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Investigation of plasma species, etch products and surface modification during etching of Ge, Sb and Se-based materials in CH₄-H₂-Ar plasmas

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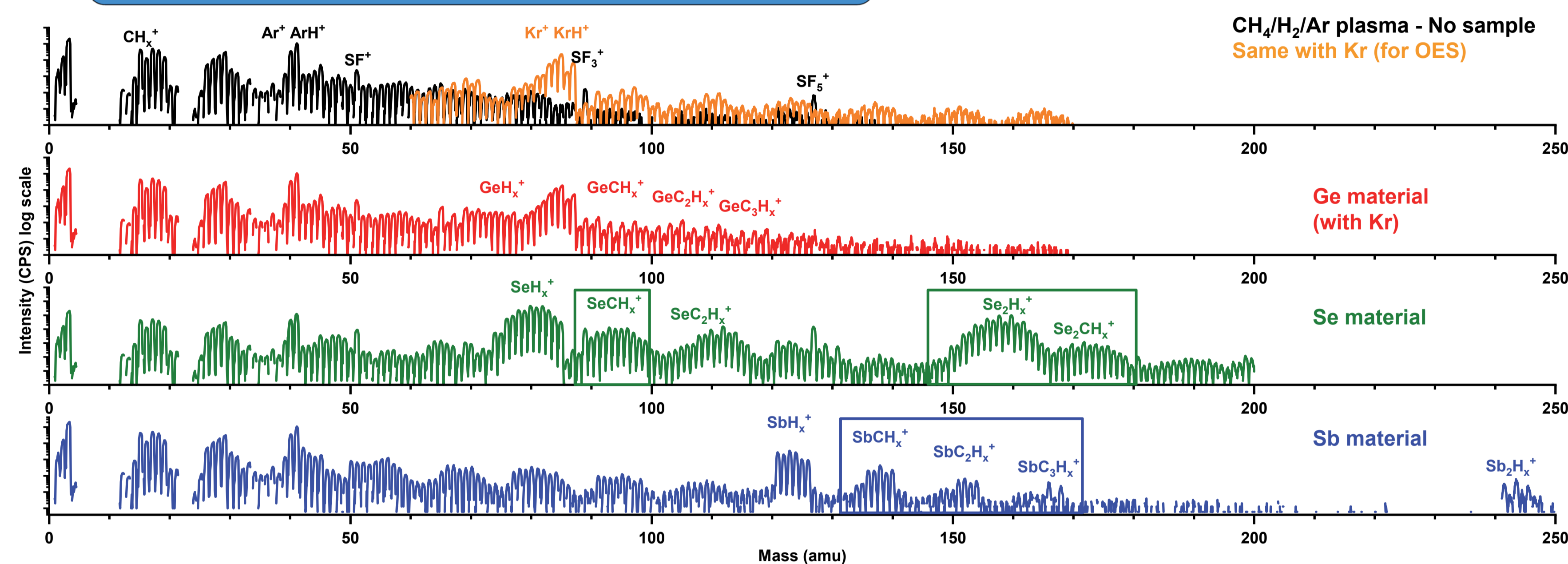
Context & objectives

- Plasma etching of Ge-Sb-Se materials in methane-based mixtures for photonic applications and advanced microelectronics.
- Identify the etch products, characterise the surface chemistry after etching.
- Ge-Sb-Se: a complex ternary material!
- Study the etching of Ge, Se, Sb first, then GeSe₂ and Sb₂Se₃, finally GeSbSe.
- Start with H₂/Ar mixtures, then add CH₄.
- Plasma study using mass spectrometry.
- Surface characterisation after etching by means of XPS (vacuum transfer).

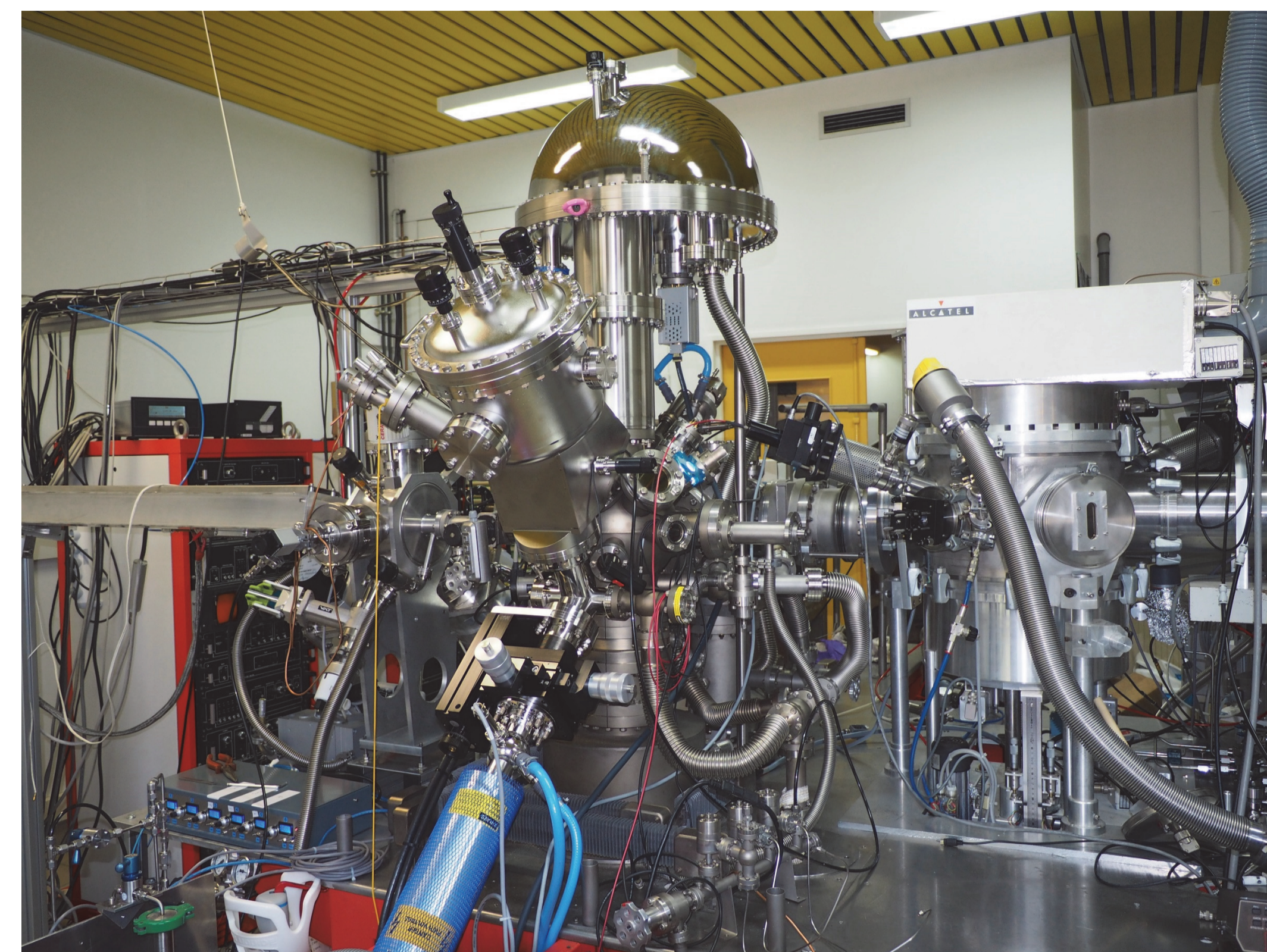
Experimental

- Typical plasma parameters: ICP plasma source, 700W, 4mTorr, 100sccm total flow, -200V bias, 4%CH₄ in H₂/Ar, H₂/Ar = 1,5.
- Mass spectrometry: EQP1000 (Hiden Analytical) - analysis of the plasma positive ions.
- XPS: (Specs) mono Al Ka source (14kV-20mA), 14eV PE, 0.1eV step, charge neutralisation.

Mass spectrometry data (example)



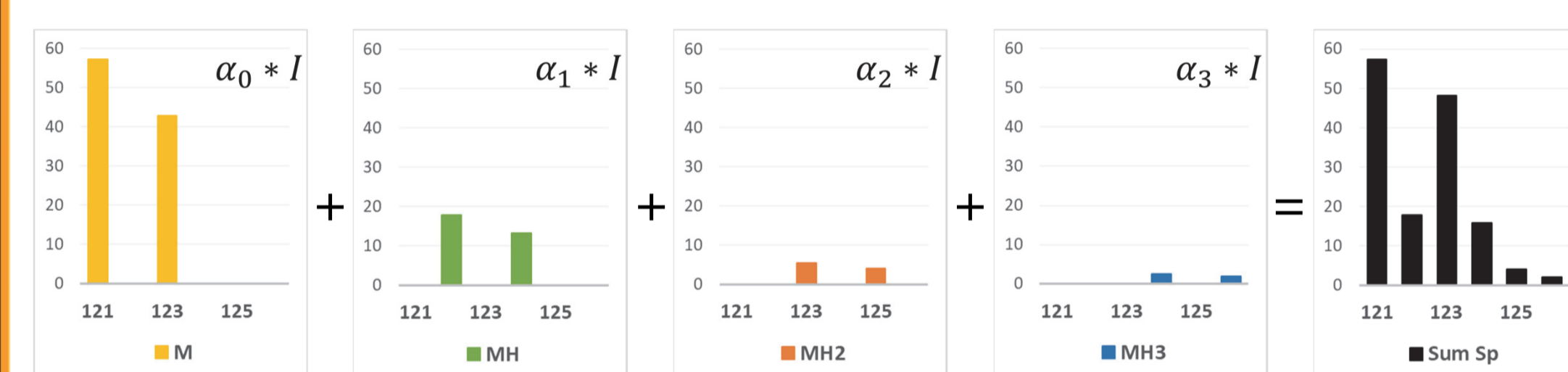
Ion mass spectra in CH₄/H₂/Ar plasma **without sample** and with **Ge, Se, and Sb** materials



Surface analysis & Plasma etching equipment

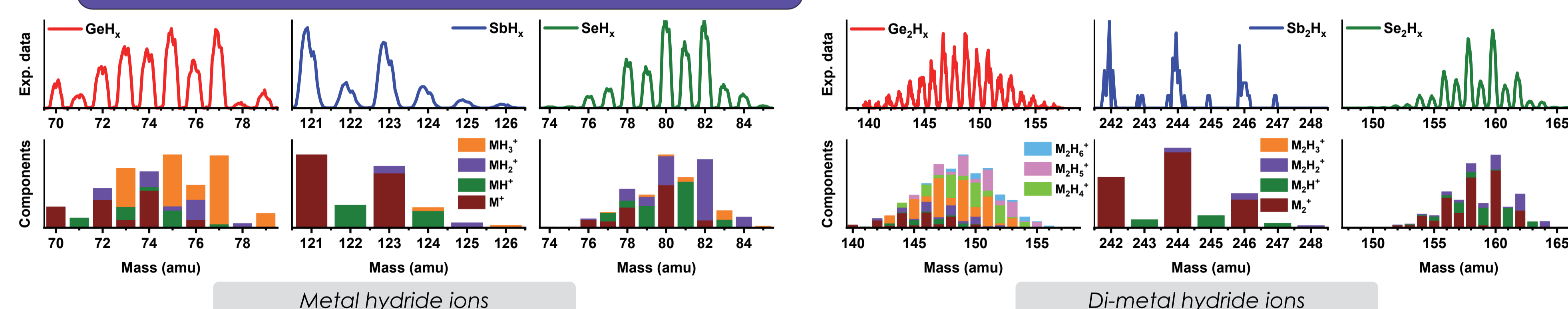
Multi-Linear Regression analysis

- Consider the experimental data S for a MH_x^+ ion cluster.
- Using the isotopic distribution of M , purpose is to determine the coefficients α_p allowing to represent the data as $S_p = \alpha_p * I + e$, with I the matrix containing the $x+1$ isotopic distributions, e the disturbance.



- α_p is determined to minimise the sum of squared residuals $\sum_j [s_j - s_{j_p}]^2$.

MLR results, identification of species



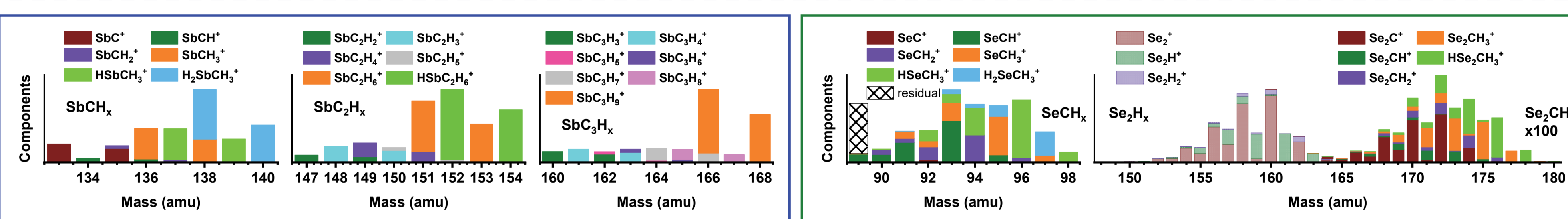
Elementary processes in H₂/Ar plasma (etching Ge, Sb and Se)

Molecular ions:

- GeH₃⁺ (GeH₄)
- SeH₂⁺, SeH⁺ (SeH₂)
- **Chemical etching:** Ge, Se

Elementary ions:

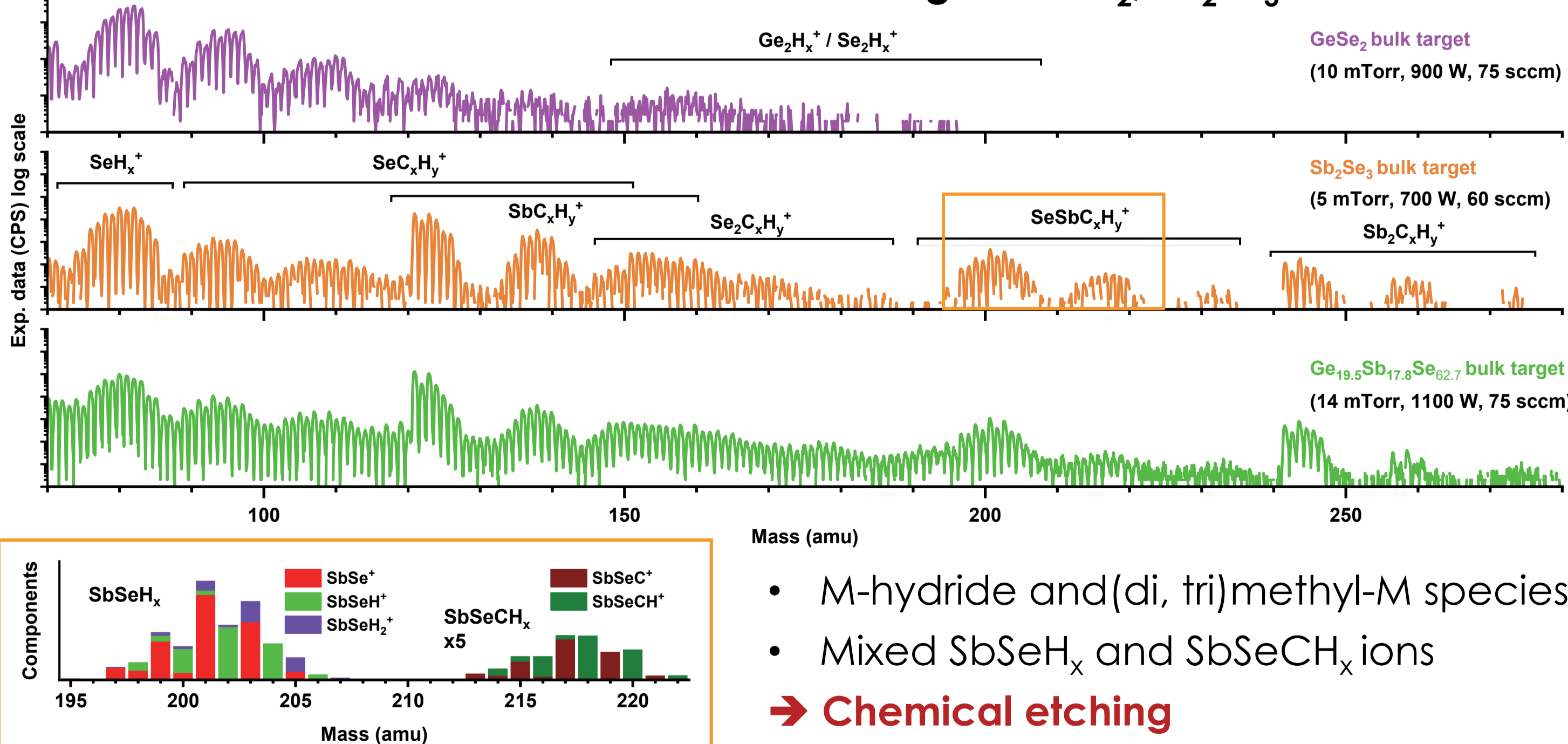
- Ge⁺, Sb⁺, Se⁺
- **Sputtering**
- Binary ions:**
- Ge₂H₃⁺, Ge₂H₄⁺, Ge₂H₅⁺
- Sb₂⁺, Sb₂H⁺
- Se₂⁺, Se₂H⁺, Se₂H₂⁺
- **Recombination (plasma)**



Benefit of CH₄/H₂/Ar plasma for Ge, Sb, Se etching

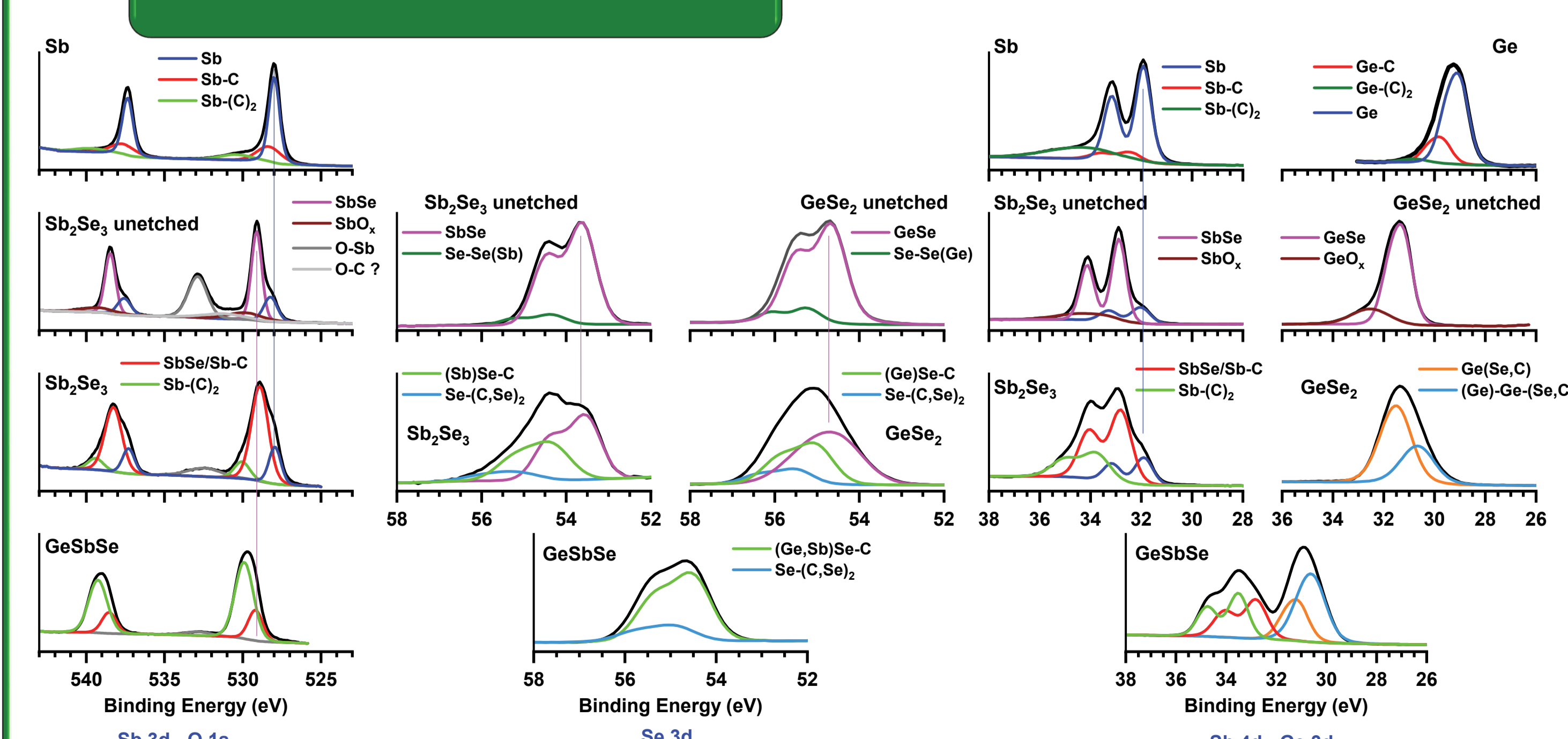
- Presence of di, tri, methyl-Sb and -Se
- **Chemical etching:** Se, Sb
- Presence of M₂-CH_x ions → **Recombination**

Etching of GeSe₂, Sb₂Se₃ and GeSbSe



- M-hydride and (di, tri)methyl-M species
- Mixed SbSeH_x and SbSeCH_x ions
- **Chemical etching**

XPS Surface analysis



Evidence for Ge-C and Sb-C species, Se-C species are less certain