Applications of GD-TOFMS for direct analysis of innovative materials

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OUTLINE

- **Motivation:** Fast Direct Solid Analysis.
- **Introduction** to Glow Discharge Time-of-Flight Mass Spectrometry.
- **Capabilities and limitations** of GD-TOFMS for direct analysis of innovative materials.
- **Comments and conclusions.**

Motivation

Many **innovative materials** (i.e. photovoltaic cells, glasses, hard-disks, alloys, polymers, etc.) are based on the deposition of thin and ultra-thin coatings and/or on the use of high-purity materials.

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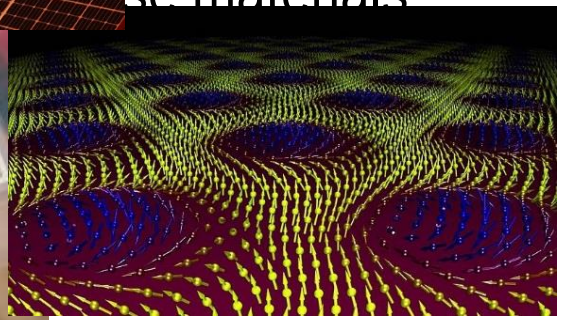
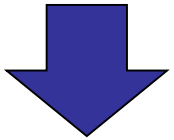


Motivation

The characterization of these innovative materials is demanding the development of **direct solid analytical techniques** able to provide **fast qualitative/quantitative multi-elemental analysis with high depth resolution and/or high sensitivity.**



✓ Glow Discharge Spectroscopy: GD-OES and GD-MS

They complement other well-establish analytical techniques for near-surface analysis and/or depth profiling, including:

- ❑ Auger Electron Spectroscopy (**AES**)
- ❑ X-ray Photoelectron Spectroscopy (**XPS**)
- ❑ Secondary Ion Mass Spectrometry (**SIMS**)

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Introduction

GD-OES

Multi-elemental depth profiling with high depth resolution.

Limited sensitivity for the determination of ultra-traces.

GD-TOFMS

Multi-elemental depth profiling with high depth resolution.

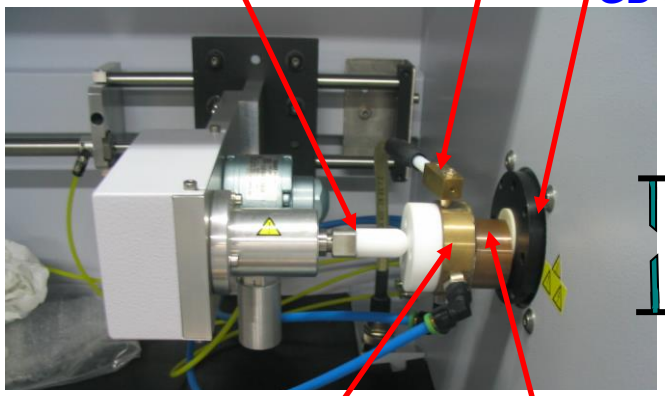
Improved sensitivity.
Isotopic information.

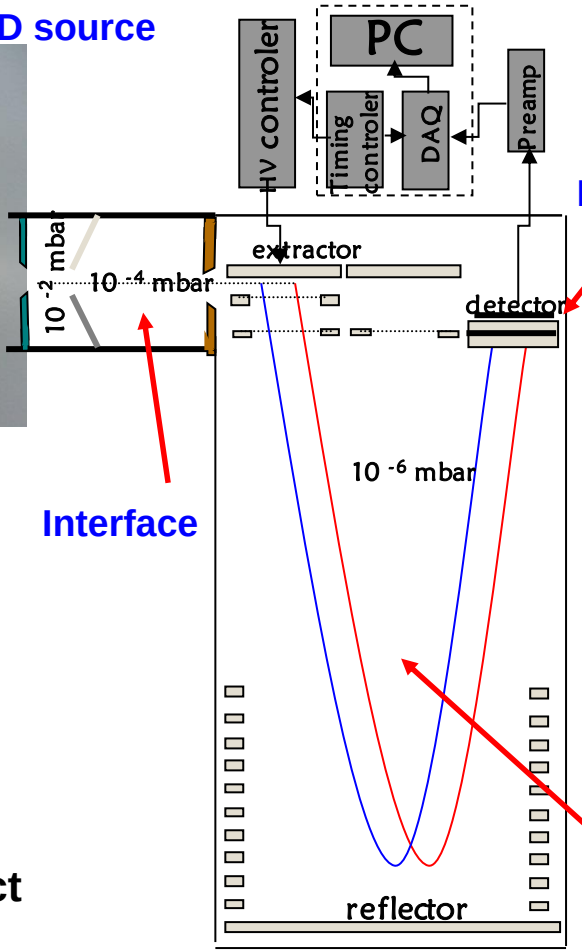
GD-SFMS

Multi-elemental depth profiling with limited depth resolution.

High sensitivity.
Isotopic information.
High spectral resolution.

GD-TOFMS

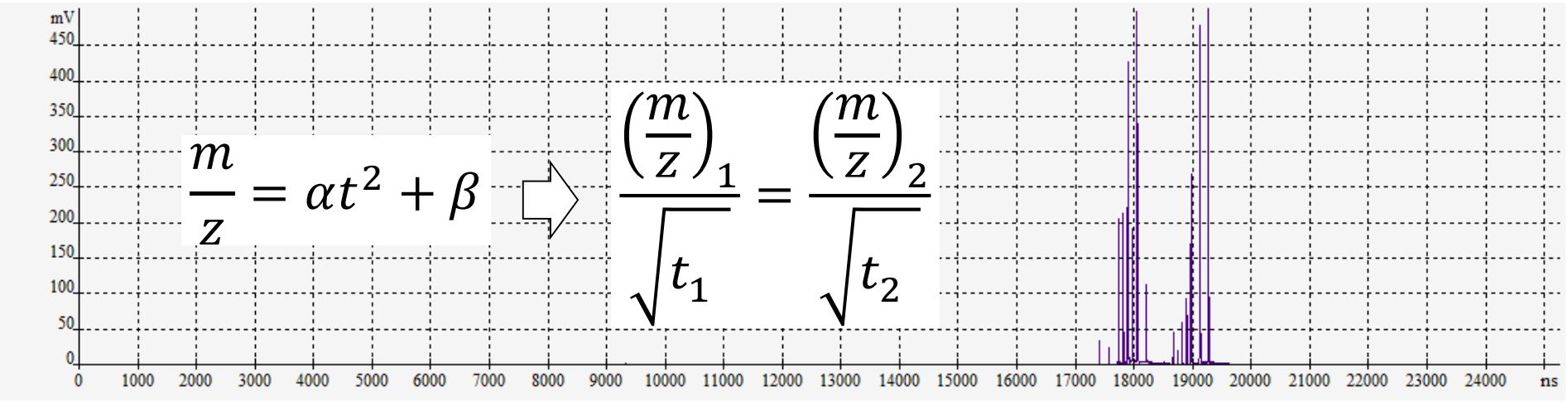


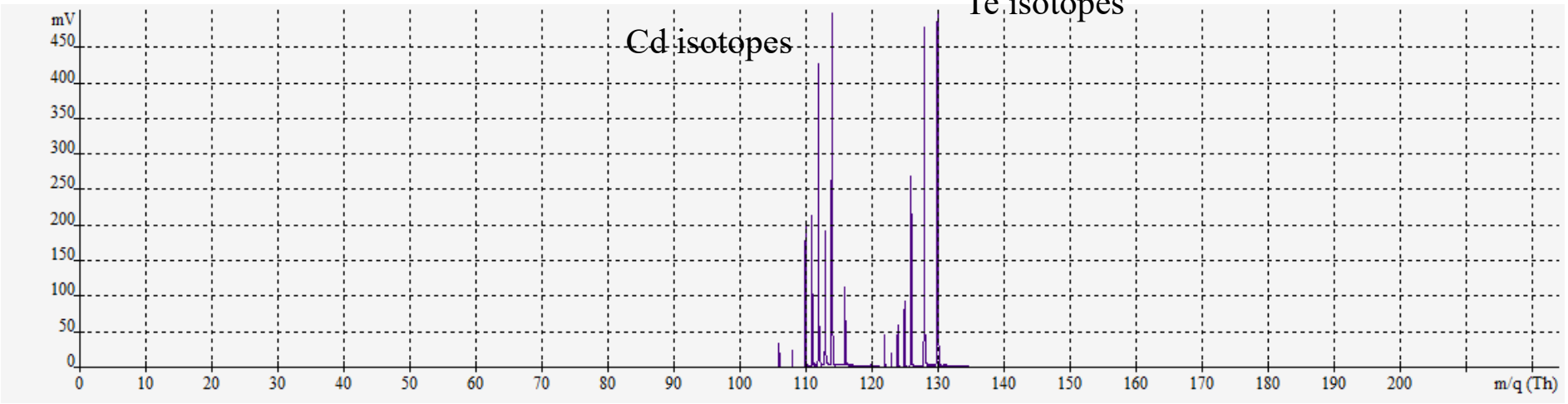


$$\frac{m}{z} = 2eU\frac{t^2}{L^2}$$

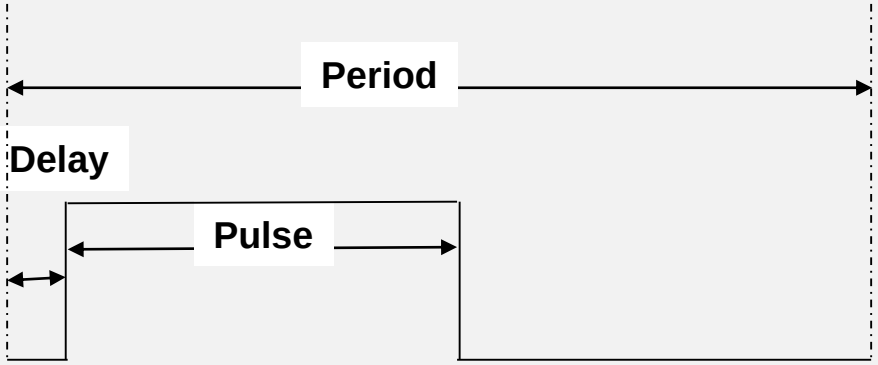
Prototype: European Project STREP 032202 EMDPA.

$$\frac{m}{z} = \alpha t^2 + \beta \Rightarrow \frac{\left(\frac{m}{z}\right)_1}{\sqrt{t_1}} = \frac{\left(\frac{m}{z}\right)_2}{\sqrt{t_2}}$$





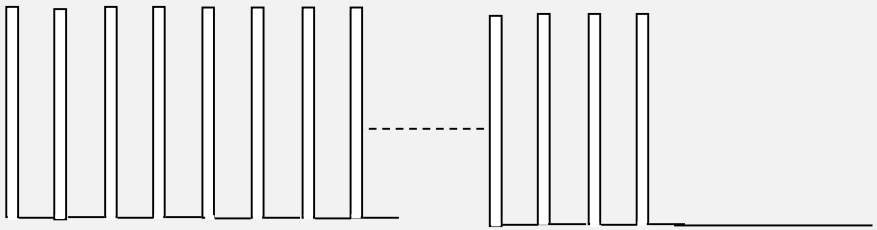
Pulsed-rf-GD ion source



Pulse Width = 1-2 ms
Period = 2-4 ms

Power = 20-100W
Pressure = 150-900 Pa

TOFMS

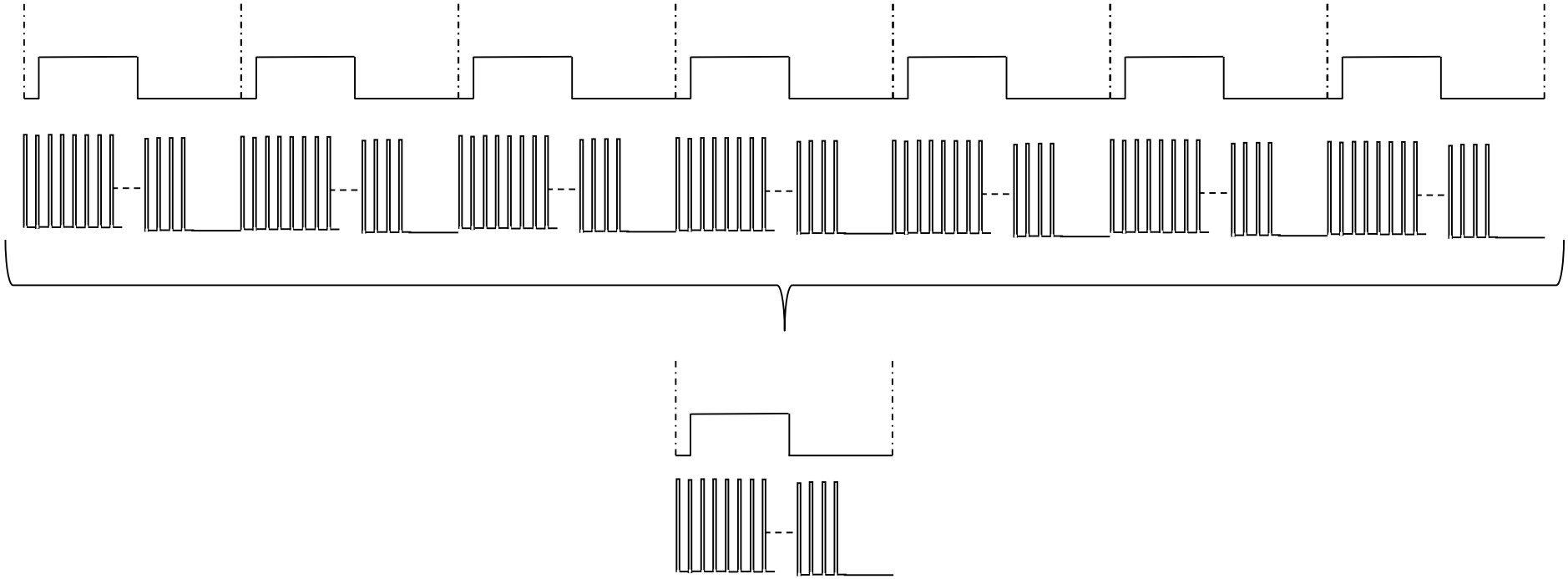


Extractions to TOFMS → every 30 µs a complete mass spectrum is collected. (up to 242 m/z)

The number of extractions per GD Period can be selected.

Pulsed-rf-GD-TOFMS

- In order to **improve statistics**, mass spectra are collected at each temporal position along a selected number of pulse periods → This process is continuously repeated (e.g. every 50 ms) → **All data are available for later evaluation.**



Pulse Profiles (Variation of ion signals along the pulse period)

Sample: Ir thin layer (Average of first 7 GD pulses)

Each ion signal should be integrated in the most appropriate temporal region of the pulse domain
→ Proper depth profile of each analyte.

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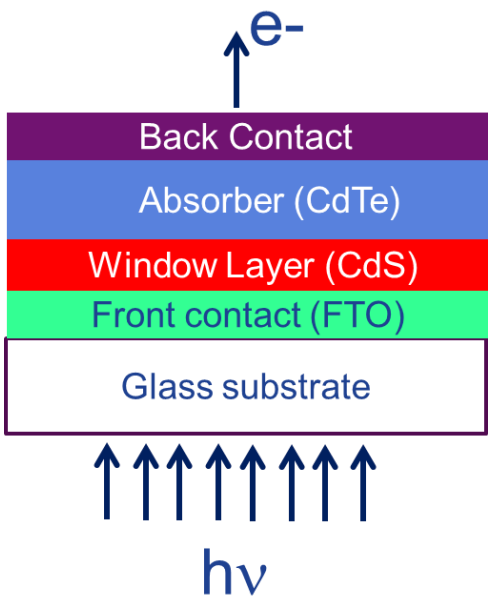
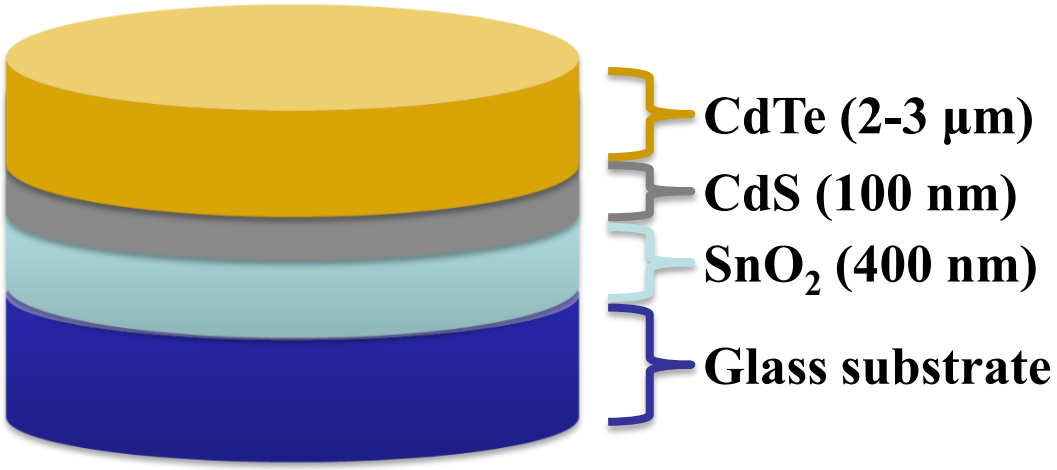
Photovoltaic application

Depth profile analysis of a commercially available CdTe solar cell with Glass Substrate, **using GD-TOFMS, SIMS, and LA-ICP-MS.**



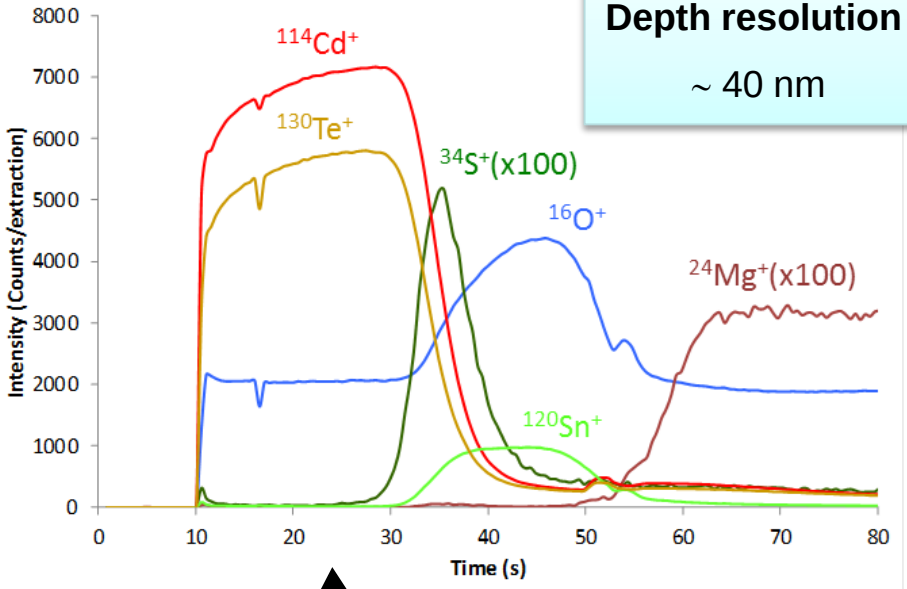


Depth profiling of CdTe PV cell

by pulsed-RF-GD-TOFMS

Depth resolution

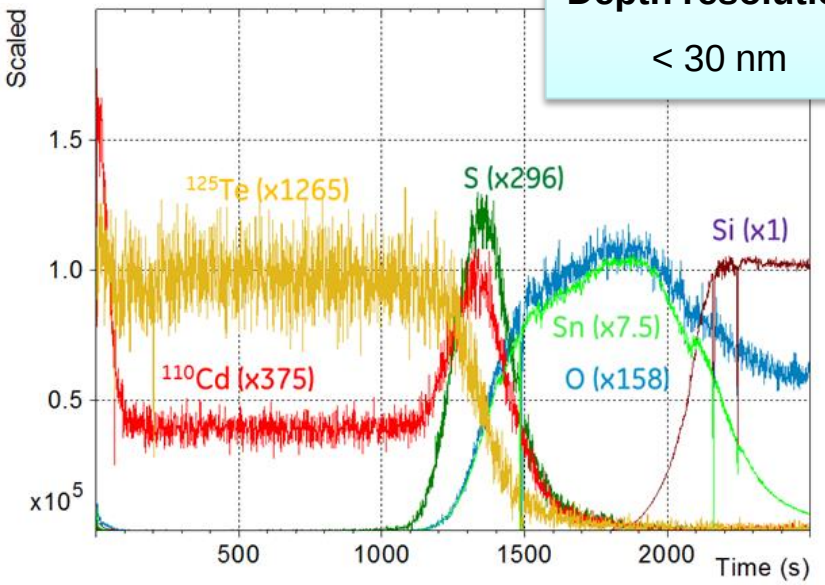
~ 40 nm



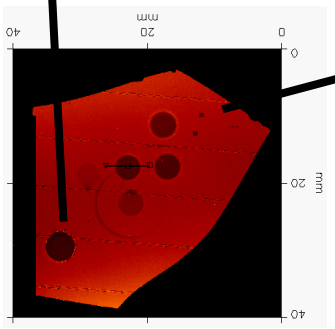
by TOF-SIMS

Depth resolution

< 30 nm



300Pa
70W

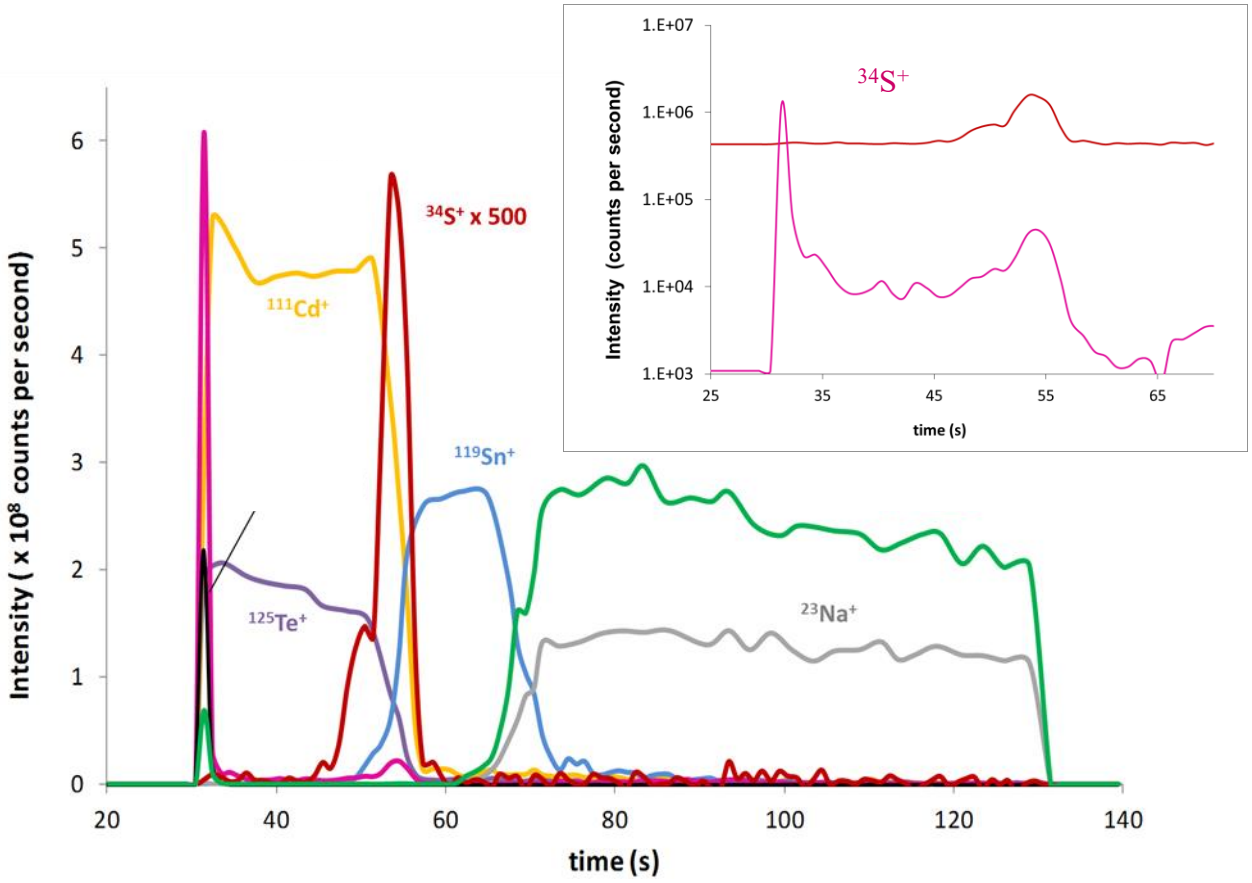


TOF.SIMS5 (ION-TOF, Münster, Germany)
Sputtering by Ar+ ions (2kV, 600nA) over a 600 µm by 600 µm area.
Analysis by Bi^+ ion beam (200 µm x 200 µm area, centered with eroded area).
The sample was eroded for 1s intervals between successive analysis cycles

C. Gonzalez-Gago et al., Journal of Vacuum Science and Technology, 2013.
http://dx.doi.org/10.1116/1.4824164

LA-ICP-MS for depth profiling of CdTe PV cell

Qualitative depth profile of a CdTe PV cell obtained by LA-ICP-MS: ∅65µm at 1 Hz + mathematical smoothing process.



Depth profiling of CdTe PV cell

Figures of merit of the evaluated techniques for depth profile analysis of CdTe Photovoltaic cells:

	Analysis spot size	Depth resolution at CdS layer	Sample Pressure Conditions	Coating Analysis time
Pulsed-RF-GD-TOFMS	∅4mm	**~40 nm**	300 Pa	**<100s**
LA-ICP-QMS	**∅65µm ∅160µm**	<100 nm	**Atmospheric pressure**	**<100s**
TOF-SIMS	600x600µm^2 sputtering 200x200µm^2 analysis	**<30 nm**	<10^{-6} Pa	~2000s

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Conclusions

- **Pulsed-rf-GD-TOFMS** shows a **great potential for fast depth profiling** of **innovative materials**, including thin and ultra-thin coatings of different nature (inorganic/organic) on conducting, semiconducting and non-conducting substrates.

- **Excellent complement for other direct solid analytical techniques (e.g. SIMS, GD-OES, GD-SFMS, LA-ICP-MS, AES, etc.)**

Comments

- **Integration intervals in the pulse profile should be carefully selected to avoid contributions from interferences.**
- **Ionization process along the GD pulse period not fully understood.**
- **Background ion signals from non-metals need to significantly reduced.**
- **Sensitivity for the analysis of trace elements needs to be enhanced.**
- **Quantification methods should be further improved.**

Acknowledgements

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THANK YOU FOR YOUR ATTENTION !!!

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