Exploring glass surface with high-resolution XPS and LEIS:

Examples of Fundamental Studies and Applications

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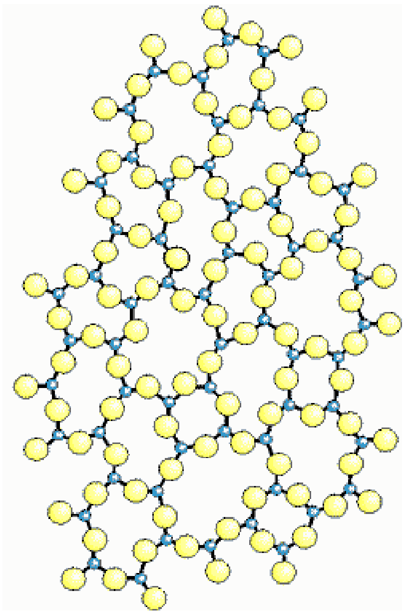
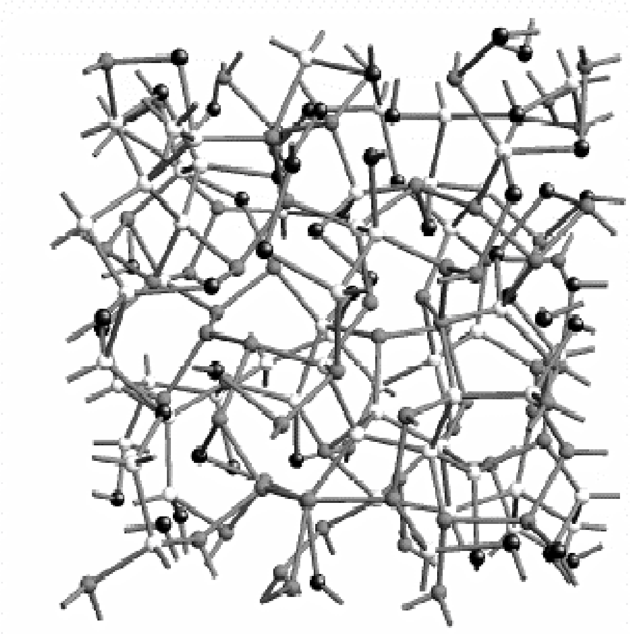
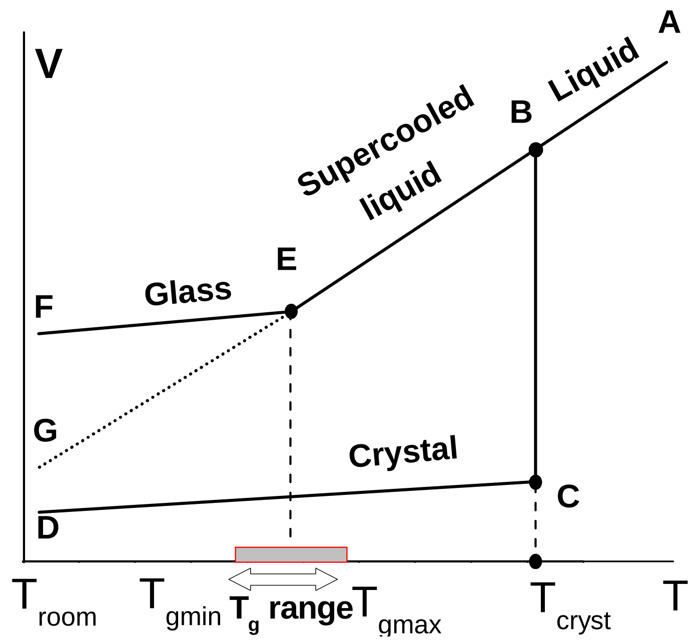
"The surface was invented by the devil"
Wolfgang Pauli

Glass structure – lack of translational symmetry







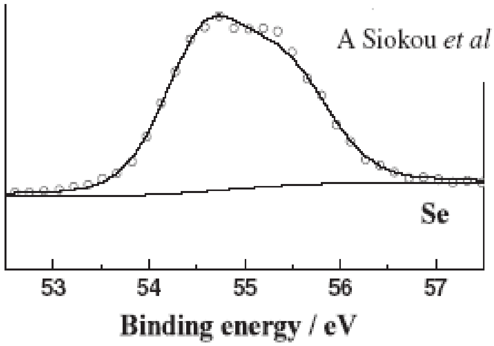
High-resolution XPS:

one of the fundamental structural methods in glass science

Other methods:

Raman/FTIR spectroscopy, EXAFS, NMR

State of the art high resolution XPS vs “normal” XPS



G.J. Adriaenssens et al. / Journal of Non-Crystalline Solids 266–269 (2000) 898–903 901

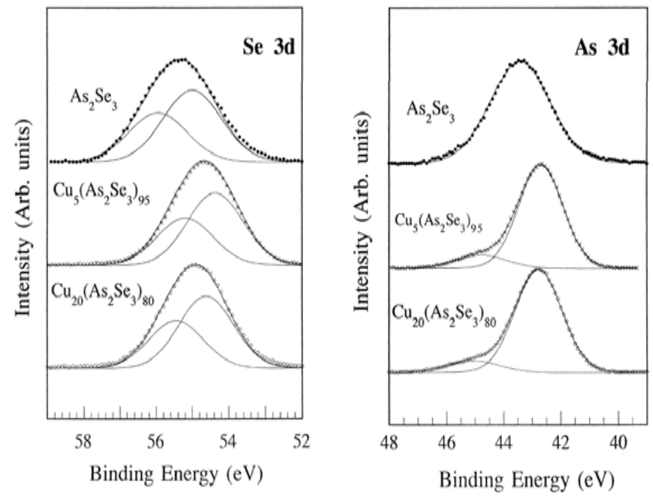
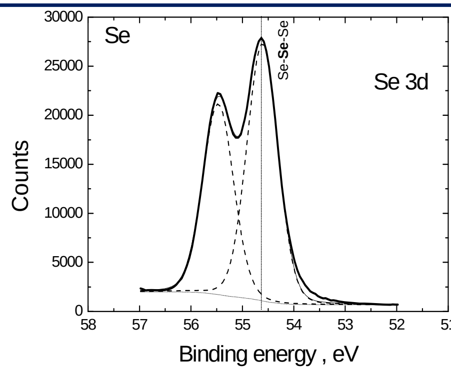
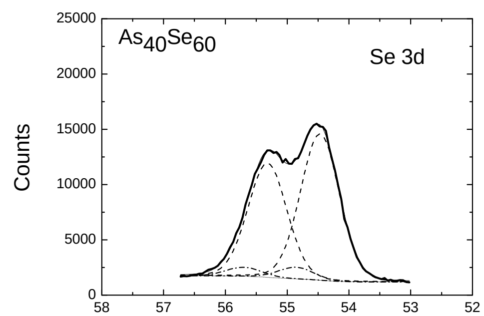
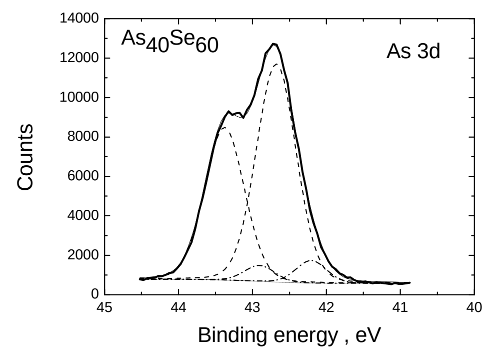


Fig. 3. XPS binding energy spectrum of the Se 3d core electrons in the indicated compounds, together with a decomposition (full lines) of the spectra into their $3d_{1/2}$ and $3d_{3/2}$ components.

Fig. 4. XPS binding energies of the As 3d core electrons for the indicated selenide compositions, also showing a decomposition (full lines) which includes the small arsenic oxide contribution that is observed in the Cu-containing samples.







PHYSICAL REVIEW B 76, 125208 (2007)

Structure of Se-rich As-Se glasses by high-resolution x-ray photoelectron spectroscopy

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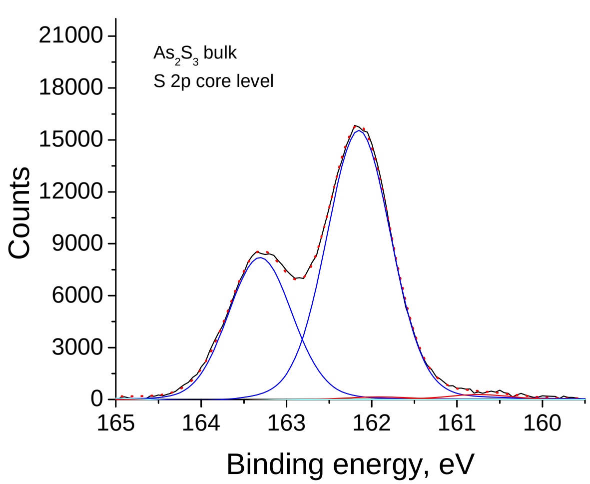
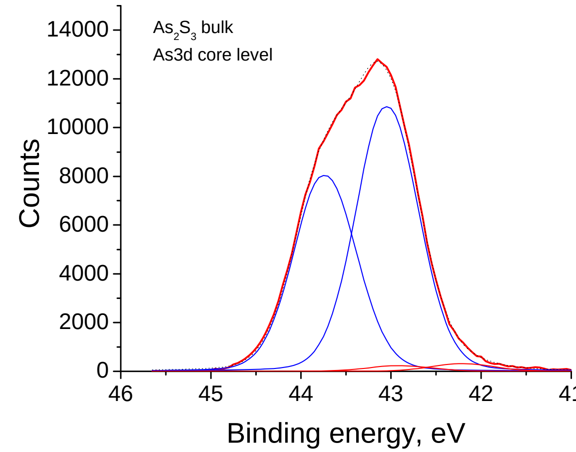
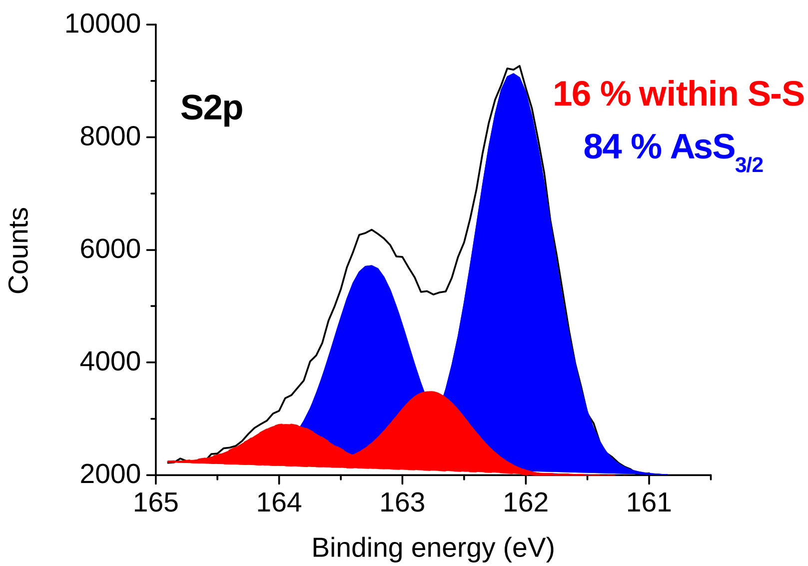
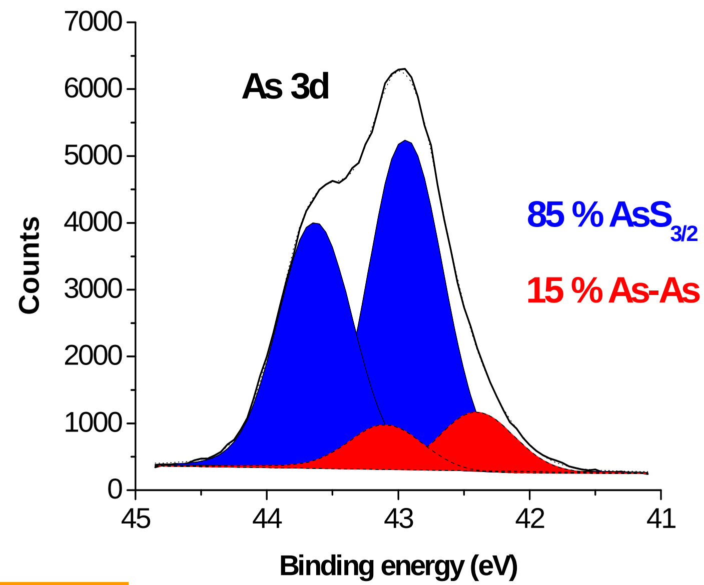
Structure of fresh cut of glass vs freshly deposited thin film





Bulk As_2S_3





Freshly deposited As_2S_3 film

Thin films: photostructural transformations by XPS

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Thin Solid Films 516 (2008) 7511 – 7518
thin solid films
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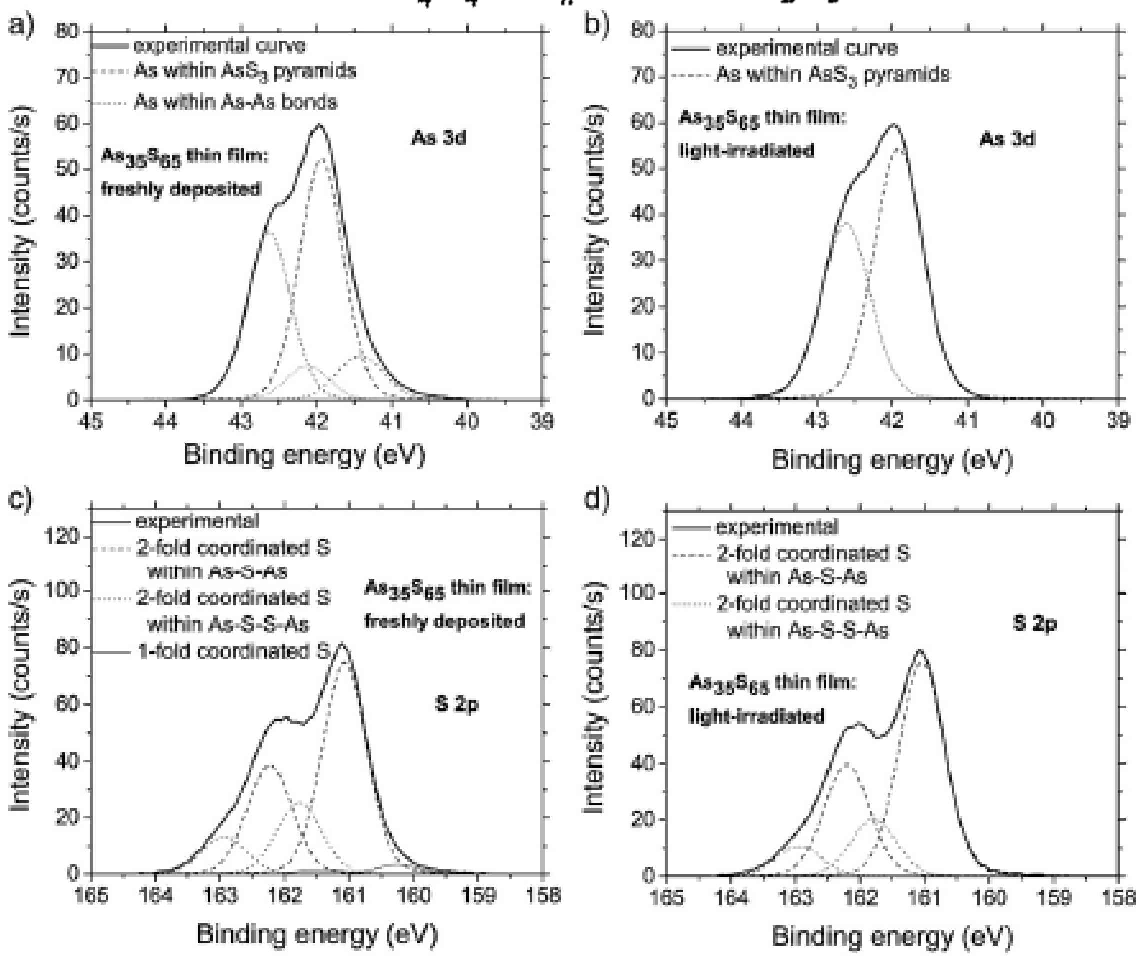
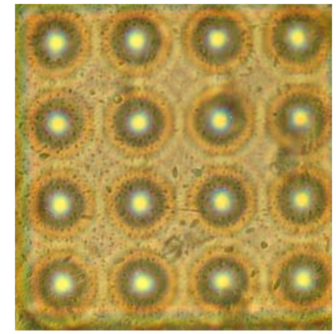
Comparative study of electron- and photo-induced structural transformations on the surface of $As_{35}S_{65}$ amorphous thin films

A. Kovalskiy [a,*], J.R. Neilson [a], A.C. Miller [a], F.C. Miller [b], M. Vlcek [c], H. Jain [a]

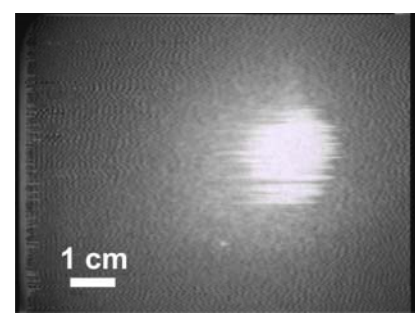
$$As_4S_4 + S_n \xrightarrow{h\nu} As_2S_3$$





Array of Fresnel lenses with focal point ~300 μm

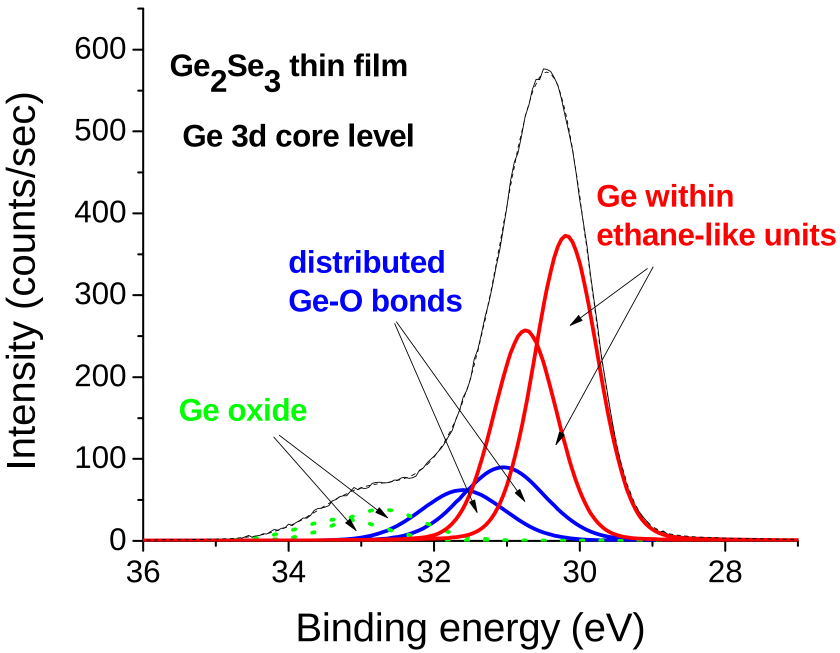
Fresnel lens with focal point ~5.38 mm



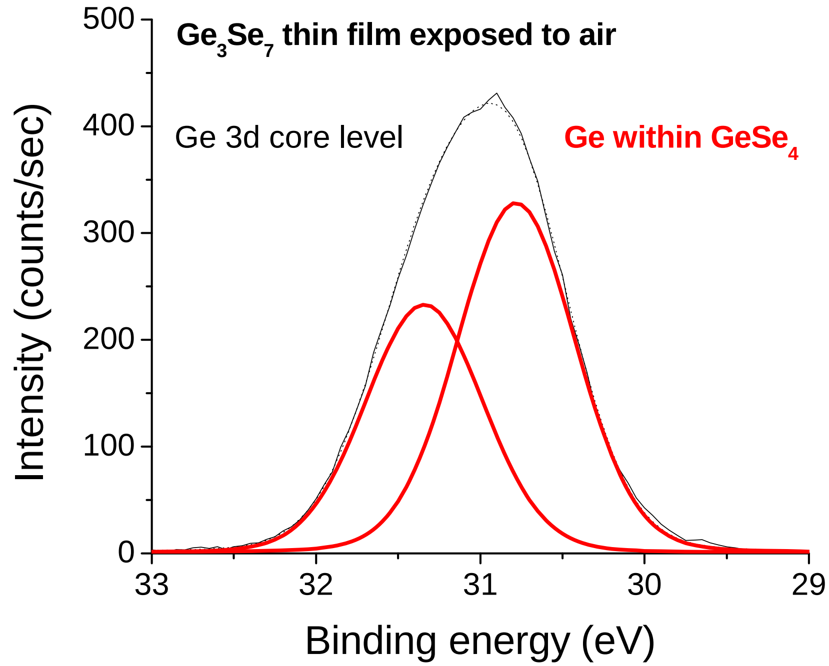
IR laser beam (1.55 μm) focused by Fresnel lens on Si substrate

Photooxidation on the surface of ChG

Oxidation in air strongly depends on Ge content



Strong oxidation in air



No oxidation in air

E-beam Patterning of Chalcogenide Glasses

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Journal of Non-Crystalline Solids 353 (2007) 1427–1430

JOURNAL OF
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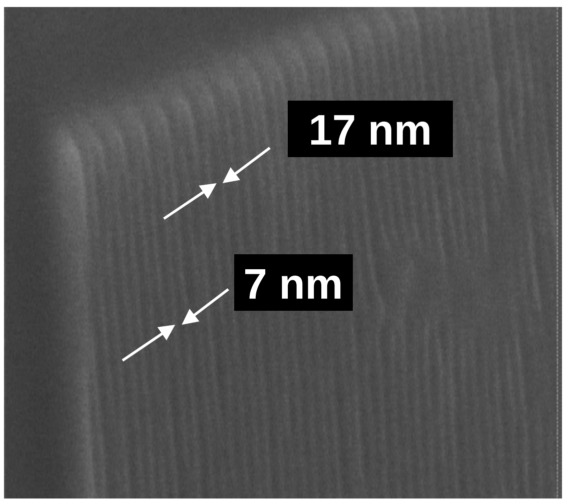
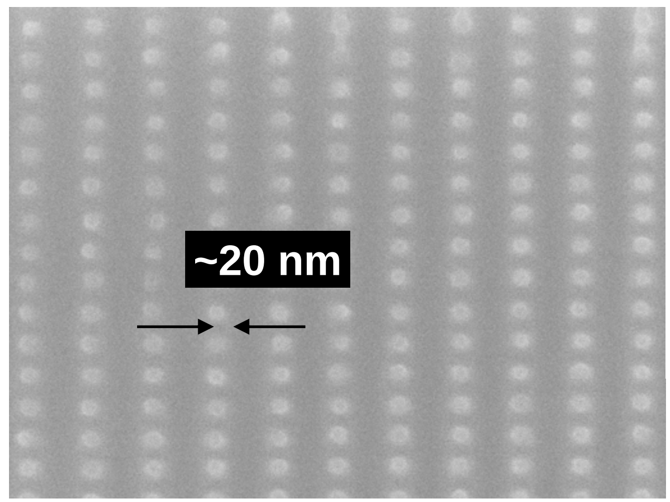
Fabrication of nano-gratings in arsenic sulphide films

J.R. Neilson [a], A. Kovalskiy [a], M. Vlček [b], H. Jain [a,*], F. Miller [c]

What is the resolution limit for ChG?



Finest structural features on glasses



Direct observation of separate e-beam spots

Wet Etching in Amine Solution

Structural Origin of E-beam Patterning of Chalcogenide Glasses

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Thin Solid Films 516 (2008) 7511 – 7518

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Comparative study of electron- and photo-induced structural transformations on the surface of $As_{35}S_{65}$ amorphous thin films

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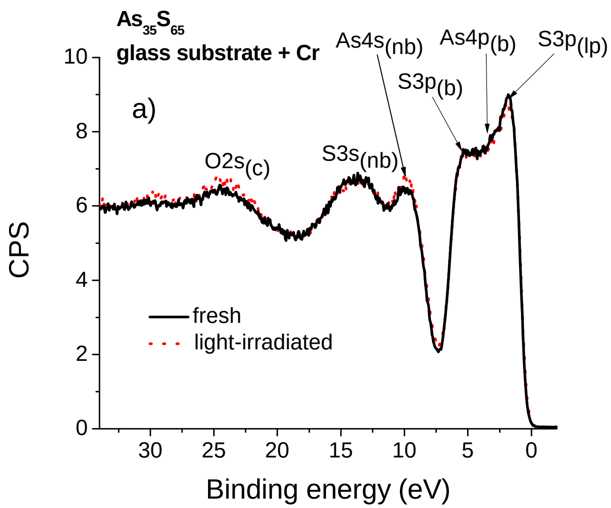
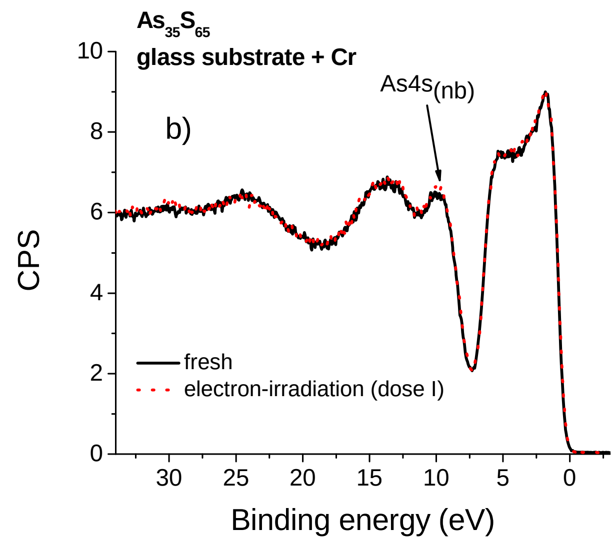
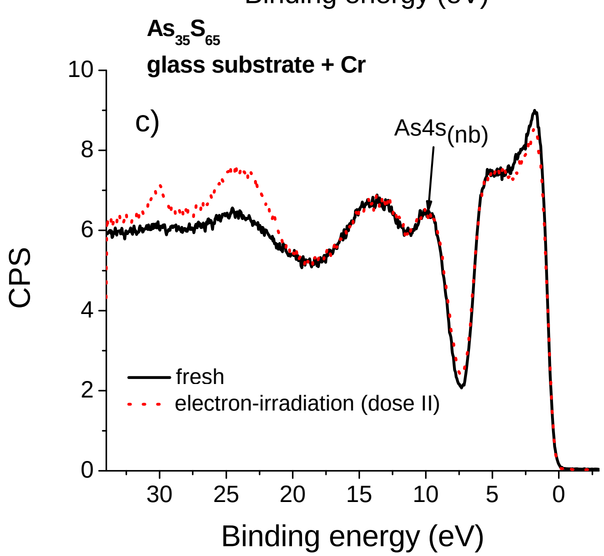
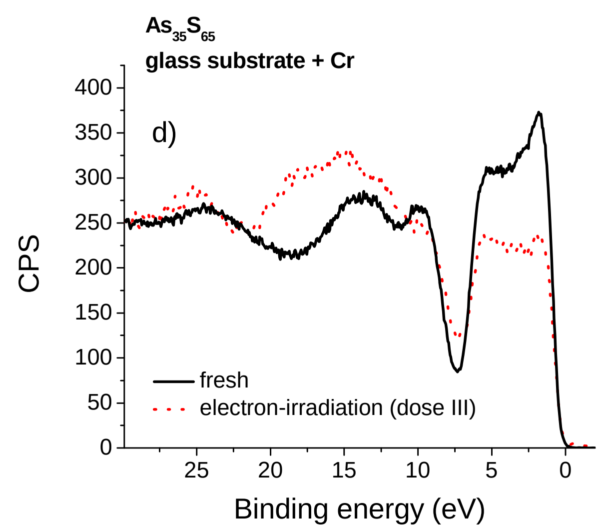


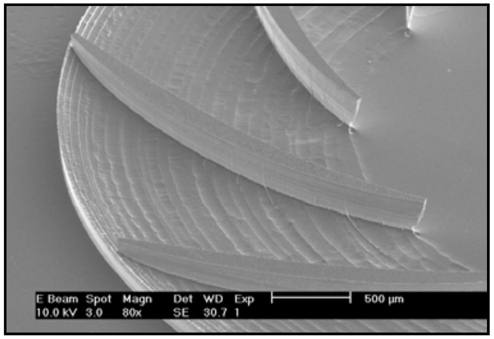


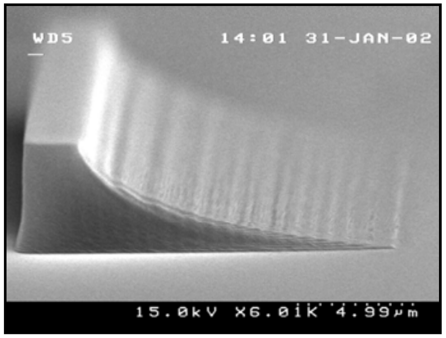




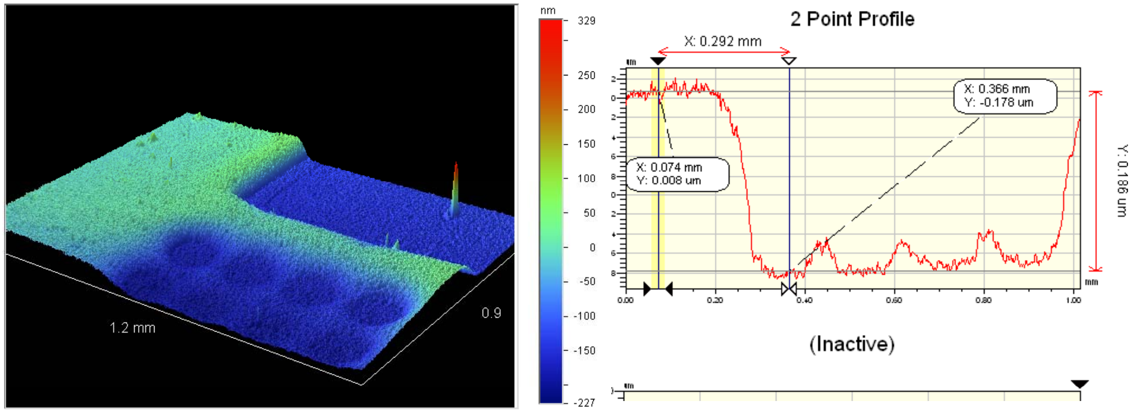
Gray Scale Lithography based on Ag Photodiffusion in Chalcogenide Glass Thin Films

Motivation: **3-D profiles in photoresist film for development of microturbine compressor with smooth blades**





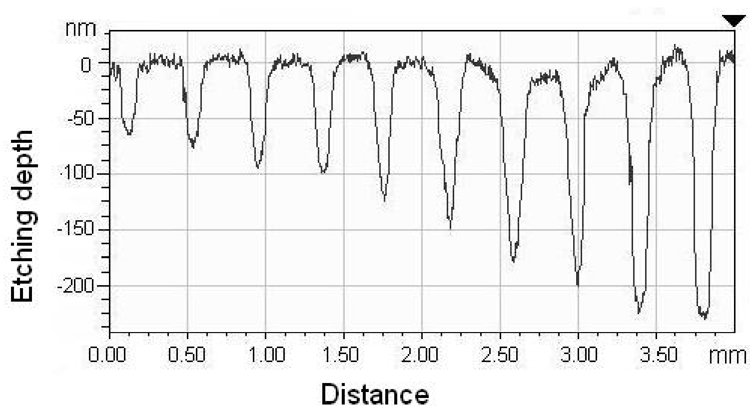
Example of complex shape structure on the surface– negative dry etching



Si substrate to ChG thickness transfer ratio of > 10 is achieved

Gray Scale Lithography based on Ag Photodissolution into Chalcogenide Glass Thin Films

- Ag dissolves into As-S glass in step like mode
- depth of dissolution - function of exposure dose



Profilogram demonstrating the change of etching depth with gradual variation of transparency of mask fragments.

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JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

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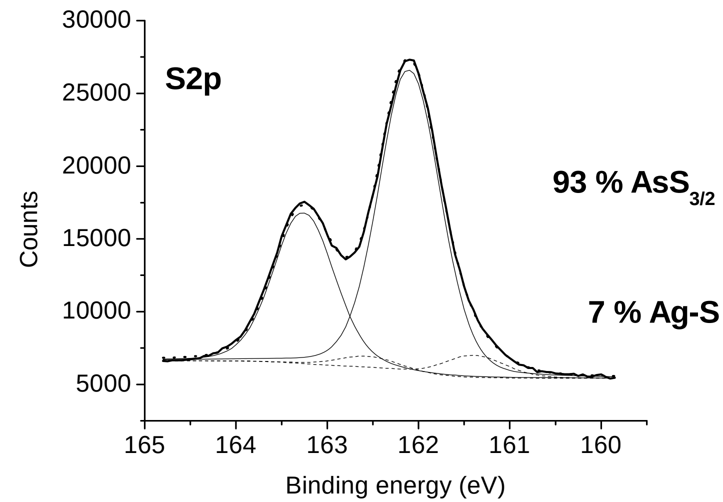
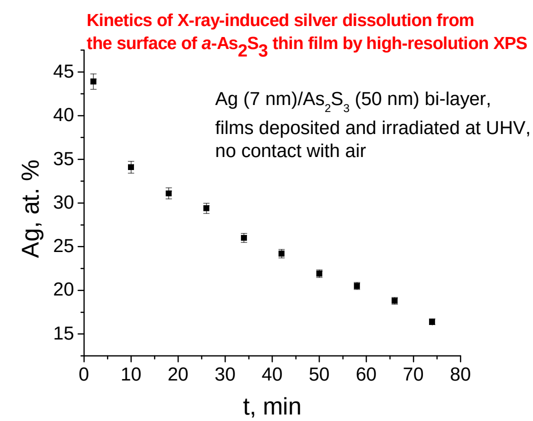
On the mechanism of gray scale patterning of Ag-containing As_2S_3 thin films

A. Kovalskiy[a,*], H. Jain[a], J. Neilson[a], M. Vlcek[b], C.M. Waits[c], W. Churaman[c], M. Dubey[c]



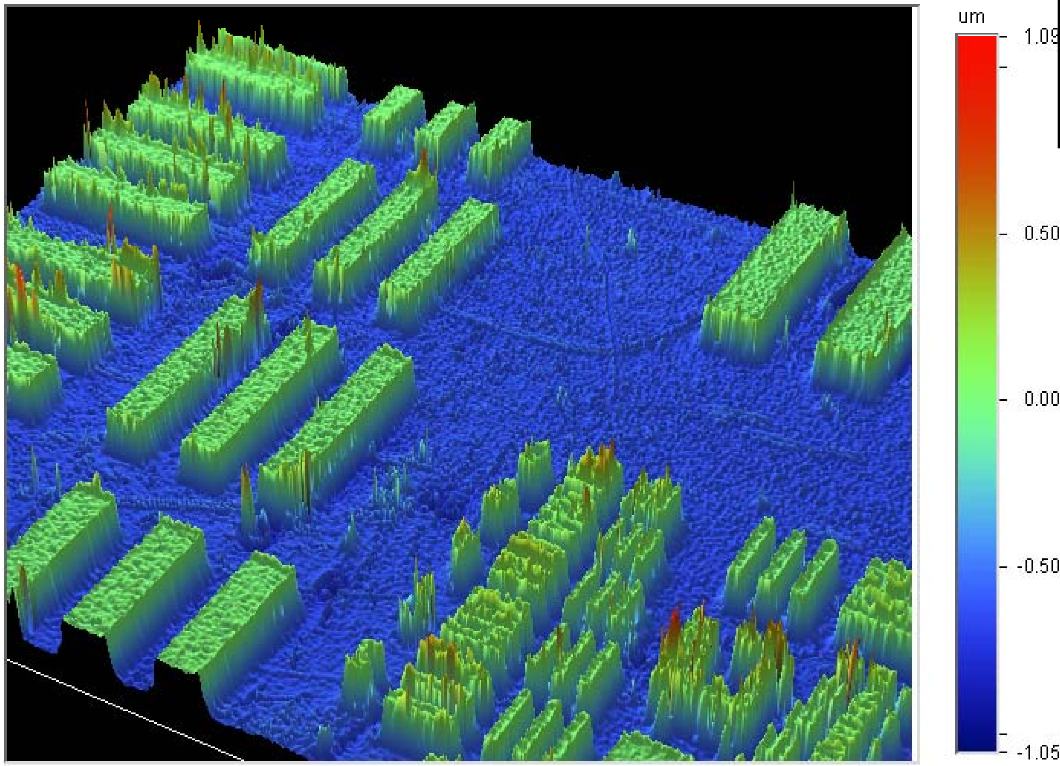
Control of composition



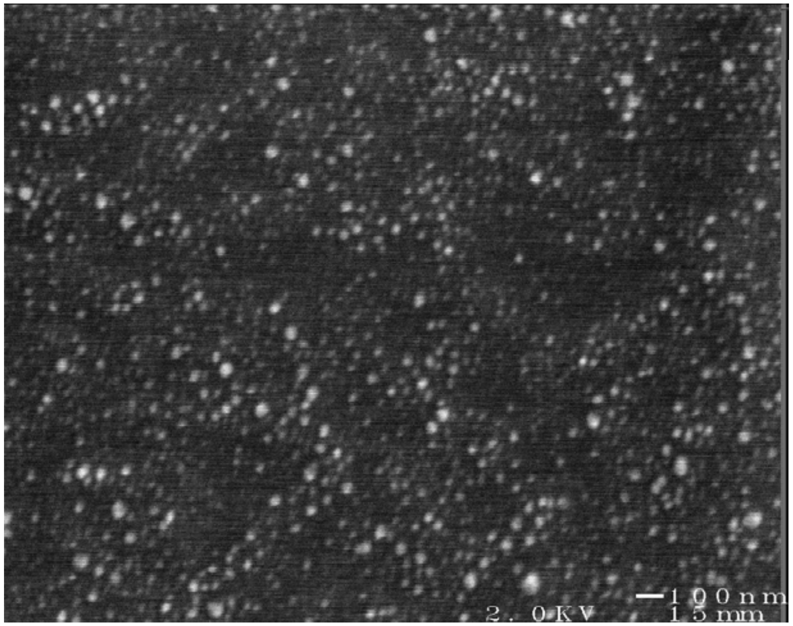
Kinetics of X-ray-induced Ag dissolution

Ag Photodiffusion into As_2S_3

Influence of surface oxidation?



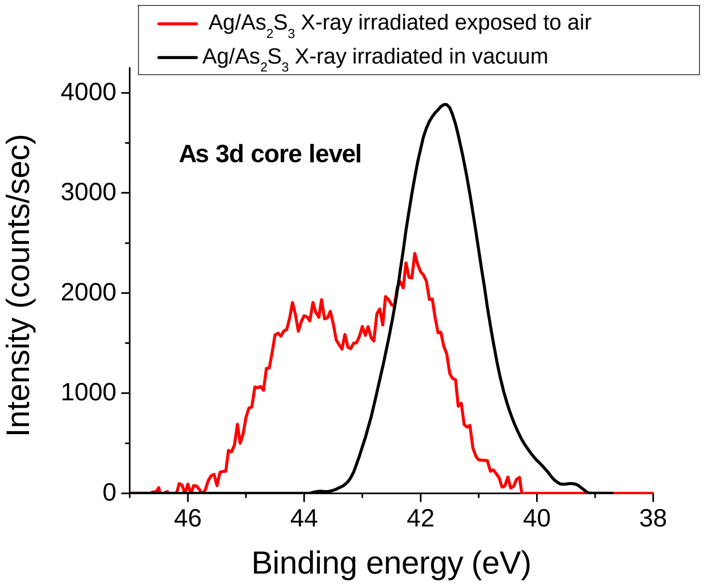
ChG Surface after Photodiffusion and Treatment in HNO_3 solution

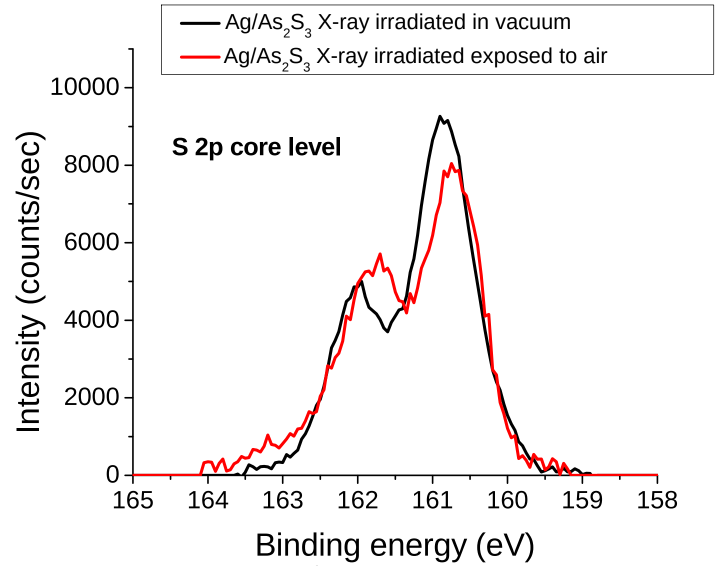


Spikes are due to: oxide clusters which etch differently.

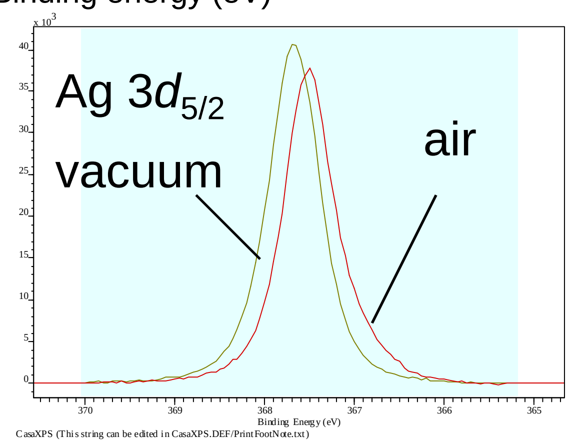
Ag Photodiffusion into ChG

Compare final products





FINAL PRODUCTS of Ag diffusion in vacuum and air:



•S chemical environment is similar, except that formation of ternary is slowed down by arsenic oxidation

•As chemical environment differs drastically:
- phase separation due to oxidation in air;
- some clustering of As in vacuum

•Ag chemical environment slightly differs due to As

Strong Glasses for Solar Energy

Concentrated Solar Thermal (CST)

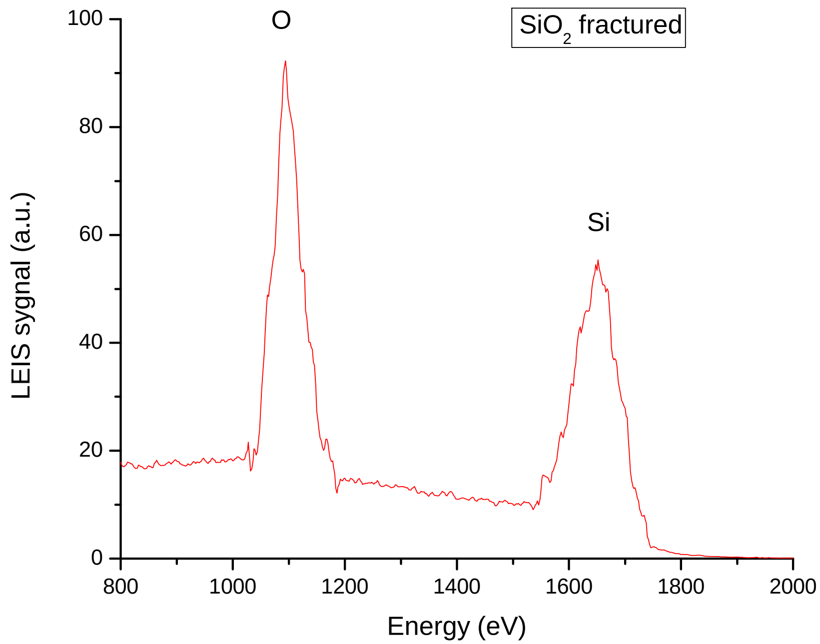
Photovoltaics: Increased strength to weight (thickness) to permit larger thin film module size

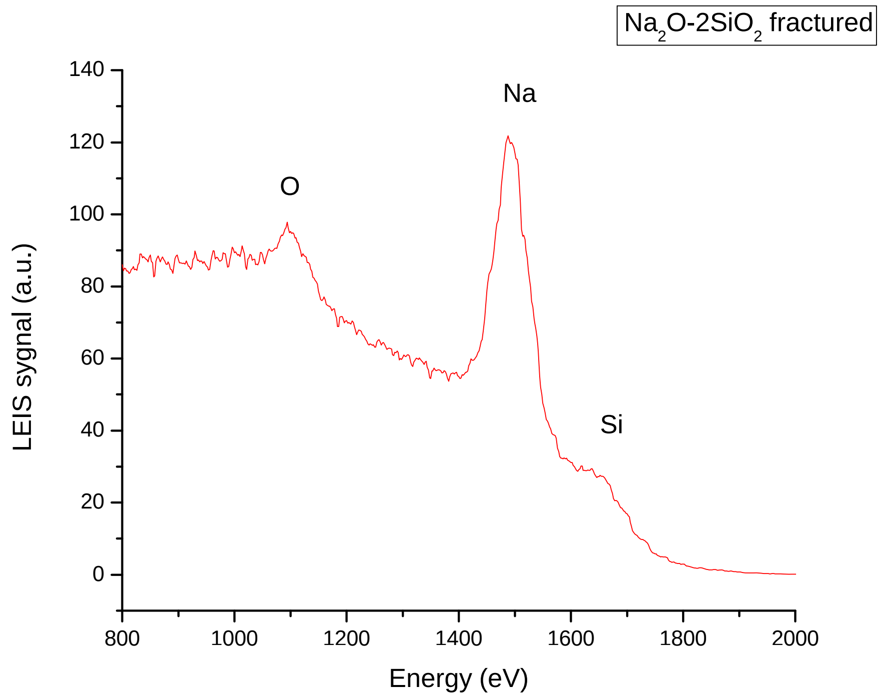
Methods: XPS, LEIS

Sodium silicate glasses – breaking path

Sample	Na	O	Si	Na/Si	BO/ NBO
Sodium disilicate, 90	21	55	24	0.875	2.2
Sodium disilicate, 25	19	59	22	0.86	2.3
Sodium disilicate heat treated, 90	20	55	25	0.80	2.3
Sodium disilicate heat treated, 25	21	54	25	0.84	2.2
Sodium trisilicate, 90	14	60	26	0.54	3.0
Sodium trisilicate, 25	24	56	20	1.20	2.4

Ion-TOF low energy ion scattering: first results





Low Energy Ion Scattering: Preliminary results

Sample	Si, at. %	O, at. %	Na, at. %	Na/Si
SiO_2 fractured	35	65	-	**-**
$Na_2O{\cdot}2SiO_2$ fractured	8	17	75	**9.4**
$Na_2O{\cdot}2SiO_2$ treated 1 h at 620 °C, fractured	5	24	71	**14.2**
$Na_2O{\cdot}3SiO_2$ fractured	3	19	78	**26.0**

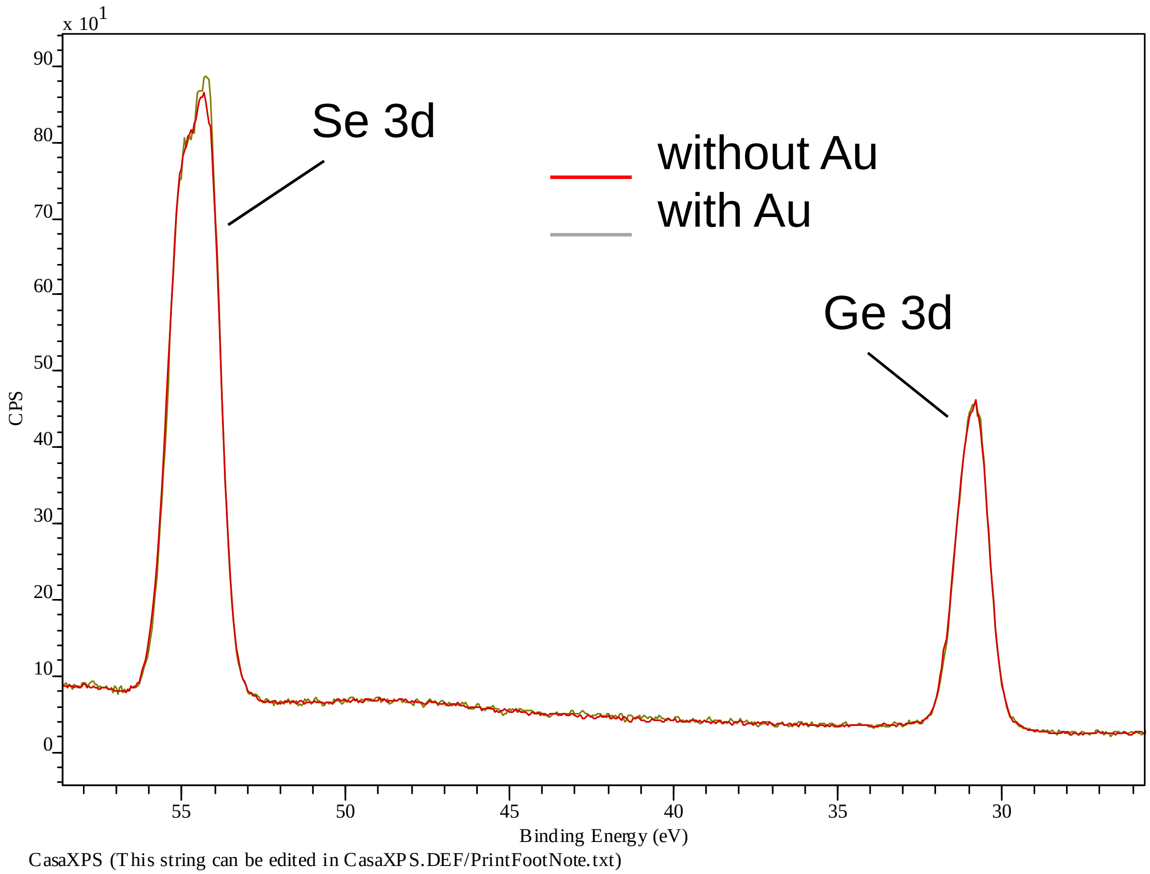
Conclusions

Binding Energy Referencing

Surface charge energy E_{ch} can be determined by electrically calibrating the instrument to a spectral feature.

C1s at 284.8 eV

Au4f$_{7/2}$ at 84.0 eV



Ge_3Se_7 – ideal referencing of Ge 3d to Au 4f$_{7/2}$