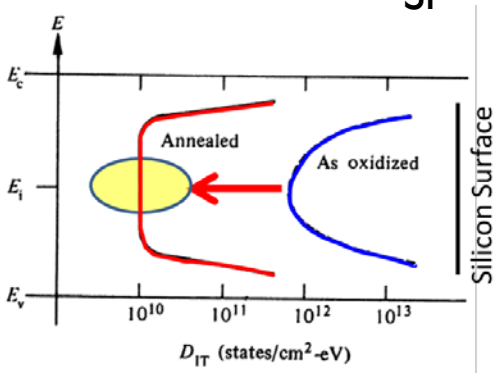
Consider 1 monolayer of Si/SiO2 at the interface

(0.5 monolayers of each: 0.5 atoms of Si/1.5 atoms of SiO2)

(1) Silicon is highly over-coordinated, because …

$Si \rightarrow 0.5 \times N_{Si} = 0.5 \times 4 = 2$ bonds.

Average bonds = 2 bonds/0.5 = 4



(2) SiO2 is optimally coordinated …

$SiO_2 \rightarrow 1.5 \times (0.33 \times 4 + 0.66 \times 2) = 4$ bonds.

Average bonds $\rightarrow$ 4 bonds/1.5 atoms = 2.66

(3) Si/SiO2 is over-coordinated, so prone to defect formation …

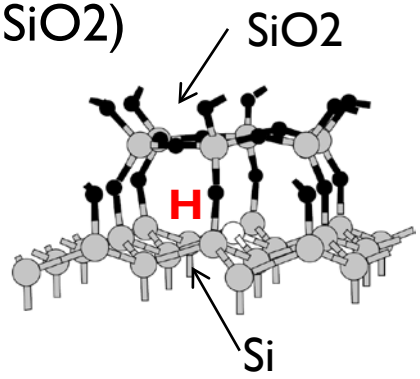
Average coordination at the interface

$\rightarrow (4+2)$ bonds/(1.5 atoms+0.5 atoms) = 3.

Hydrogenation improves Si/SiO2 interface

Consider 1 monolayer of $Si_{0.9}H_{0.1}/SiO_2$ at the interface

(0.5 monolayers of each: 0.5+0.05 atoms of Si and H/1.5 atoms of SiO2)



(4) SiH/SiO2 is relaxed, with reduced defect density

$$Si_{0.9}H_{0.1} \rightarrow 0.55\times(0.9N_{Si}+0.1N_H)=2.03 \text{ bonds.}$$

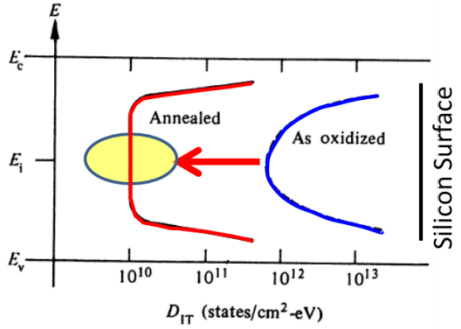
$$SiO_2 \rightarrow 1.5\times(0.33\times 4+0.66\times 2)=4 \text{ bonds.}$$

Average coordination

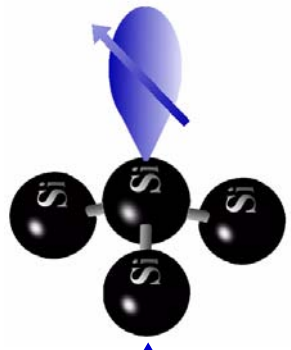
$\rightarrow$ 6.03 bonds/(1.5 atoms+0.55 atoms) =2.94

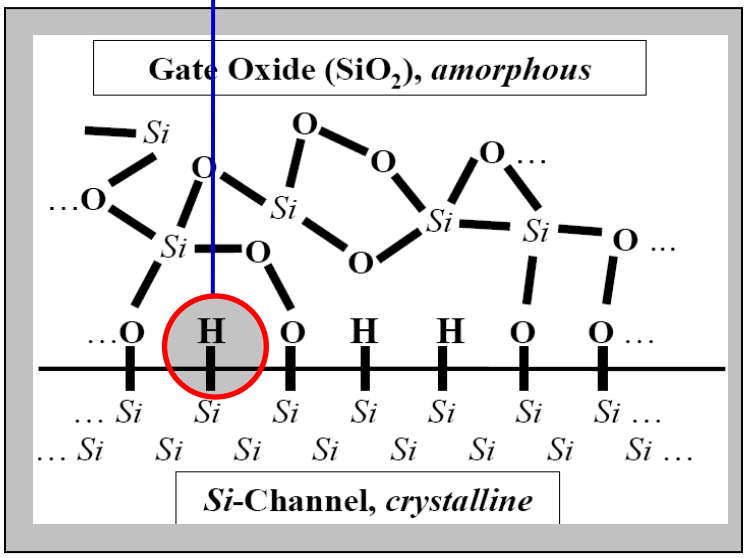
To conclude, defects at interface

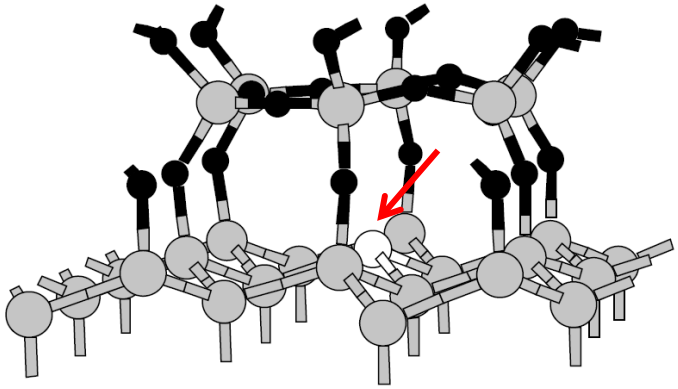
SiO2 < $SiH\text{-}SiO_2$ < $Si\text{-}SiO_2$ < Si



Pb centers – interface traps

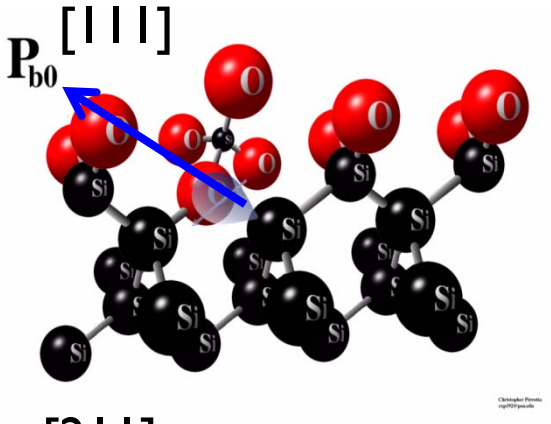




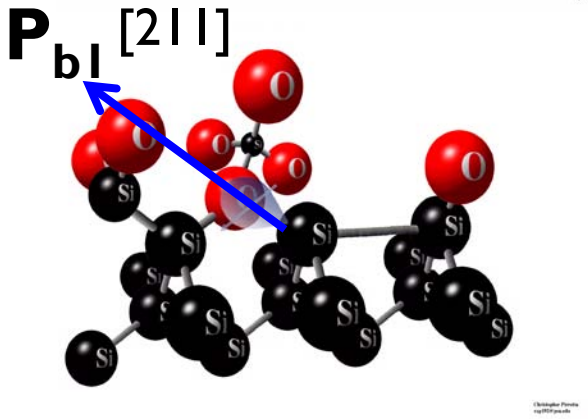


[111] surface
P_b along [111]

Stirling, PRL, 2000.



[100] surface
Pb_0 along [111]



[100] surface
Pb_1 along [211]

Of Pa, Pb, Pc -- only Pb survives
Related to NBTI degradation

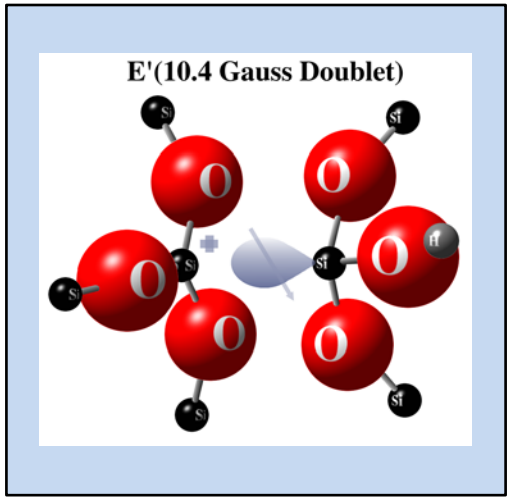
Outline

1. Strain in materials/origin of defects
2. Examples: bulk defects
3. Examples: interface defects
4. Measurements
5. Conclusions

Electron spin resonance: a 'microscope' for defects

10 GHz Microwave

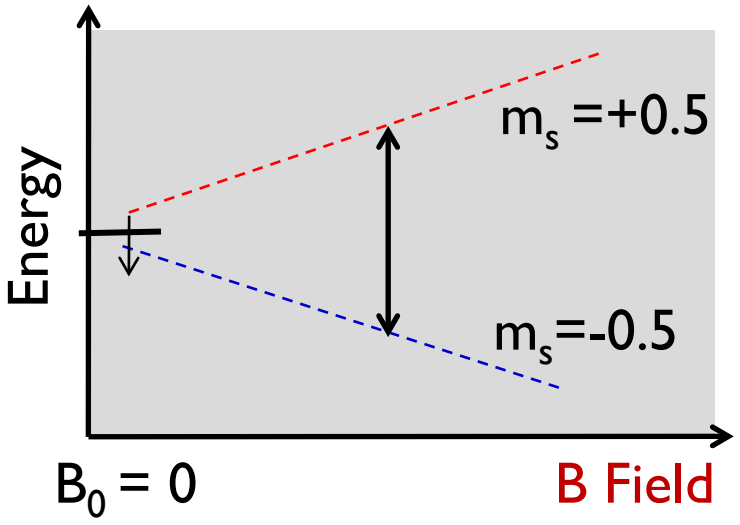
Variable B-field



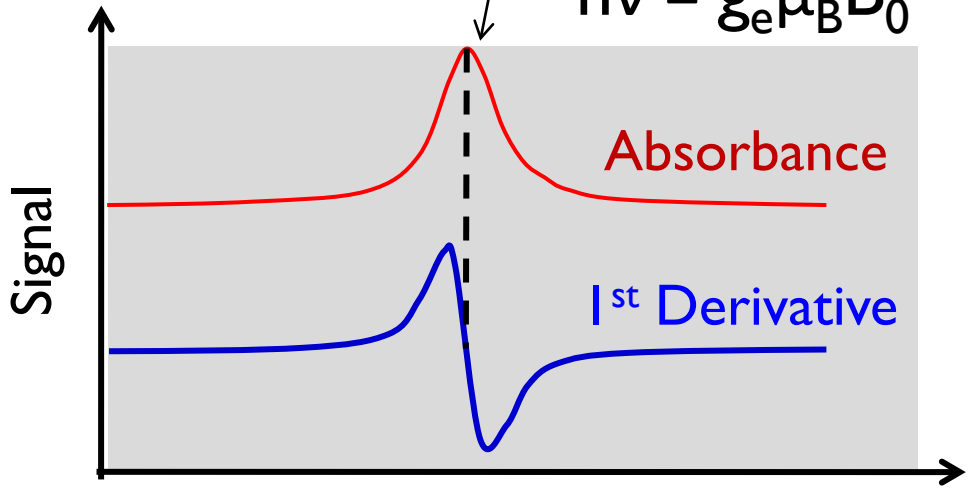
Absorption spectra

B-value suggests local environment

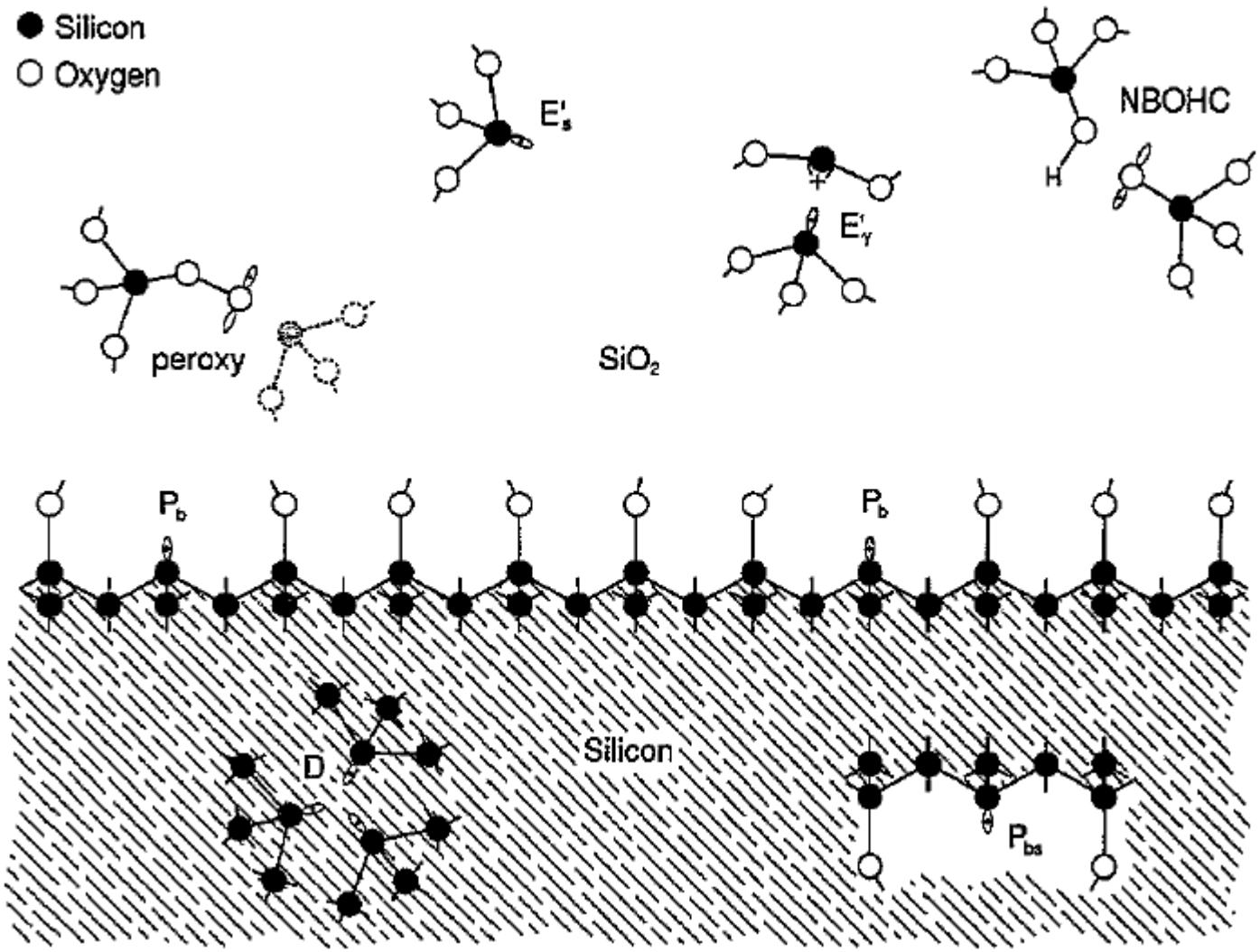
$\Delta E = g_e \mu_B B_0$



$h\nu = g_e \mu_B B_0$



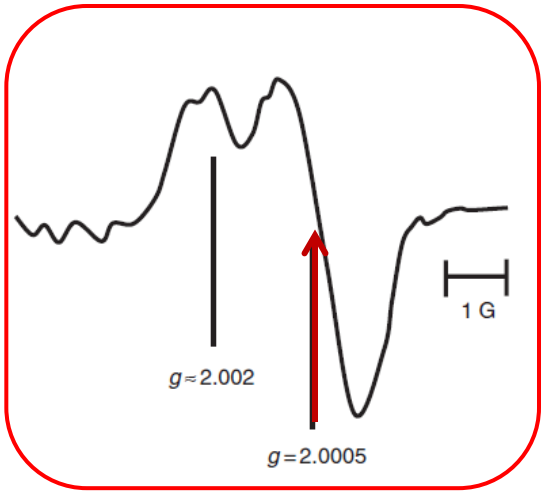
Different types of ESR-visible defects

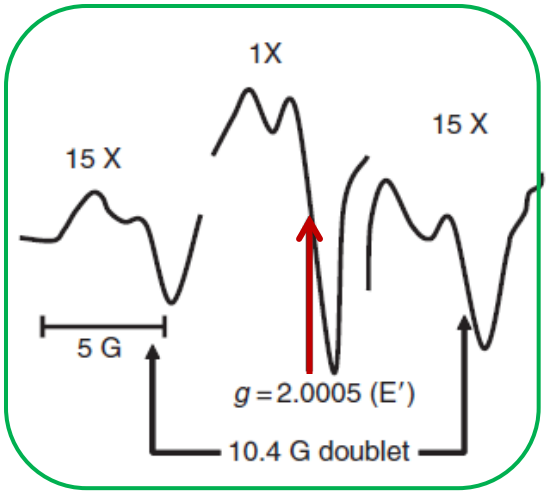


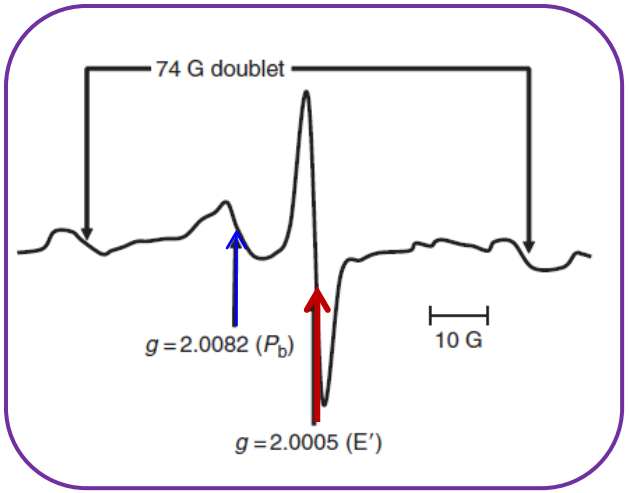
Nonbridging oxygen hole center

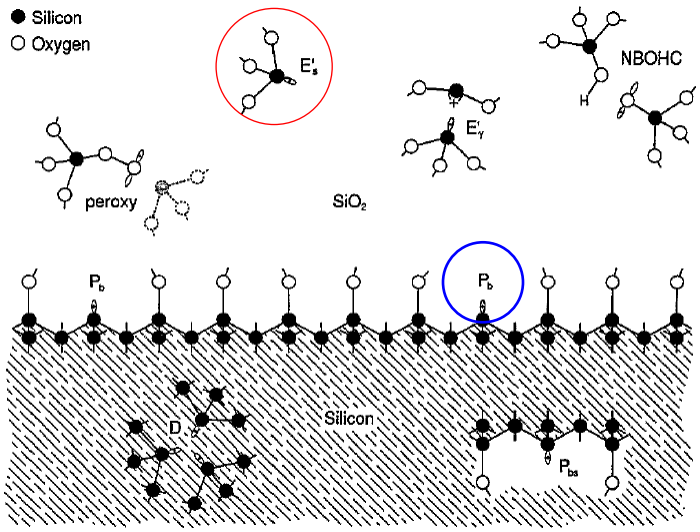
Helms and Poindexter, 1994.

ESR signature of different defects



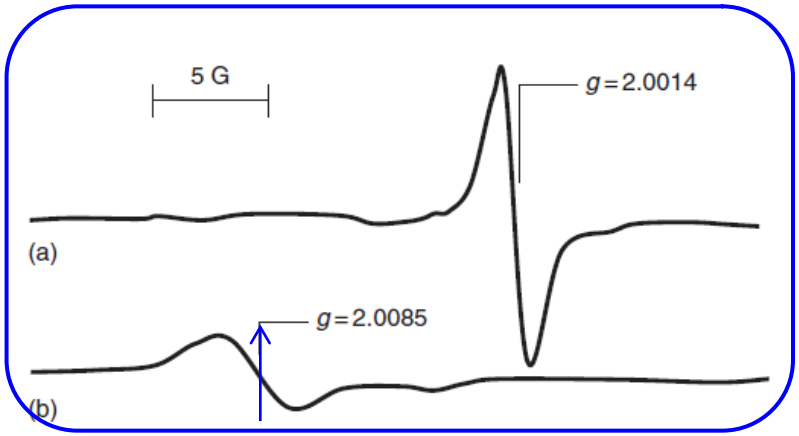




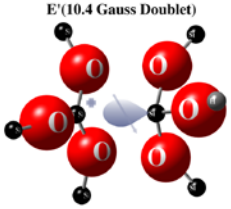


P. M. Lenahan, 2004.

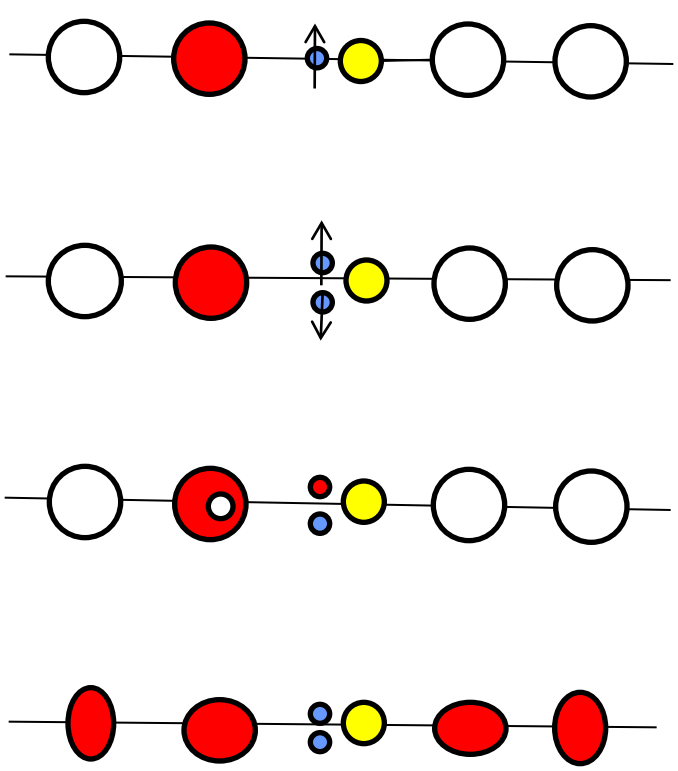
Pb parallel and perpendicular to <111>



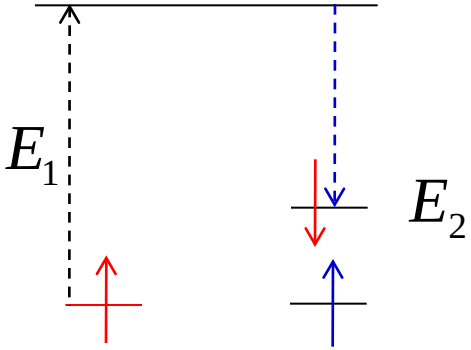
ESR invisible defects (negative U traps)



Paramagnetic materials may appear diamagnetic



$$D_0 + E_1 = D^+ \qquad D_0 - E_2 = D^-$$



$$2D_0 + (E_1 - E_2) = D^+ + D^-$$

$$2D_0 + (E_1 - E_2) - U_{e-h} = D^+ + D^-$$

Like superconductivity with phonon assisted e-e attraction

Conclusions

- Maxwell relationship anticipates bulk and interface defects as a consequence of excessive coordination. In SiO2, bulk defects are called E' centers and at the Si/SiO2 interface, interface defects are called Pb centers.
- The theory also explains how small atoms like H relaxes the structure and reduces defect density.
- Determining the precise number of angle constraints is sometime difficult. If the angle are very floppy, we assign the constraint to zero as an initial guess.
- Electron spin resonance (ESR) techniques are often used to determine types of defects in a systems. There are ESR-invisible many body defects that can be detected by other methods.

References

- A. Stirling et al., Dangling bond defects at Si-SiO2 interfaces: Atomic structure of the Pb1 center, PRL, 85(13), p. 2773, 2000.
- A. Bongiorno, Transition structure at the Si(100)-SiO2 Interface, 18, 186101, 2003.
- A nice review by C. R. Helms and E. H. Poindexter, "The silicon-silicon dioxide system: its microstructure and imperfections," Rep Prog Phys 57 791-852, 1994. P.M. Lenahan is well known for his work on defect characterization by ESR For example see his chapter in "Defects in Microelectronic Materials and Devices" edited by Fleetwood, 2004.
- First-Principles Investigations of Low Energy E' center Precursors in Amorphous Silica, PRL, 106, 206402, 2011 provides a sophisticated MD-DFT perspective of these defects. Another review by J. Robertson, "Interfaces and defects of high-K oxides on Slicon, Solid State Electronics, 49, 283,2005.

Review questions

G1: Why do we not account for angle constraint in for oxygen in SiO_2?

G2: Explain why amorphous structures actually have fewer types of defects

G3: If you needed to calculate HfO_2/SiO_2 interface properties – How many monolayers of atoms should you consider in HfO_2 side?

G4: What is the difference between a Pb center and E' center?

G5: Support the statement that "Hydrogen incorporation in c-Si makes the structure amorphous".

G6: 10.4 GHz doublets and 74GHz doublet indicates the backbonding of which atom?

G7: Name a technique other than ESR that might be used to characterize defects?

G8: Why is negative U traps invisible to ESR?