nano-scales order in non-crystalline oxides: strain minimizing chemical bonding self-organizations in SiO2

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*presented by [1]Wenchang Lu, NCSU

i) non-crystalline SiO$_2$

fused silica (glass) high-quality optical material for lenses
**no strain induced birefringence**

thin film - thermally grown SiO$_2$ on Si - gate dielectric of choice
for field effect transistors until ~ 1990
scaled from > 1000 nm to 15 nm with excellent performance low
defect density, excellent e interface
but, increased tunneling leakage ~ 1 A/cm^{-2} for
1.5 nm thickness limited further scaling

vacuum ultra-violet reflection features at same photon
energies in crystalline a-quartz and SiO$_2$ glass

# VUV reflectivity features of crystalline SiO₂ (α-quartz) and glass (fused silica)SiO₂ at same photon energies*
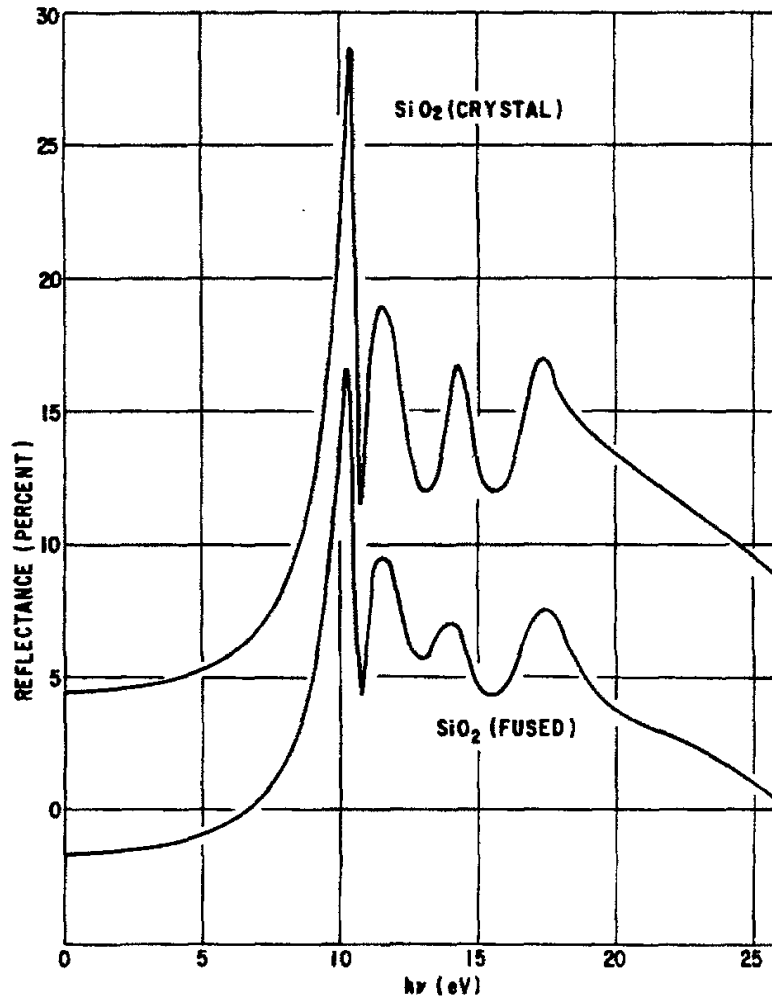
photon energies from VUV

10.2 , 11.7, 14, 17 eV (± 0.3 eV)

same energies observed in other spectroscopic studies of non-crystalline SiO₂**

additionally in Griscom review

band-gap of non-crystalline SiO₂

8.9 ± 0.2 eV

*HR Phillipp - *Solid State Commun.* 4, 73 (1966)

**DL Griscom, *J. Non-Cryst. Solids* 24, 155 (1974)

results from Lucovsky group -- X-ray absorption spectroscopy of deposited and annealed thin films

1.5 nm to 10 nm thick deposited by remote plasma CVD on Si and annealed at 900°C in Ar
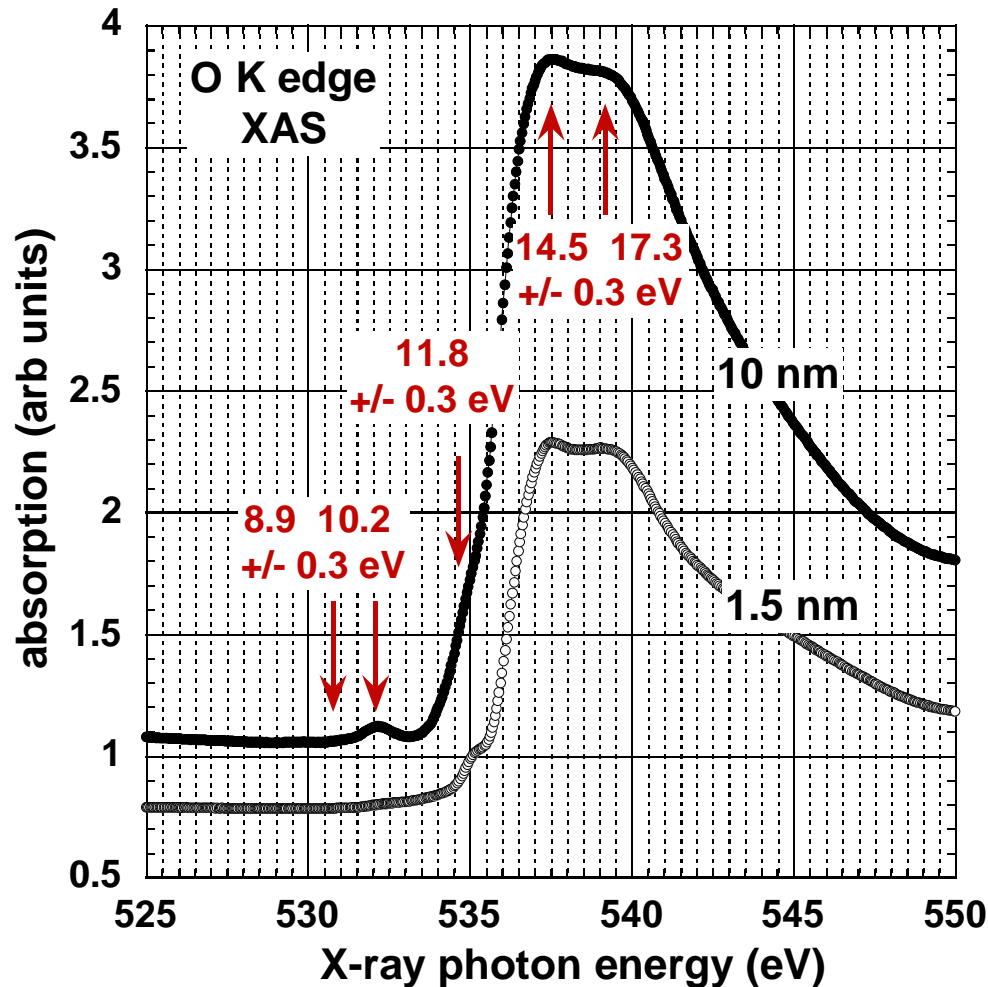
features at same energies as glass and crystal

from minima in 2nd derivative of XAS absorption

Issues *addressed and answered* in this presentation

➔**What is the scale of order for optical properties ?,**

➔**What is the limiting thickness for thin film SiO_2 to be "SiO_2"?**

➔**Can limiting thickness be related to fundamental electronic structure, if so on what length scale?**

➔**Why is non-crystalline SiO_2 strain free? and**
➔**What is scale of order?**

X-ray diffraction I

approach for amorphous solids*

determine radial distribution function

pair correlations between nearest, next-nearest neighbors

ball and stick modeling > 500 atoms

compare RDF with experiment and
obtain partial pair correlations from
short range order (SRO),
into medium range order (MRO) regimes

computer modeling*

substantially the same as Bell and Dean

*R Zallen, Physics of Amorphous Solids, 1983
**RJ Bell and P Dean, Nature, 1966; Phil Mag, 1972
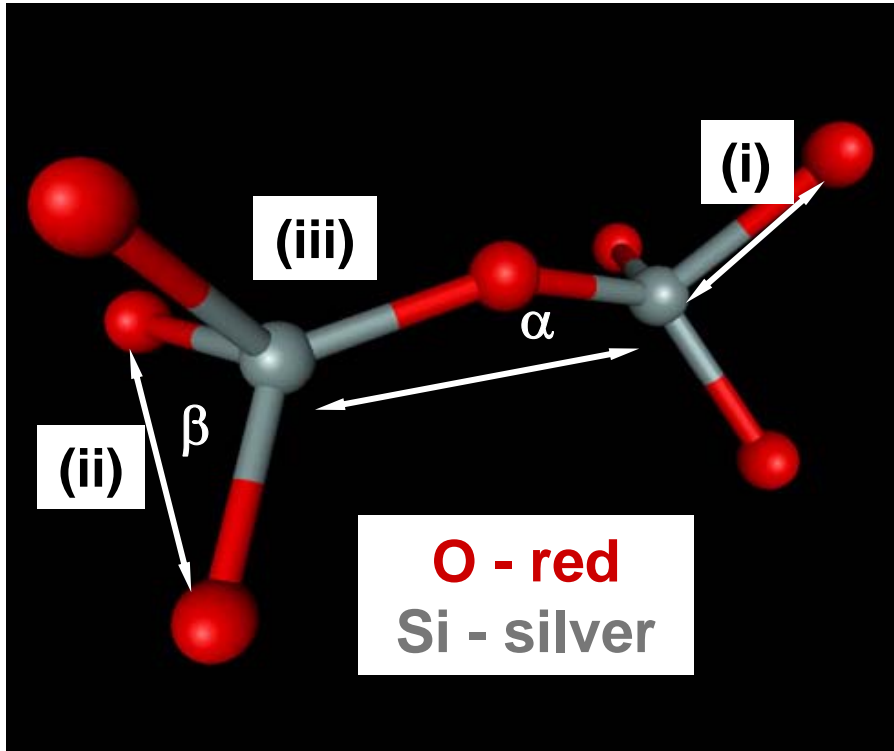***A Tadros, G Lucovsky and MJ Klenin, J Non-Cryst Solids 1983,1984

nano-regime length scales for non-crystalline oxides

short range order - bond-lengths and bond-angles

bond-lengths - 1st nearest neighbors
bond-angles - 2nd (next) nearest neighbors
combine first and second nearest neighbors ➜ bond angles

O - red
Si - silver

(i) Si-O 1st neighbor distance

combined with

(ii) Si-Si and (iii) O-O
2nd neighbor distances

equivalent to
Si-O-S and O-Si-O
bond-angles - α and β,
respectively

SiO$_2$ diffraction (Mozzi and Warren)
Si-O ~ 1.6Å
O-O ~ 2.6Å - β ~ 109 degrees
Si-O ~ 3.1Å - α ~ 145 degrees

comparison between RDFs - ball and stick from continuous random network (CRN) model of Bell & Dean and experimental x-ray RDFs

SRO <0.35 nm (3.5Å)

first peak
Si-O bond length
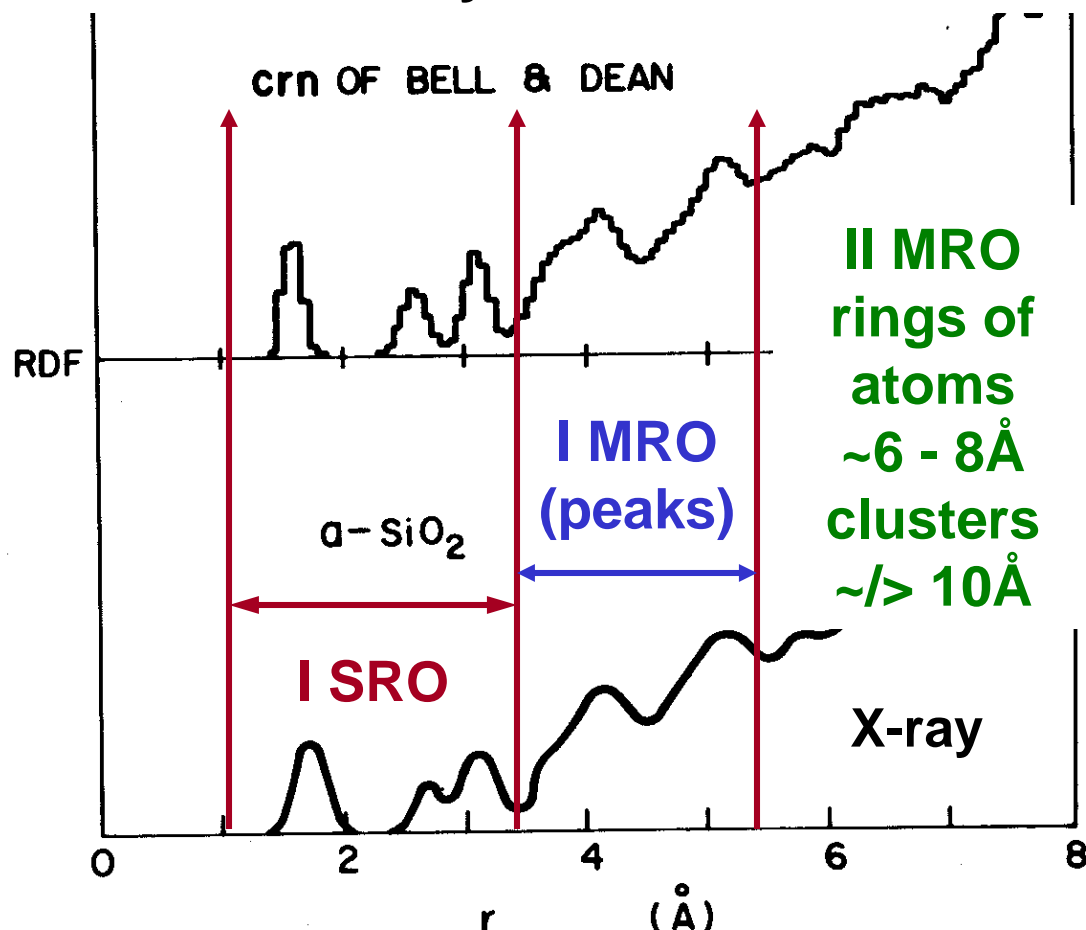
second and third peaks
2nd neighbor distances

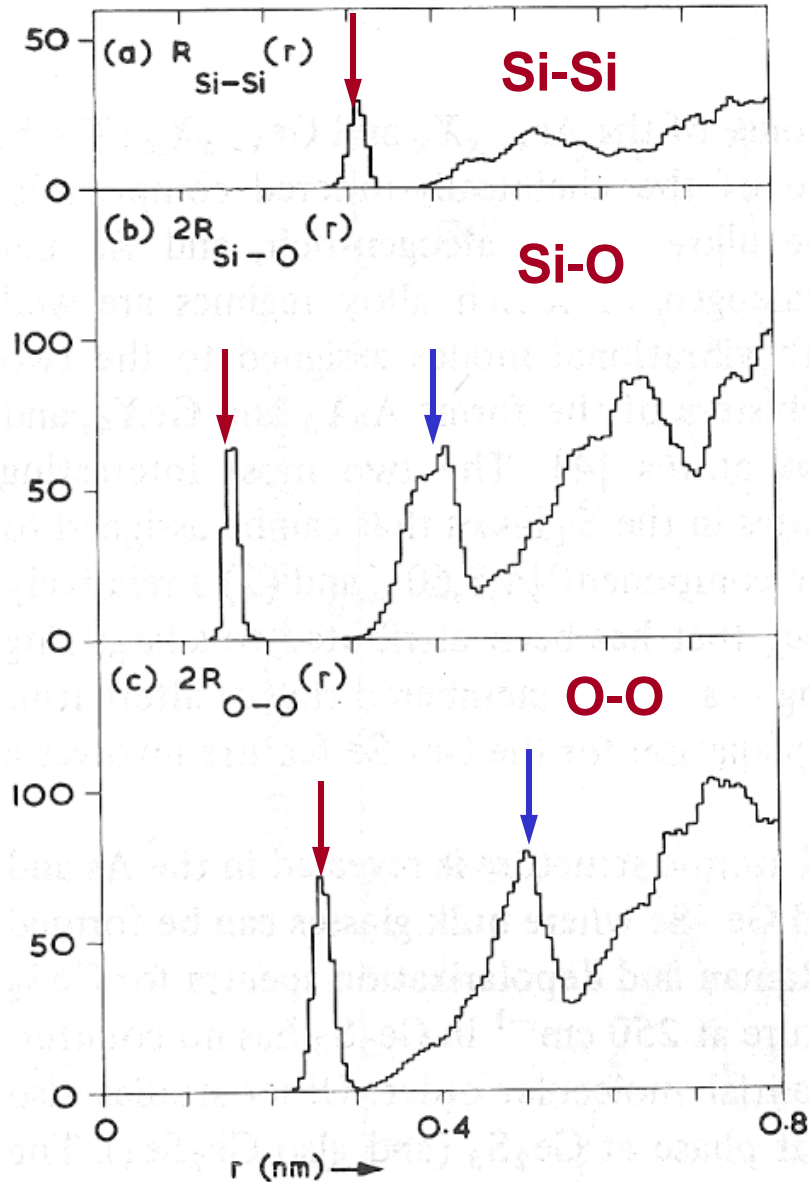**i) O-O ➡ O-Si-O bond angle**

ii) Si-Si ➡ Si-O-Si bond angle

additional peaks

discussed on next slide

radial distribution function from x-x-ray diffraction

crn OF BELL & DEAN

RDF

a-SiO$_2$

I SRO

I MRO (peaks)

II MRO rings of atoms ~6 - 8Å clusters ~/> 10Å

X-ray

r (Å)

partial pair distribution functions for Si-Si, Si-O and O-O

first peak in pair correlation functions

from nearest neighbor shells - SRO - red arrows

second peak in pair correlation function for Si-O, O-O - more distant neighbors - MRO - blue arrows will show these contribute to first sharp diffraction peak, FSDP

0.6 - 0.8 nm and beyond these features are *associated with* 5, 6 and 7 member rings

by definition medium range order (MRO)
is order beyond bond-lengths and bond angles
type I MRO with sharp diffraction features in last slide, and
Si-O and O-O distances below
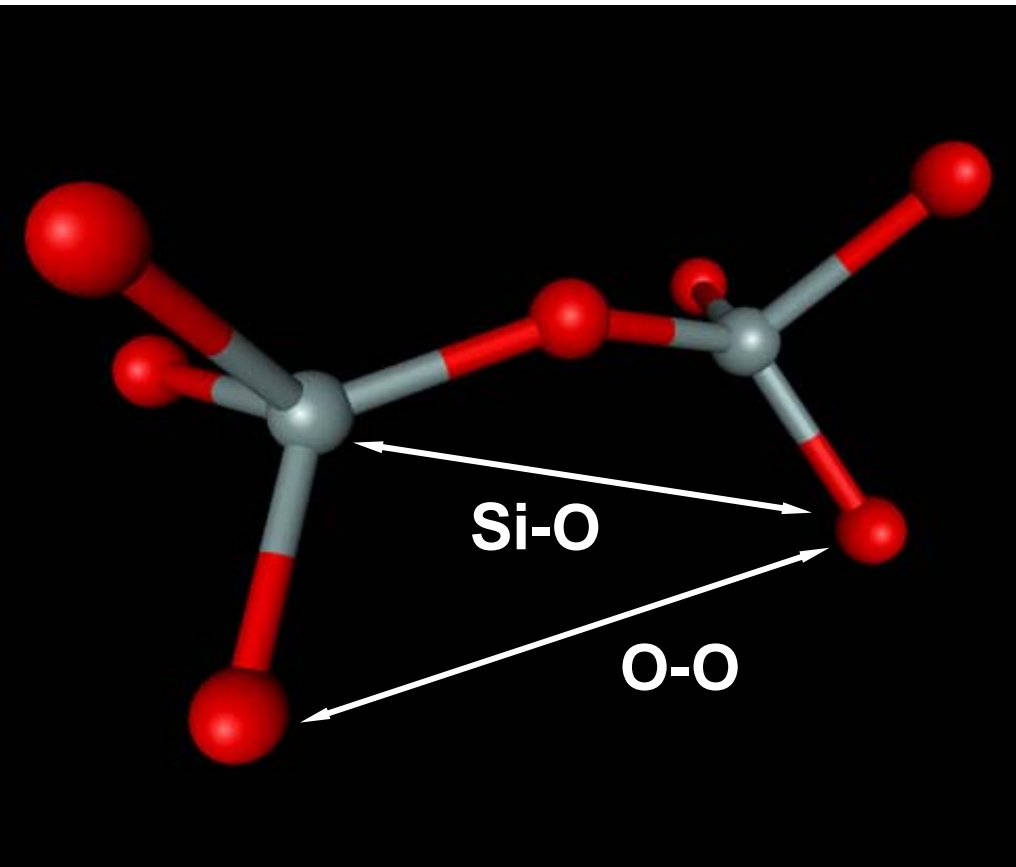
**Si-O, and O-O distances
in this cluster *can be*
ring segments**

**are they all equivalent, or
are they random and change
with dihedral angles ?**

**CRN network model and
*conventional wisdom***

**dihedral angles random - not
likely that they contribute to
contribute to MRO**

**wrong - not consistent with
electronic structure**

they are equivalent!

introduction to FSDP

what is the first sharp diffraction peak, FSDP?

1st peak in Fourier transform of diffraction intensity

why has it received so much attention? *medium range order-MRO*

real space distances beyond nearest and next nearest neighbors

part of answer was there all the time for SiO_2

the Bell and Dean "ball and stick model" 1967-1972

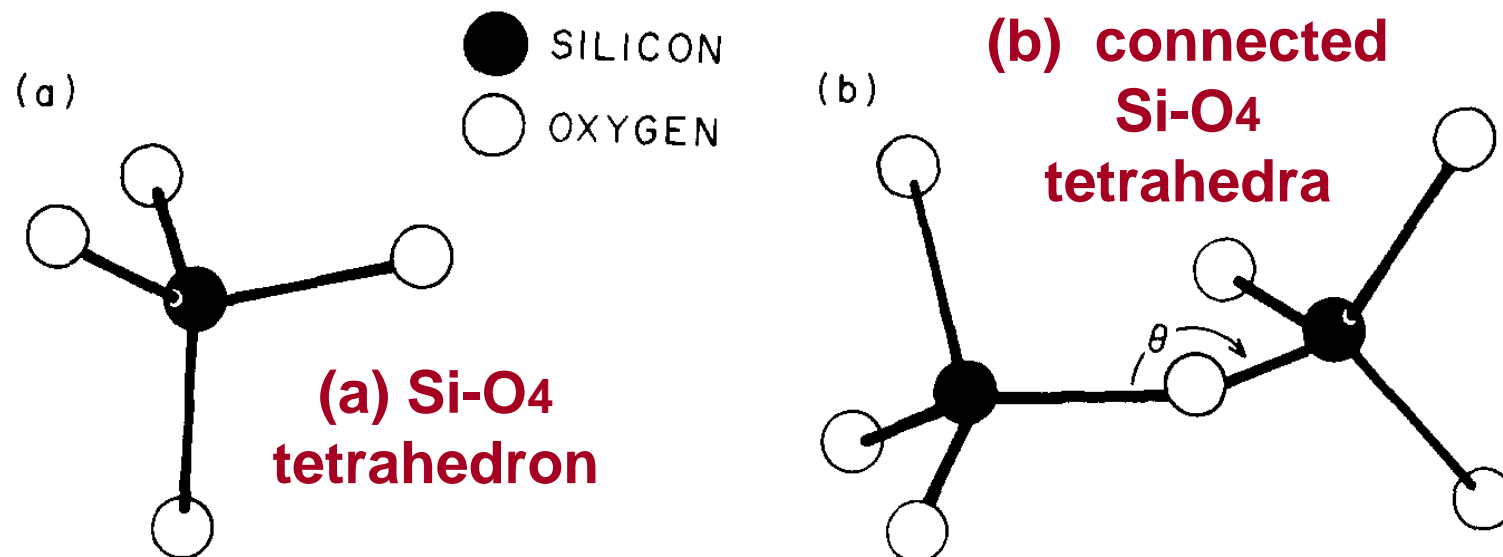**model calculations of (i) Tadros, Lucovsky and Klenin, NCSU**
and also (iii) the Gaskell group at Cambridge

all revealed MRO in SiO_2

A STRUCTURAL MODEL FOR AMORPHOUS SiO₂ INCLUDING THE EFFECTS OF INTERMEDIATE RANGE ORDER

A. TADROS, M.A. KLENIN and G. LUCOVSKY

(b) connected Si-O₄ tetrahedra

(a) Si-O₄ tetrahedron

paper considered ring structures, and arrangements in (b) three terminal O-atoms were either staggered or eclipsed

important for symmetry determined alignments source of MRO - in next group of slides

the first sharp diffraction peak (FSDP)

the FSDP in the structure factor, S(Q), has been determined from X-ray and neutron diffraction studies of oxide, silicate, germanate, borate and chalcogenide glasses

consensus that the position and width of the FSDP feature derive from medium range order, MRO, order extending beyond the length scale of nearest- and next-nearest neighbor distances

there has been much speculation, not supported by diffraction theory, and/or electronic structure, regarding the microscopic nature of the local atomic bonding in MRO regime, e.g., rings of bonded atoms, inter-layer distances, and/or void clustering.

➡ however, one paper by Moss and Price on the next slide *gets it completely correct*, and
provides the basis for interpretation of FSDP in the structure factor S(Q)

basis for the interpretation of structure factor for SiO_2 and other glasses, and non-crystalline solids in general

Moss and Price*, have noted that the position of the FSDP, Q_1(Å^{-1}), "can be related, via an approximate reciprocal relation, to a distance R in real space by the expression $R = 2\pi/Q$".

"such a diffraction feature (the FSDP) thus represents the build up of correlation whose basic period is well beyond the first few neighbor distances" the SRO, and

"In fact, the width of this feature is used to estimate a correlation range over which the period in question survives"

*S.C. Moss and D.L. Price: in Physics of Disordered Materials, edited by D. Adler et al. (Plenum Press, New York, 1985), p. 77.

first sharp diffraction peak in structure factor - SiO_2
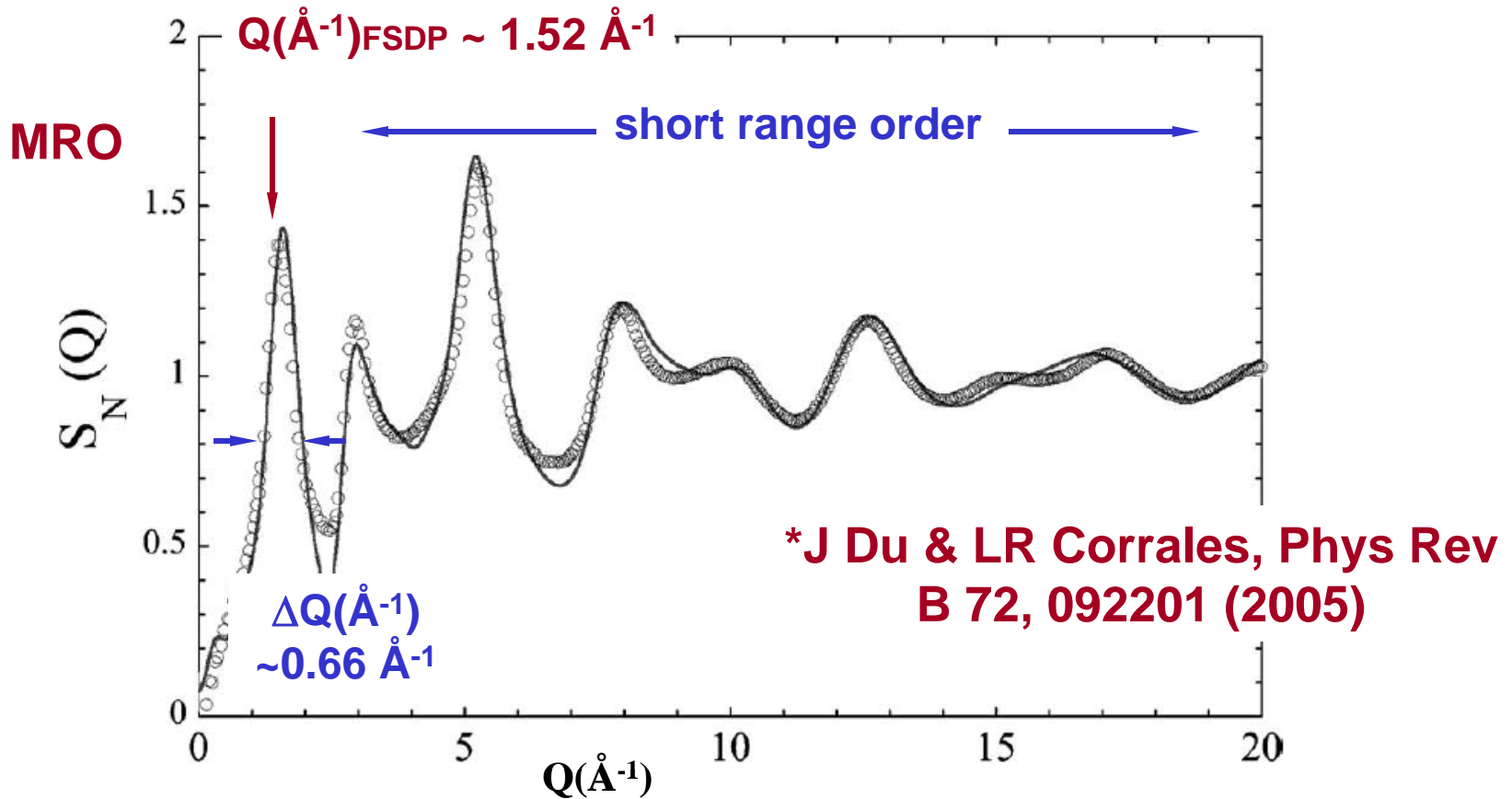
$S_N(Q)$ is Fourier transform of diffraction intensity

two MRO length scales

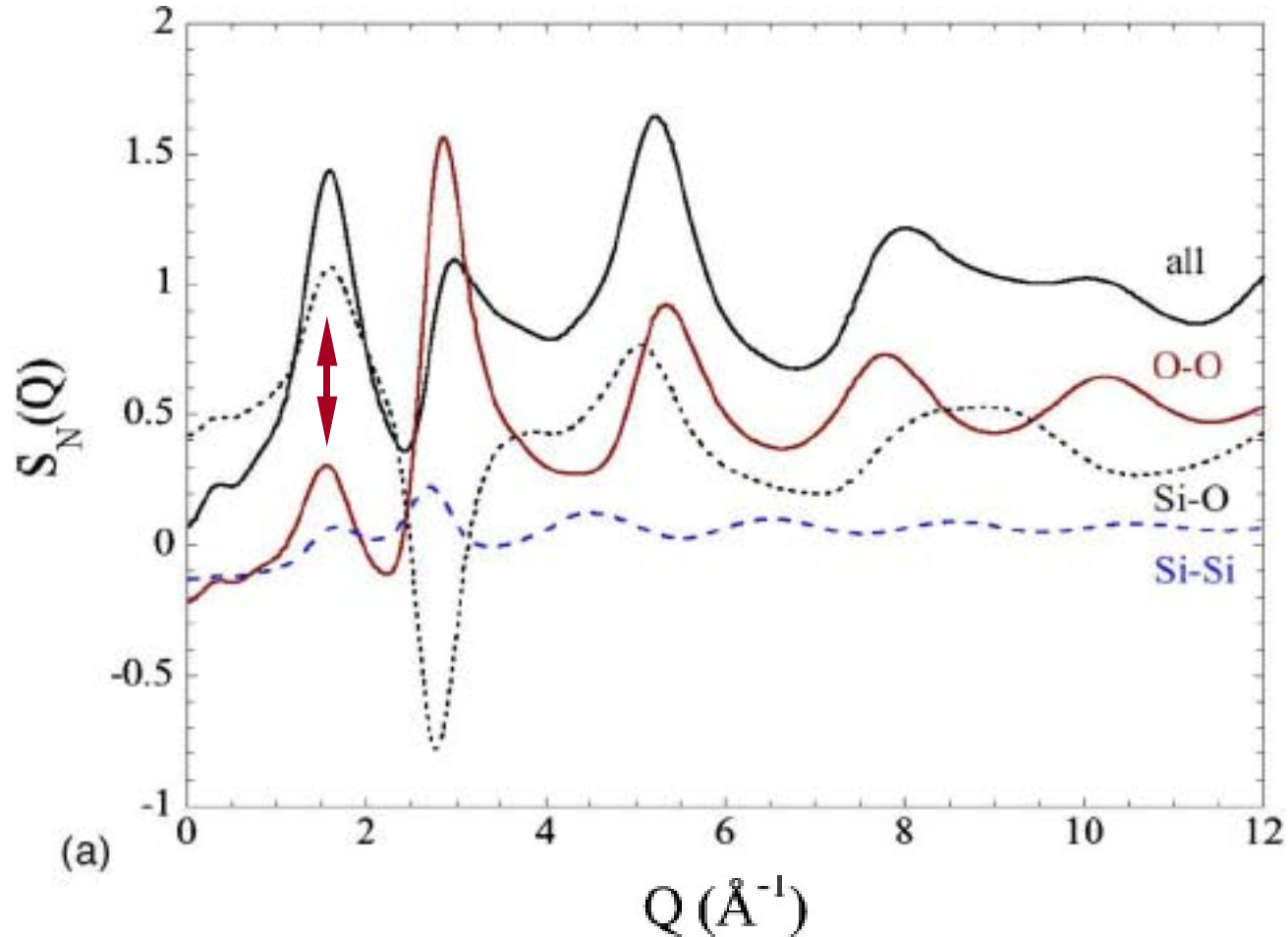correlation length, $\lambda_{corr} \sim 2\pi / Q(\text{Å}^{-1})$, ~0.41 nm

coherence length ~ $\lambda_{coh} \sim 2\pi / \Delta Q(\text{Å}^{-1})$, ~0.95 nm

also, S Sussman...DL Price, Phys. Rev. B 43, 11076 (1991)
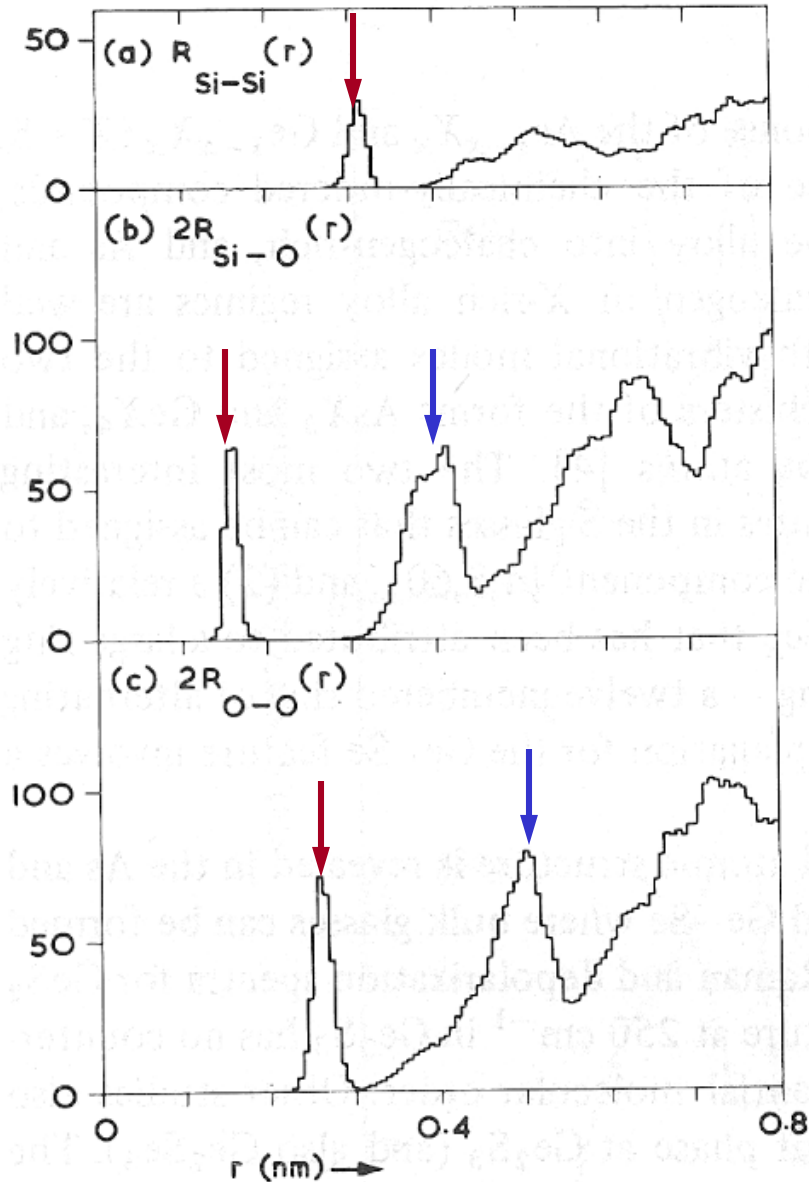
$S_N(Q) = \Sigma \; S_{N,ij}$ - $ij =$ O-O, Si-O, Si-Si

2 strongest partial structure factors contributors
O-O - solid red, Si-O ---- dotted black

(a)

analysis of Bell and Dean model -- Fourier components
length scale - which neighbors? in MRO beyond SRO

partial pair distribution functions for Si-Si, Si-O and O-O

first peak in pair correlation functions

from nearest neighbor shells - SRO - red arrows

second peak in pair correlation function for Si-O, O-O - more distant neighbors - MRO - blue arrows these contribute to first sharp diffraction peak, FSDP
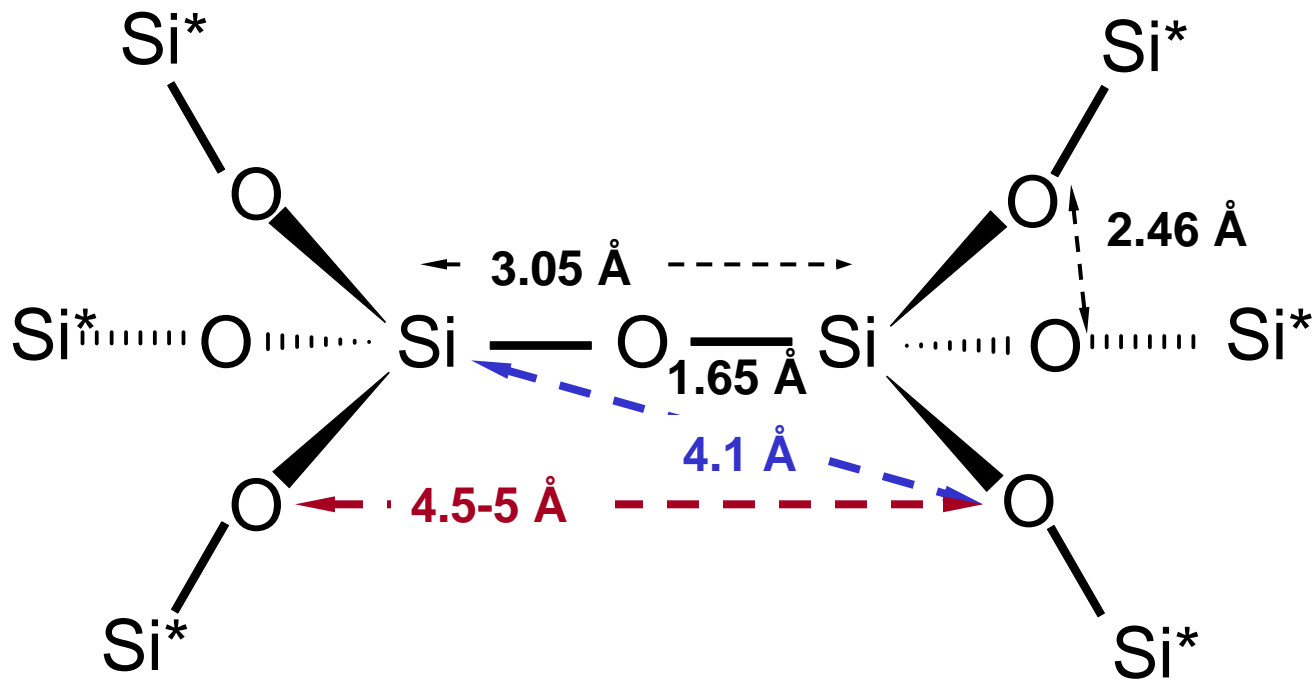
0.6 - 0.8 nm and beyond these features are *associated with* 5, 6 and 7 member rings and contribute to FWHM of FSDP

medium range order (MRO)

contribute to position of FSDP in structure factor as determined by partial structure factor analysis
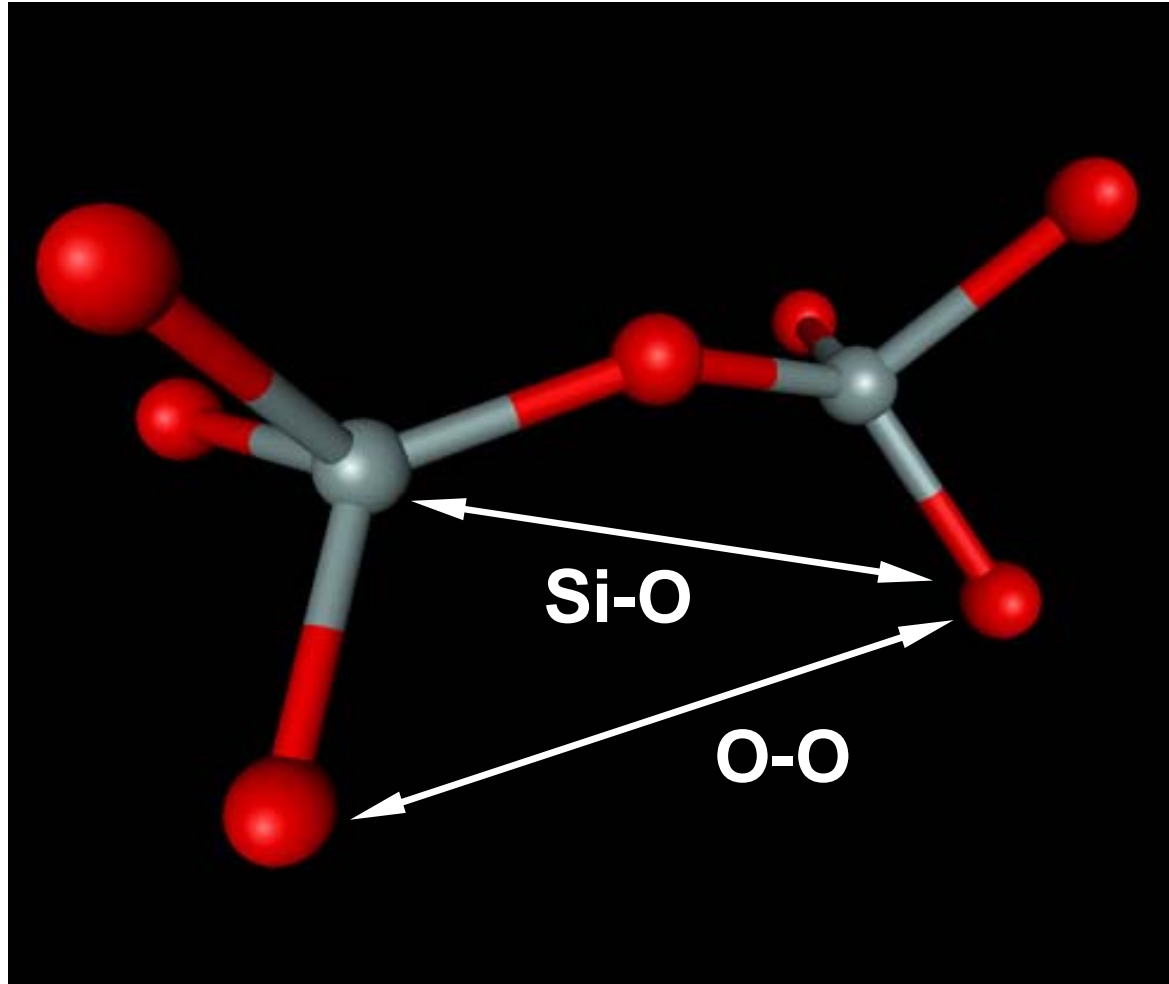
MRO bonding identifies
coherence length as determined from FSDP
partial structure factor analysis and Bell & Dean model

what is origin of correlation length features?

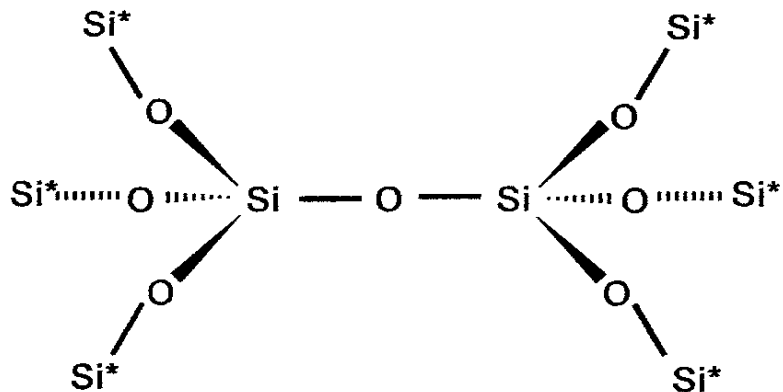**inherent in many-electron theory, ab initio cluster calculations for non-crystalline SiO2**

Fig. 2. Schematic representation of the Si–O–Si terminated cluster used for the ab-initio calculations of this paper. The Si–O–Si bond angle, α, is 180° in this diagram, and will be varied from 120° to 150° for the calculations. The Si* represent an embedding potential that Si core eigenvalues are correct.
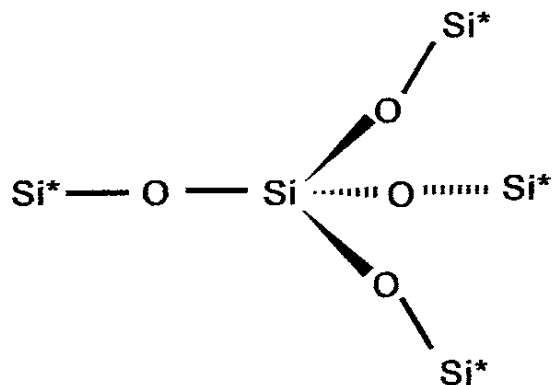

Fig. 3. Schematic representation of a second Si–O–Si cluster that establishes the validity of the embedding potentials, Si*.

calculations small clusters
Si–O–Si groups connected through O atoms to embedding Si atom terminators Si* emulating connectivity to SiO_2 continuous random network
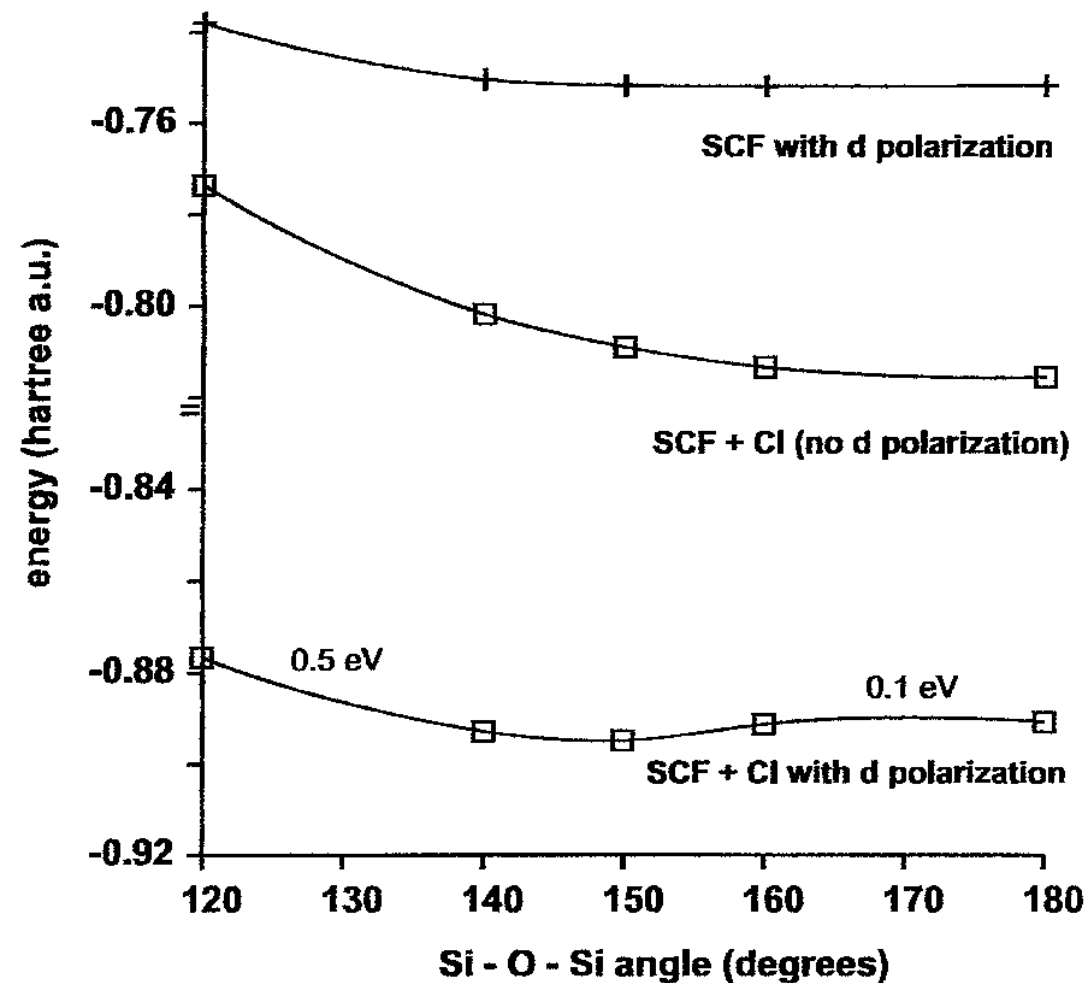
basis sets
Si s-type, p-type Gaussians, and Si $3d$ state
O s-, p-type Gaussians

test
Si* sp^3 hybrid pseudo-atoms correct core state energies zero dipole moments for clusters in Fig. 2 and Fig. 3

JL Whitten,...G Lucovsky, J. Vac. Sci. Technol. B 20, 1710 (2002).

inclusion of d-polarizations on Si -- shallow minimum at bond angle corresponding to recent X-ray studies*

Hartree-Fock (SCF) with gaussian d-polarizations on Si start with Mozzi-Warren coordinates**
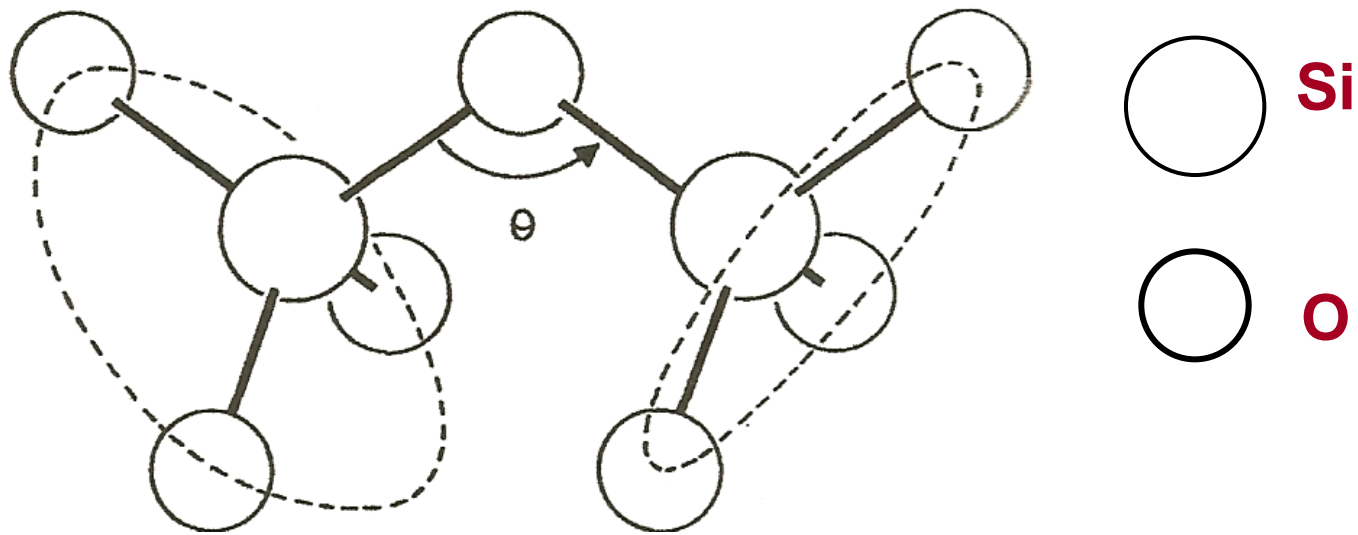Δ(Si-O-Si)~30±2°

SCF + configuration interaction (CI) - no d-polarization

SCF + CI with d-polarization optimized distances same as Neufieind-Liss coordinates**
Δ(Si-O-Si)~18±2°

*J. Neufeind and K.-D. Liss, Bur Bunsen Phys Chem 100, 1341 (1996).
**R.L. Mozzi and B.E. Warren, J. Appl. Cryst. 2, 164 (1969).

are all rotations equivalent? no
constrained by electronic structure

O $2p\pi$ lone pair - perpendicular to Si-O-Si, *out of slide*

d orbital symmetries for Si and $p\pi$-$d\pi$ back donation narrows
2nd neighbor Si-O pair correlation distances
symmetries of Si d-states for pairs of Si atoms connected
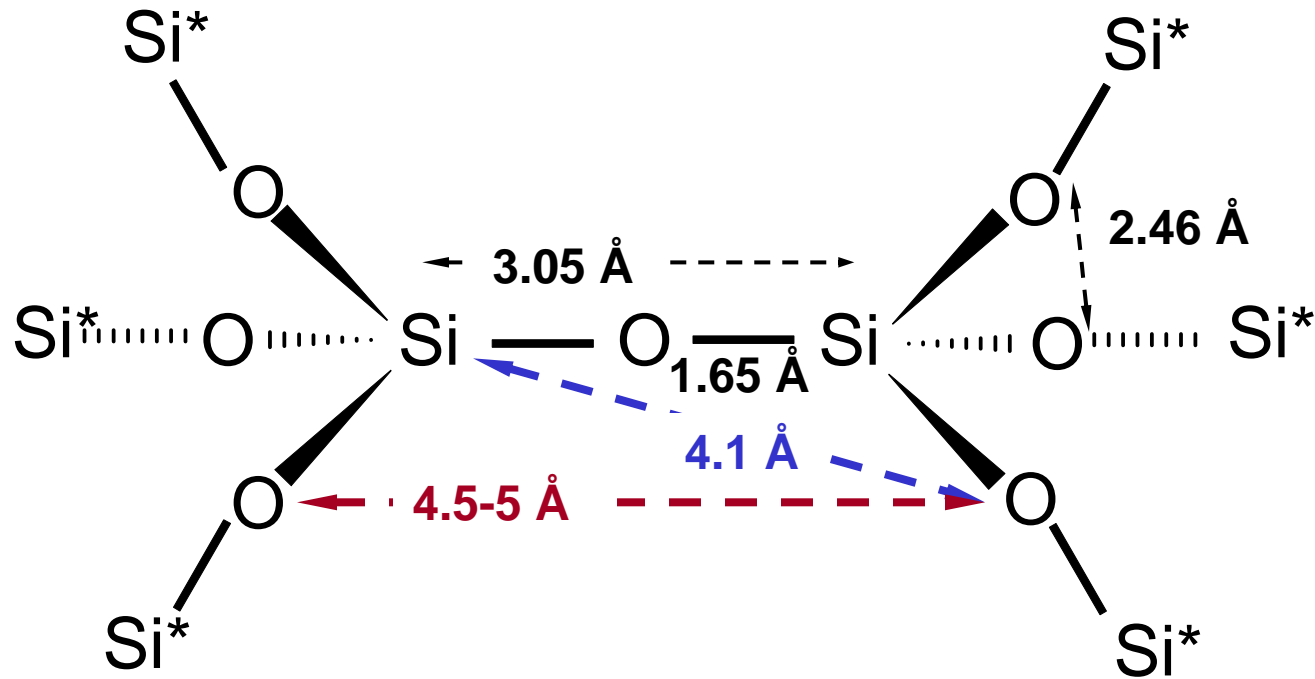**through intervening O atom are strongly correlated**

correlations extend bonding coherence and constraints
into MRO regime*

***this nullifies the original bond constraint theory!! of Phillips**
and co-workers (GL included)

MRO bonding correlations
coherence length regime of FSDP
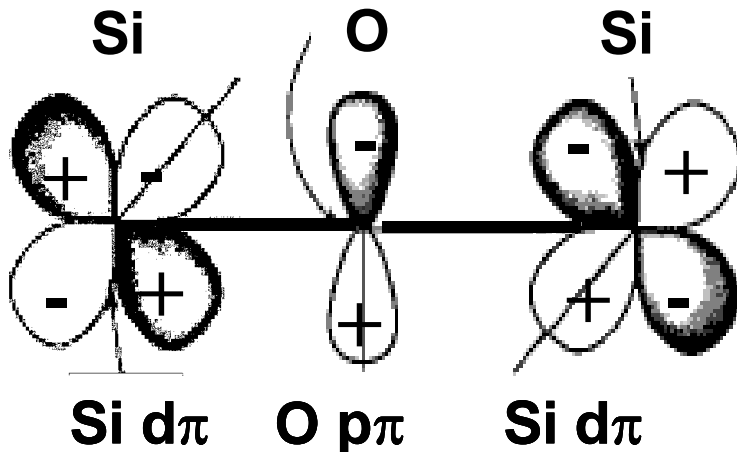### partial structure factor analysis and Bell & Dean model

Si*

Si*

O

O — 2.46 Å

← 3.05 Å ---→

Si*·······O·······Si — O $\overline{1.65\ Å}$ Si·······O·······Si*

4.1 Å

O ← 4.5-5 Å ---→ O

Si*

Si*

Si   **O**   **Si**

Si dπ   O pπ   Si dπ

back-donation of charge from O to Si atoms

shortens bond-length and stabilizes geometry - similar to

anti-ferromagnetic coupling

1st row transition metals and O

coherence length ~ λ_{coh}~2π / ΔQ(Å^{-1}), ~0.95 nm

connected pairs of rings through common Si-atom

this gives SiO_2 its unique properties and the scale of order that determines good glass formation and low defect densities

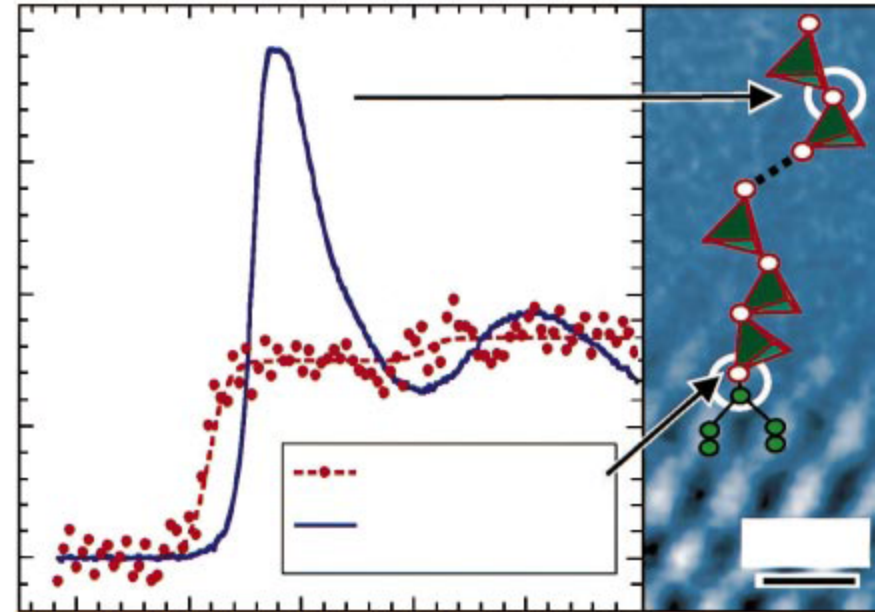**minimum thickness for SiO_2 film for gate dielectric next slide**

and

B_2O_3 glass

O K edge can also be obtained via electron energy loss spectroscopy (EELS)

introduction: nano-regime scales of order for gate dielectric materials

➔i) SiO_2 -- what is thinnest SiO_2 layer with bulk properties?

DA Mueller et al., O K edge EELS Nature 399, 758 (1999)

introduction: nano-regime scales of order for gate dielectric materials

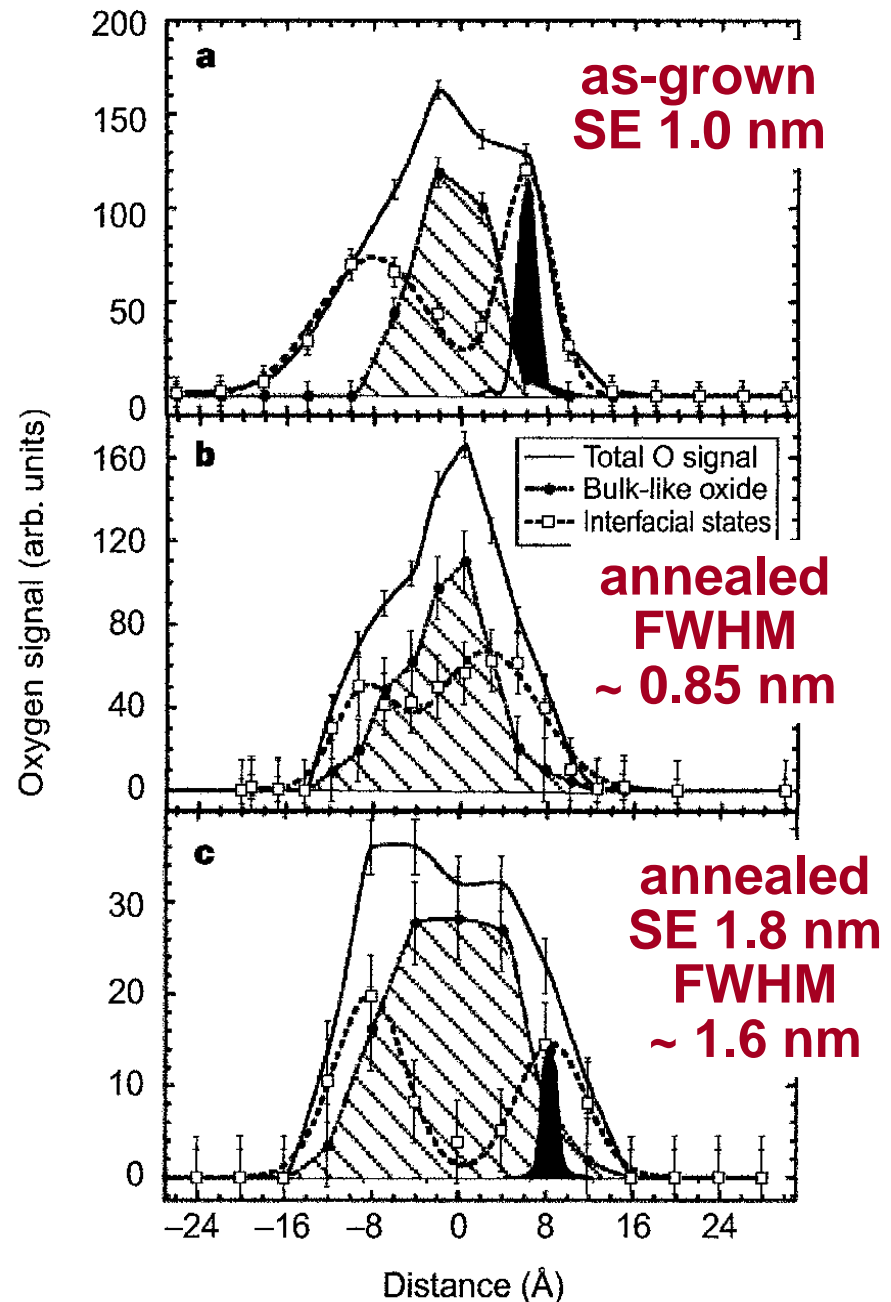➔ i) SiO_2 -- what is thinnest SiO_2 layer with bulk properties?

DA Mueller et al., O K edge EELS Nature 399, 758 (1999)

➔ 0.85 nm

the analysis of S(Q) gives a value for coherence length of

➔ 0.95 nm

this correspondence as well as XAS analysis of resonant absorptions provides the basis for the interpretation of coherence length

a. as-grown SE 1.0 nm

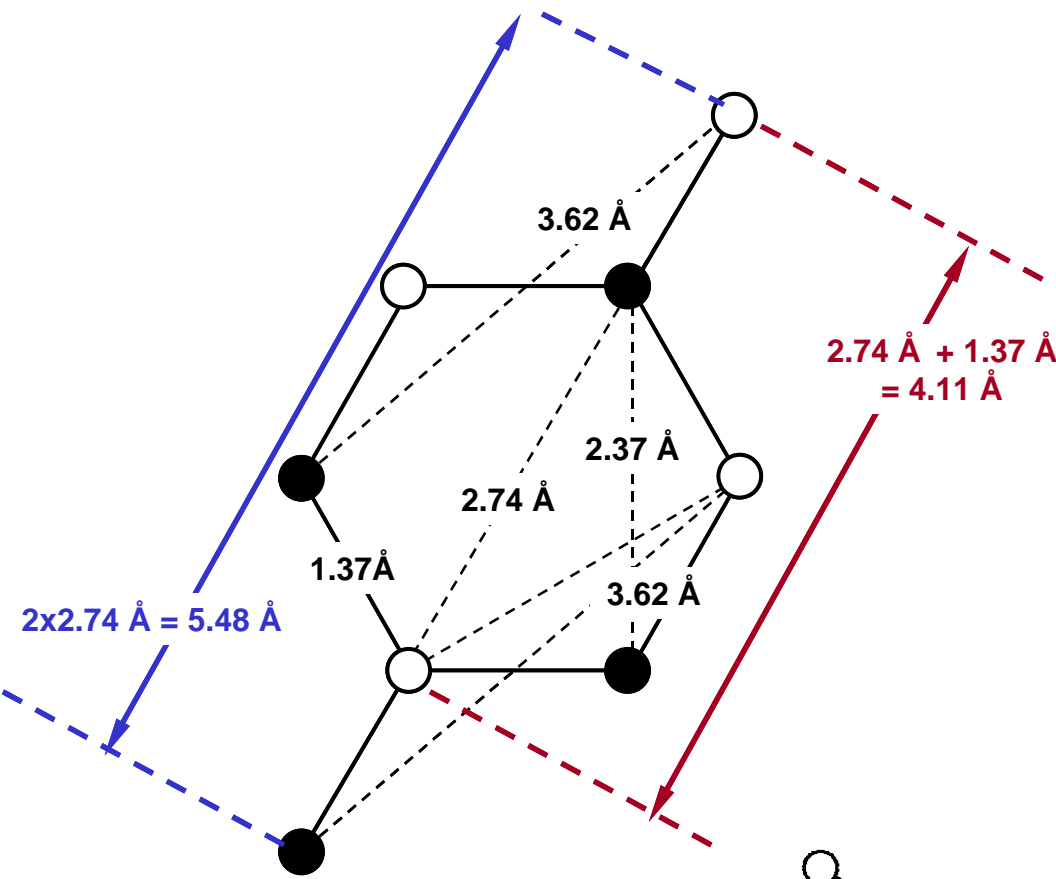b. Total O signal / Bulk-like oxide / Interfacial states
annealed FWHM ~ 0.85 nm

c. annealed SE 1.8 nm FWHM ~ 1.6 nm

Oxygen signal (arb. units)

Distance (Å)

B$_2$O$_3$ - boroxol ring model
planar ring symmetry - FL Galeener Raman spectra

B2O3 structure factor

$Q(Å^{-1})_{FSDP} \sim 1.57\ Å^{-1}$

$\Delta Q(Å^{-1}) \sim 0.66\ Å^{-1}$
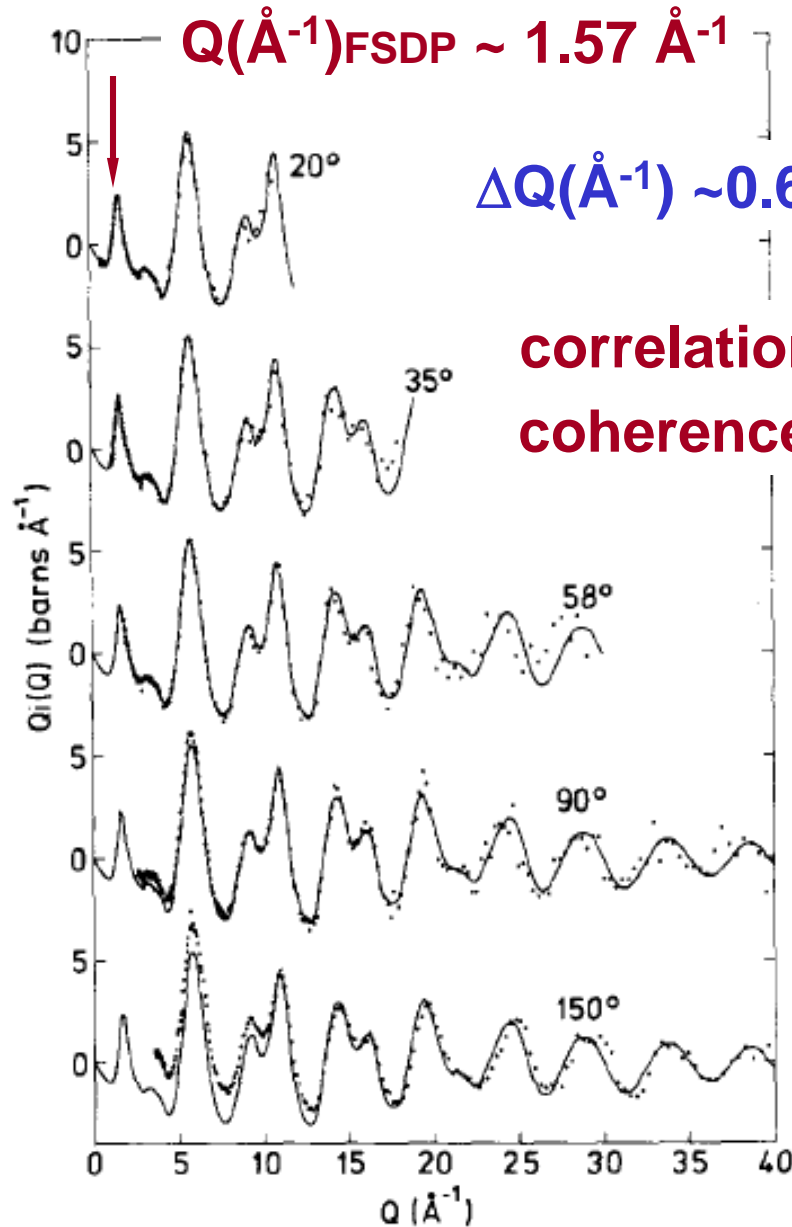
correlation length, $\lambda_{corr} \sim 2\pi/Q(Å^{-1})$, ~0.4 nm

coherence length, $\lambda_{coh} \sim 2\pi/\Delta Q(Å^{-1})$, ~1.1 nm

correlation length ~0.4 nm
2nd O-O distance *same* **as in SiO$_2$**

3.62 Å

2.74 Å + 1.37 Å = 4.11 Å

2.37 Å

2.74 Å

1.37Å

3.62 Å

2x2.74 Å = 5.48 Å

coherence length ~1.1 nm
coupling of two boroxol rings *similar* **to SiO$_2$**

B-O-B Angle

B-O-B Angle

Boroxol Rings

~11 Å
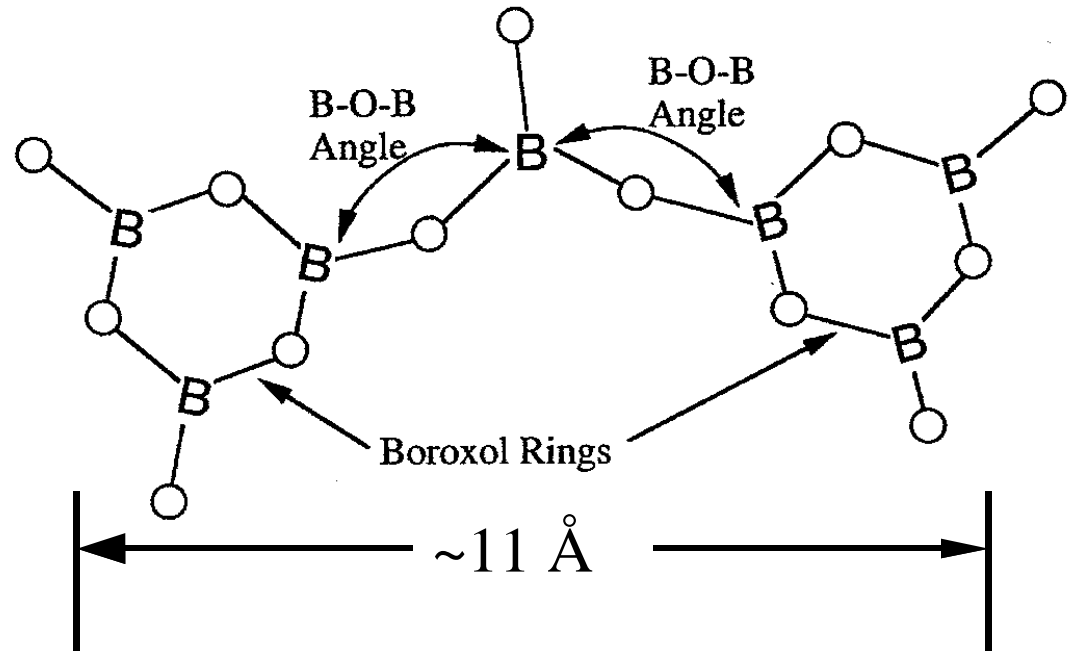
O pπ - B pπ - O pπ coupling - between central B and 3 O's
analogous to ferromagnetic ordering

O   B   O

O pπ   B pπ   O pπ
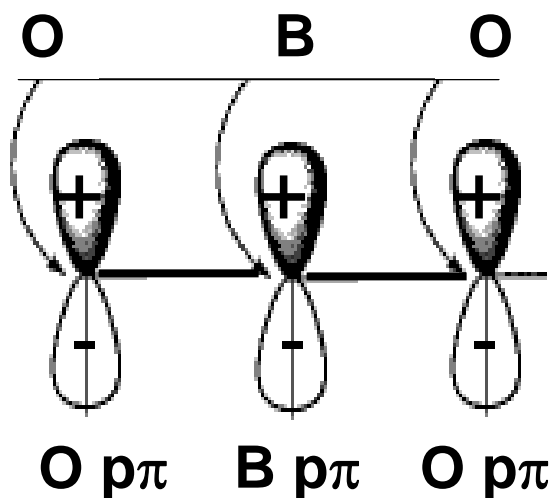
back-donation of charge from O filled to B empty π-orbitals
shortens bond-length
stabilizes geometry

B-O-B Angle

B-O-B Angle

Boroxol Rings
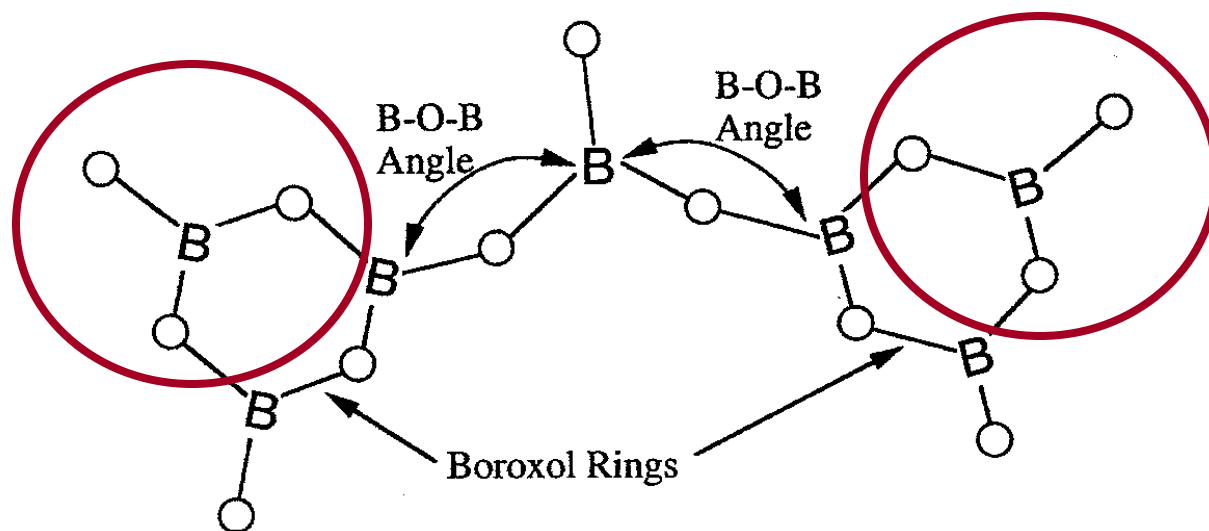
First Sharp Diffraction Peak obtained from X-ray Diffraction structure factor, S(Q) gives 2 length scales associated for Medium Range Order (MRO) in SiO2 and other non-crystalline solids

a correlation length, λ_{corr} ~2π / Q(Å^{-1}), ~0.41 nm

a coherence length ~ λ_{coh}~2π / ΔQ(Å^{-1}), ~0.95 nm
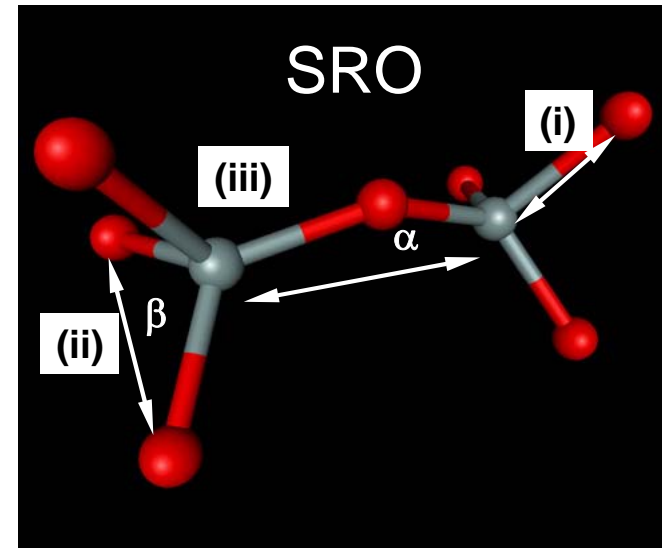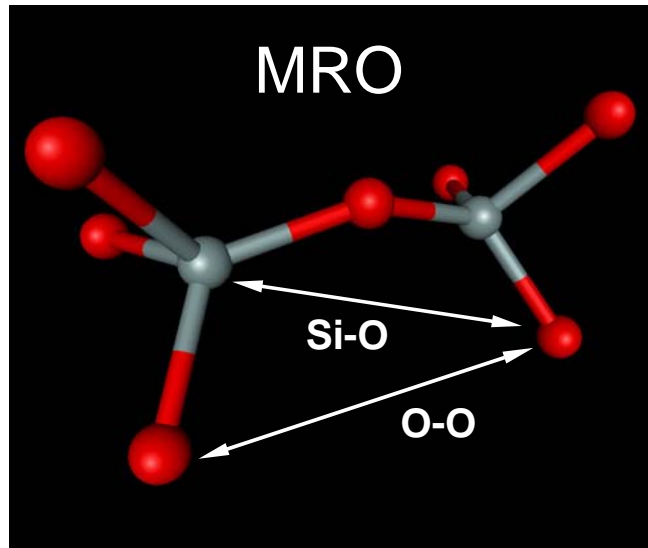
spectroscopy studies establish VUV features, 8.9 – 20 eV from excitations on a scale of the correlation length, and

EEELs and electrical studies establish that coherence length establishes the scale, and limit for SiO2 downscaling in ULSI devices