Lecture 8
Chemical/Electronic Structure of Glass

Syllabus Topic 6. Electronic spectroscopy studies of glass structure

Fundamentals and Applications of X-ray Photoelectron Spectroscopy (XPS)

a.k.a. Electron Spectroscopy for Chemical Analysis (ESCA)

Review of Lecture 7

XPS data come with Auger as by-product.

XPS of solids consists of core levels and valence band.

Intensity of core levels decreases with decreasing BE.

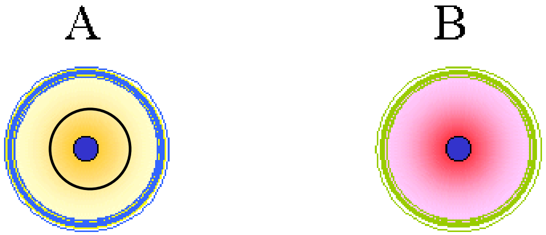
BE of a given level is unique to the particular element.

ARXPS allows depth profile by varying the angle between the detector and sample surface normal.

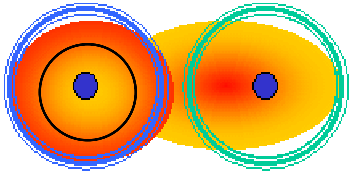
XPS probes <10 nm of the surface region.

The area under the peak of a core level peak is directly proportional to the concentration of that particular element.

Chemical Structure by XPS
Charge potential model for bonds



Free atoms



Bonded atoms

Consider valence electrons as hollow charged sphere. Neglecting relaxation effects:

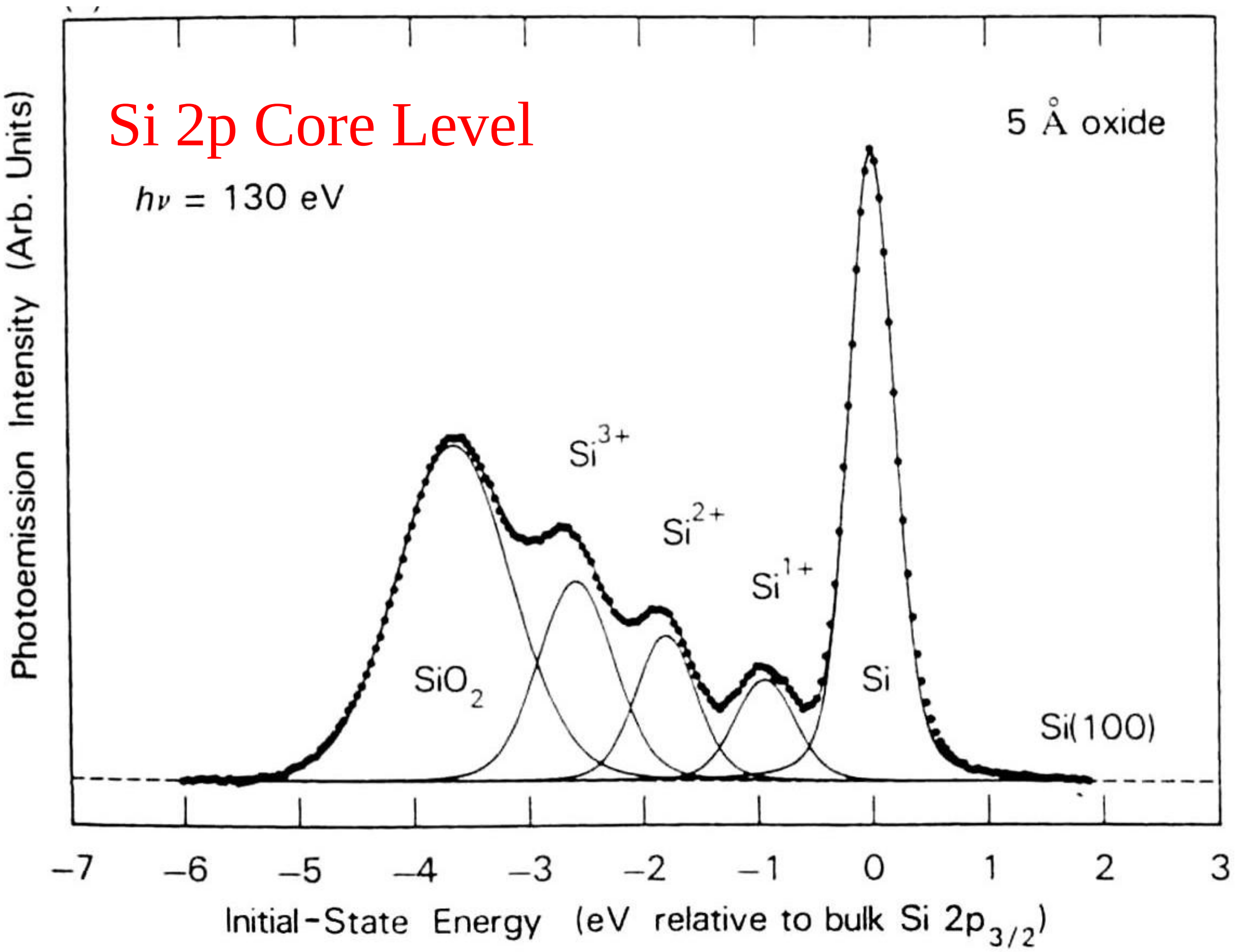
$$E_i = E_{i0} + q_i/r_v + \Sigma_{i=j}\ q_i/r_{ij}$$

$$\Delta E_i = \Delta\ q_i/r_v + \Delta(\Sigma_{i=j}\ q_i/r_{ij})$$

Δq_i for valence electrons => change in energy of all inner level by $\Delta q_i/r_v$ where r_v is the valence shell radius.

http://ligand-depot.rcsb.org/marvin/chemaxon/marvin/help/Charge.html

Chemical Shifts of Si oxide



Si 2p Core Level

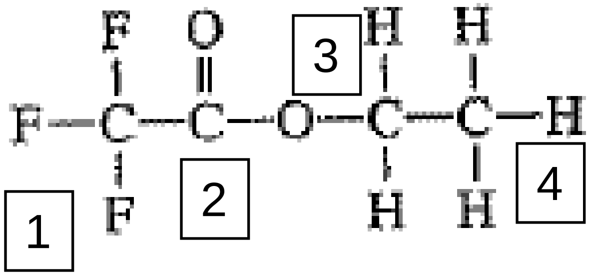
- ❖ Binding energy increases with increasing oxidation state of the cations.

http://www.emsl.pnl.gov/new/emsl2002/tutorials/engelhard_xps.pdf

Sensitivity of core levels to local bonding

Map the peaks for the four kinds of C in the molecule!

C 1s spectrum of ethyl trifluoroacetate



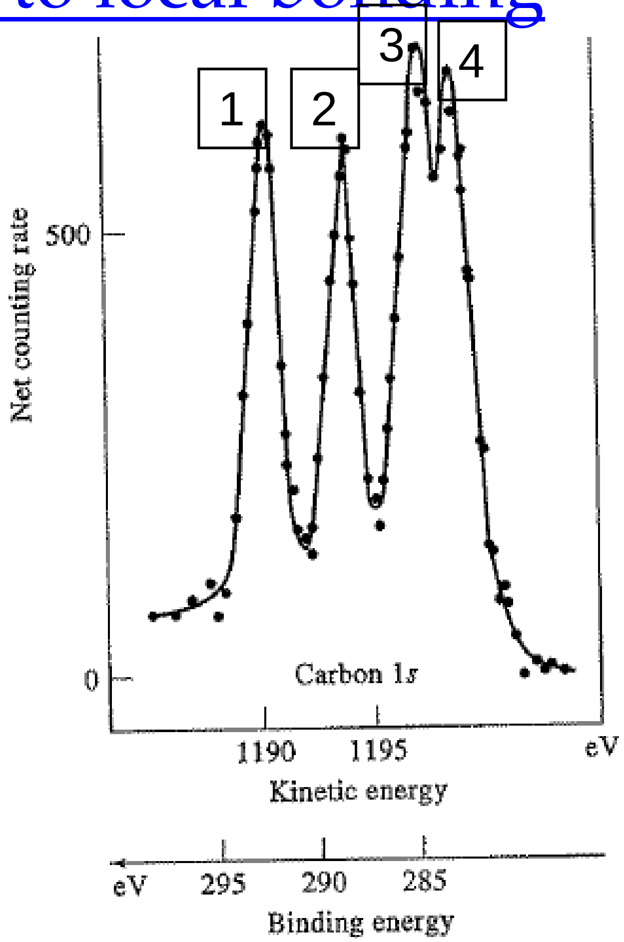
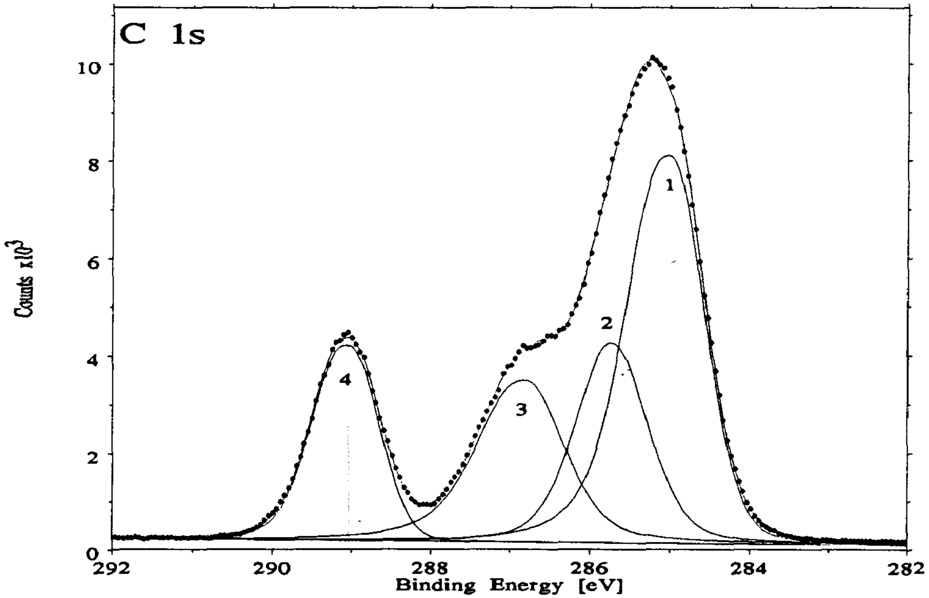
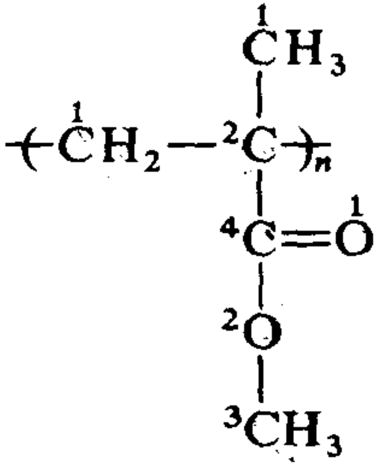
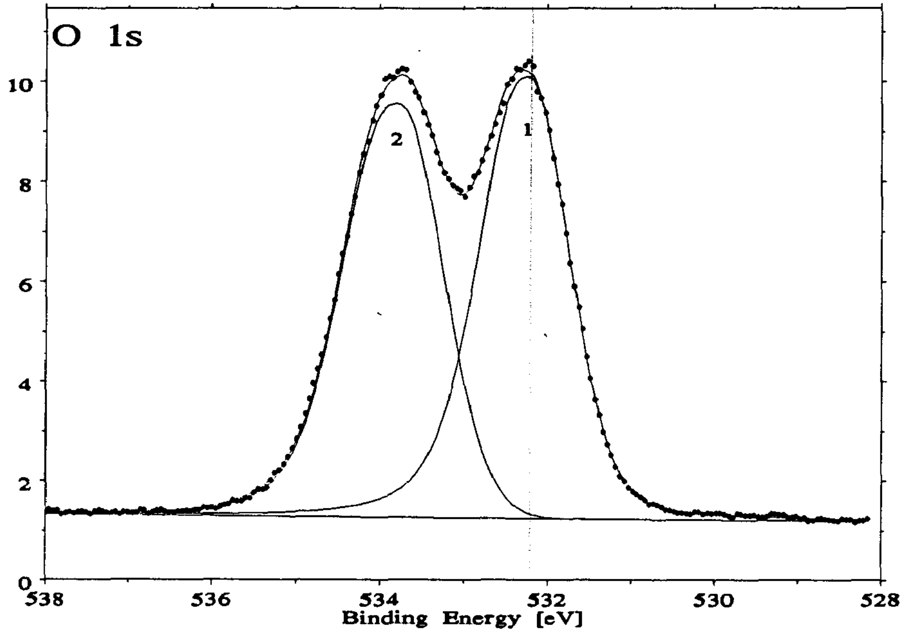


Figure 21-5 Carbon 1*s* X-ray photoelectron spectrum for ethyl trifluoroacetate. *(From K. Siegbahn et al.,* ESCA: Atomic, Molecular, and Solid-State Studies by Means of Electron Spectroscopy, *p. 21. Upsala: Almquist and Wiksells, 1967. With permission.)*

Polymethylmethacralate (PMMA)



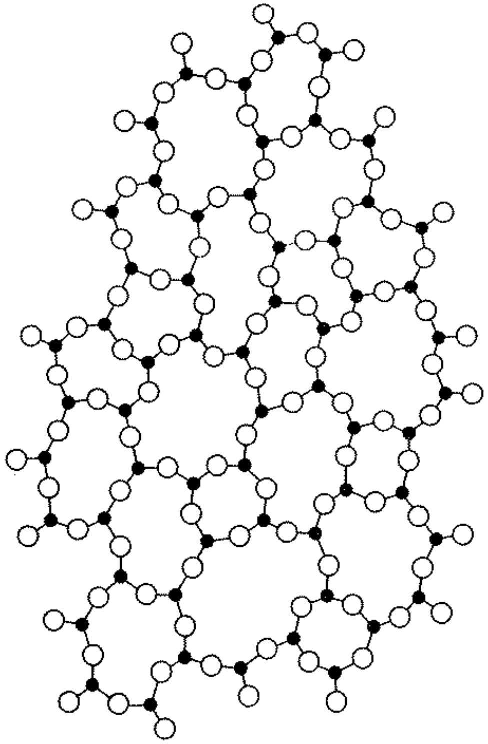

$$\left(\overset{1}{C}H_2-{}^{2}\overset{\overset{1}{C}H_3}{\underset{{}^{4}C(=\overset{1}{O})-{}^{2}O-{}^{3}CH_3}{C}}\right)_n$$

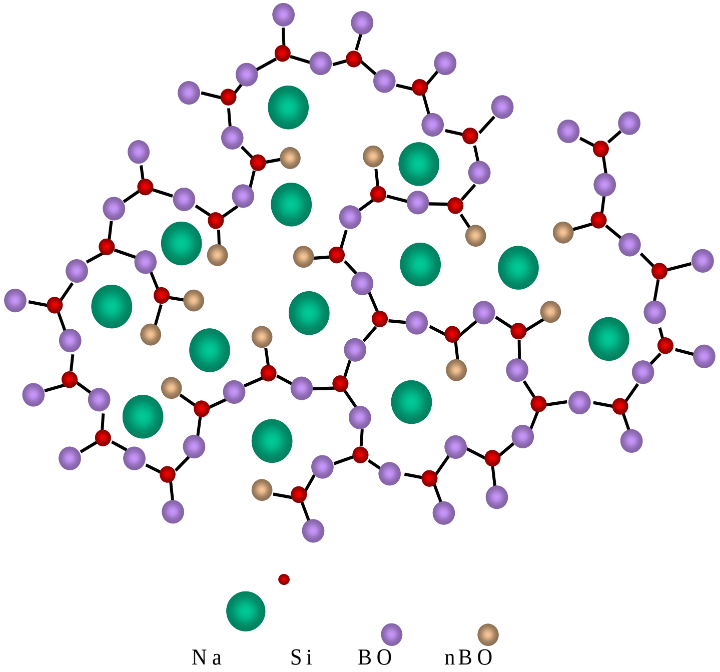


A deconvolution procedure may be needed when the components are not resolved.

To obtain unique decomposition of spectrum, additional information may be required, including estimates from ab initio simulations.

Silica glass structure modification by alkali oxide addition

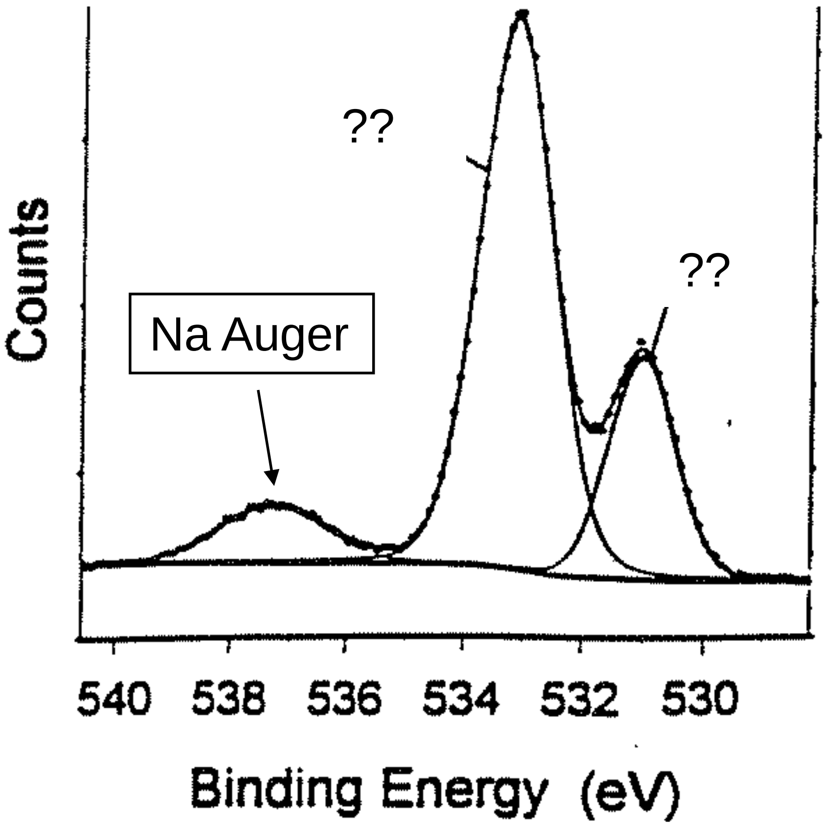




Formation of NBO with the addition of M_2O

O 1s spectrum of sodium silicate glass

What do the two ?? marked peaks represent?



C. H. Hsieh et al. J. Non-cryst. Solids 168, 247-257 (1994).

O 1s Chemical shift (Δ_{NBO-BO}) in silicate glasses

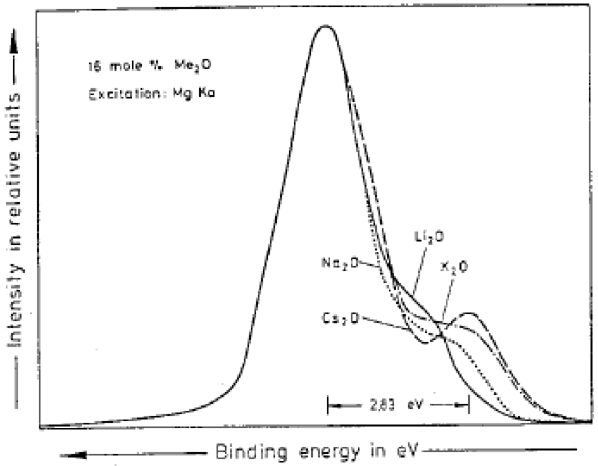
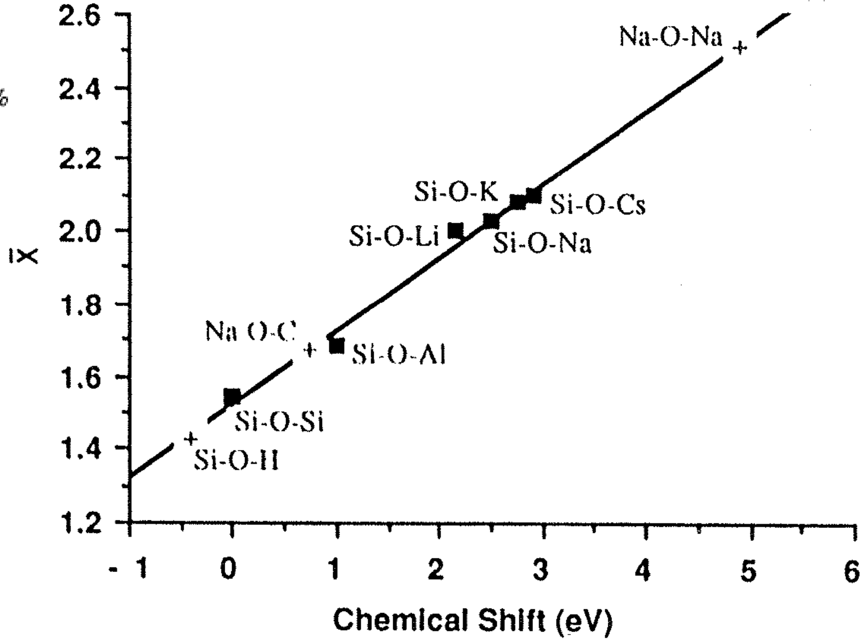


Figure 9. High-resolution Ols spectra of alkali silicate glasses with 16 mol-% Me_2O where Me = Li, Na, K or Cs [from 2.3].

2.3. R. Bruckner, H.-U. Chun, and H. Goretzki, "Photoelectron Spectroscopy (ESCA) on Alkali Silicate and Soda Aluminosilicate Glasses," Glastechn. Ber., 51[1], 1-7 (1978).

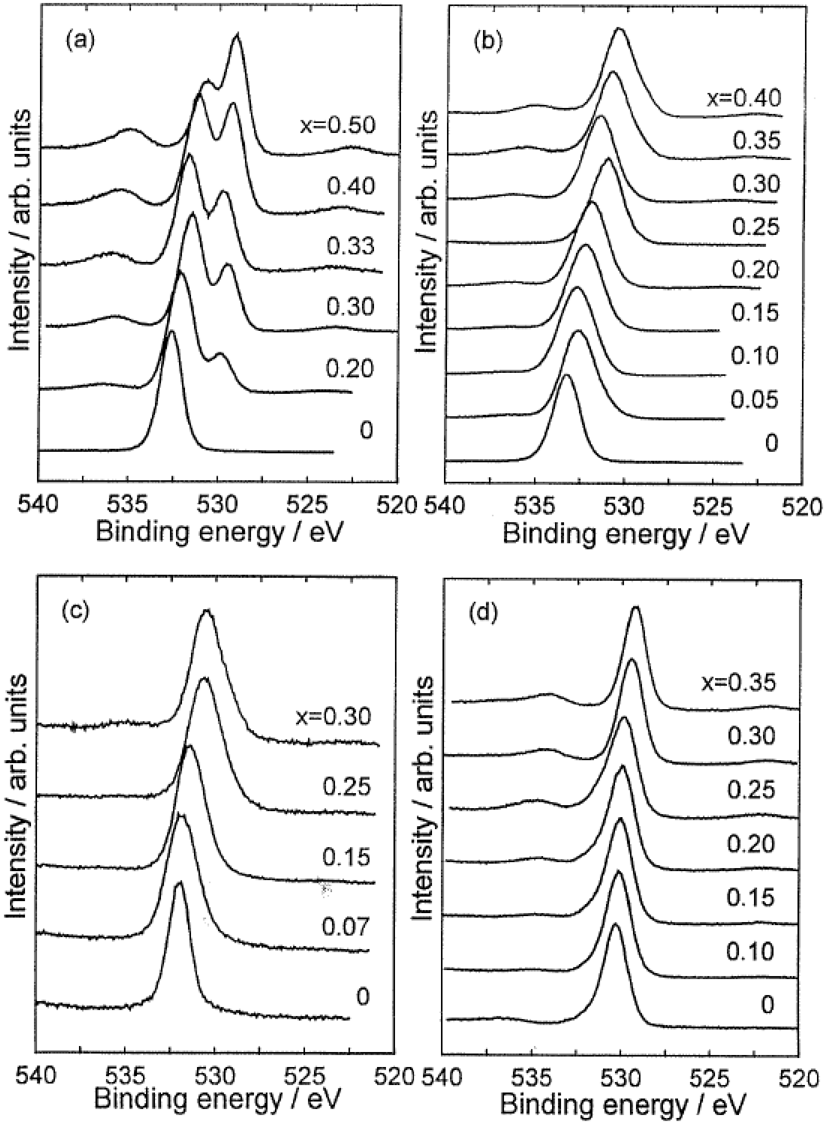


nical shift of the O_{1s} photoelectron band between non-bridging and bridging oxygens as a function of the mean electronegativity differences ($\bar{X}$).

Nasu et al. JNCS 99, 140 (1988)

O 1s spectra of sodium silicate, borate, germanate and tellurite glass series

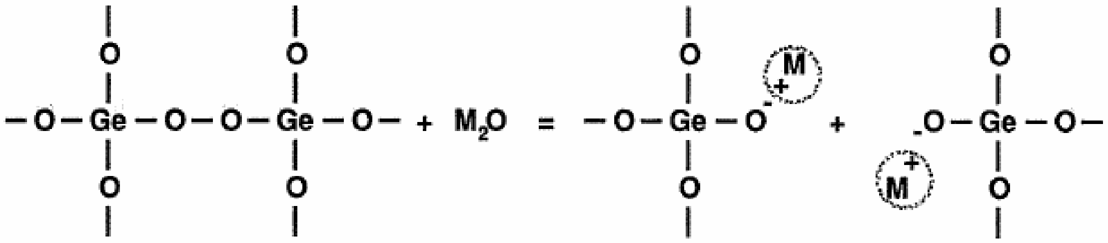
(a). $xNa_2O-(1-x)SiO_2$
(b). $xNa_2O-(1-x)B_2O_3$
(c). $xNa_2O-(1-x)GeO_2$
(d). $xNa_2O-(1-x)TeO_2$



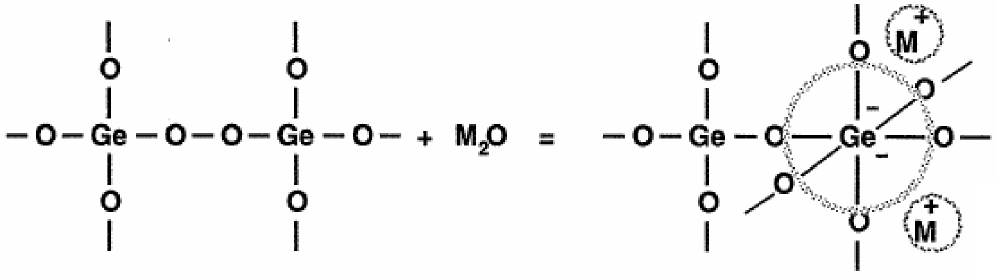
What question was raised earlier in the course with regard to the difference in the structure of alkali silicates and germanates?

Nanba and Miura

Network modification in alkali germanate glasses



(4-fold + 2NBO)



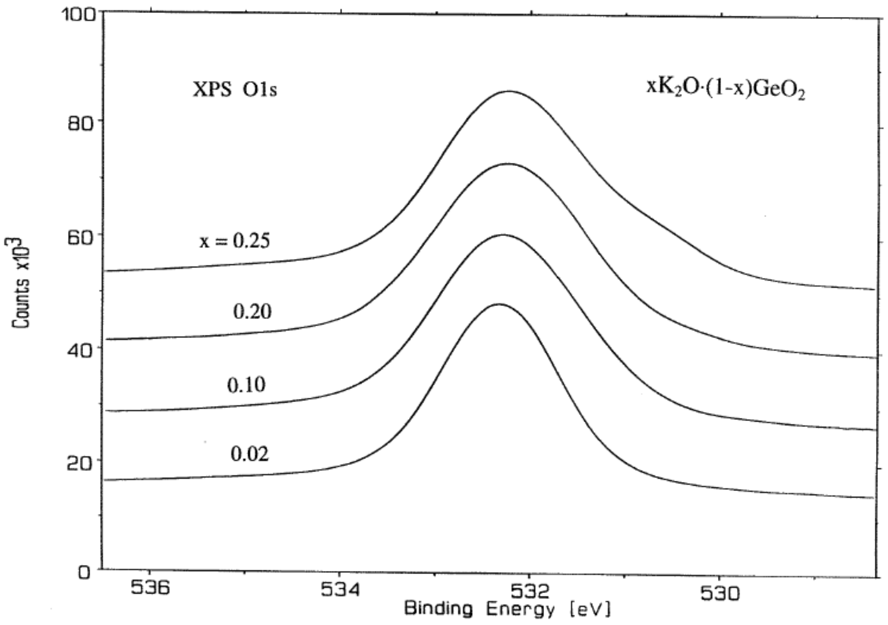
(6-fold, no NBO)

Addition of alkali means two choices:

Creation of NBO as in silicates

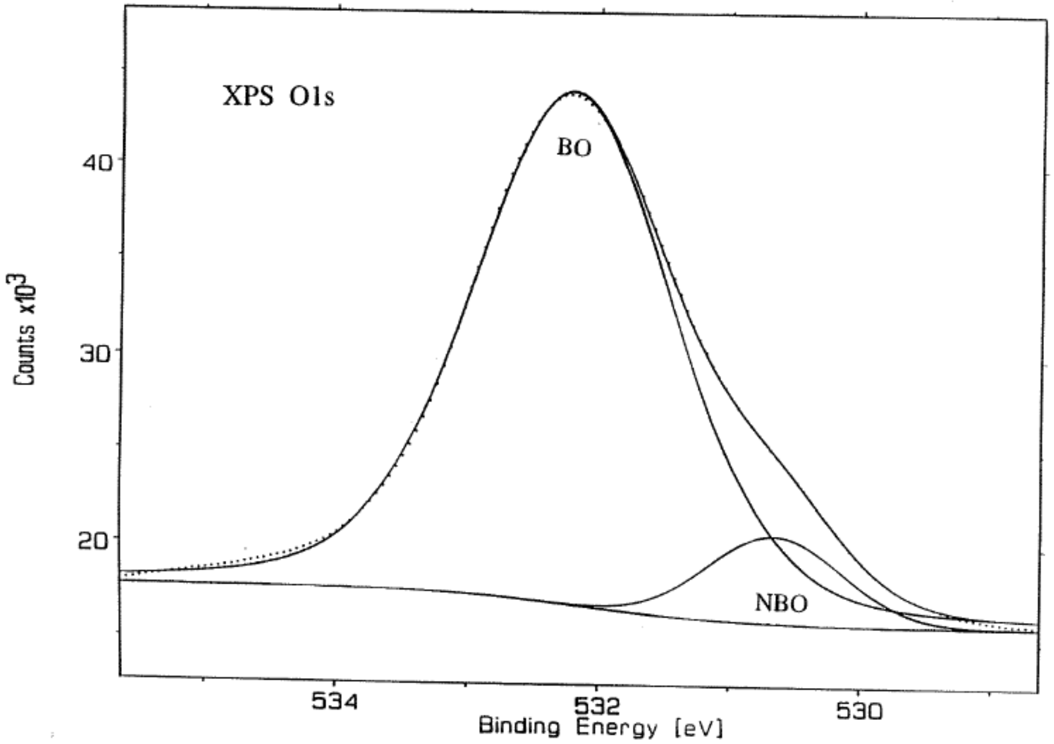
or

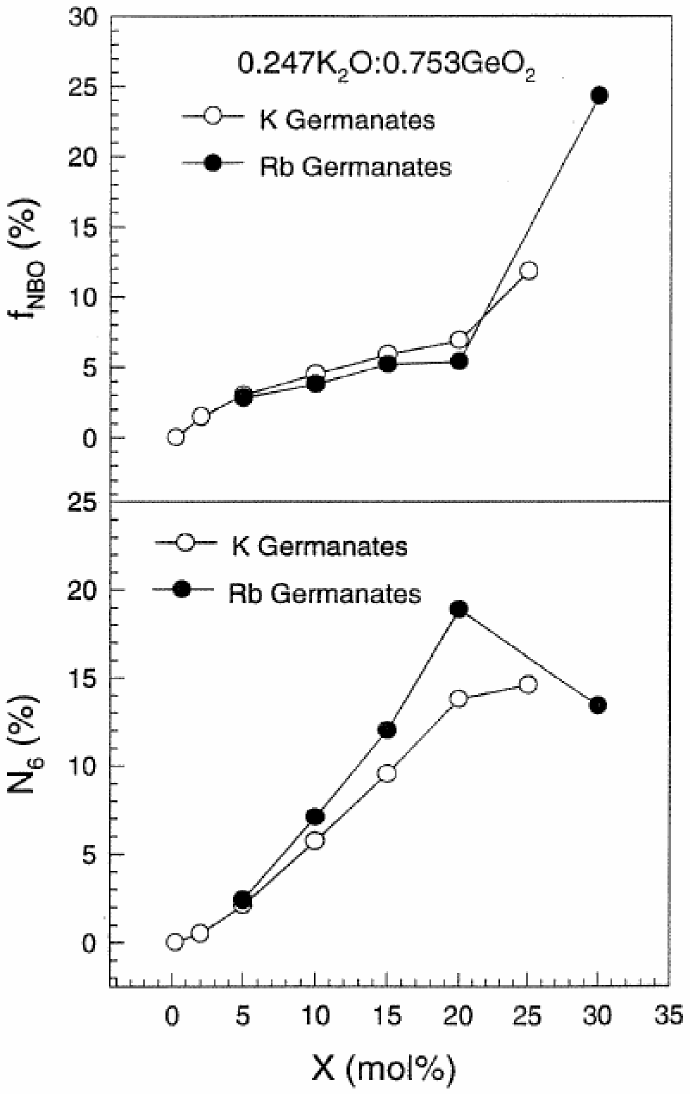
Change of Ge from tetrahedral to octahedral coordination



Xu et al. Phys Chem Glass (1996)

NBOs vs Ge-octahedra?



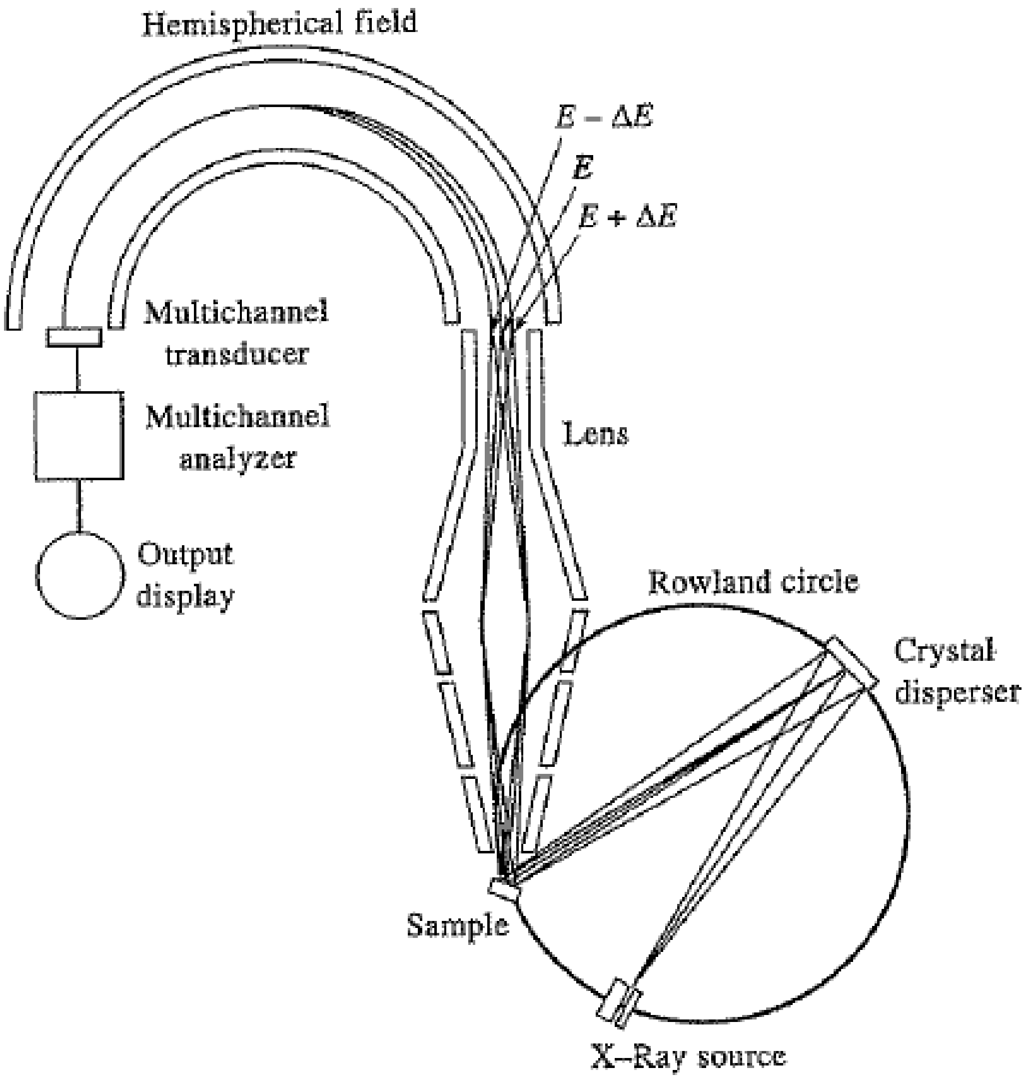


O-1s BE for SiO_2

533.0	Polycrystalline powder of stishovite, natural mineral from meteor crater Arizona, the densest modification of SiO2
533.2	Alpha-quartz
532.9	pelletized, composition determined by XPS is SiO2.08
533.8	Thermal oxide - SiO2.1.
532.7	Thermaly grown SiO2
532.7	Fused quartz.
532.8	alpha phase, insulator, polycrystalline
533.2	Quartz (rock crystal).
532.0	Polycrystalline powder of stishovite from meteor crater, Arizona

NIST X-ray Photoelectron Spectroscopy Database: http://srdata.nist.gov/xps/

XPS instrument schematic



Complications of XPS on glass

Charging of surface
- Error in BE
- Error in composition

Damage by sputtering (if used in depth analysis)
- Alteration of structure

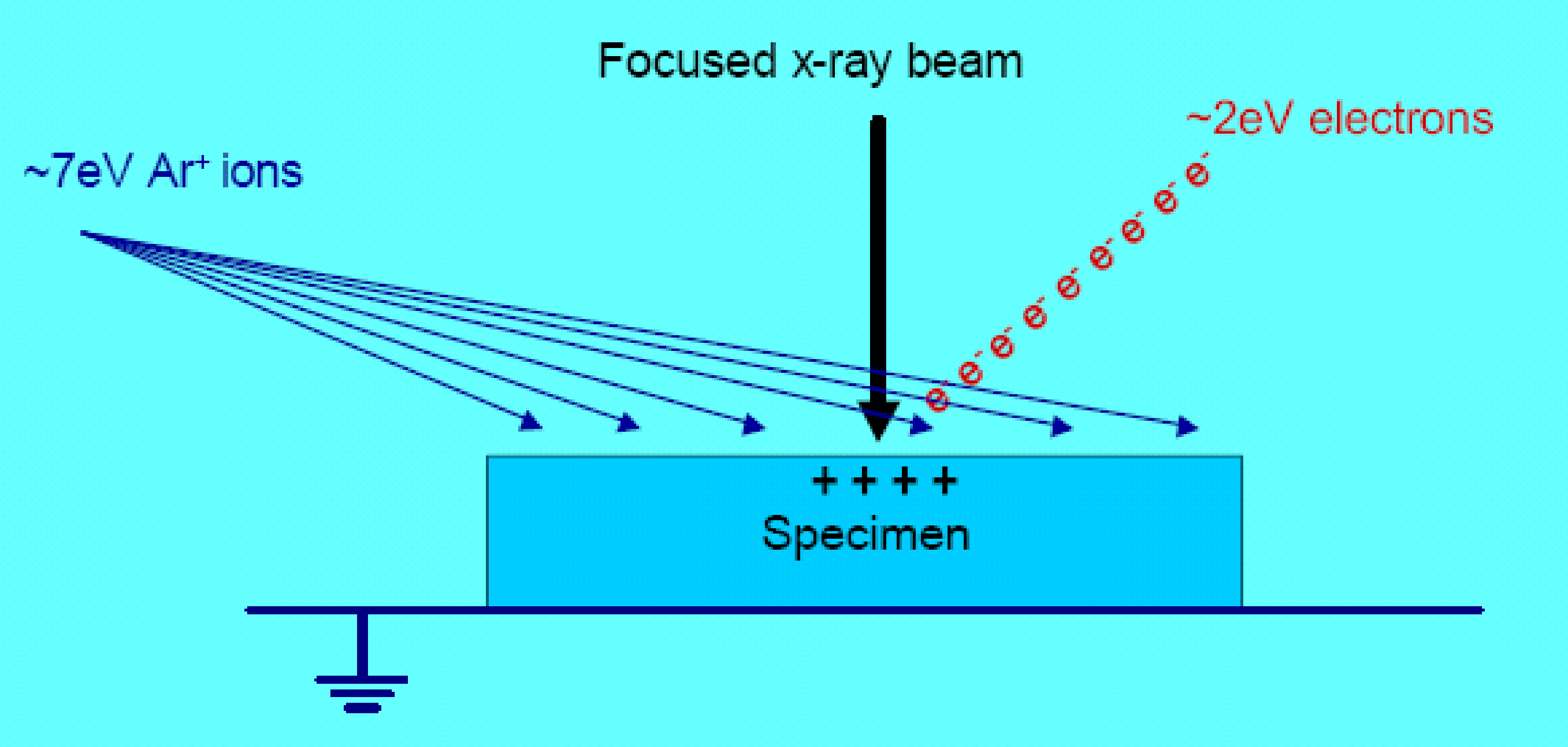
Charging of insulating sample

Net build up of charge on the surface when e loss is not compensated by inward flow => Surface at unknown +V => All peaks shifted/broadened by ~ the same amount.

Problem mostly corrected by flooding with low energy e.

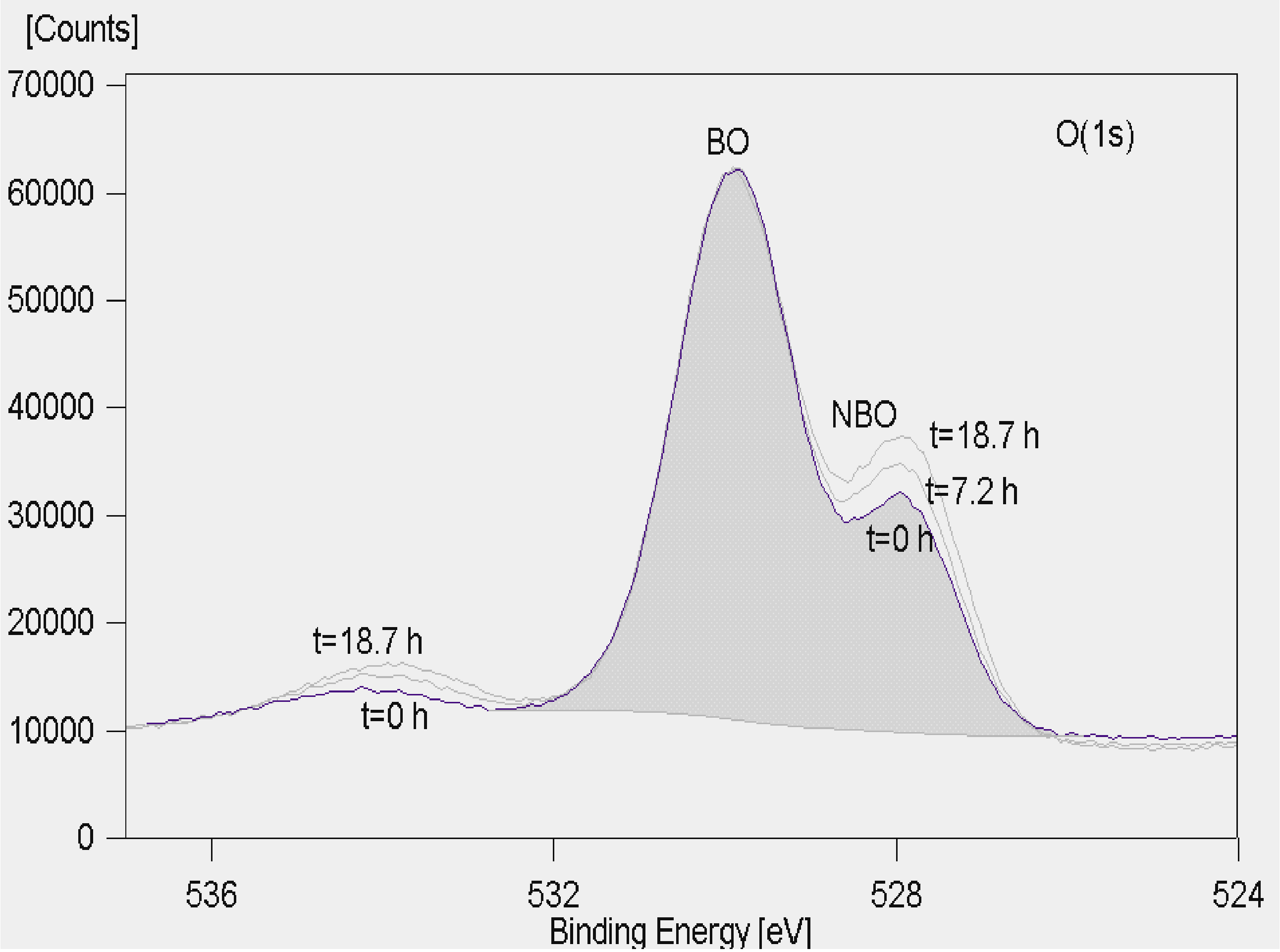
For precise b.e. values, need a reference:

1. Adventitious C-1s (may not be present on pristine surface)
2. Thin overlayer of Au
3. Internal reference e.g. Si-2p in silicate glasses.
4. Use Auger parameter



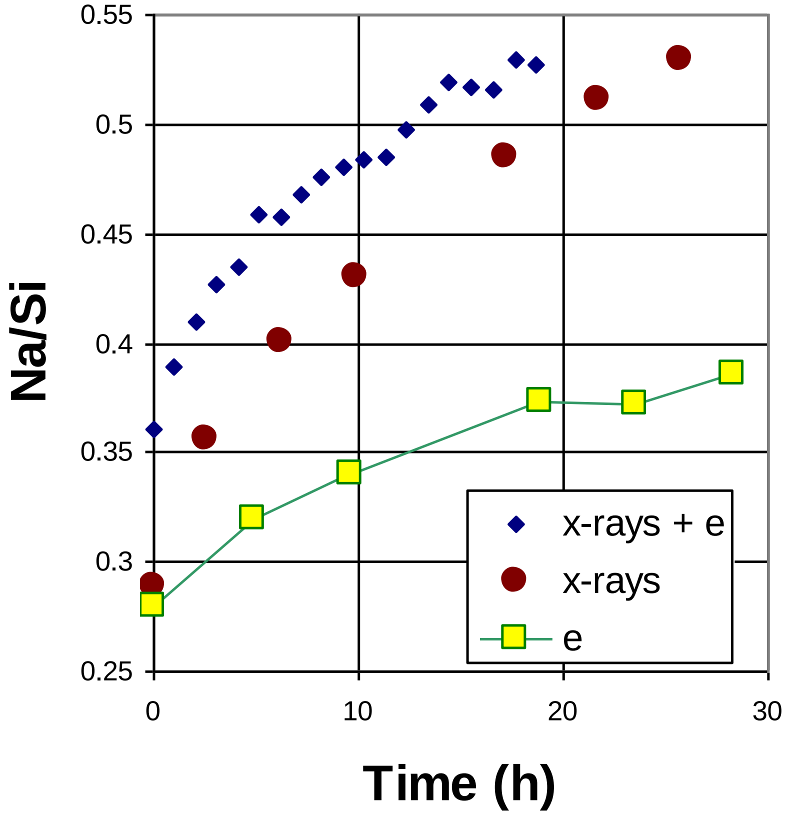
- Low-energy electrons from a cold cathode flood gun alleviates positive charging
- Low-energy source of positive ions alleviates the surrounding negative charge

f_{NBO} vs. time of XPS experiment



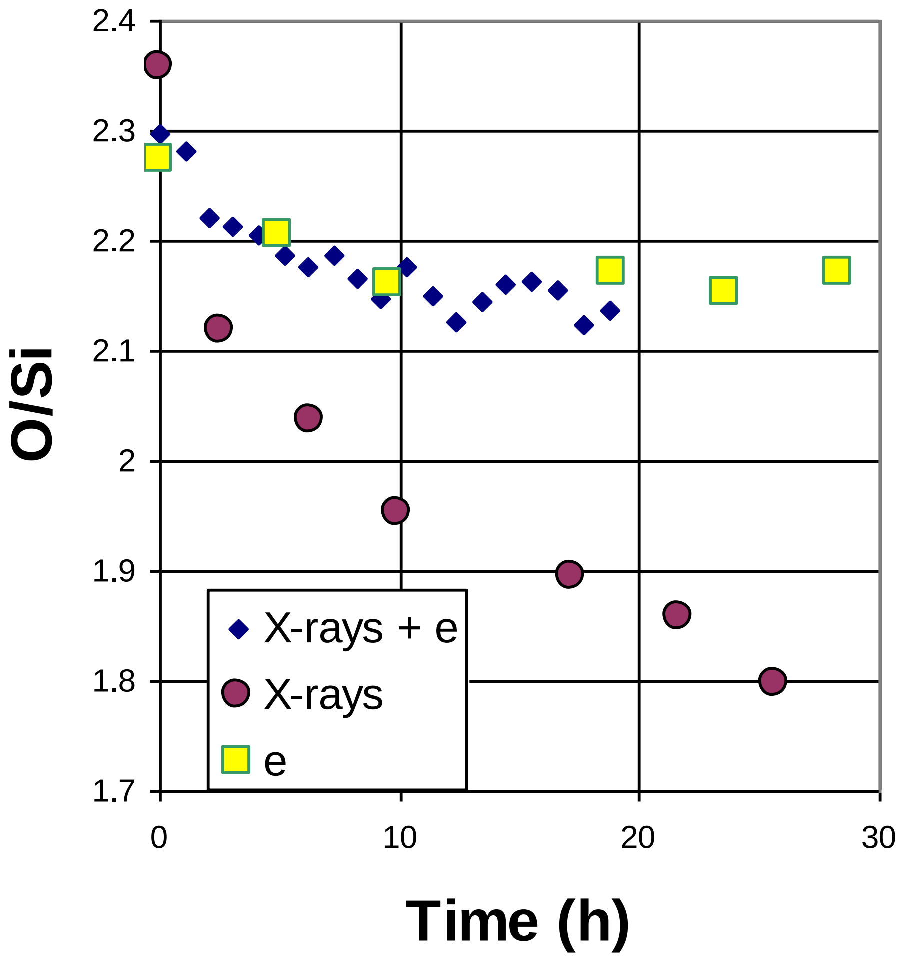
Soda-Lime-Silicate Glass 13.30Na_2O 11.62CaO 73.86SiO_2 (mole %)

Na conc. vs time



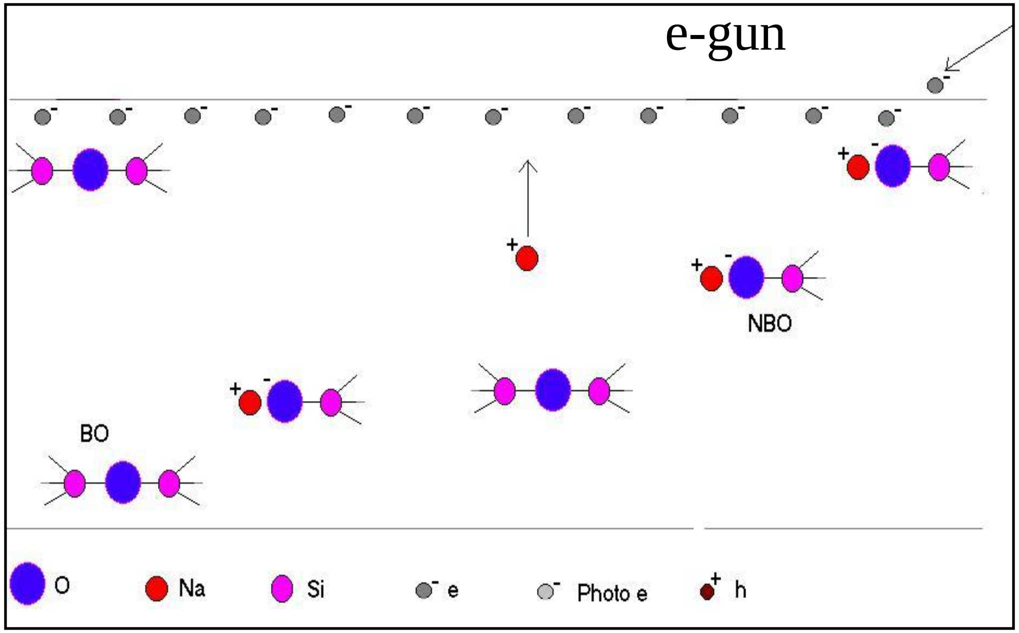
X-irradiation is the primary cause for Na accumulation. Once liberated, Na can migrate to the surface very quickly, if e-field is present.

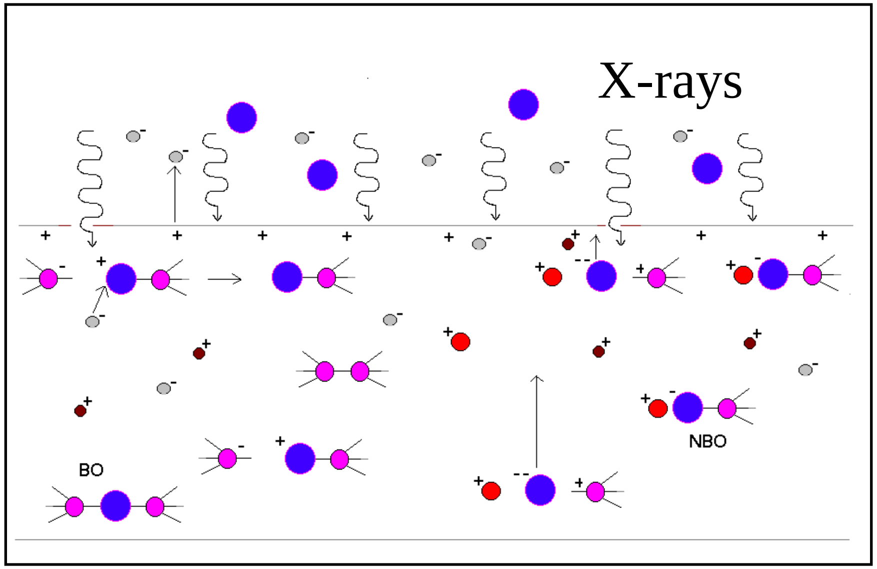
Total oxygen vs time

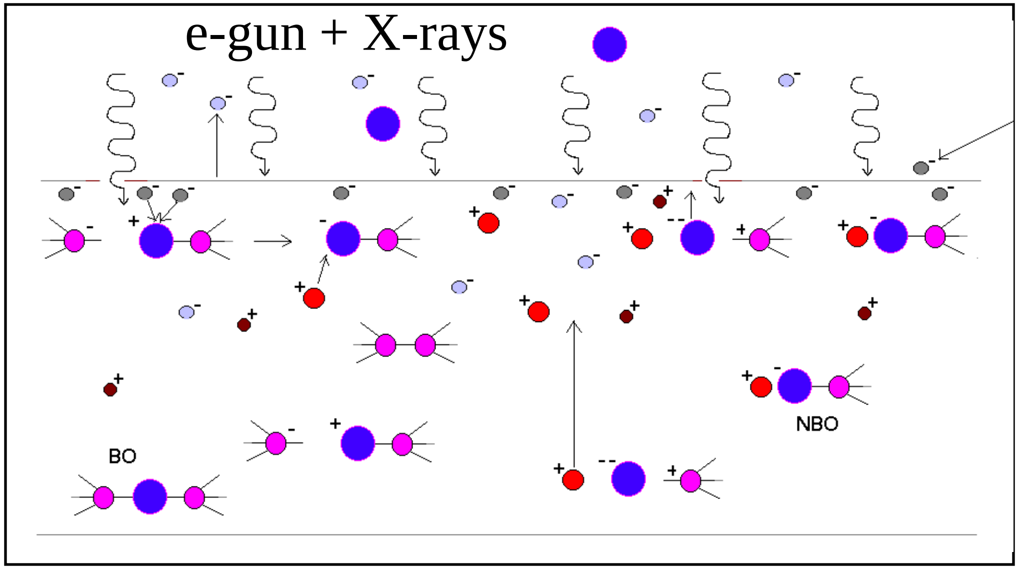


The loss of oxygen is mostly determined by x-ray dose; electrons retard it.

Contrast of x-ray and e-gun effects







For experimental reasons, both e-gun and x-rays had to be used *during* analysis of all cases.

Summary: XPS capabilities

- Elements detected from Li to U.
- Nondestructive (x-ray beam damage in certain materials?)
- Quantitative.
- Chemical bonding (e-density) analysis.
- Surface sensitivity from 5 to 75 angstroms.
- Conducting and insulating materials.
- Detection limits that range form 0.01 to 0.5 atom percent.
- Spatial resolution for surface mapping from >10 μm.
- Depth profiling (non-destructive as well as destructive).