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Thibaut Meyer, Aurélie Girard, Christophe Cardinaud, Marek Bouška, Emeline Baudet, Marion Baillieul, Petr Němec, Virginie Nazabal

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# Investigation of plasma species, etch products and surface modification during etching of Ge, Sb and Se-based materials in CH<sub>4</sub>-H<sub>2</sub>-Ar plasmas

Thibaut MEYER, Aurélie GIRARD, Christophe CARDINAUD, Université de Nantes, CNRS, IMN, Nantes, France

Marek BOUŠKA, Emeline BAUDET, Marion BAILLIEU, Petr NĚMEC, Dep<sup>t</sup>. Graphic Arts & Photophysics, University of Pardubice, Pardubice, Czech Republic

Virginie NAZABAL, Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes, Rennes, France

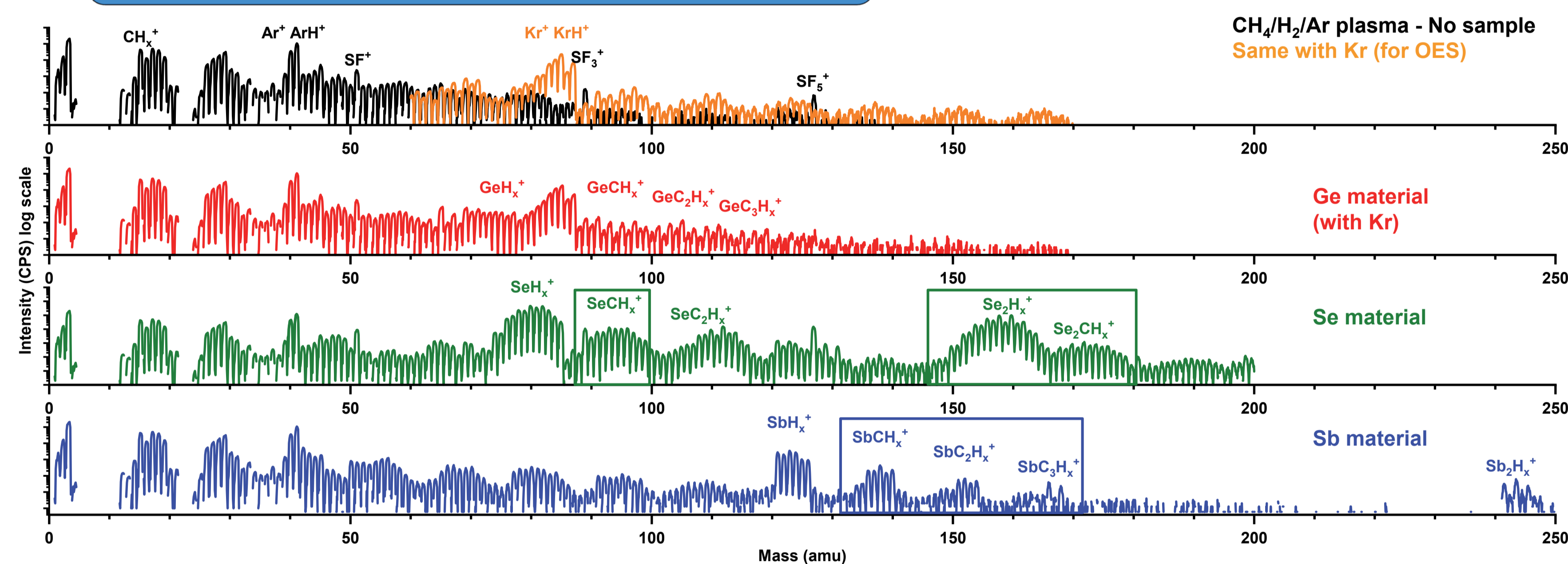
## Context & objectives

- 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 GeSe<sub>2</sub> and Sb<sub>2</sub>Se<sub>3</sub>, finally GeSbSe.
- Start with H<sub>2</sub>/Ar mixtures, then add CH<sub>4</sub>.
- Plasma study using mass spectrometry.
- Surface characterisation after etching by means of XPS (vacuum transfer).

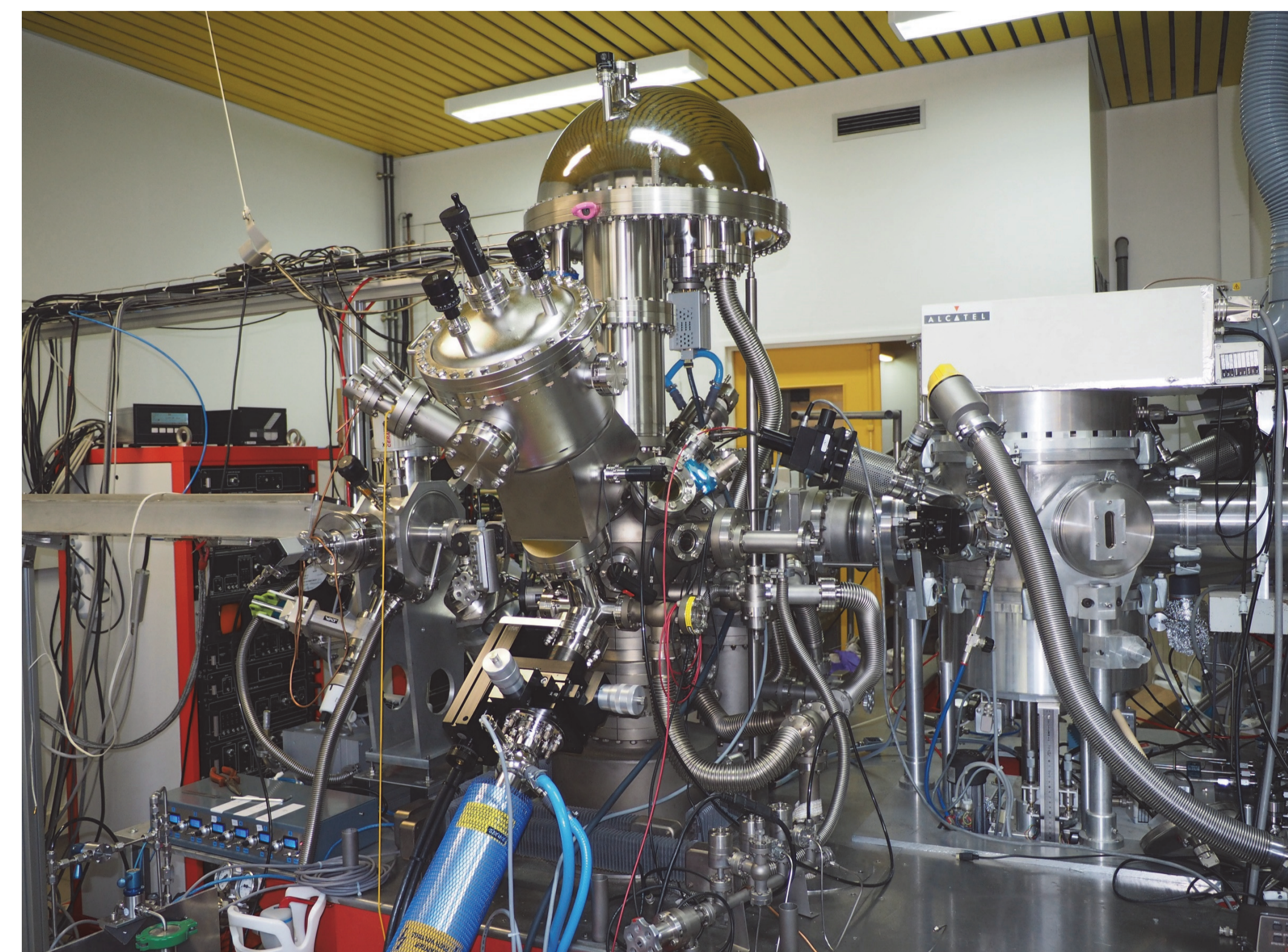
## Experimental

- Typical plasma parameters: ICP plasma source, 700W, 4mTorr, 100sccm total flow, -200V bias, 4%CH<sub>4</sub> in H<sub>2</sub>/Ar, H<sub>2</sub>/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)



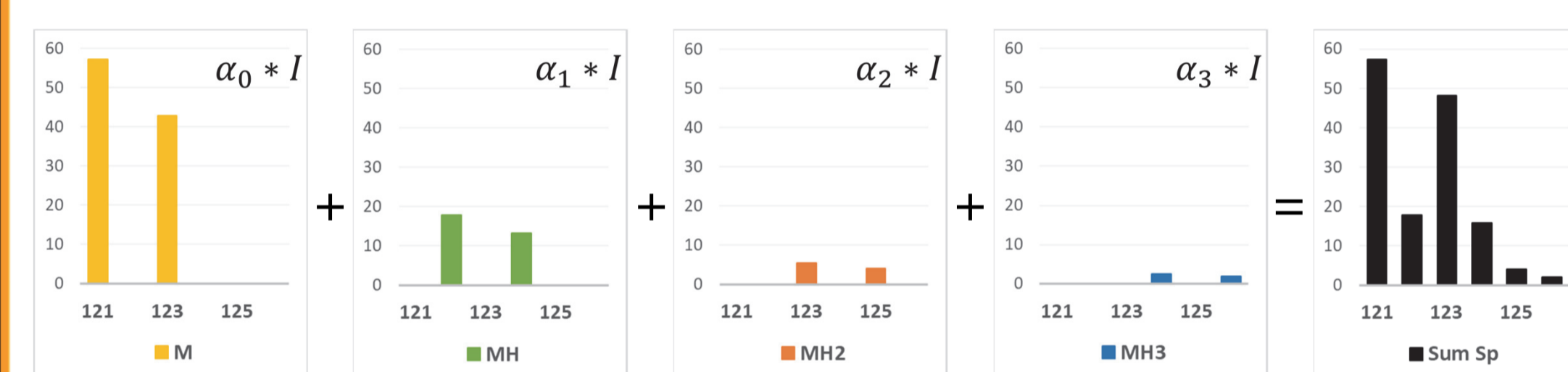
Ion mass spectra in CH<sub>4</sub>/H<sub>2</sub>/Ar plasma **without sample** and with **Ge, Se, and Sb** materials



Surface analysis & Plasma etching equipment

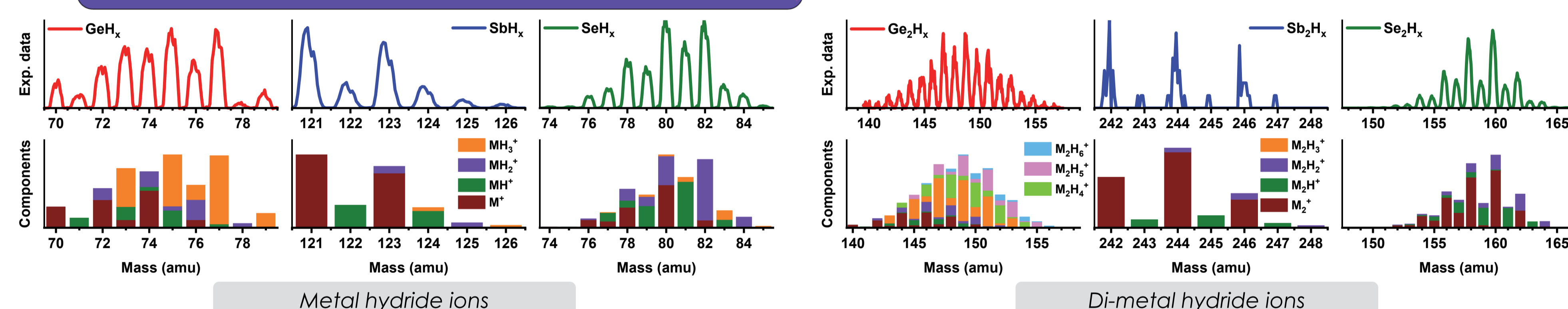
## Multi-Linear Regression analysis

- Consider the experimental data  $S$  for a  $MH_x^+$  ion cluster.
- Using the isotopic distribution of  $M$ , purpose is to determine the coefficients  $\alpha_p$  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.



- $\alpha_p$  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 H<sub>2</sub>/Ar plasma (etching Ge, Sb and Se)

### Molecular ions:

- GeH<sub>3</sub><sup>+</sup> (GeH<sub>4</sub>)
- SeH<sub>2</sub><sup>+</sup>, SeH<sup>+</sup> (SeH<sub>2</sub>)
- **Chemical etching:** Ge, Se

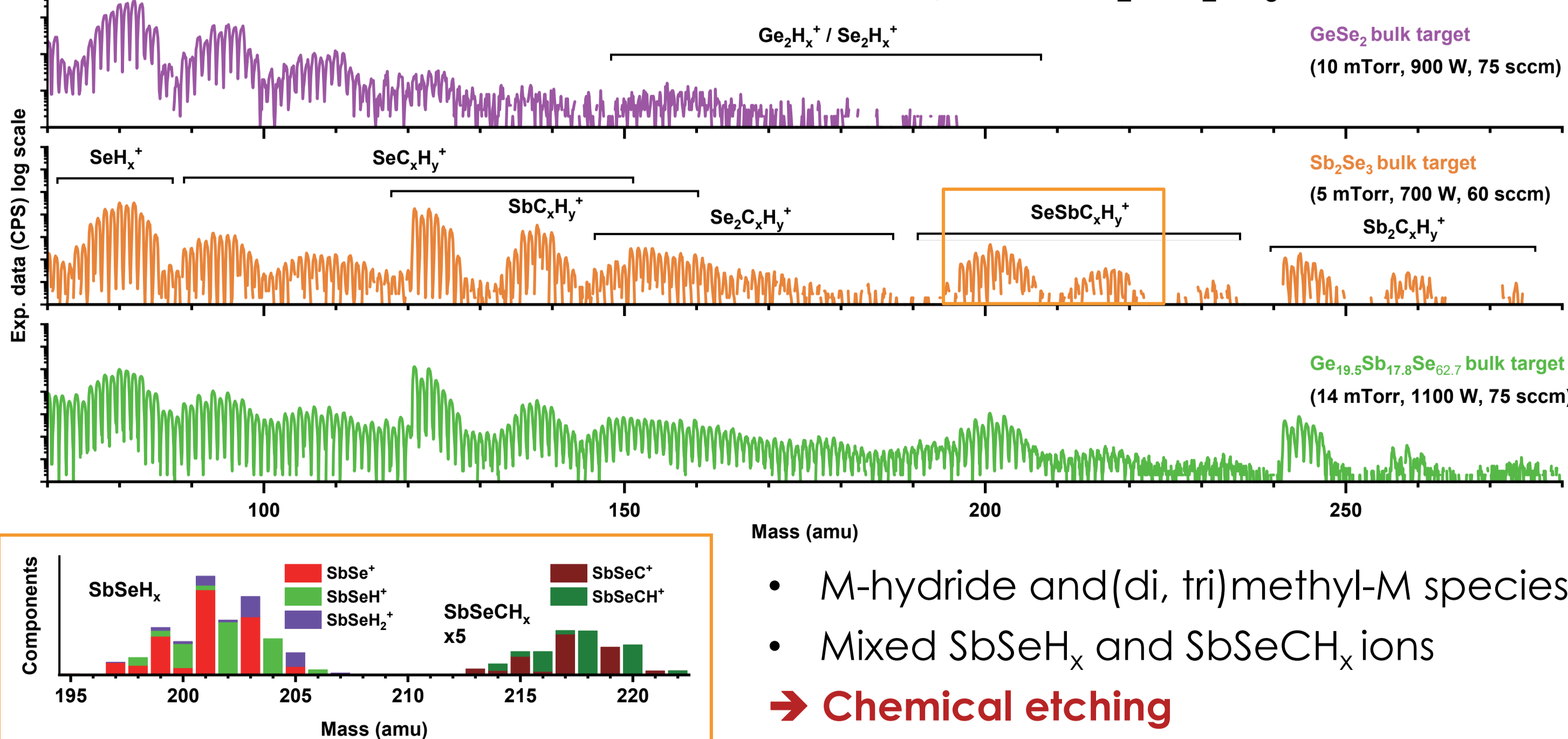
### Elementary ions:

- Ge<sup>+</sup>, Sb<sup>+</sup>, Se<sup>+</sup>
- **Sputtering**
- Binary ions:**
- Ge<sub>2</sub>H<sub>3</sub><sup>+</sup>, Ge<sub>2</sub>H<sub>4</sub><sup>+</sup>, Ge<sub>2</sub>H<sub>5</sub><sup>+</sup>
- Sb<sub>2</sub><sup>+</sup>, Sb<sub>2</sub>H<sup>+</sup>
- Se<sub>2</sub><sup>+</sup>, Se<sub>2</sub>H<sup>+</sup>, Se<sub>2</sub>H<sub>2</sub><sup>+</sup>
- **Recombination (plasma)**

## Benefit of CH<sub>4</sub>/H<sub>2</sub>/Ar plasma for Ge, Sb, Se etching

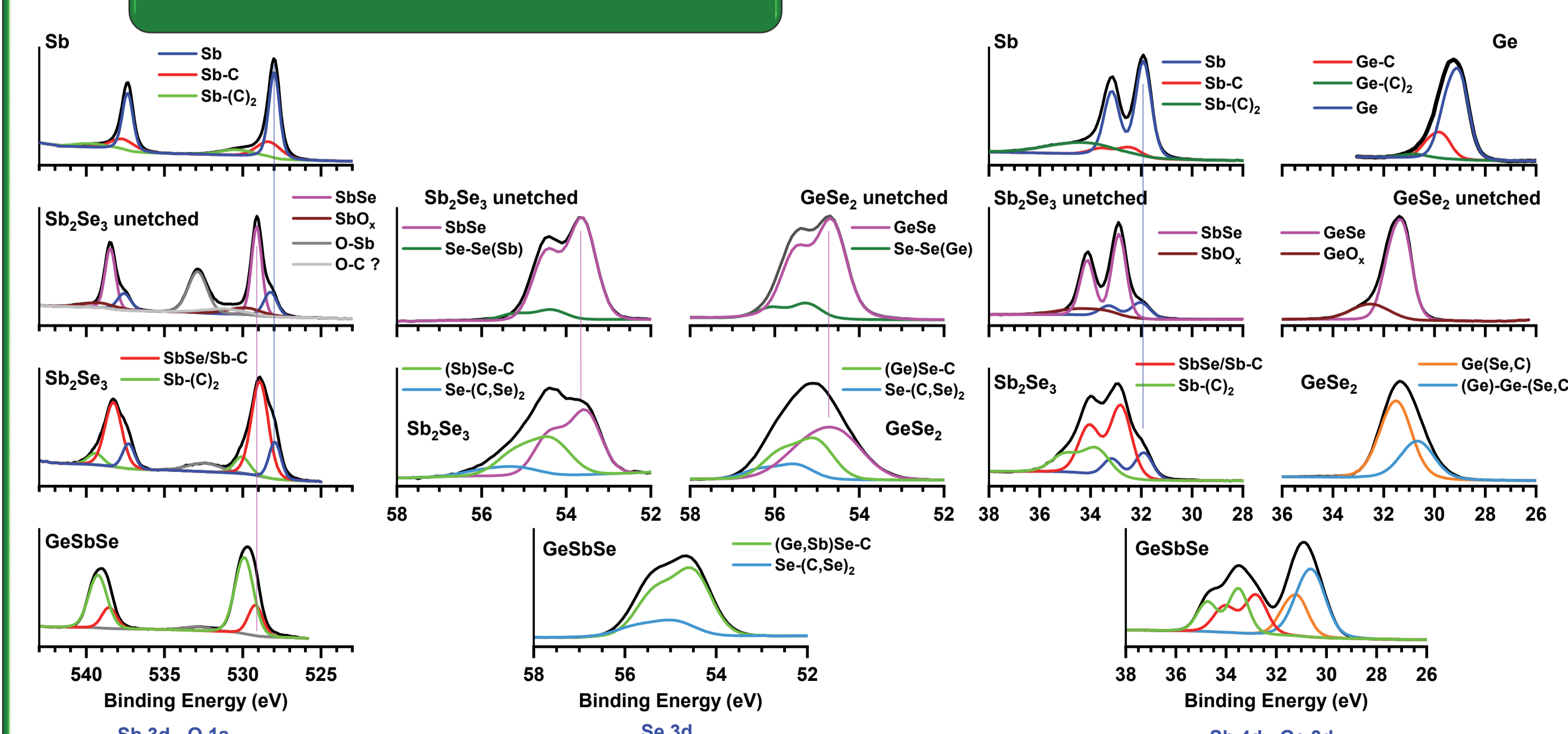
- Presence of di, tri, methyl-Sb and -Se
- **Chemical etching:** Se, Sb
- Presence of M<sub>2</sub>-CH<sub>x</sub> ions → **Recombination**

## Etching of GeSe<sub>2</sub>, Sb<sub>2</sub>Se<sub>3</sub> and GeSbSe



- M-hydride and (di, tri)methyl-M species
- Mixed SbSeH<sub>x</sub> and SbSeCH<sub>x</sub> ions
- **Chemical etching**

## XPS Surface analysis



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