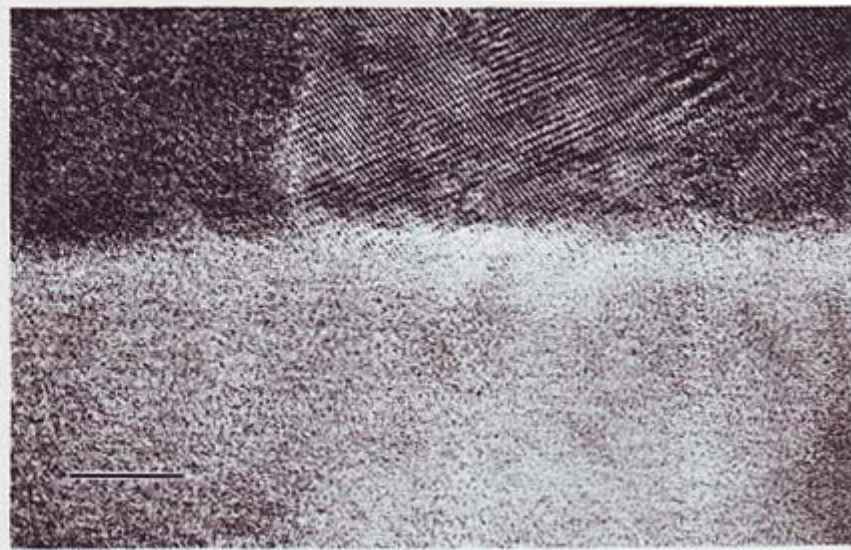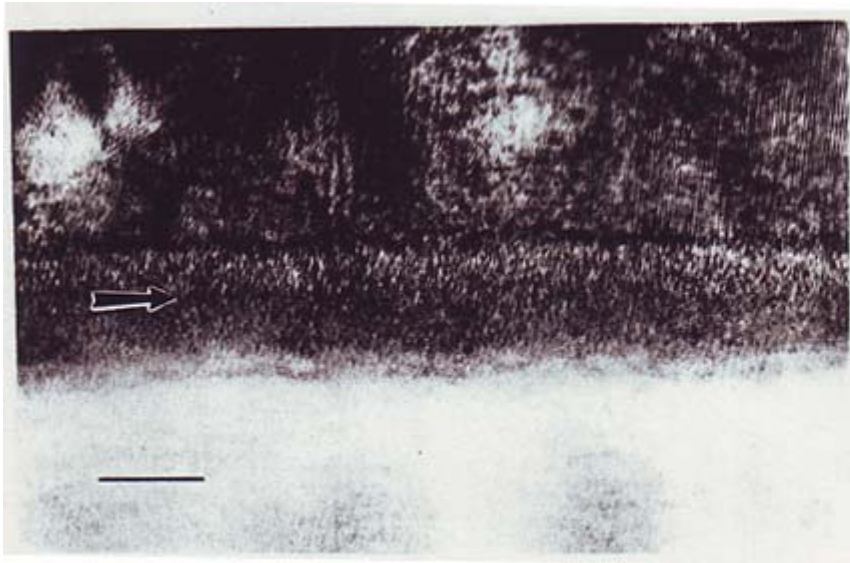# Thermochemical Effects at Multicomponent Glass Surfaces

Carlo G Pantano
Department of Materials Science and Engineering
Materials Research Institute
The Pennsylvania State University

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**Materials Research Institute**

outline

- surface composition changes during fiberglass processing

- surface segregation during the fabrication of micro-sheet for display glass

- composition <<>> structure effects at surfaces…. BORON-OXIDE

- surface atomic structure models and their validation by adsorption

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crystallized amorphous
silicon on various
glass substrates….

note interphases
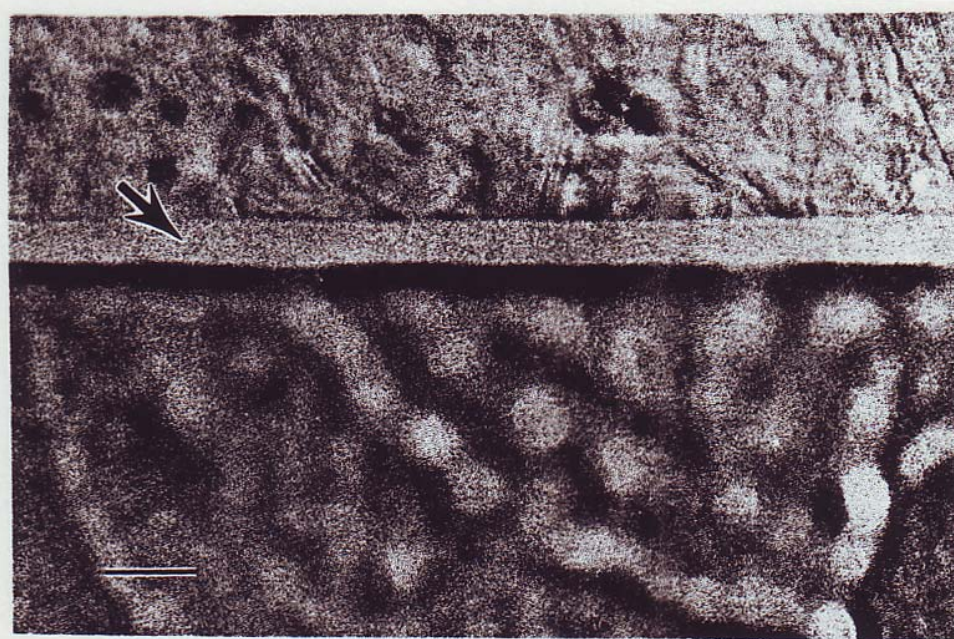
some opportunities for glass surface modification

- controlled electrical conductivity
- 'primed' for adhesion
- 'hardened' for abrasion resistance
- anti-reflective or highly reflective
- soluble or insoluble

Commercial Glass Dielectrics

- Large scale processes have been developed for producing thin glass sheets.
- Commercial market is growing rapidly for flat panel displays.
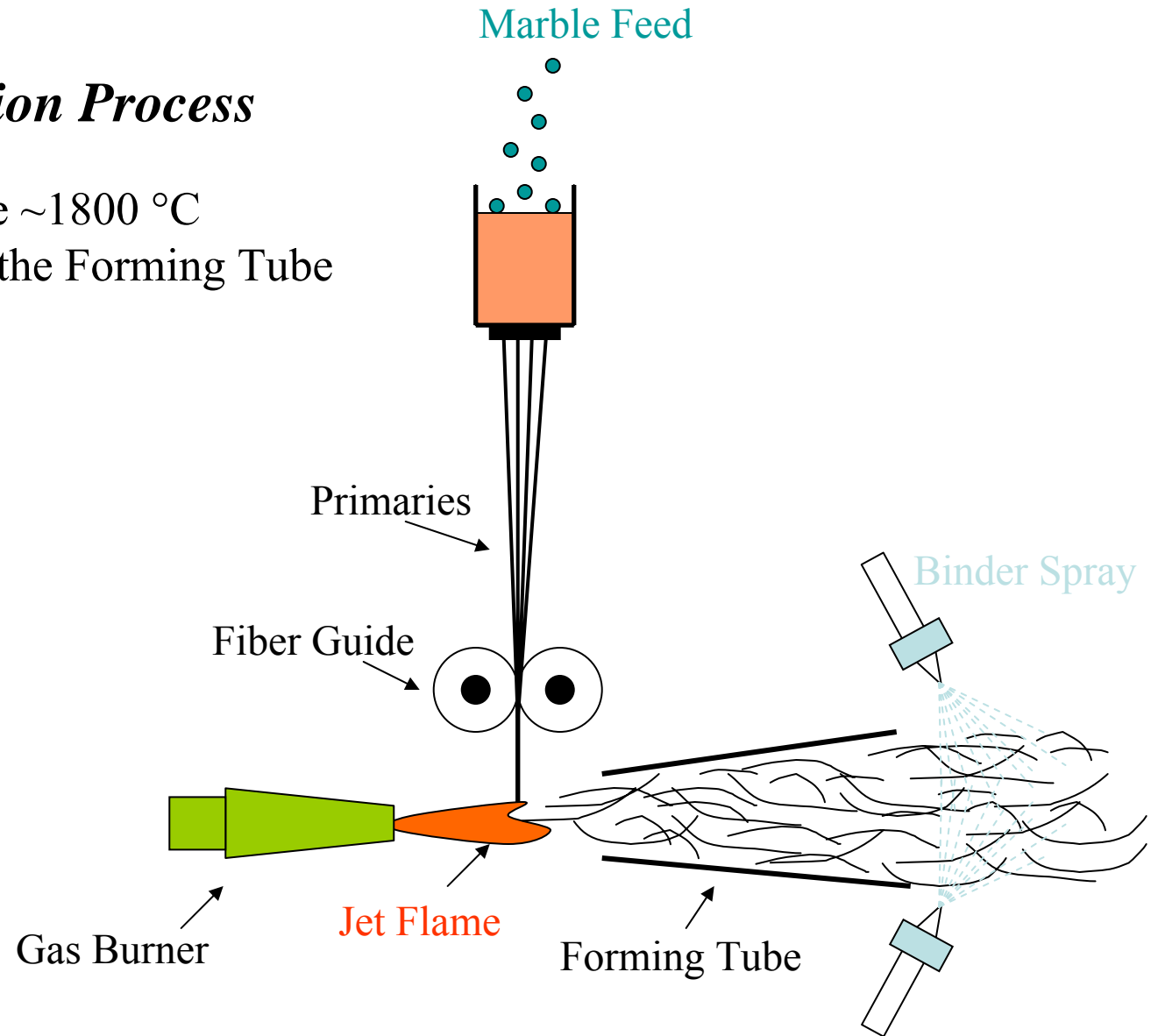- Companies are interested in exploring new markets flat panel glass.
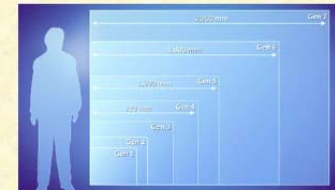
Projected glass plate dimensions for active matrix liquid crystal displays. The glass may be an excellent commodity material for high temperature capacitors for use in hybrid electric vehicles.

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the 'surfaces' of most functional glasses come into existence in a temperature range where surface energy can be minimized through composition and/or structure changes, where evaporation of volatile species occurs, and where local redox equilibria can be established through adsorption and/or ion transport
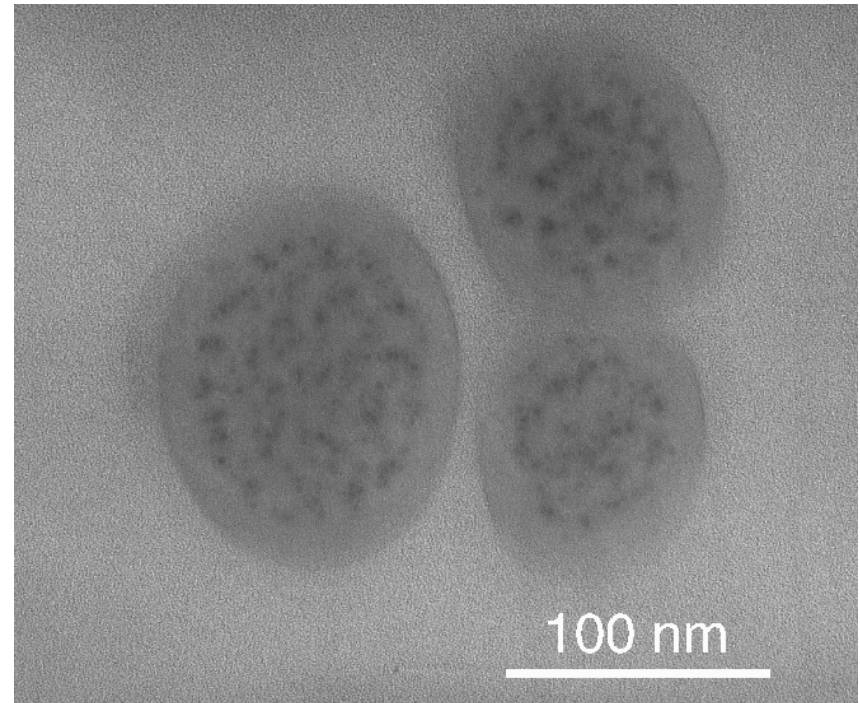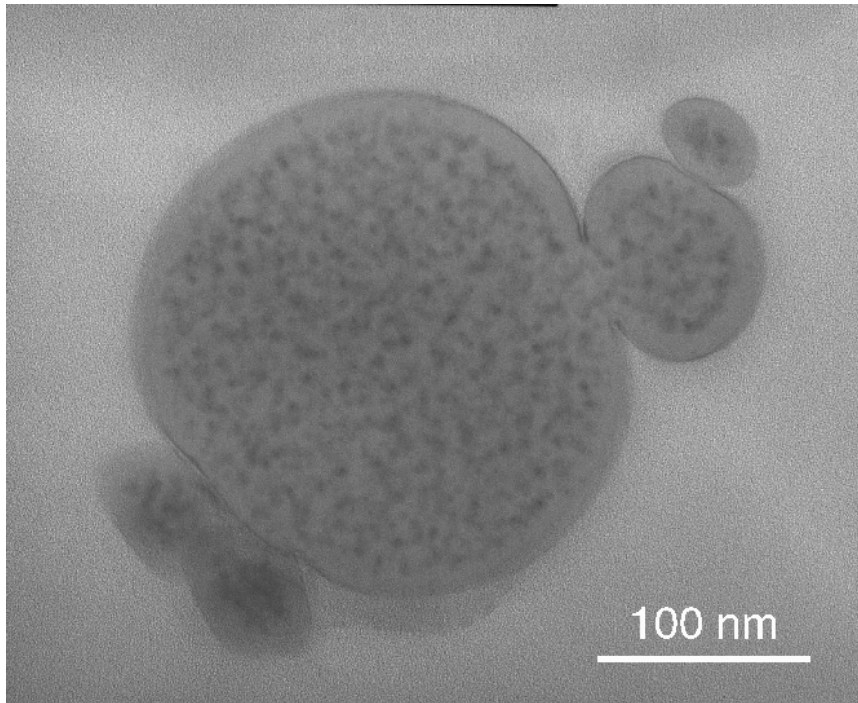
- thermal segregation
- changes in local coordination..B_2O_3
- alkali, alkali borate, etc evaporation
- cation out-diffusion usually faster than O_2 in-diffusion
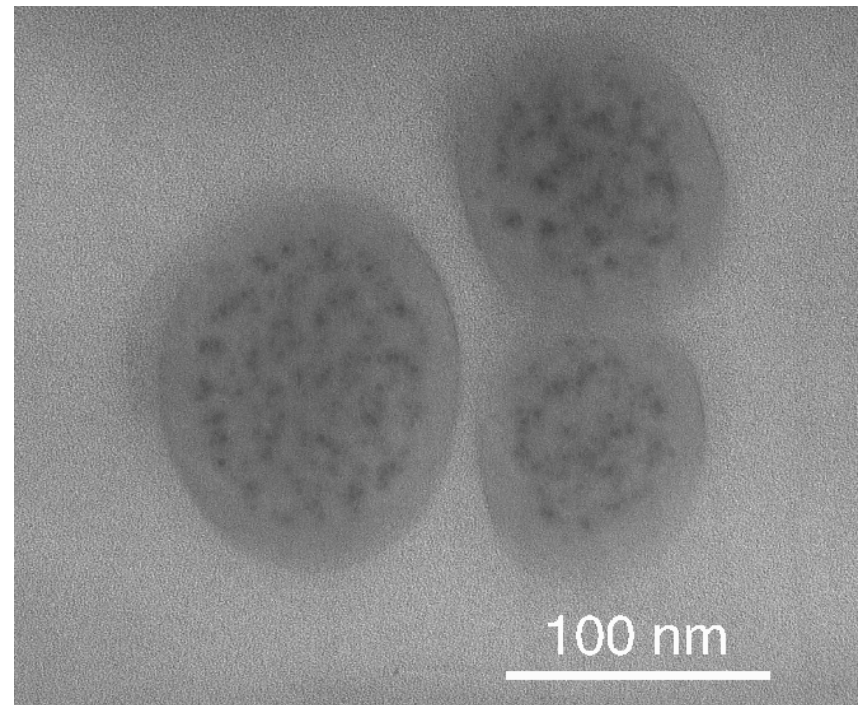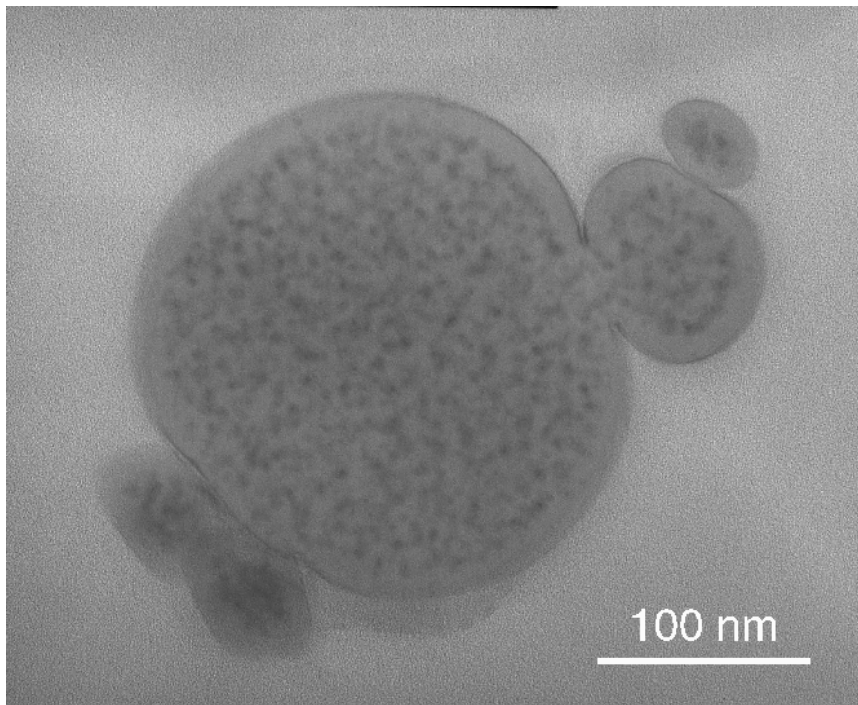- redox equilibria drives cation oxidation on cooling

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Flame Attenuation Process

Flame Temperature ~1800 °C
Slower Cooling in the Forming Tube

Marble Feed

Primaries

Binder Spray

Fiber Guide
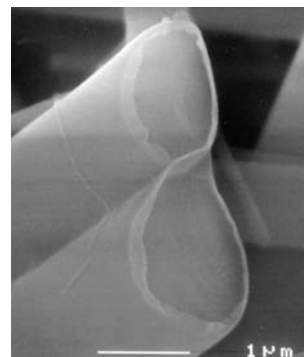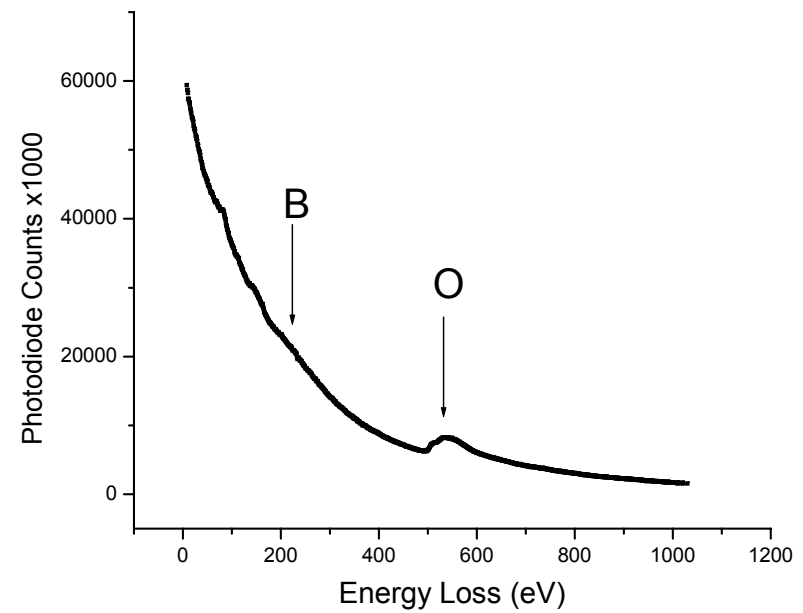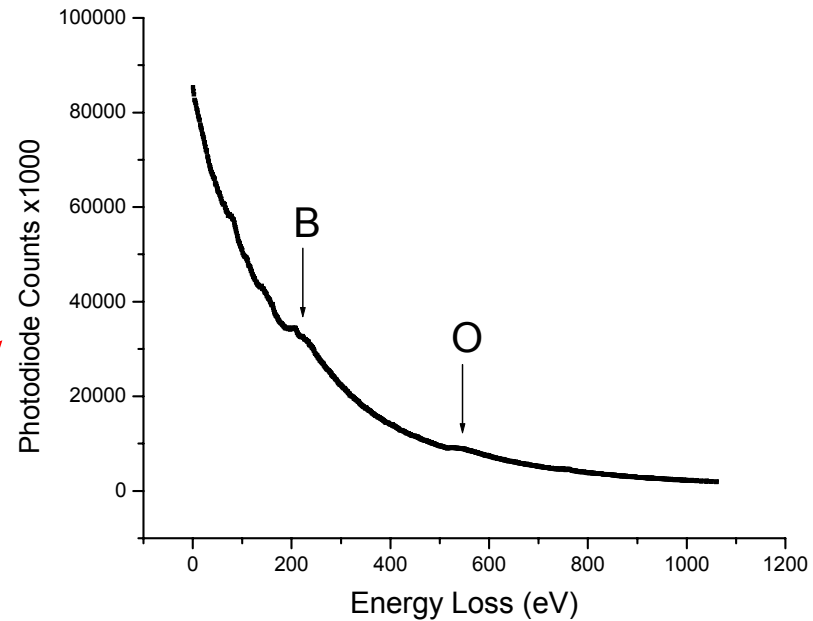
Gas Burner

Jet Flame

Forming Tube

TEM of FA Nano Fibers

TEM of FA Fibers (Glass A)

100 nm

100 nm

after leaching $\longrightarrow$

1 μm

PSUMCL 30KV X70,000 13mm   100nm

1 μm
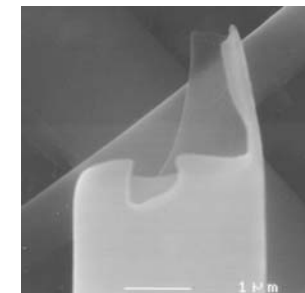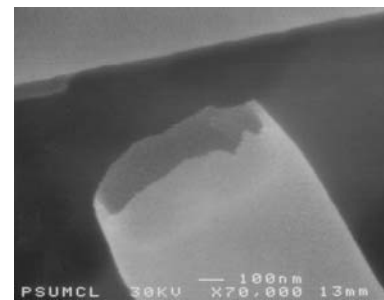
EELS (and XPS) confirm that this surface layer is depleted in boron.
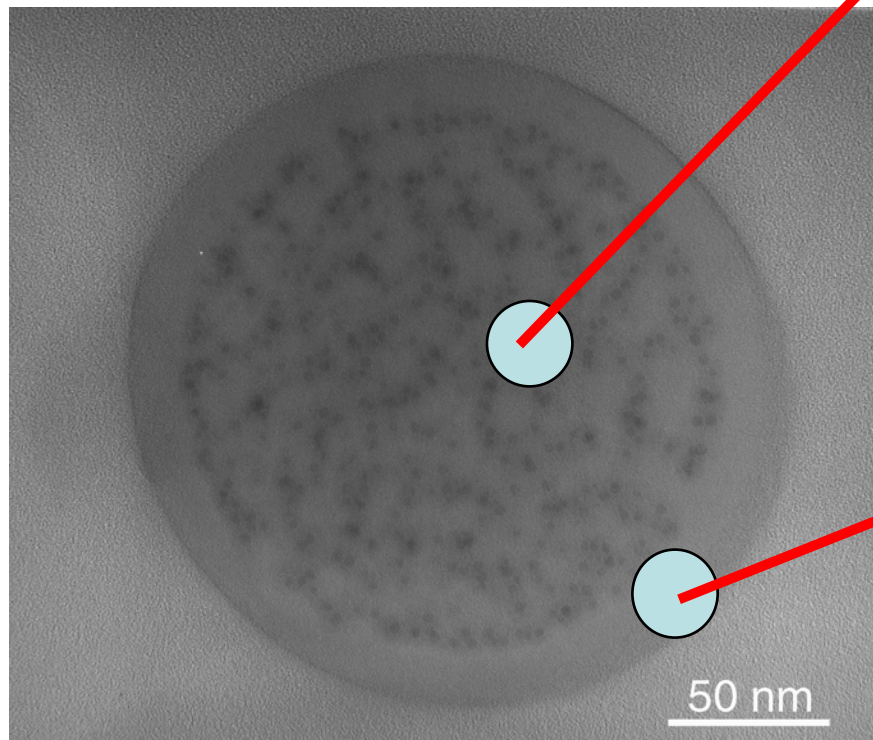
The thickness of the surface layer is NOT related to the fiber diameter (FA)
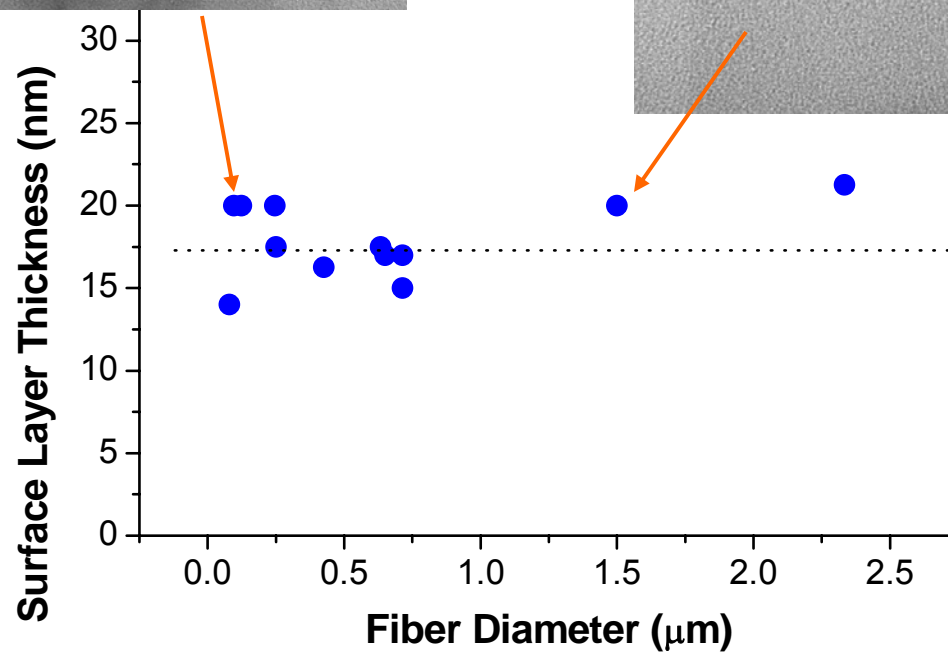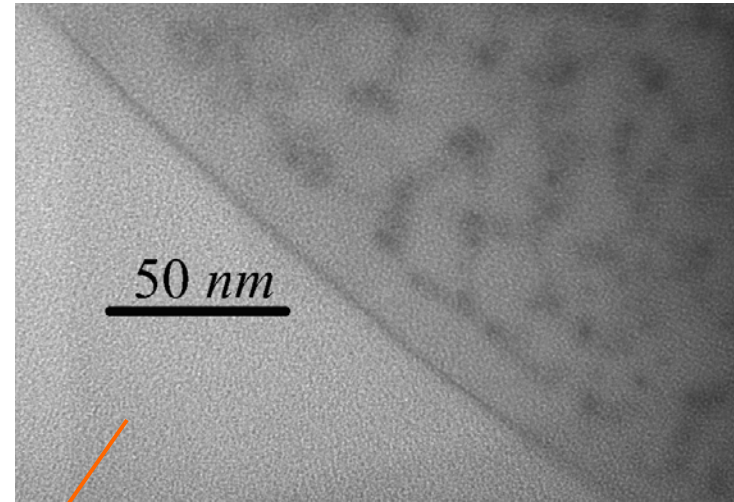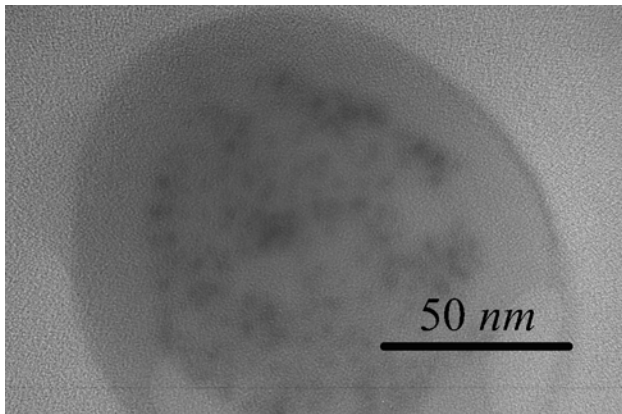
'Isothermally' Freezing in the Surface Composition
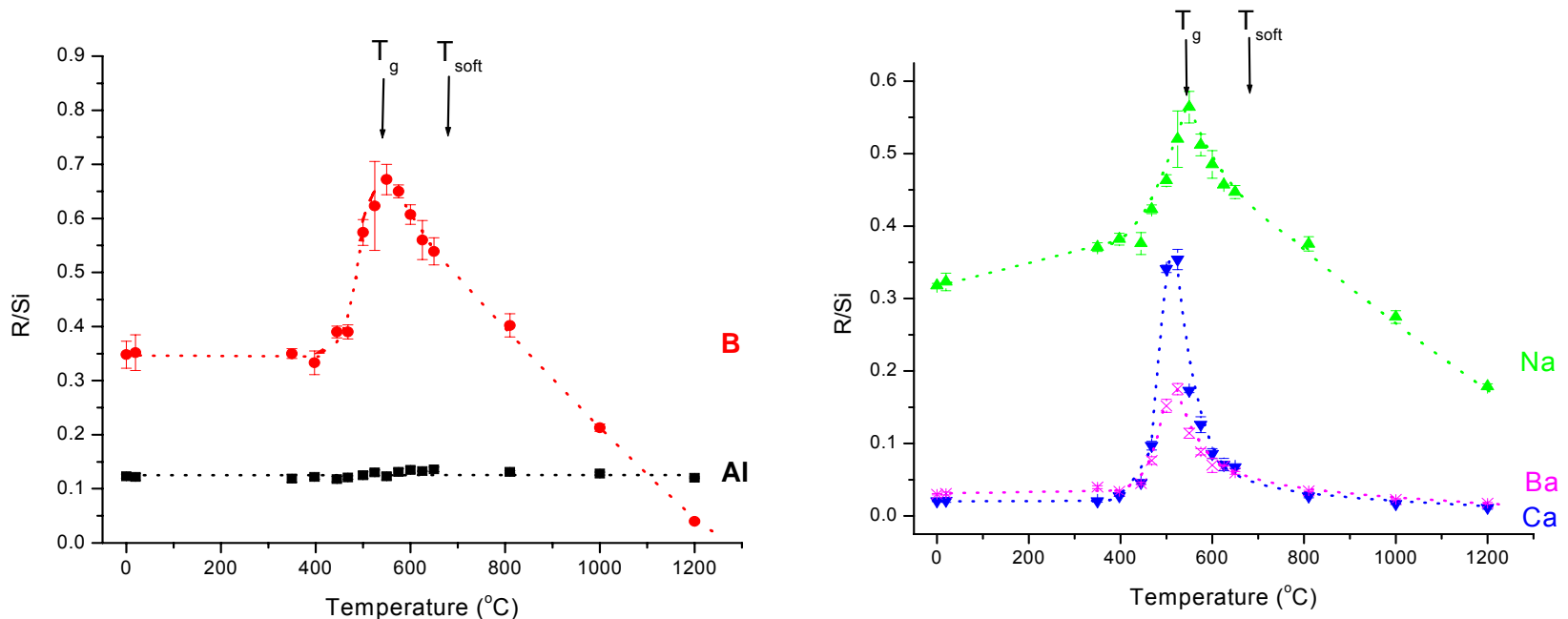
- after heat-treatment at T_g, the surface is depleted in Si. The concentrations of B, Na, Ba and Ca increase significantly on the surface, especially Ca and Ba.

- At temperatures > 800 °C, the surface is depleted in B and Na.

- The Al/Si ratio does not change over the entire temperature range.

Glass VII

XPS Depth Profiling:
air-fracture surface of glass I,
"equilibrated" at 525 °C.
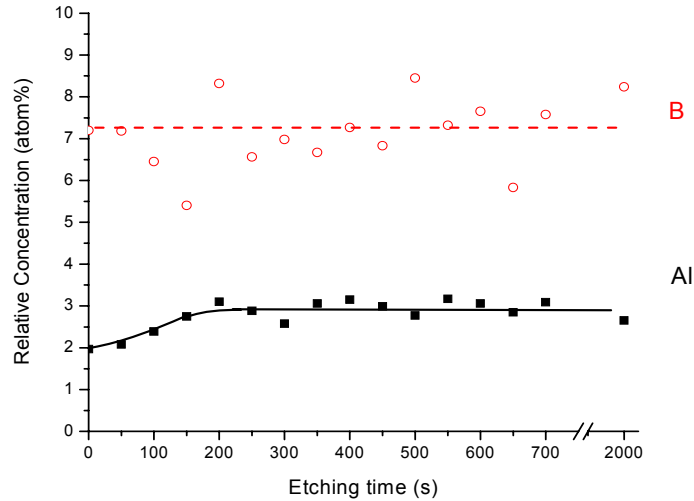
- Sputtering rate ~ 1 Å/s.
- The Si-depleted layer ~200 Å thick.
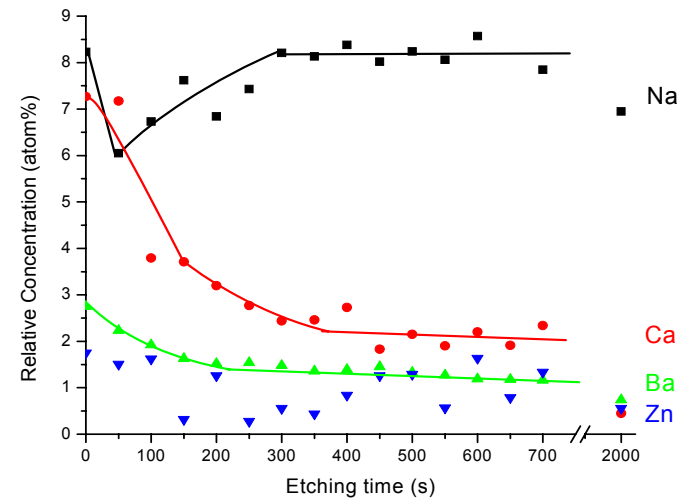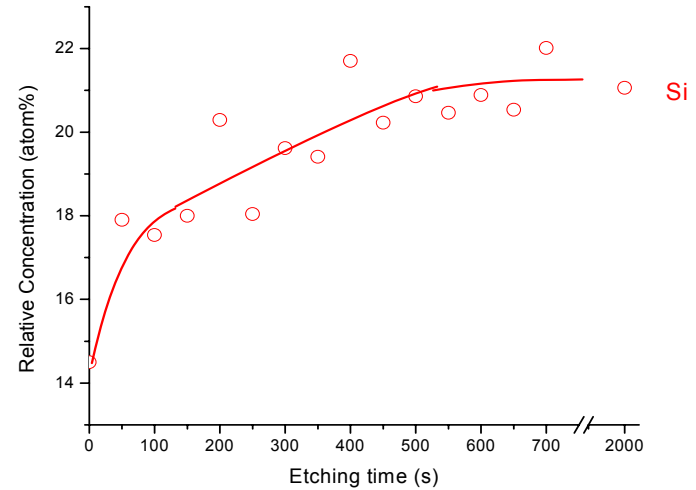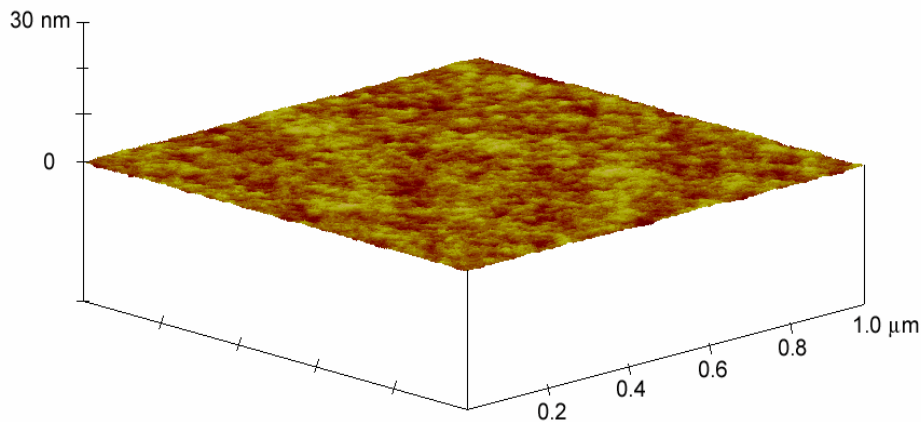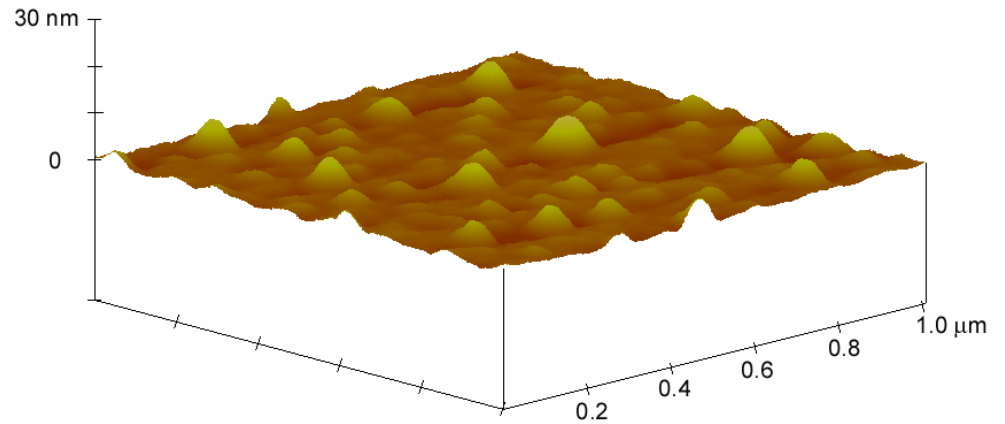
After: RMS = 0.93 nm

Before: RMS = 0.14 nm

After heat-treatment, features (4-7 nm in height) appear on the surface.

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Phenomenological Model
for "Phase Segregation/Migration" to the Surface

 Network modifier rich region

 Network former rich region
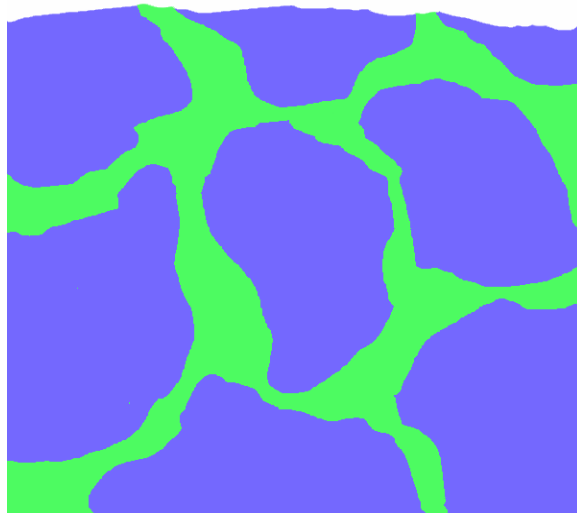
Before Heat-treatment
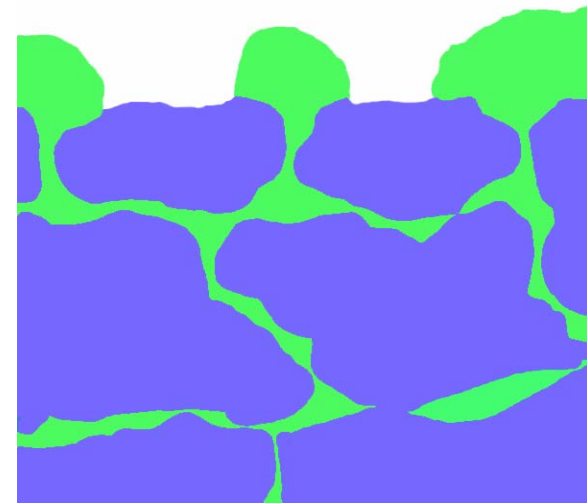
After Heat-treatment
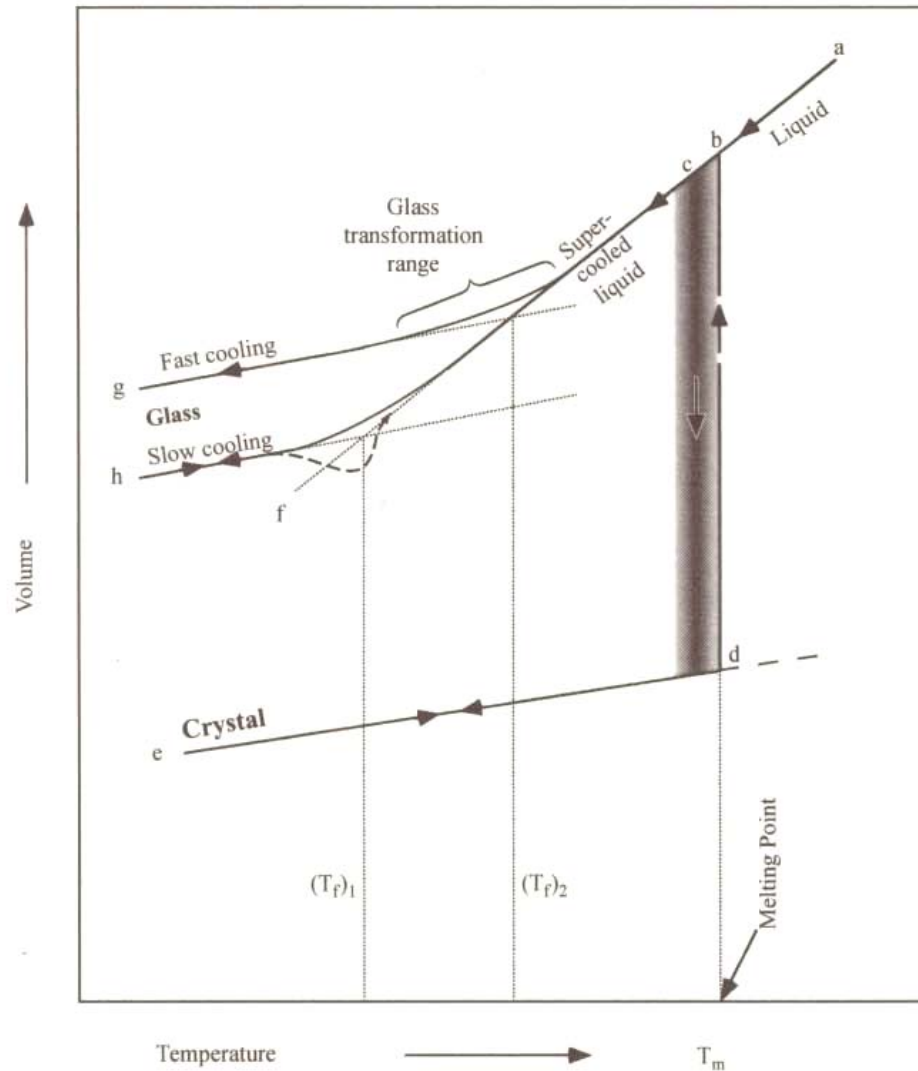
FIGURE 5.1 The volume-temperature diagram. (*After A. K. Varshneya, Fundamentals of Inorganic Glasses, Fig. 2-1, p. 15, Academic Press, 1994.*)

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FUSION PROCESS FOR MICROSHEET GLASS FABRICATION

Trough

Homogeneous glass delivered from melting unit

Root

Sheet drawn downward
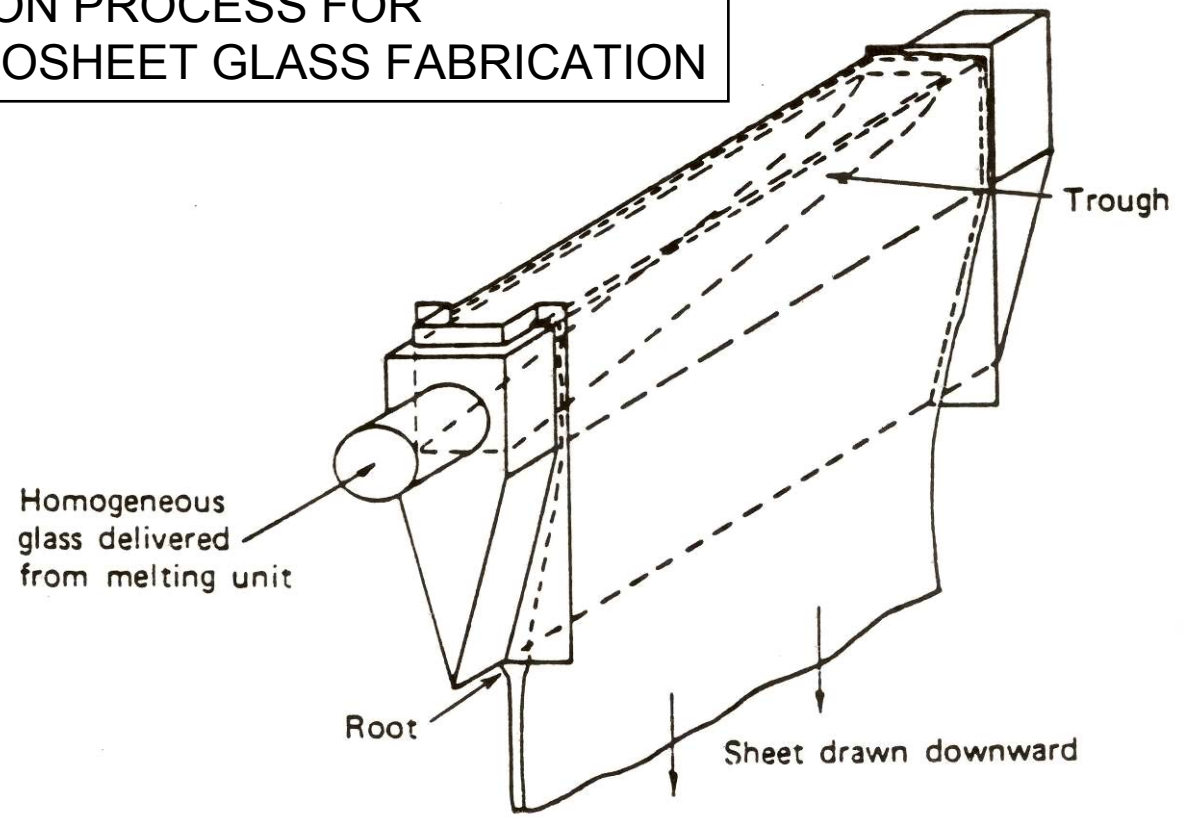
5X surface segregation of Sb (.5% in the bulk for fining)

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Angle Resolved XPS Depth Profiling

Beer-Lambert Law

$$I = I_0 e^{-z/\lambda \sin \theta}$$

Observed intensity, I, as a function of depth, z where λ is escape depth, θ is takeoff angle (w.r.t. surface plane).

Case 1. Atomically clean surface;

no angular effect

Angle Resolved Depth Profiling in XPS

??

??

?

?

?sin(?)
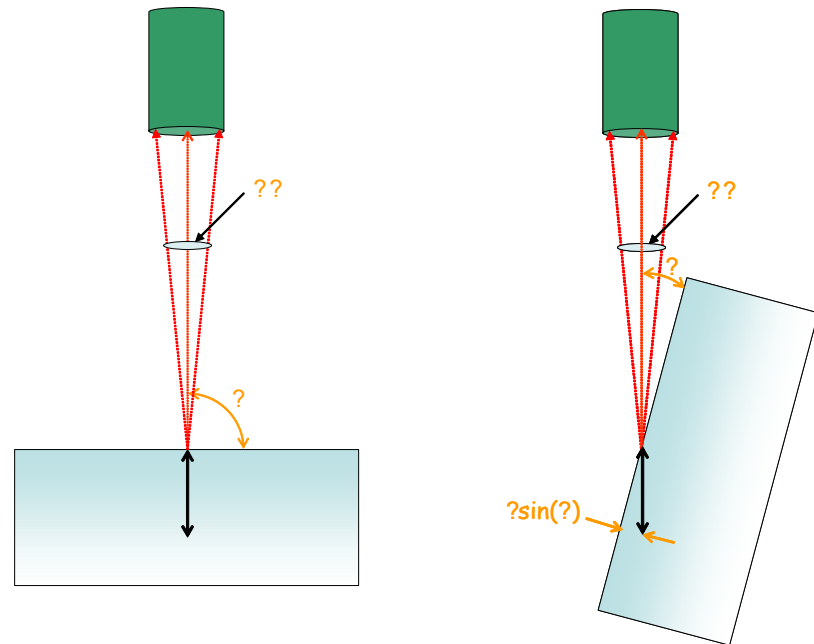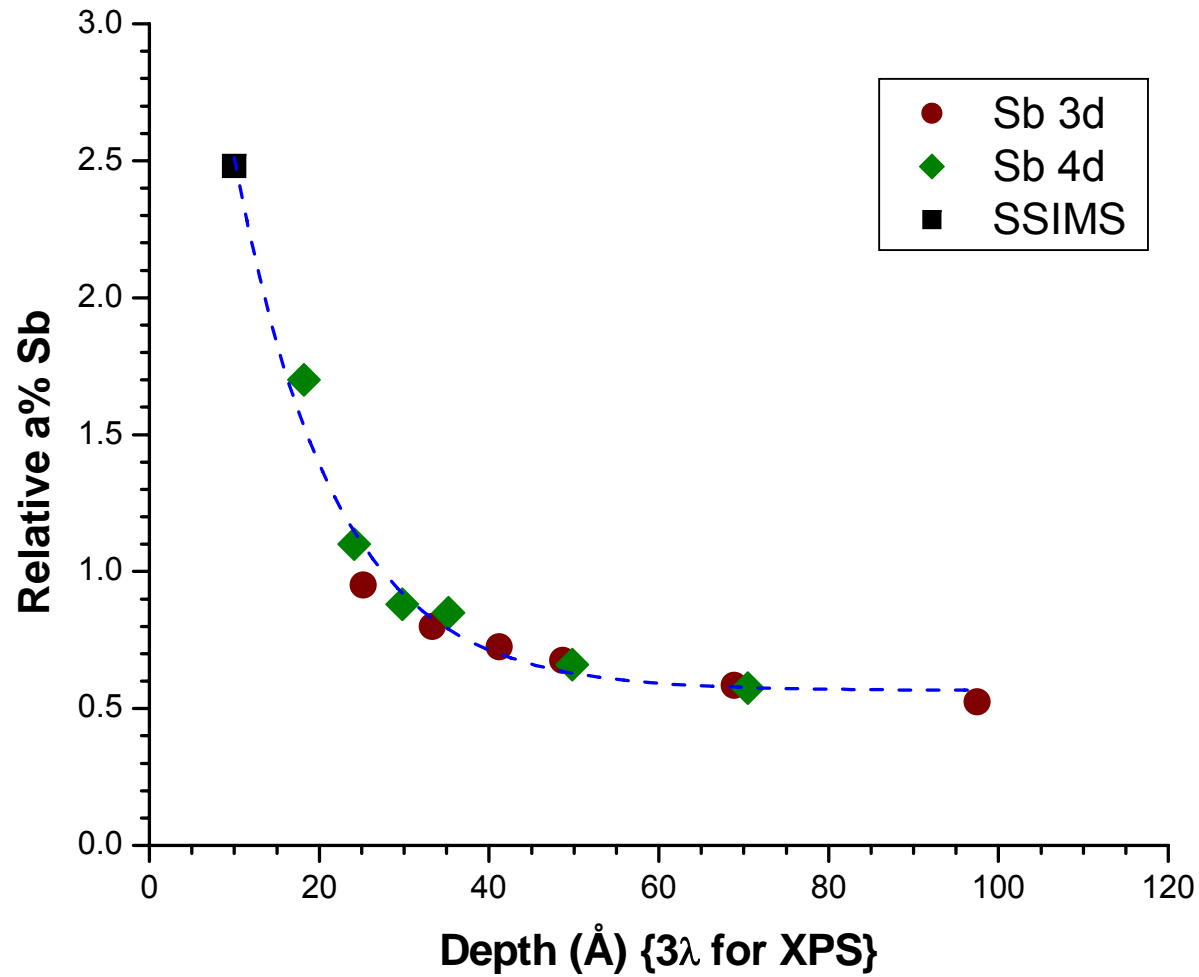
Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS
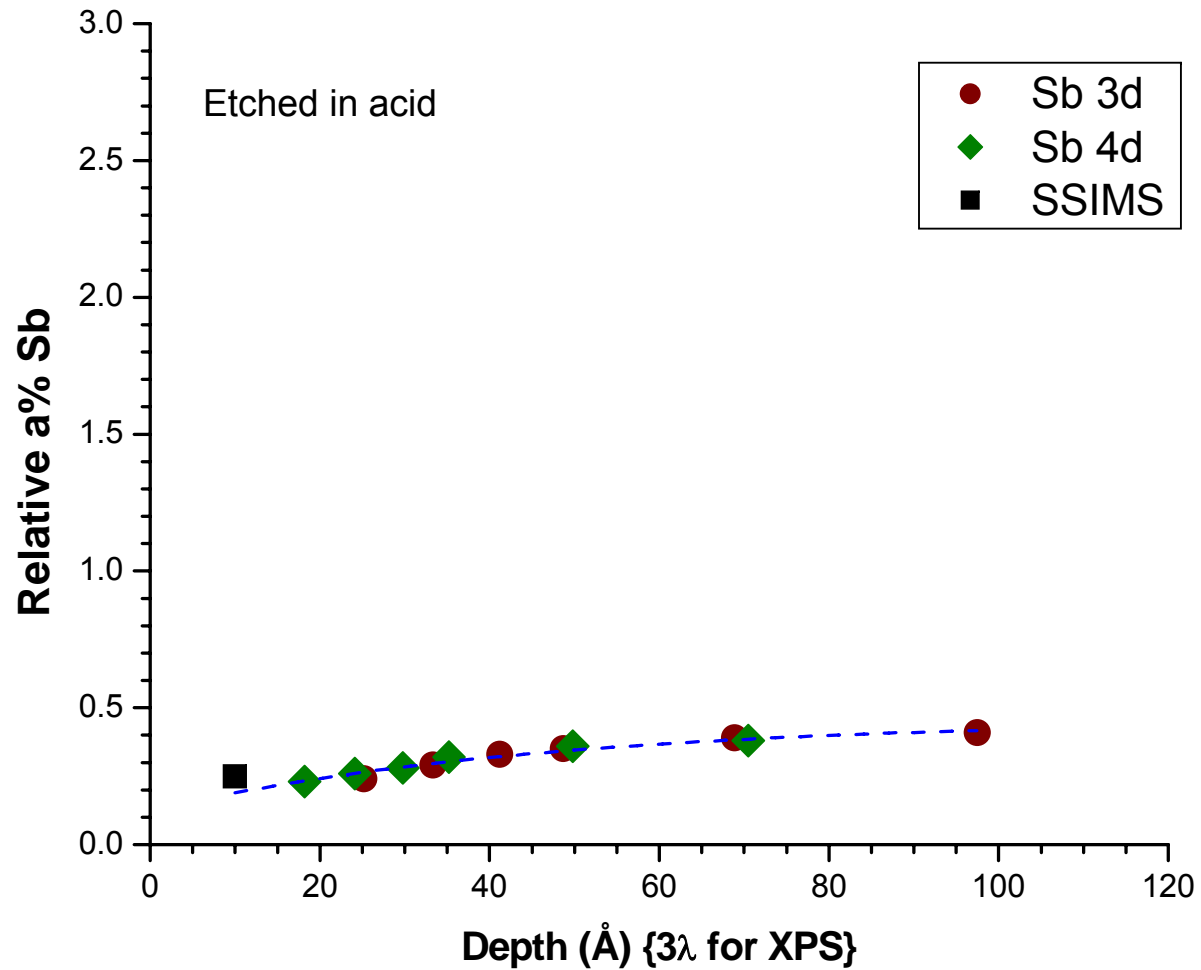
Etched in acid

Legend:
- Sb 3d
- Sb 4d
- SSIMS

Y-axis: Relative a% Sb

X-axis: Depth (Å) {3λ for XPS}

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Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

*Heat Treatments were for 10 minutes; samples were then air quenched.

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Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

*Heat Treatments were for 10 minutes; samples were then air quenched.

Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS
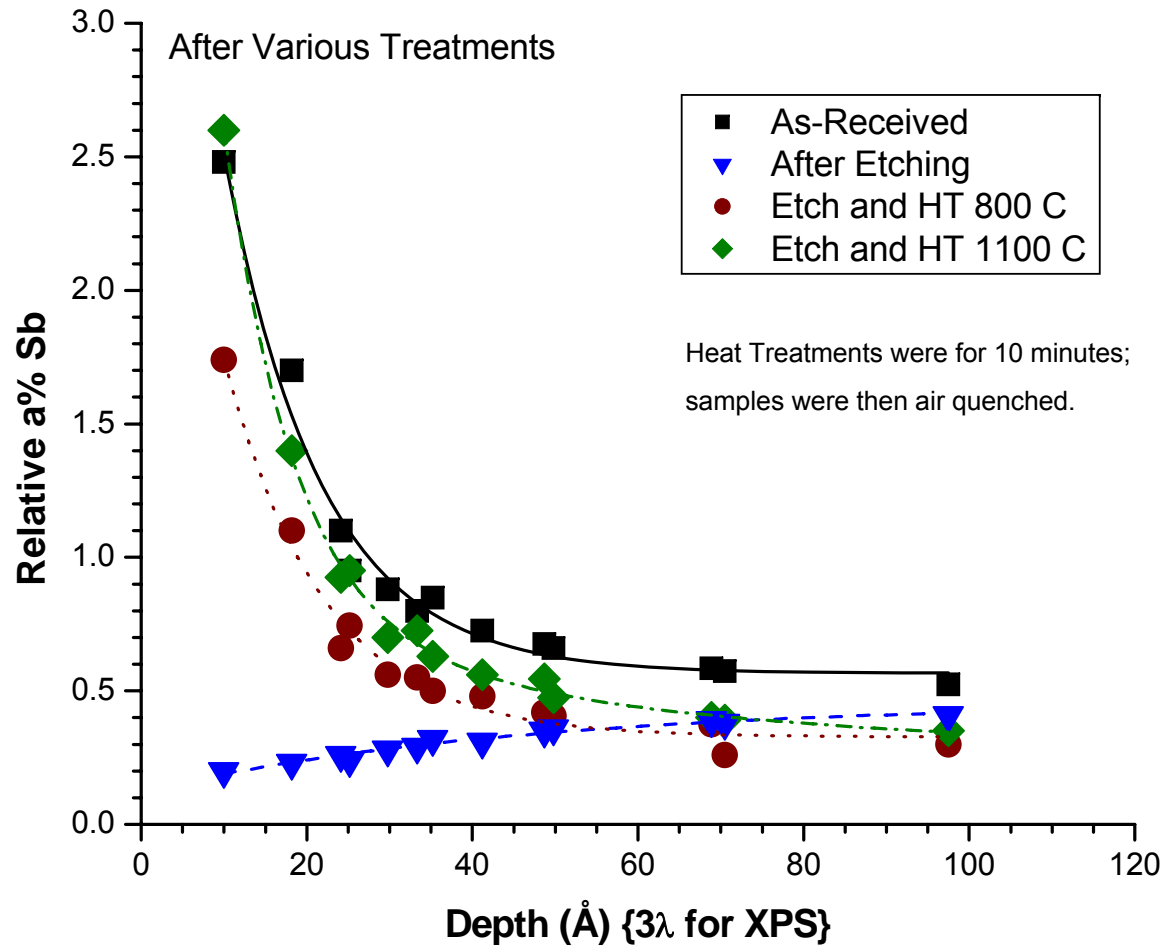
Case 2. Thin, uniform layer A of thickness, t, on top of substrate B
(where $E_{k, A} = E_{k, B}$)

$$I_A = I_A^\infty \left[1 - \exp^{(-t/\lambda_A \sin \theta)} \right]$$

$$I_B = I_B^\infty \exp^{(-t/\lambda_B \sin \theta)}$$

Ratio,

$$\frac{I_A}{I_B} = \frac{I_A^\infty}{I_B^\infty} \frac{\left(1 - \exp^{-t/\lambda_A \sin \theta} \right)}{\left(\exp^{-t/\lambda_B \sin \theta} \right)}$$

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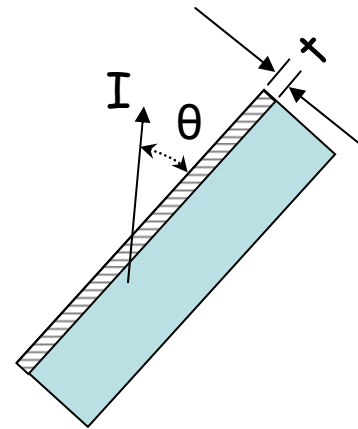
Case 3. Thin, patched layer A of thickness, t, on top of substrate B where γ is the fractional coverage of A

$$\frac{I_A}{I_B} = \frac{I_A^{\infty}}{I_B^{\infty}} \frac{\gamma\left(1 - \exp^{-t/\lambda_A \sin\theta}\right)}{\left[(1-\gamma) + \gamma\left(\exp^{-t/\lambda_B \sin\theta}\right)\right]}$$
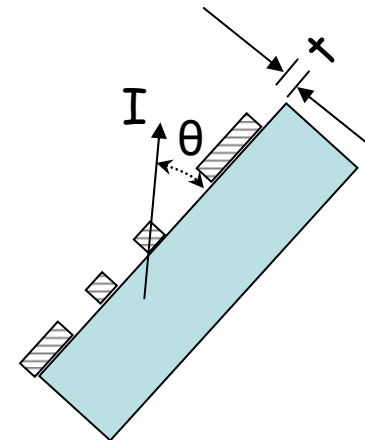
Reconstructed Angle Resolved XPS Depth Profiles

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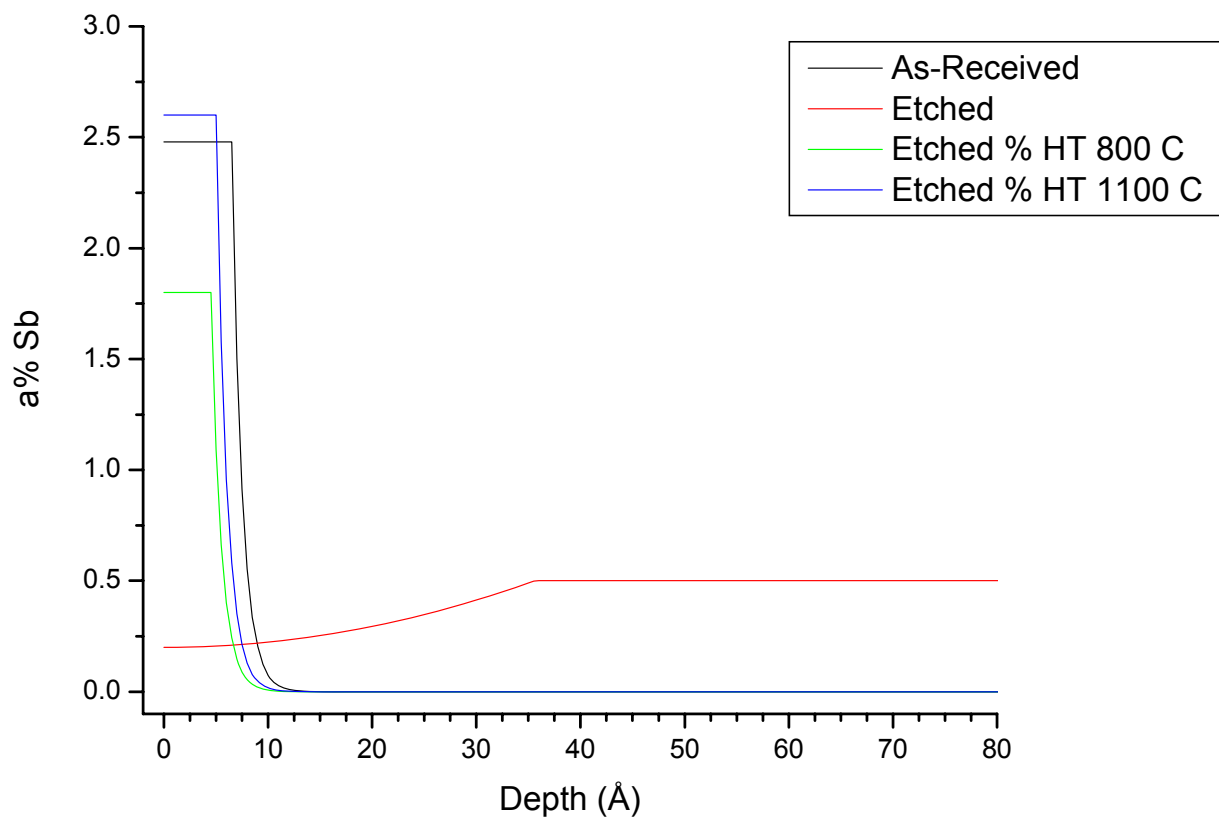
FAB-Static SIMS Analysis of Sb segregation versus temperature

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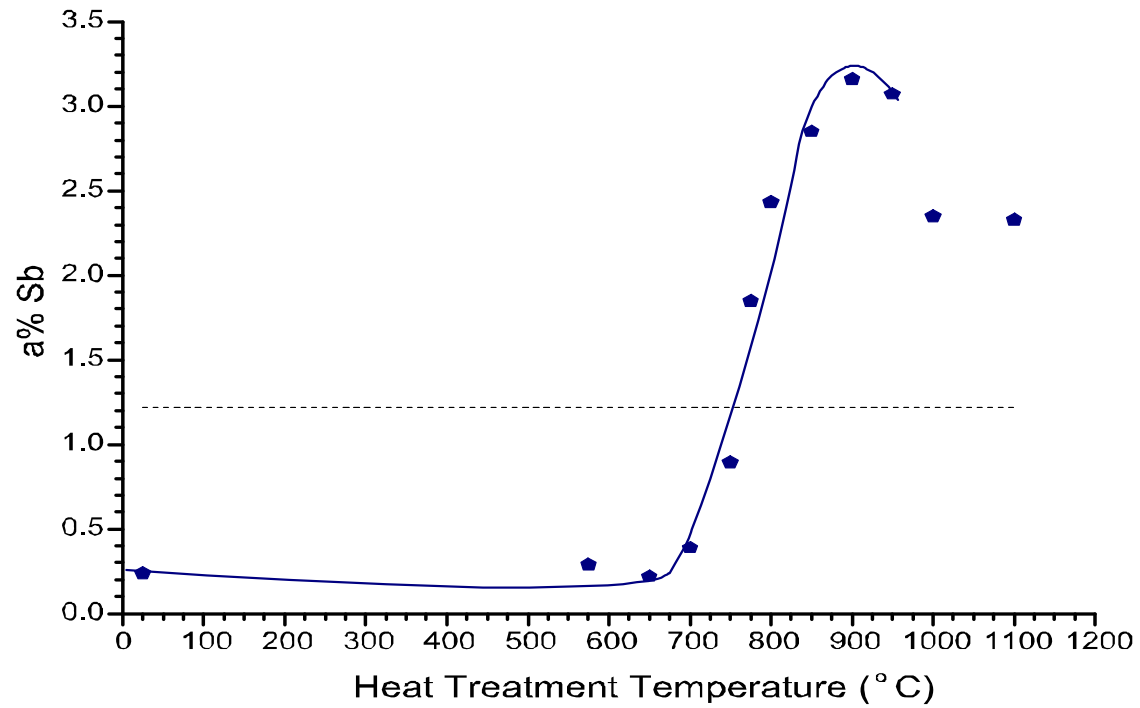
Surface Concentration of Antimony on Etched and Heat Treated Glass by Static SIMS
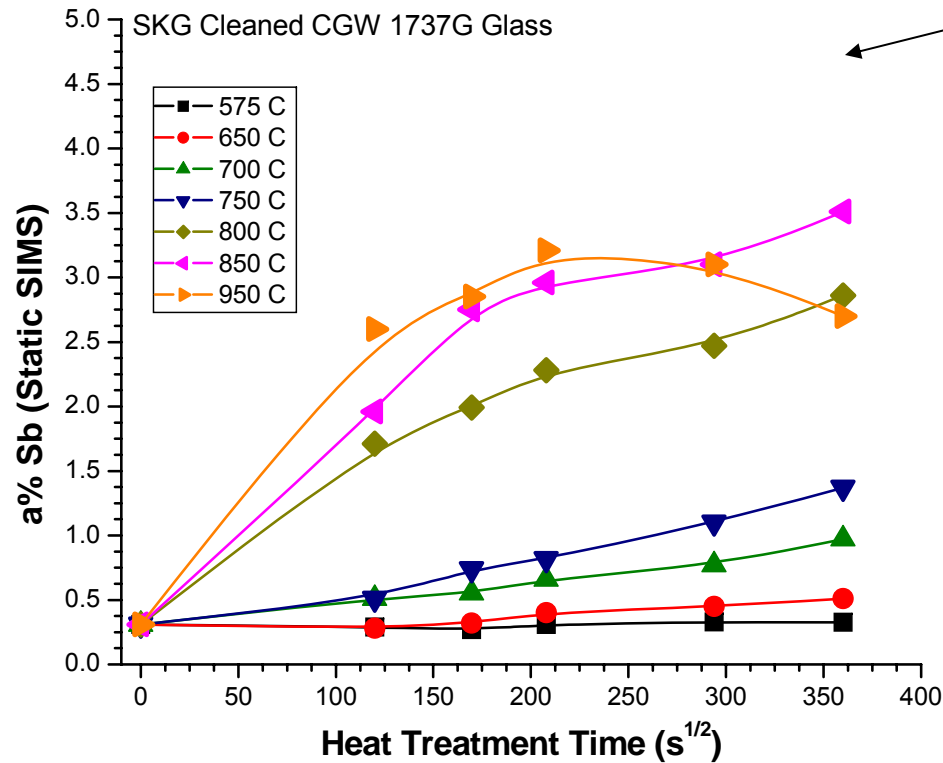
The graph on the left suggests that the enrichment of Sb occurs through bulk diffusion. Using only the linear portions of this concentration graph on the left, the activation energy for Sb diffusion is calculated below.

SKG Cleaned CGW 1737G Glass

Legend:
- 575 C
- 650 C
- 700 C
- 750 C
- 800 C
- 850 C
- 950 C

a% Sb (Static SIMS) vs Heat Treatment Time ($s^{1/2}$)

$ln(\Delta[Sb]/t^{1/2})$ vs 1/ Temp (K^{-1})

Q = 1.43 kJ

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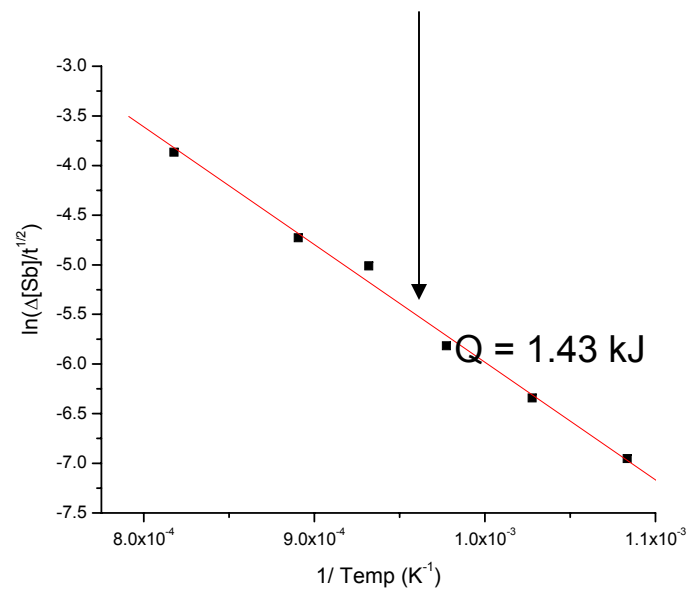
surface composition by FAB SIMS for commercial microsheet glass for FPD

Legend (left chart):
- (Silicon) / 5
- Aluminum
- Boron
- Σ (Alkaline Earths)

Left chart axes: Atom Percent vs Heat Treatment Temperature (^{o}C)

Legend (right chart):
- B_2O_3
- CaB_2O_4

Right chart axes: vapor species / sec vs Heat Treatment Temperature C
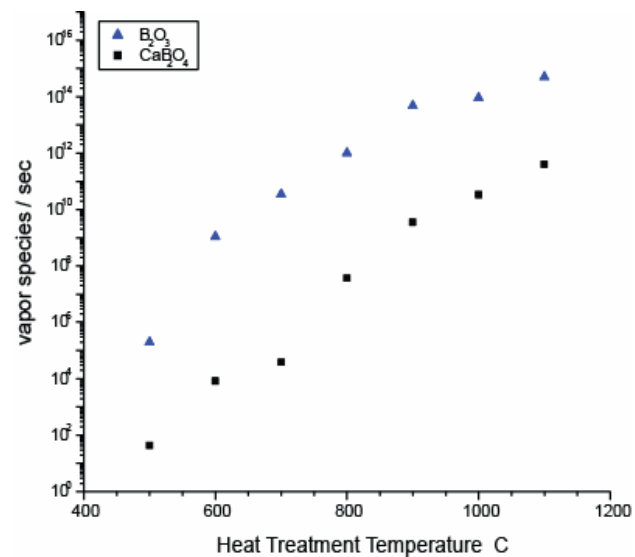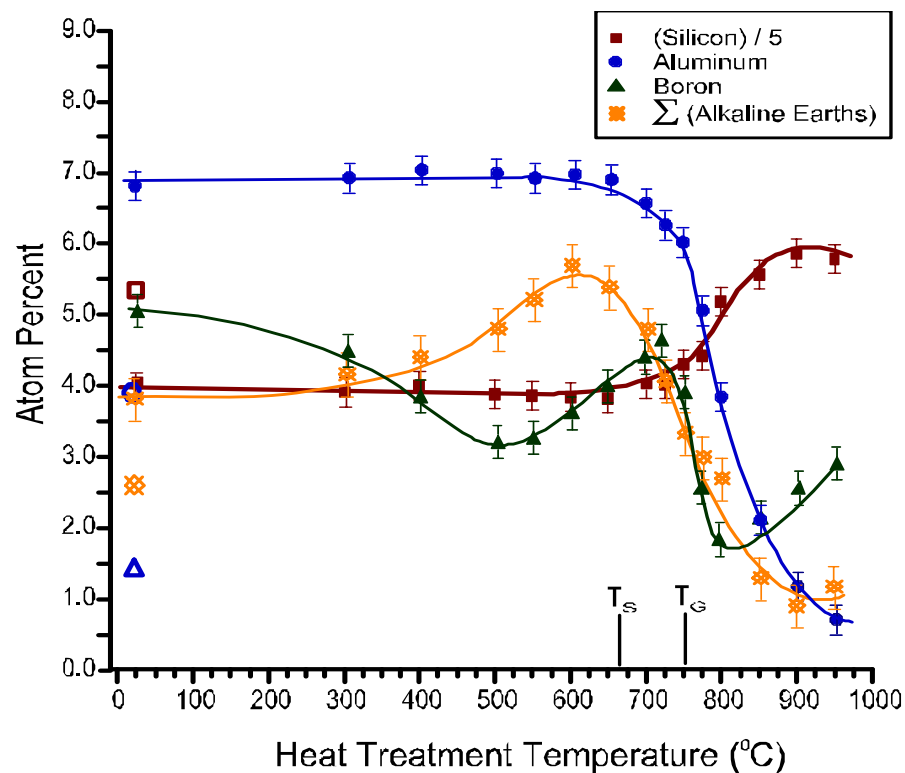
Estimated 'Initial' Molecular Flux of Boron Containing
Vapor Species from CGW 1737 Fracture Surface.

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^{29}Si MAS NMR

5.5% Sb_2O_3

4.5% Sb_2O_3

3.0% Sb_2O_3

1.5% Sb_2O_3

0.5% Sb_2O_3

0.0% Sb_2O_3

-60 -80 -100 -120 -140 -160

^{29}Si Frequency (ppm from TMS)
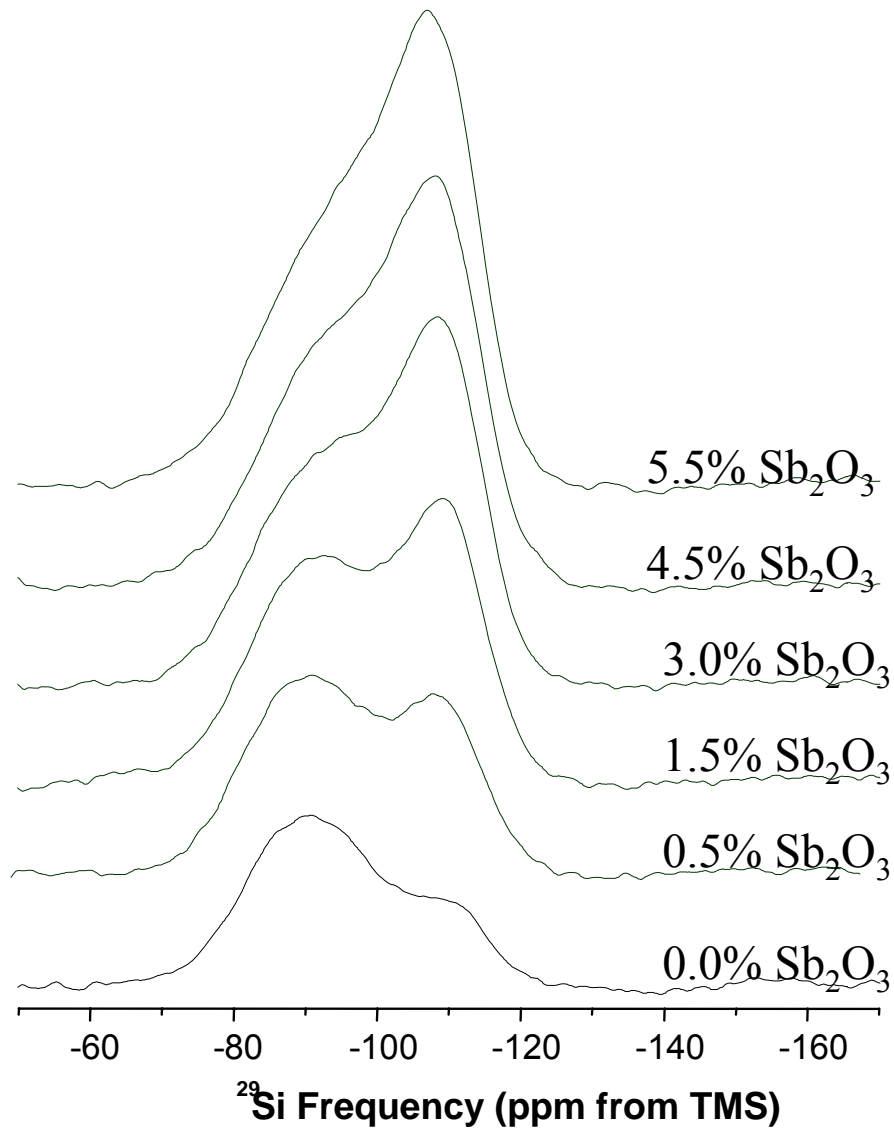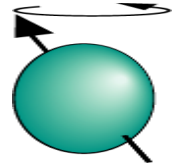
More Q^4(4Si) units are observed as the antimony oxide concentration increases.

^{11}B MAS NMR

3 fold boron   4 fold boron

5.5% Sb_2O_3

4.5% Sb_2O_3

3.0% Sb_2O_3

1.5% Sb_2O_3

0.5% Sb_2O_3

0.0% Sb_2O_3

40   20   0   -20   -40

^{11}B Frequency (ppm from BF_3)
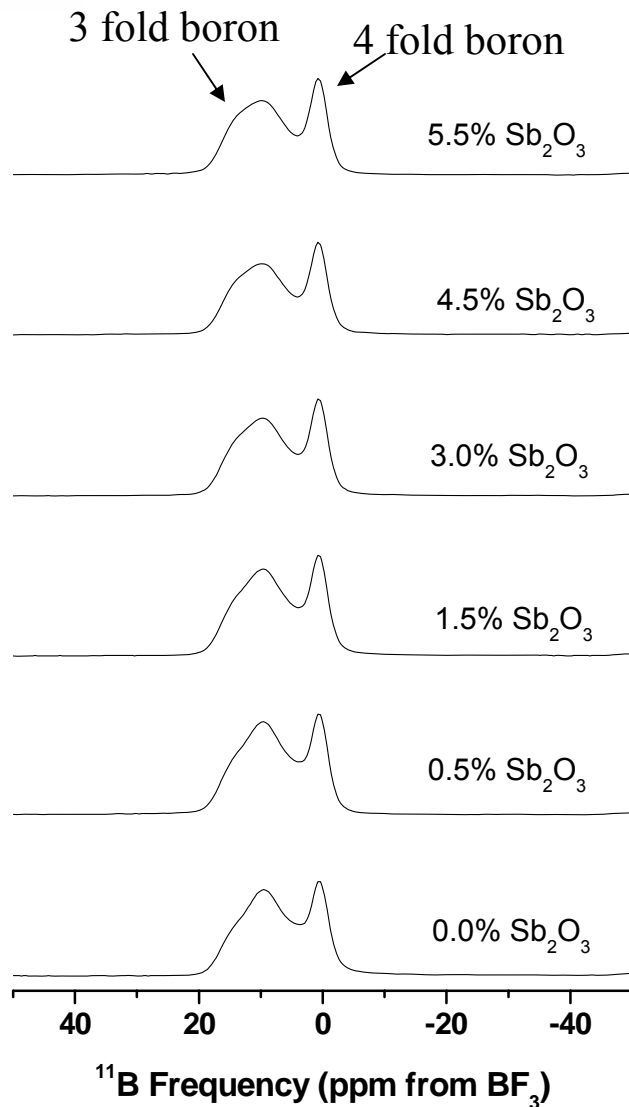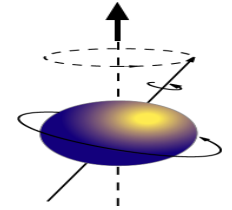
% Sb_2O_3	Ratio of 4/3 Fold Boron
0.0	0.45
0.5	0.50
1.5	0.57
3.0	0.66
4.5	0.62
5.5	0.66

With an increase in Sb_2O_3 concentration, there is an increase in tetrahedral boron units.

Boron-oxide in glass

(i)   (ii)   (iii)

Mol. % alkali modifier
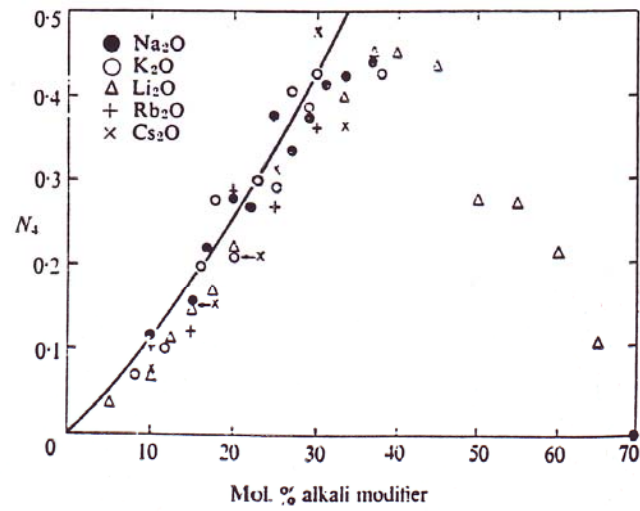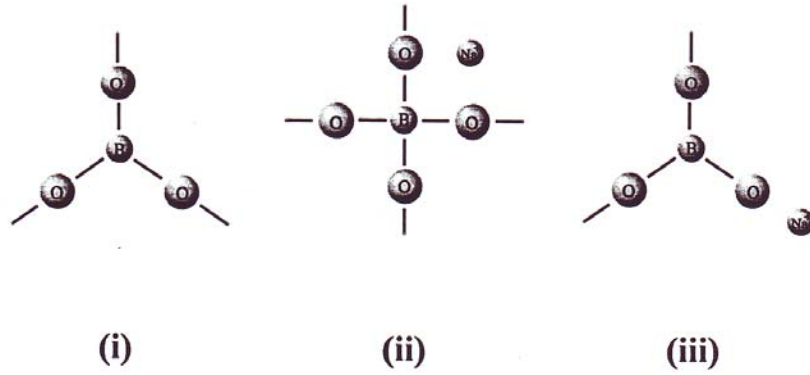
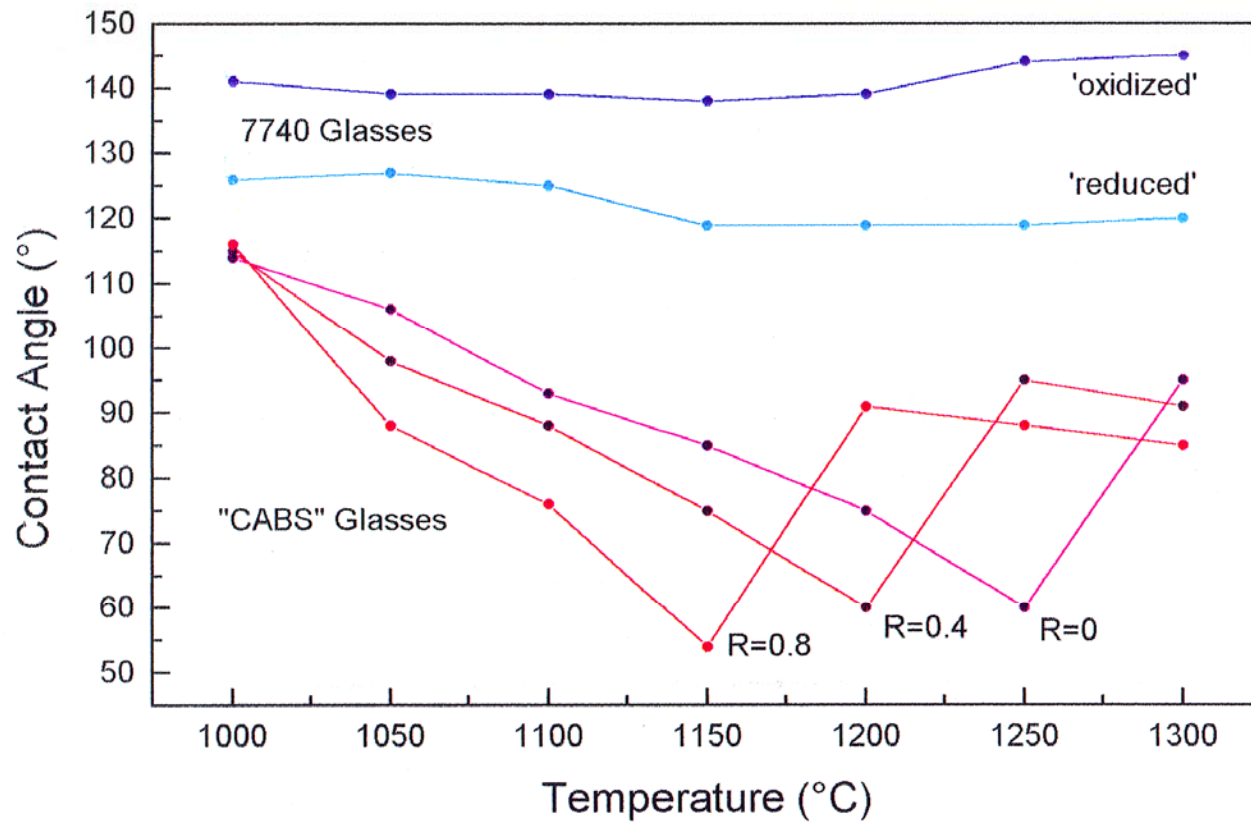$$R = \frac{x\ R_2O}{(1-x)\ B_2O_3}$$

Surface Tension of Borate Glasses

- B_2O_3 ~ 80 dyn/cm at 1000°C

- positive temperature coefficient

- exhibits boron oxide anomaly

- temperature coefficient is constant up to $20^{m}/o$ R_2O

Altogether, these data suggest the segregation and orientation of planar [BO₃] at the surface.

Contact Angles of Borosilicate Glasses on Silicon Carbide

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Boron in the bulk and at surfaces:

x=0 | 0 < x < 0.40 | 0.40 < x

$$xR_2O \cdot (1-x)B_2O_3$$

Increasing alkali oxide concentration

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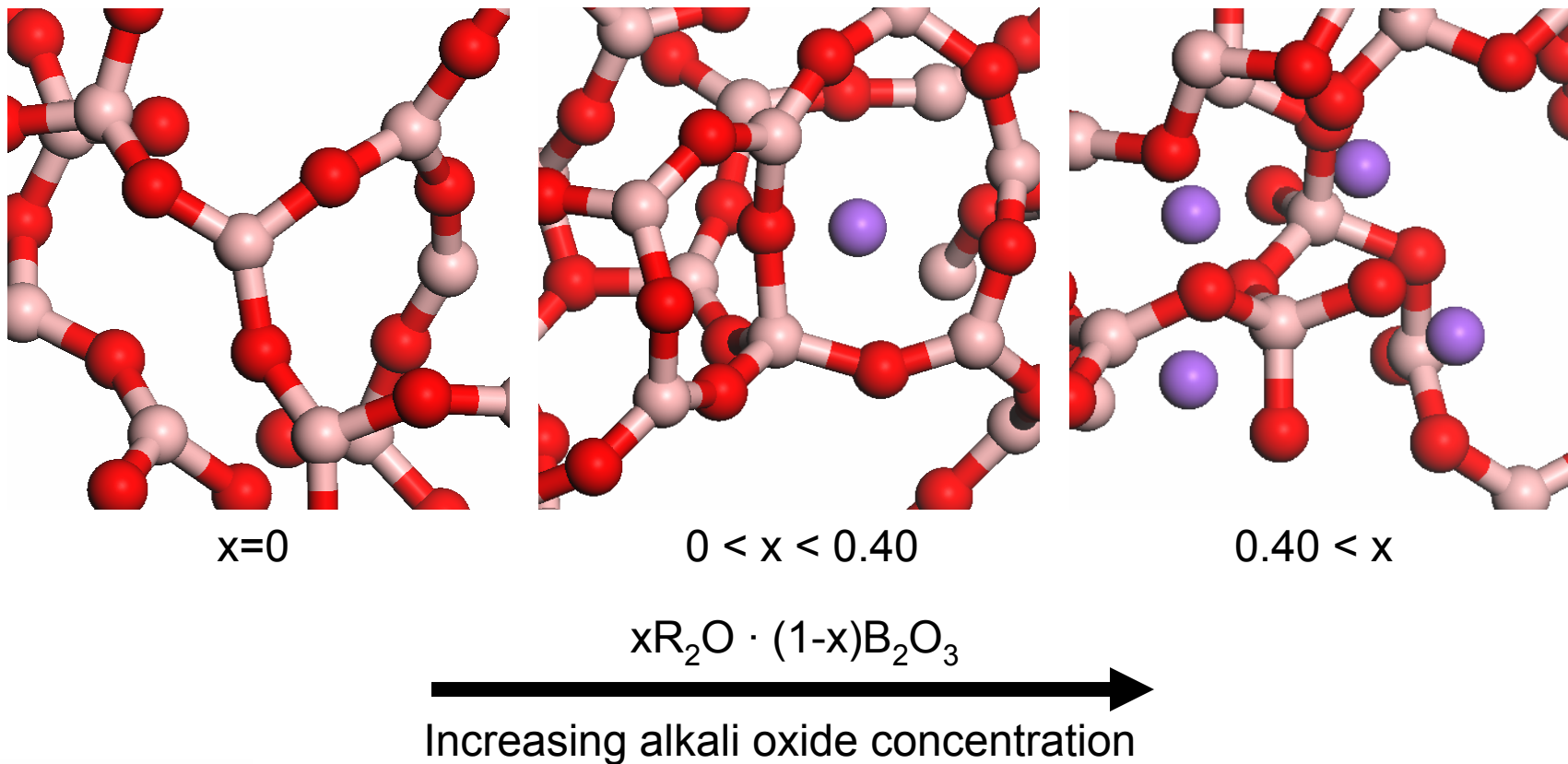
XANES vs. EXAFS
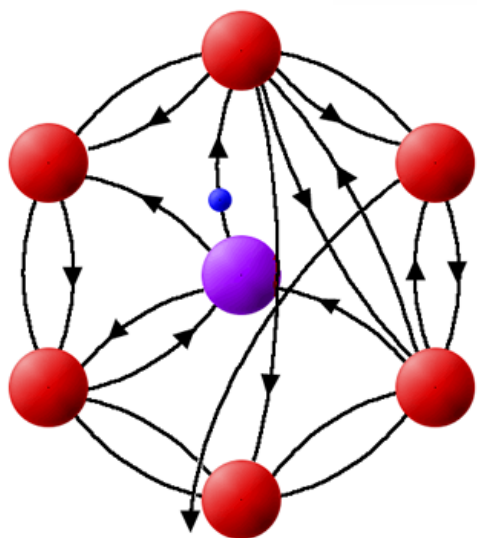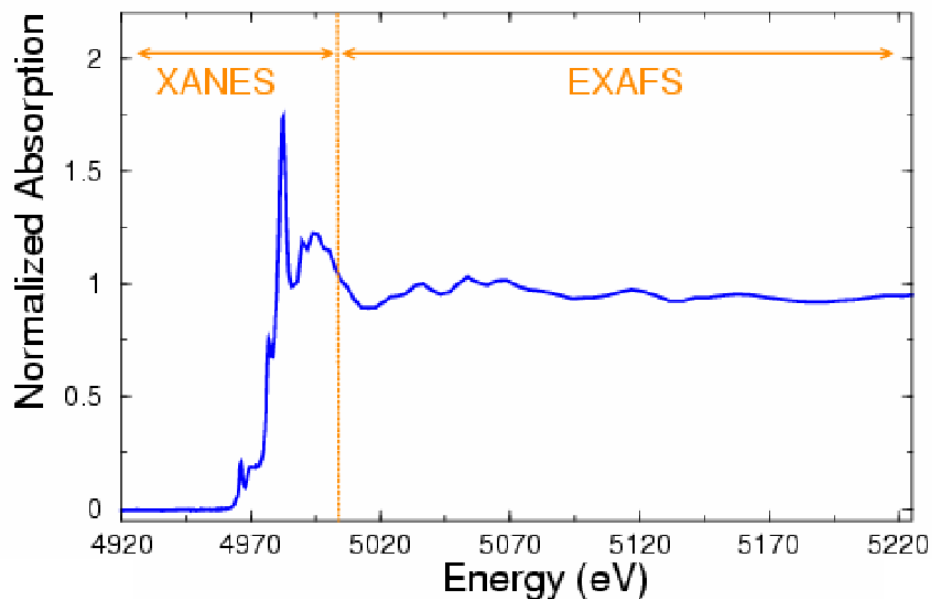
XANES is dominated by multiple scattering processes of low kinetic-energy photoelectrons.

EXAFS contains oscillations from scattering by high kinetic energy photoelectrons.
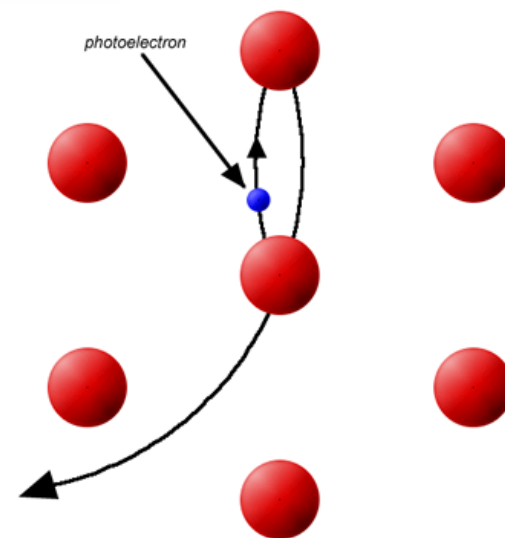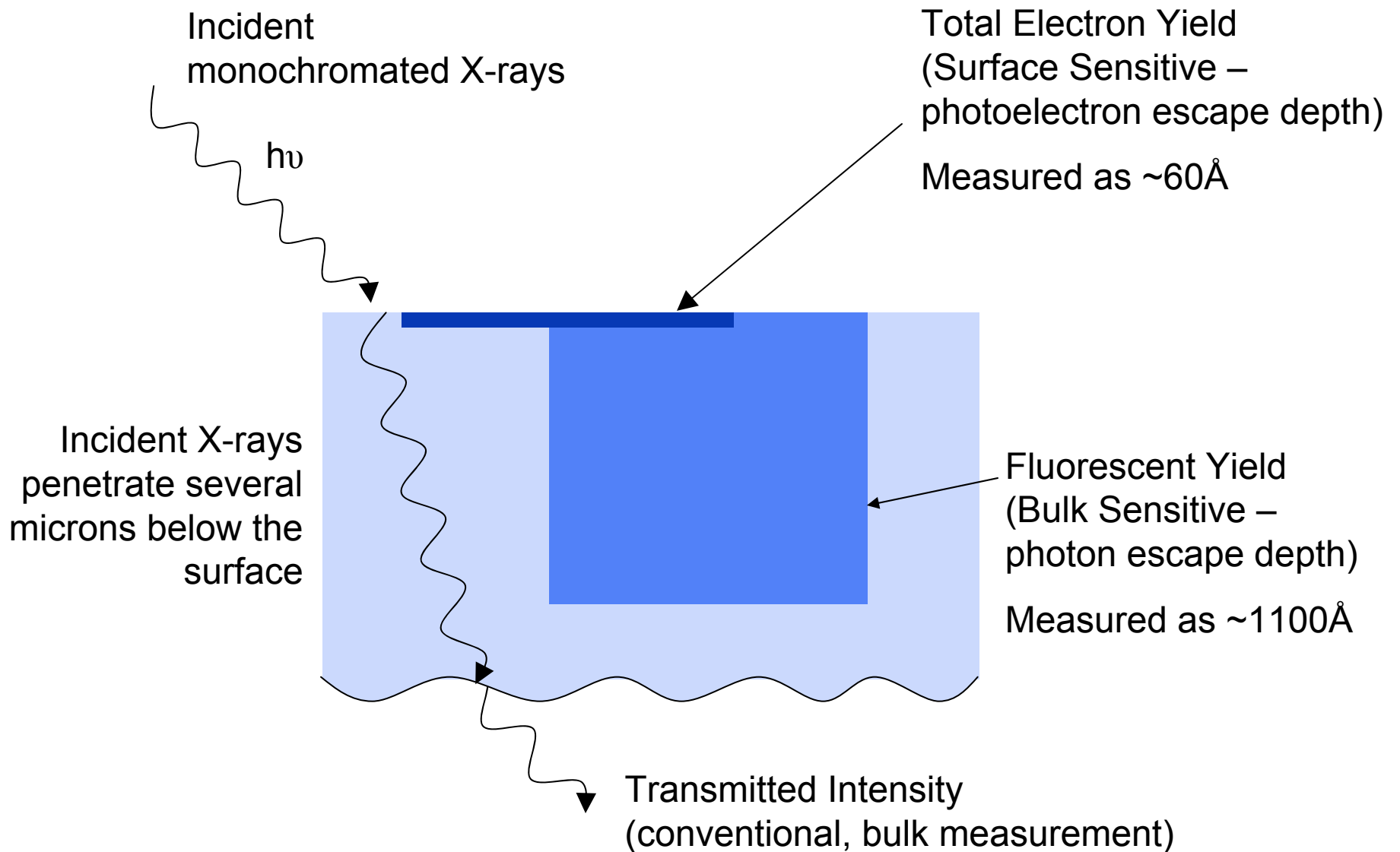
Surface Sensitivity

Incident
monochromated X-rays

hυ

Total Electron Yield
(Surface Sensitive –
photoelectron escape depth)

Measured as ~60Å

Incident X-rays
penetrate several
microns below the
surface

Fluorescent Yield
(Bulk Sensitive –
photon escape depth)

Measured as ~1100Å

Transmitted Intensity
(conventional, bulk measurement)

Boron XANES
at mineral surfaces

Peak A: only 3-fold boron
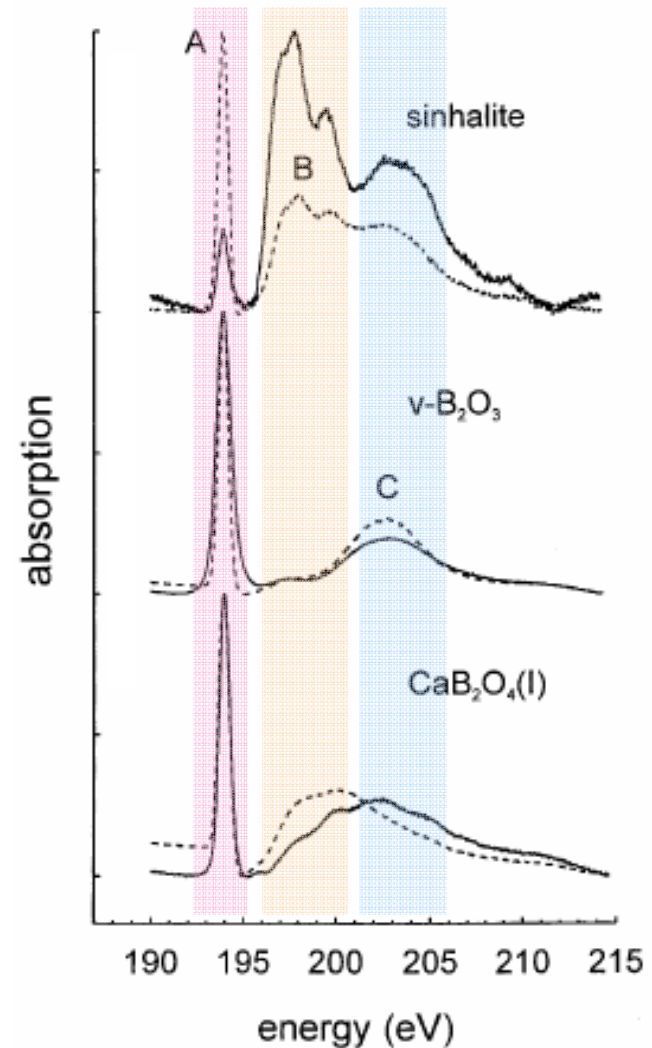
Peak B: only 4-fold boron

Peak C: contains information from both
3- and 4-fold boron

Solid spectra:
FY – bulk measurement

Broken spectra:
TEY – surface measurement

* Figures borrowed from Fleet and Lui, Phys. Chem. Minerals (2001).

SUMMARY:

opportunities for glass surface modification

- controlled electrical conductivity
- 'primed' for adhesion
- 'hardened' for abrasion resistance
- anti-reflective or highly reflective
- soluble or insoluble

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