Thermochemical effects at multicomponent glass surfaces

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Thermochemical Effects at Multicomponent Glass Surfaces

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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
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
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..$\text{B}_2\text{O}_3$
- alkali, alkali borate, etc evaporation
- cation out-diffusion usually faster than $\text{O}_2$ in-diffusion
- redox equilibria drives cation oxidation on cooling
Flame Attenuation Process

Flame Temperature $\sim 1800 \, ^\circ C$

Slower Cooling in the Forming Tube
TEM of FA Nano Fibers
TEM of FA Fibers (Glass A)

after leaching
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)
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.
Before: RMS = 0.14 nm

After: RMS = 0.93 nm

After heat-treatment, features (4-7 nm in height) appear on the surface.
Phenomenological Model for “Phase Segregation/Migration” to the Surface

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.)
FUSION PROCESS FOR MICROSELECT GLASS FABRICATION

Homogeneous glass delivered from melting unit

Root

Sheet drawn downward

Trough

5X surface segregation of Sb (.5% in the bulk for fining)
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 $\lambda$ is escape depth, $\theta$ is takeoff angle (w.r.t. surface plane).

**Case 1.** Atomically clean surface; no angular effect
Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

0.0 0.5 1.0 1.5 2.0 2.5 3.0
Relative a% Sb

0 20 40 60 80 100 120
Depth (Å) \{3\lambda \text{ for XPS}\}

- Sb 3d
- Sb 4d
- SSIMS
Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

Etched in acid

Relative a\% Sb vs. Depth (Å) \{3λ for XPS\}

- Sb 3d
- Sb 4d
- SSIMS
Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

Etched and Heat-treated at 800 °C in air

*Sb 3d
*Sb 4d
*SSIMS

*Heat Treatments were for 10 minutes; samples were then air quenched.
**Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS**

Etched and Heat Treated at 1100 °C in Air

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

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Center for Glass Surfaces, Interfaces and Coatings
Antimony Depth Distribution by Angle-Resolved XPS and FAB-Static SIMS

Heat Treatments were for 10 minutes; samples were then air quenched.
Case 2. Thin, uniform layer A of thickness, t, on top of substrate B (where $E_{k,A} = E_{k,B}$)

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

$$I_B = I_B^\infty \exp \left( -t/\lambda_B \sin \theta \right)$$

Ratio,

$$\frac{I_A}{I_B} = \frac{I_A^\infty}{I_B^\infty} \frac{1 - \exp \left( -t/\lambda_A \sin \theta \right)}{\exp \left( -t/\lambda_B \sin \theta \right)}$$
Case 3. Thin, patched layer A of thickness, $t$, on top of substrate B where $\gamma$ is the fractional coverage of A

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

- As-Received
- Etched
- Etched % HT 800 C
- Etched % HT 1100 C

Depth (Å)

a% Sb

0.0 0.5 1.0 1.5 2.0 2.5 3.0

0 10 20 30 40 50 60 70 80

Depth (Å)
FAB-Static SIMS Analysis of Sb segregation versus temperature

Heat Treatment Temperature (°C)

a% Sb

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5
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.

\[ Q = 1.43 \text{ kJ} \]
surface composition by FAB SIMS for commercial microsheet glass for FPD
More Q⁴(4Si) units are observed as the antimony oxide concentration increases.
With an increase in $\text{Sb}_2\text{O}_3$ concentration, there is an increase in tetrahedral boron units.
Boron-oxide in glass

\[ R = \frac{x \cdot R_2O}{(1-x) \cdot B_2O_3} \]
Surface Tension of Borate Glasses

- $\text{B}_2\text{O}_3 \sim 80 \text{ dyn/cm at } 1000\text{°C}$
- positive temperature coefficient
- exhibits boron oxide anomaly
- temperature coefficient is constant up to 20m/o $\text{R}_2\text{O}$

Altogether, these data suggest the segregation and orientation of planar $[\text{BO}_3]$ at the surface.
Contact Angles of Borosilicate Glasses on Silicon Carbide

![Graph showing contact angles versus temperature for different glasses and conditions.](image-url)
Boron in the bulk and at surfaces:

\[ xR_2O \cdot (1-x)B_2O_3 \]

Increasing alkali oxide concentration

\( x = 0 \)
\( 0 < x < 0.40 \)
\( 0.40 < x \)
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

Total Electron Yield
(Surface Sensitive – photoelectron escape depth)
Measured as ~60Å

Incident monochromated X-rays

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

SUMMARY:

opportunities for glass surface modification

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