

***Neue Entwicklungen der GDMS zur
Analytik für
Dünnschichtsolarzellen***

Cornel Venzago

Einführung: Historie bei AQura Glow Discharge Mass Spectrometry

1991: GDMS VG9000

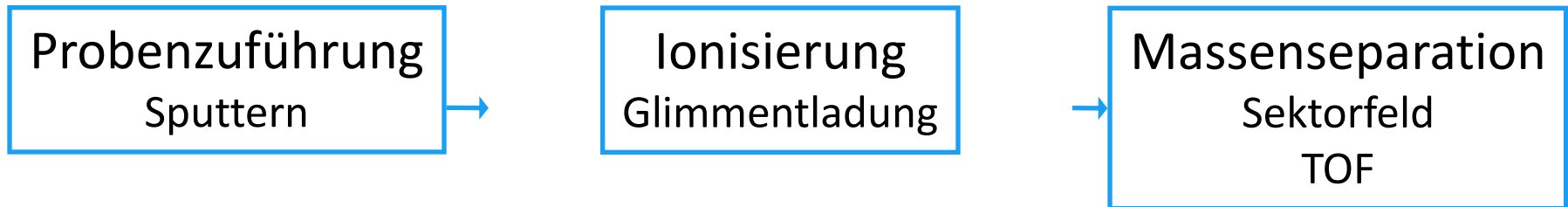
2005: ElementGD (Kooperation mit Gerätehersteller)

2010: μ s pulsed GD (Erweiterung selbst entwickelt)

2011: rf-GD TOF MS (im Rahmen einer Kooperation)



Einführung: GDMS

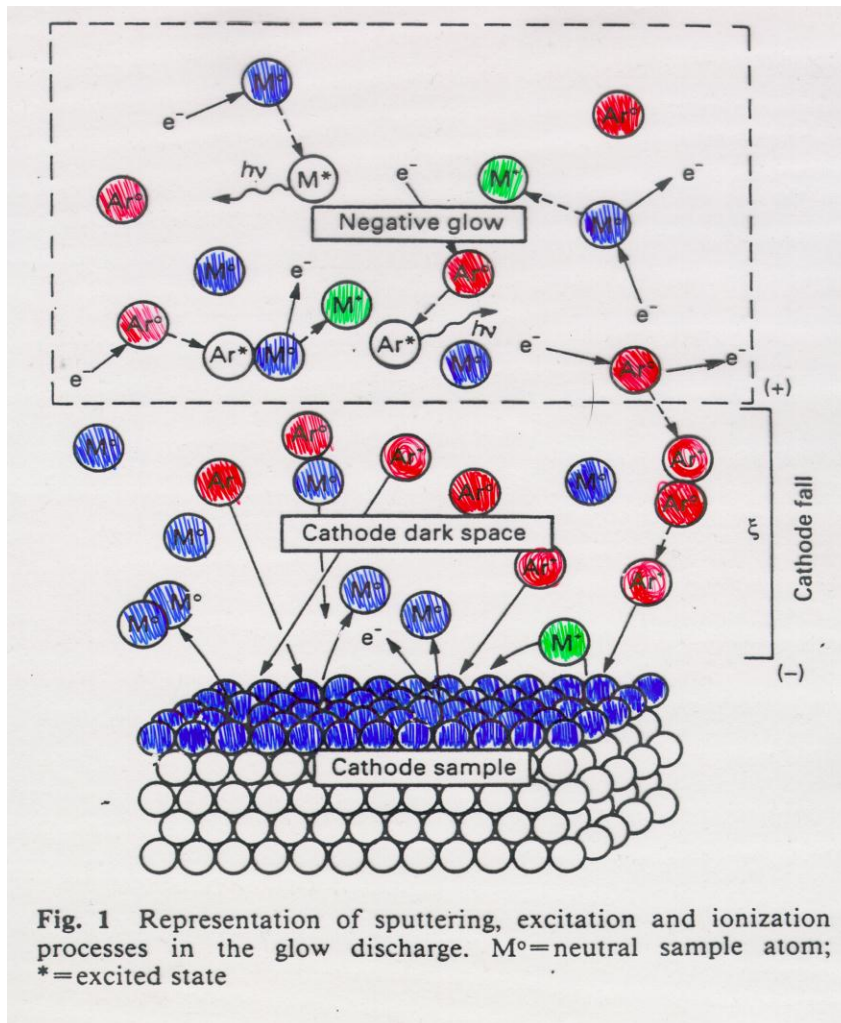


Vorteile der Massenspektrometrie als Detektor für die Elementanalytik

- **hohe Spezifität**
- **hohe Empfindlichkeit (Bestimmungsgrenzen im ppt-Bereich)**
- **Multielementbestimmungen**
- **Isotopeninformationen**
- **Schnelligkeit und Robustheit**

Einführung: GDMS

Ionisationsprozesse in der Glimmentladung



Sputterprozess getrennt von Ionisierung

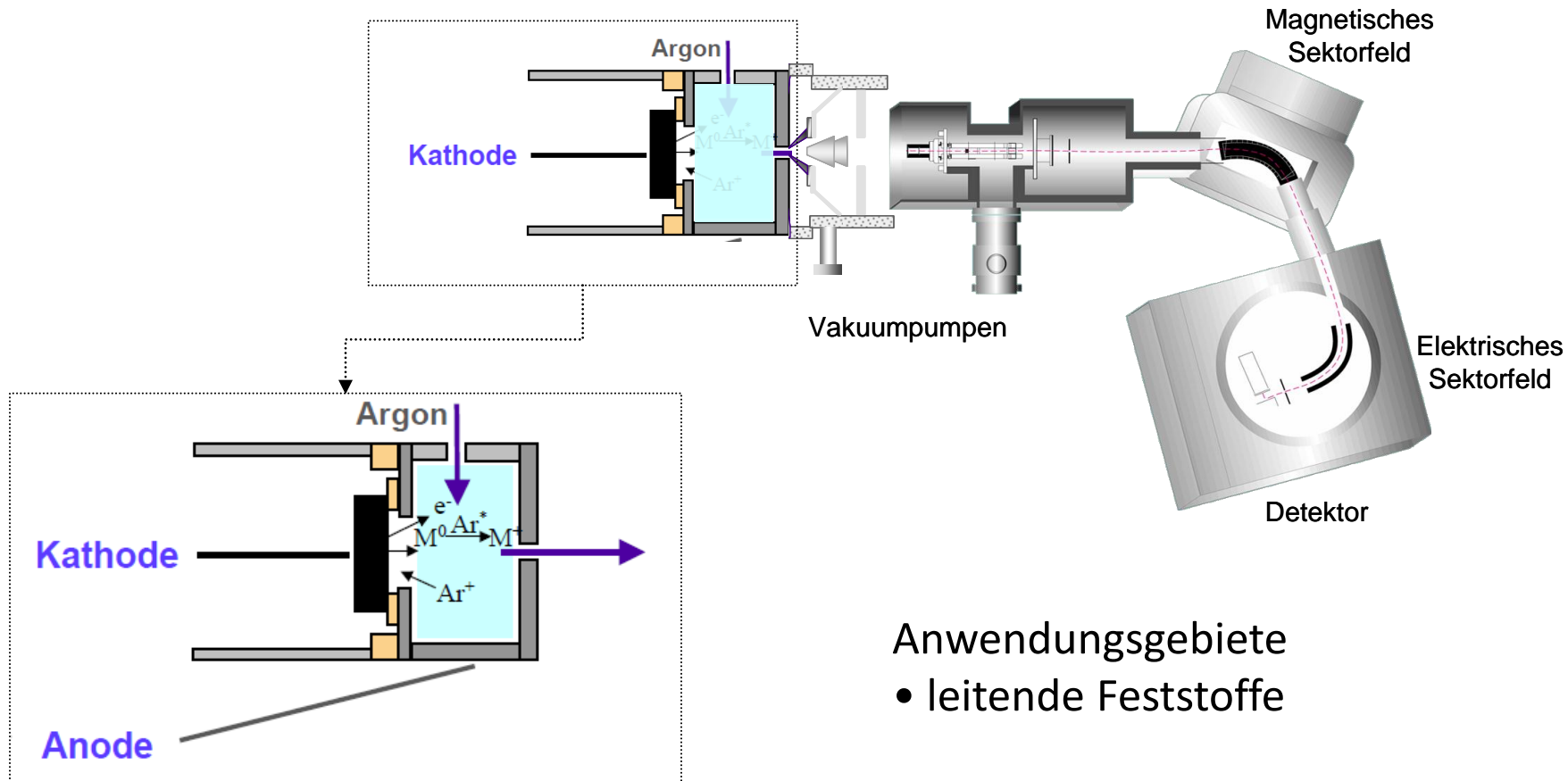
Ionisationsprozesse:

Penning

Elektronenstoß

Charge Transfer

Einführung: GDMS

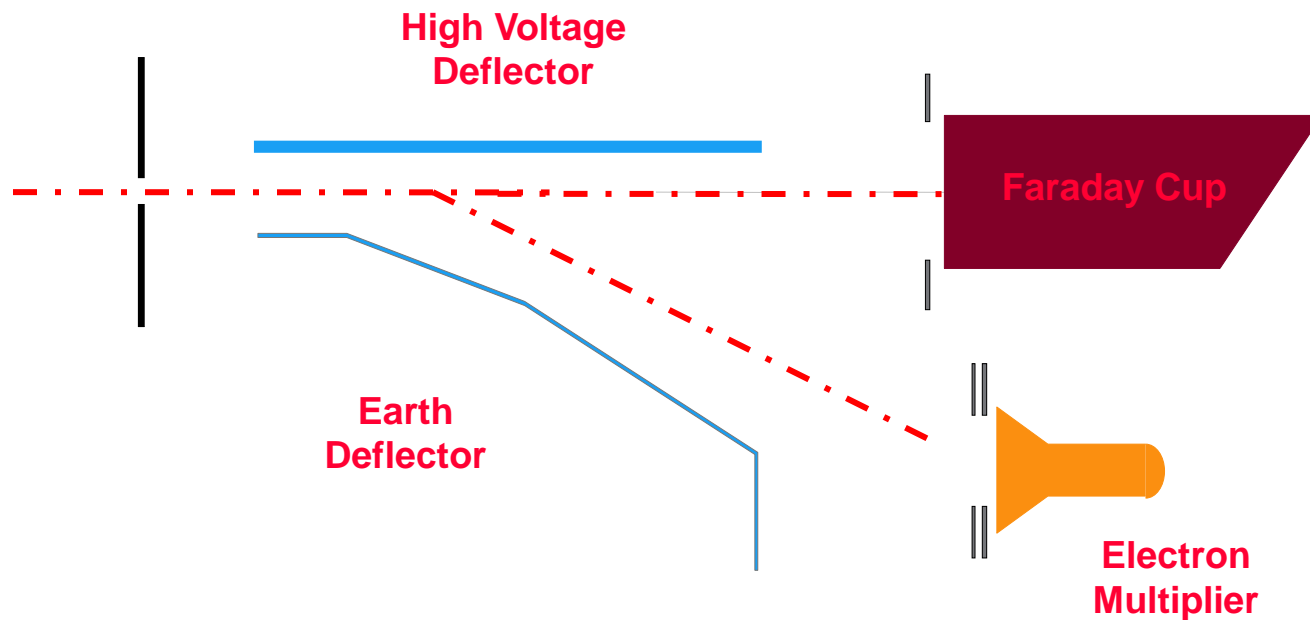


Anwendungsgebiete

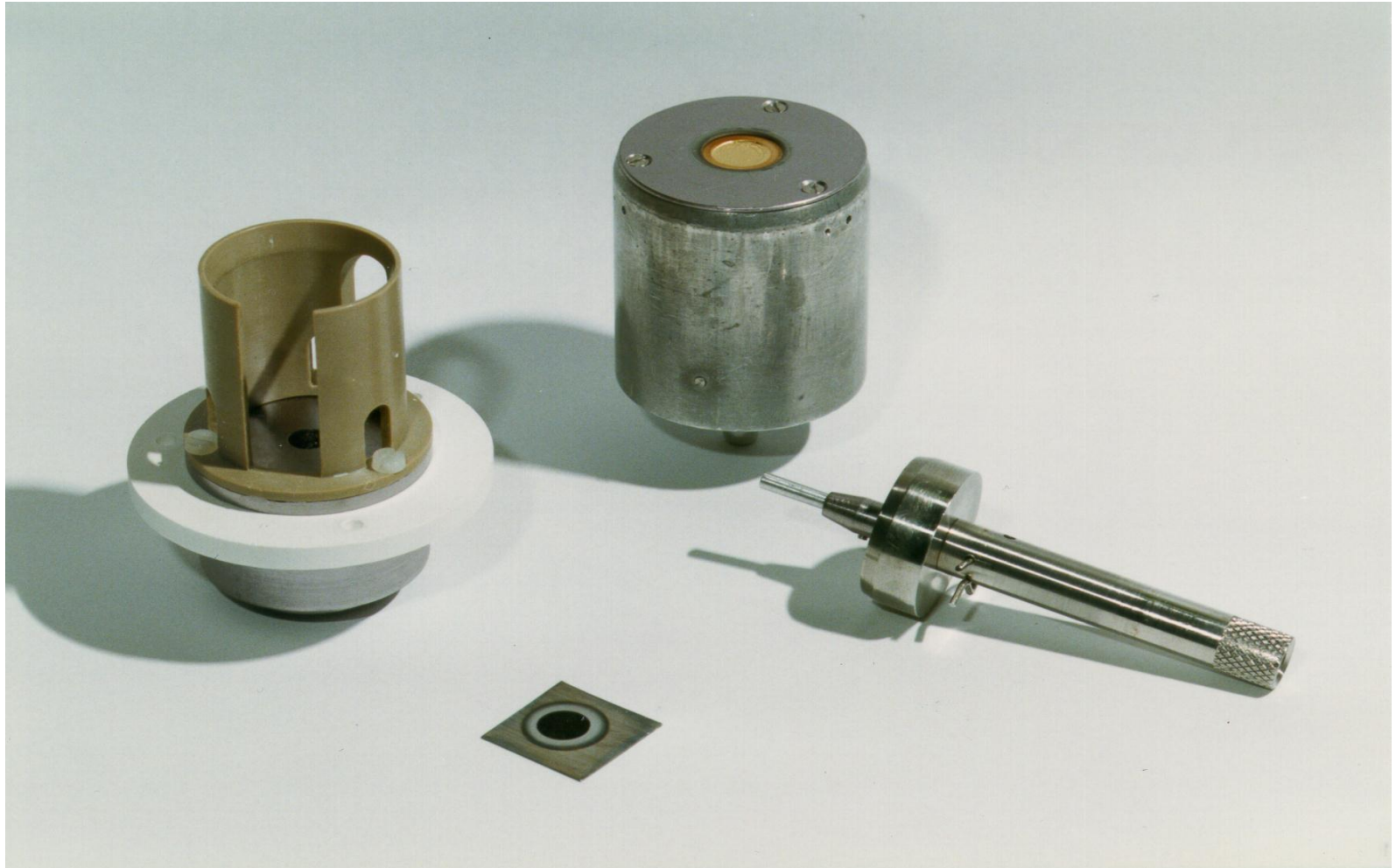
- leitende Feststoffe

Einführung: GDMS

Detektor-System



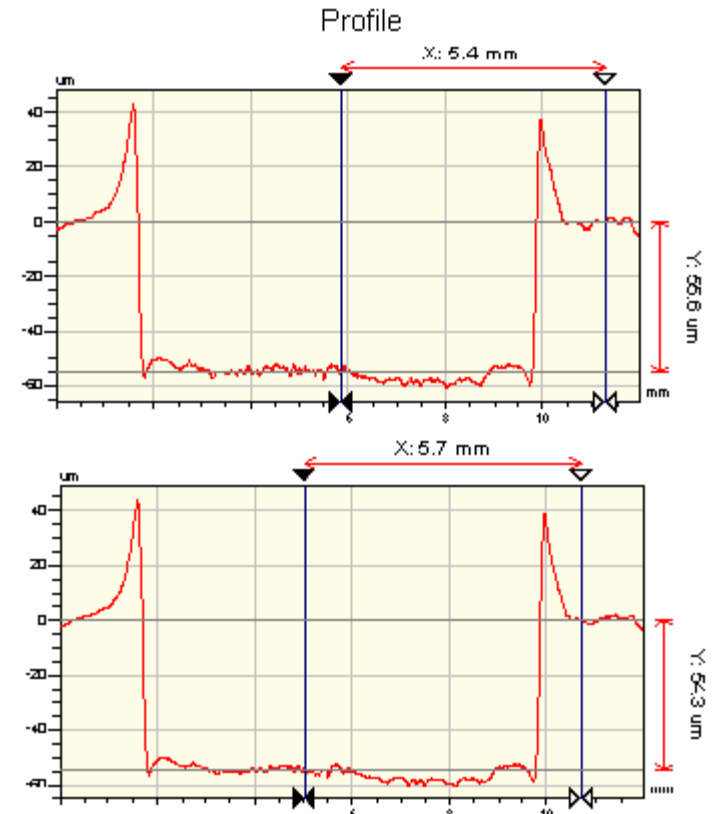
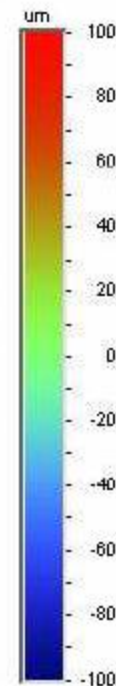
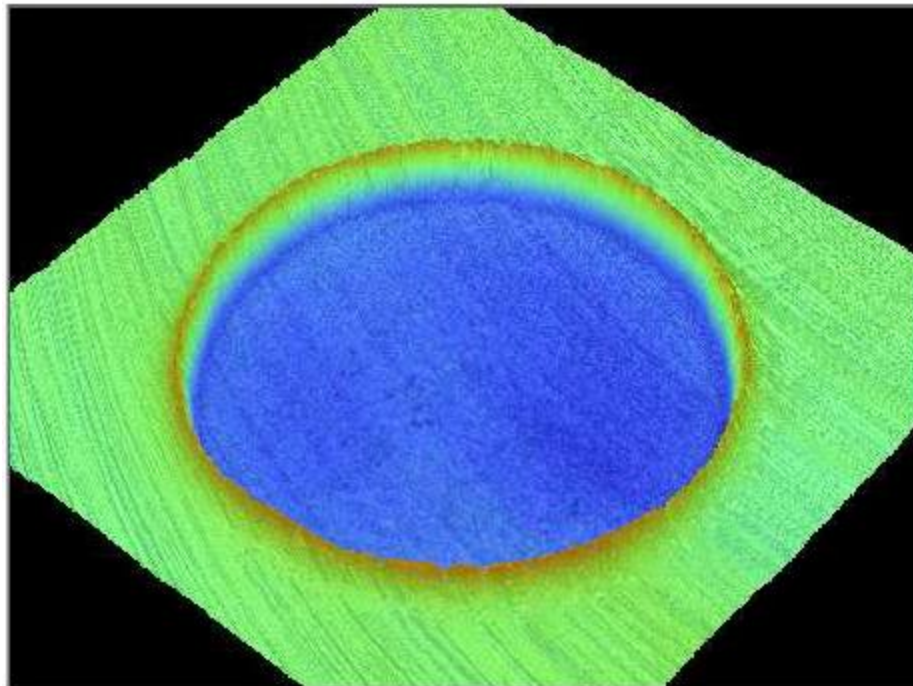
Einführung: GDMS Probengeometrie



Einführung: GDMS

Sputterkrater – Tiefenprofile

Probe: Messing

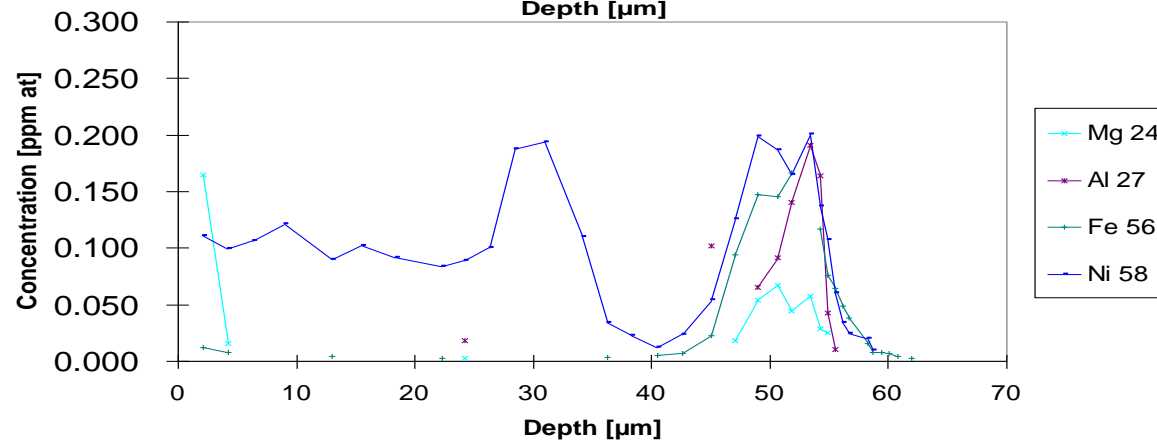
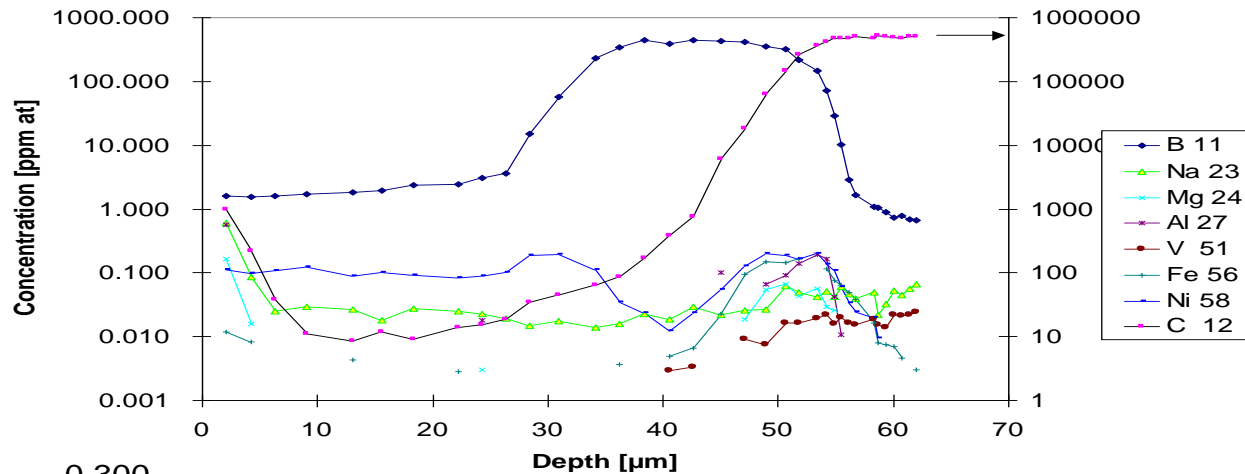


Ergebnisse: Ergebnisse an EPI-Schichten

FZ Silicon Wafer									
EPI SlotX1				EPI X2				Blank sample	
1-2 Ohm cm									
		ppba	atoms/cm3			ppba	atoms/cm3		
As	<	0,2	1,0E+13	<	0,4	2,0E+13	<	0,9	4,5E+13
B	<	0,4	2,0E+13	<	0,7	3,5E+13	<	260	1,3E+16
P	<	0,5	2,5E+13	<	0,6	3,0E+13	<	1,3	6,5E+13
Sb	<	0,3	1,5E+13	<	0,3	1,5E+13	<	1,0	5,0E+13
Al	<	1,5	7,5E+13	<	1,8	9,0E+13	<	3,1	1,6E+14
C	≤	4300	2,2E+17	≤	4400	2,2E+17	≤	5100	2,6E+17

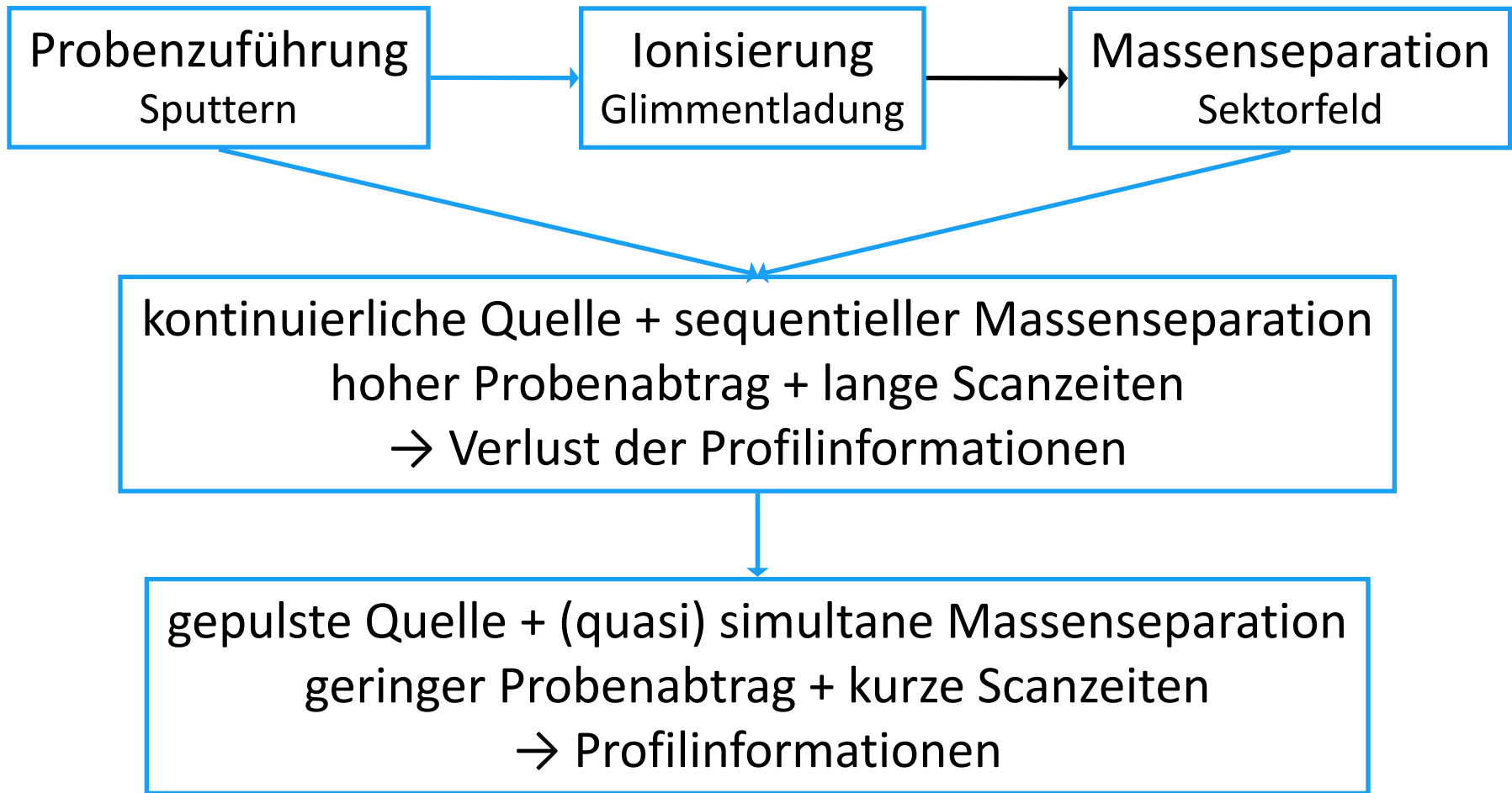
Concentrations in ppb atomic and atoms/cm3

Ergebnisse: Sputterkrater – Tiefenprofile



Concentrations in ppb atomic and atoms/cm³

Weiterentwicklung der GDMS



Erweiterung der GDMS auf dünne Schichten über eine mikrosekunden-gepulste Anregung

Die bisher angewandten GDMS-Geräte sind für ein kontinuierliches Plasma ausgerüstet

Diskontinuierliches Plasma schont die Probe und erlaubt ein langsames Sputtern

Erste Installation bei AQura wurde im Rahmen eines EU-Projektes entwickelt:

GLADNET, Marie Curie action, im FP6

M. Voronov, T. Hofmann, P. Šmíd and C. Venzago, *J. Anal. At. Spectrom.*, 2009, 24, 676-679

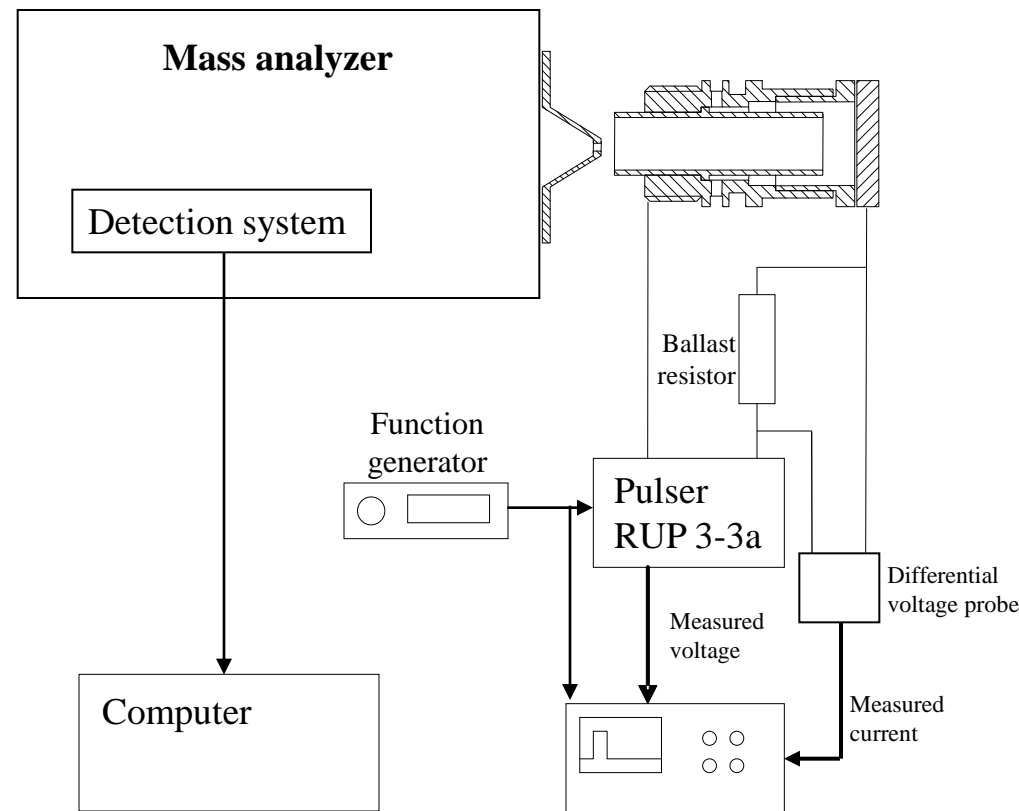
μ s pGDMS: Experimentelle Umsetzung

ELEMENT GD in DC pulsed mode:

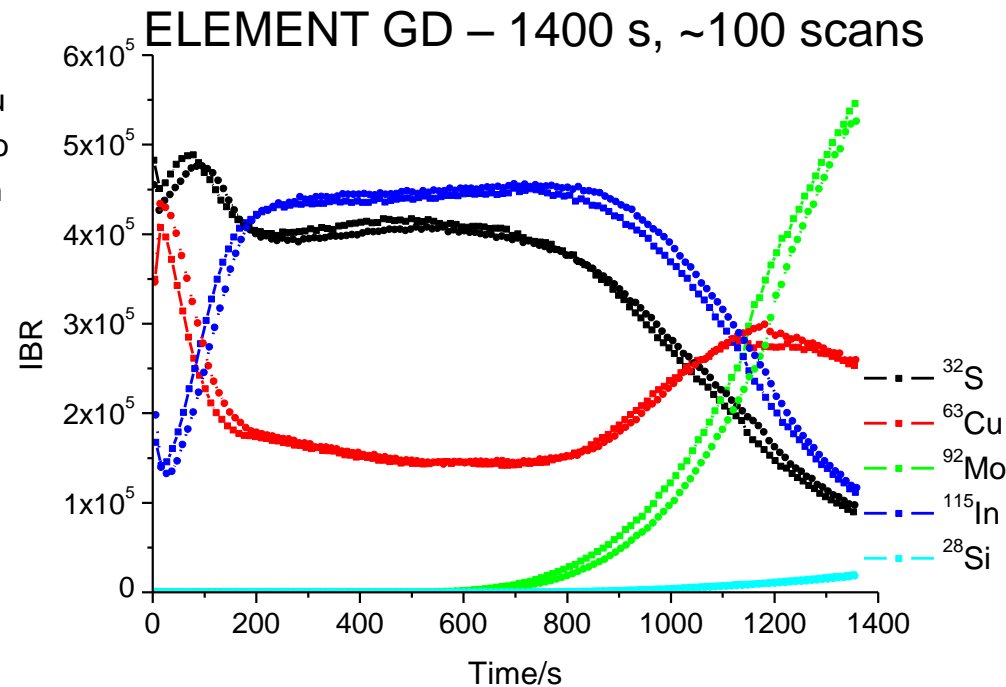
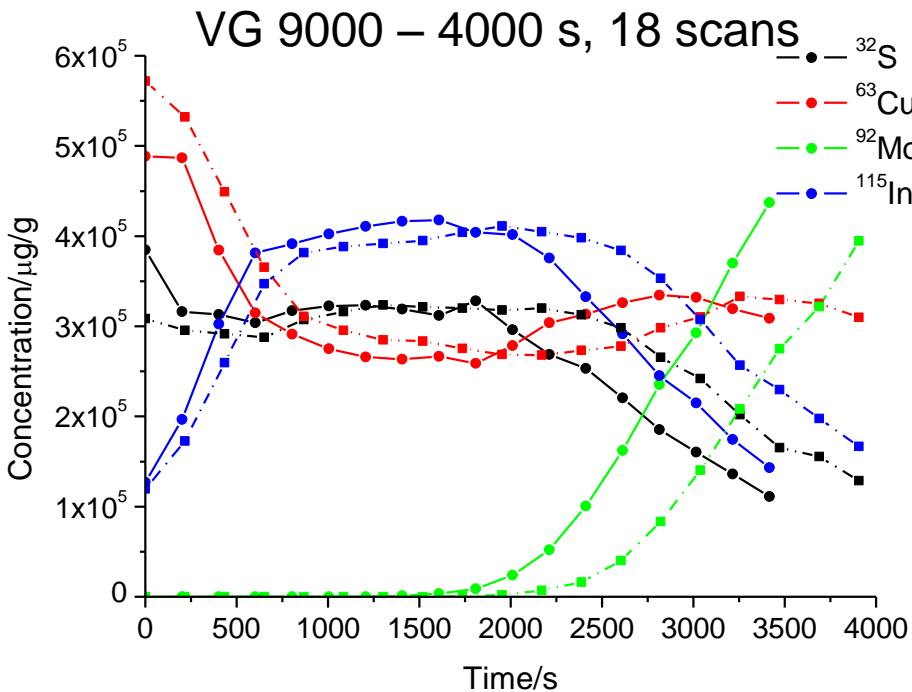
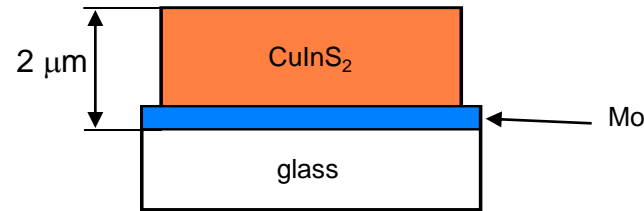
⊗ **ELEMENT GD high voltage cable** connected to the output of a DC pulse voltage generator (**RUP 3-3a**) via a **ballast resistor – current measurement**

⊗ **RUP 3-3a (GBS Elektronik):**

- Pulse voltage: 0...-3 kV
- Max mean current: 100 mA
- Max peak current: 38 A
- Max mean power: 300 W
- Switch-off time: ~80 ns!



Ergebnisse: CuInS₂/Mo-Schicht auf Glas



Weiterentwicklung – CuInS_2/Mo Schichten auf Glas

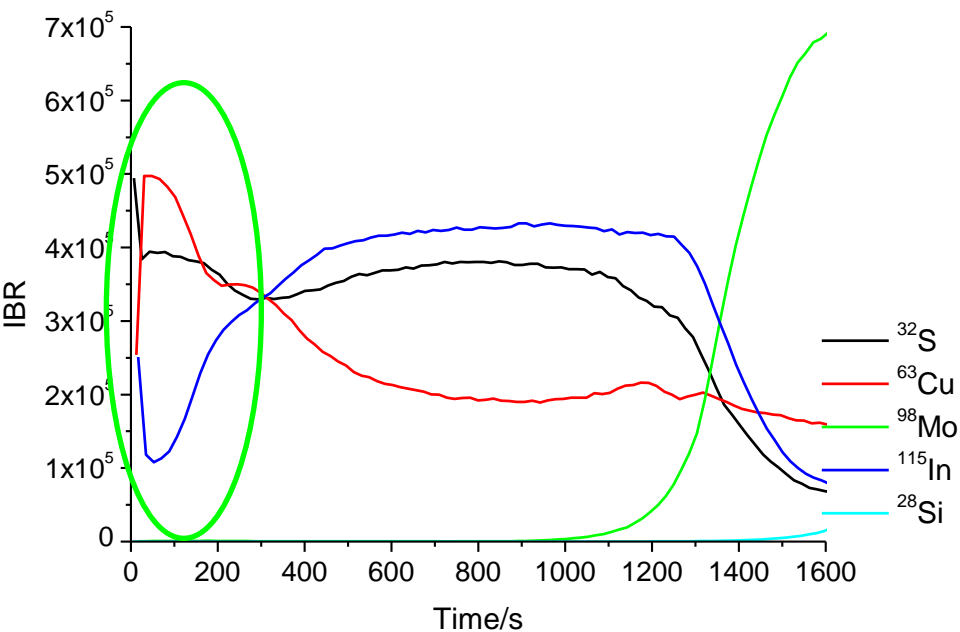
Optimierung des Kraterprofils – Effekt der flow tube Länge



Weiterentwicklung – CuInS₂/Mo Schichten auf Glas

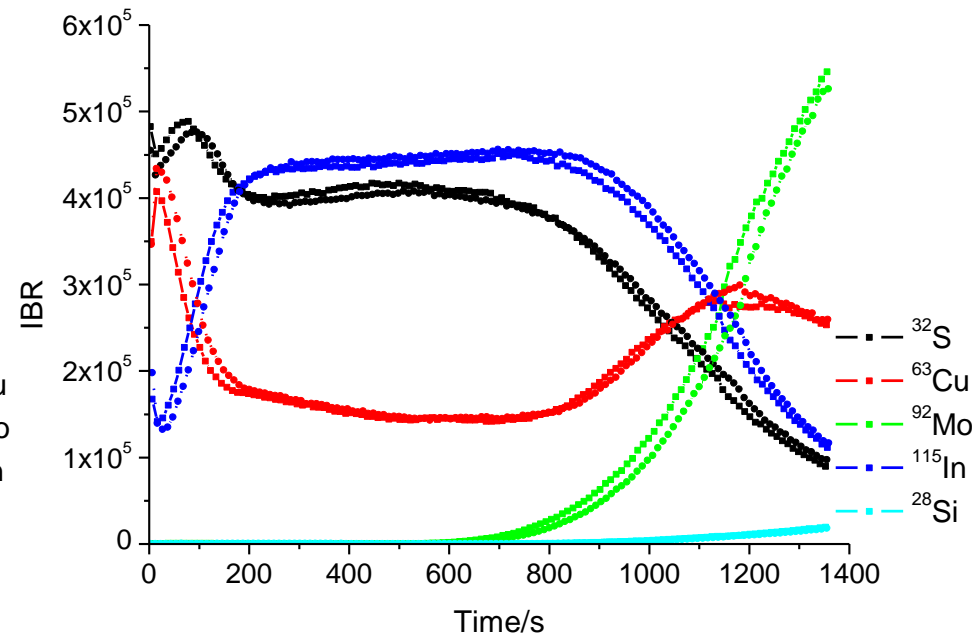
18 mm flow tube

Voltage: 900 V
Gas flow: 256 sccm
Frequency: 500 Hz
Pulse length: 100 μs



20 mm flow tube

Voltage: 900 V
Gas flow: 295 sccm
Frequency: 1 kHz
Pulse length: 50 μs



Weitere Optimierung des Kraterprofils

- Sputtering time 10 min on floatzone Si wafer

900V, 400sccm, 40% duty cycle → 5.7 μ m



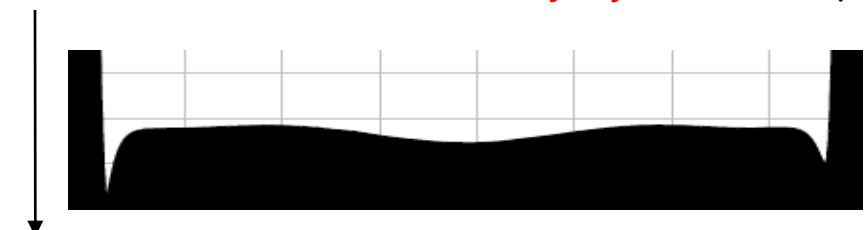
950V, 380sccm, 40% duty cycle → 6.2 μ m



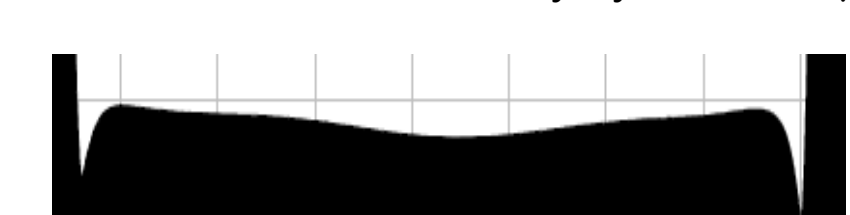
900V, 380sccm, 40% duty cycle → 5.1 μ m



950V, 380sccm, 20% duty cycle → 2.9 μ m



900V, 350sccm, 40% duty cycle → 4.5 μ m



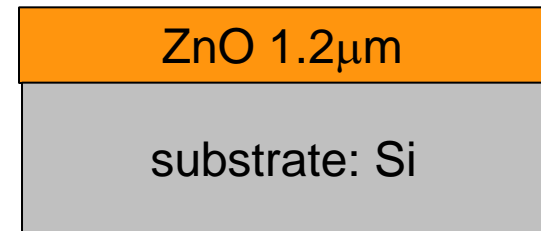
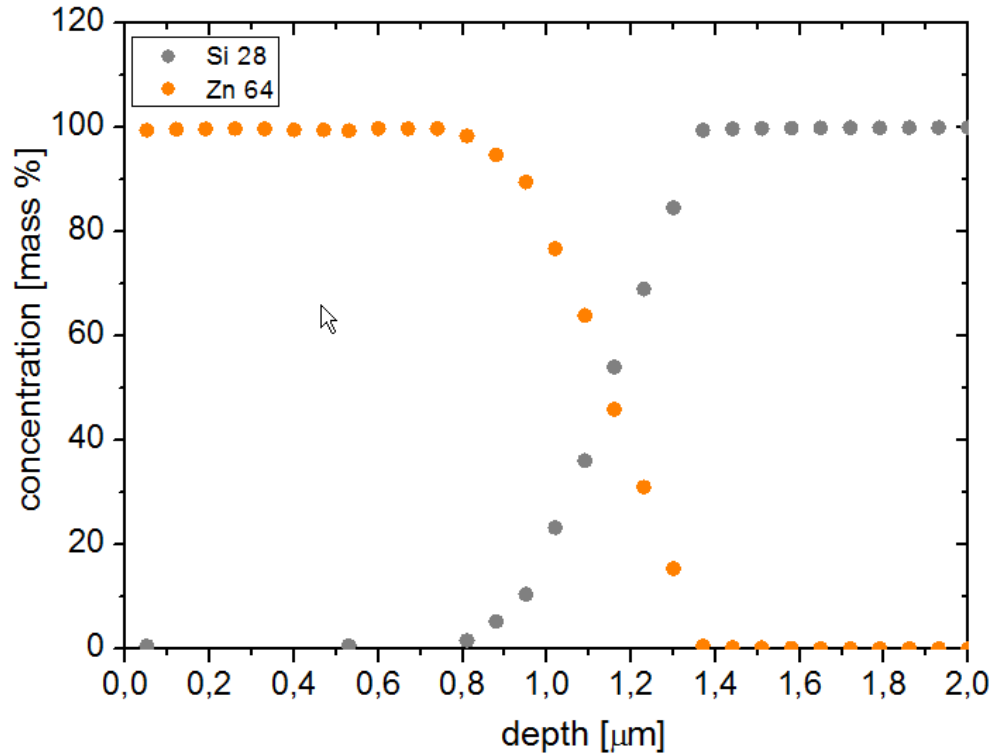
950V, 270sccm, 20% duty cycle → 1.7 μ m



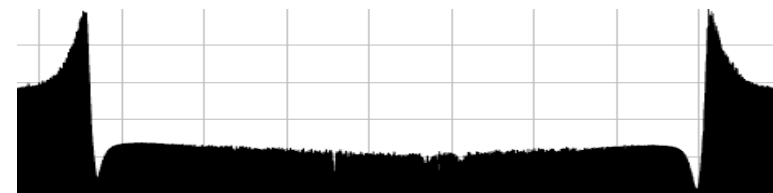
- Low pressure, high voltage → symmetric
- Low duty cycle, low pressure → flat
- It is possible to adjust crater shapes in the GD fast flow source!

Ergebnisse: ALD ZnO Schicht auf Si

- 950V, 270sccm, 20% dutycycle

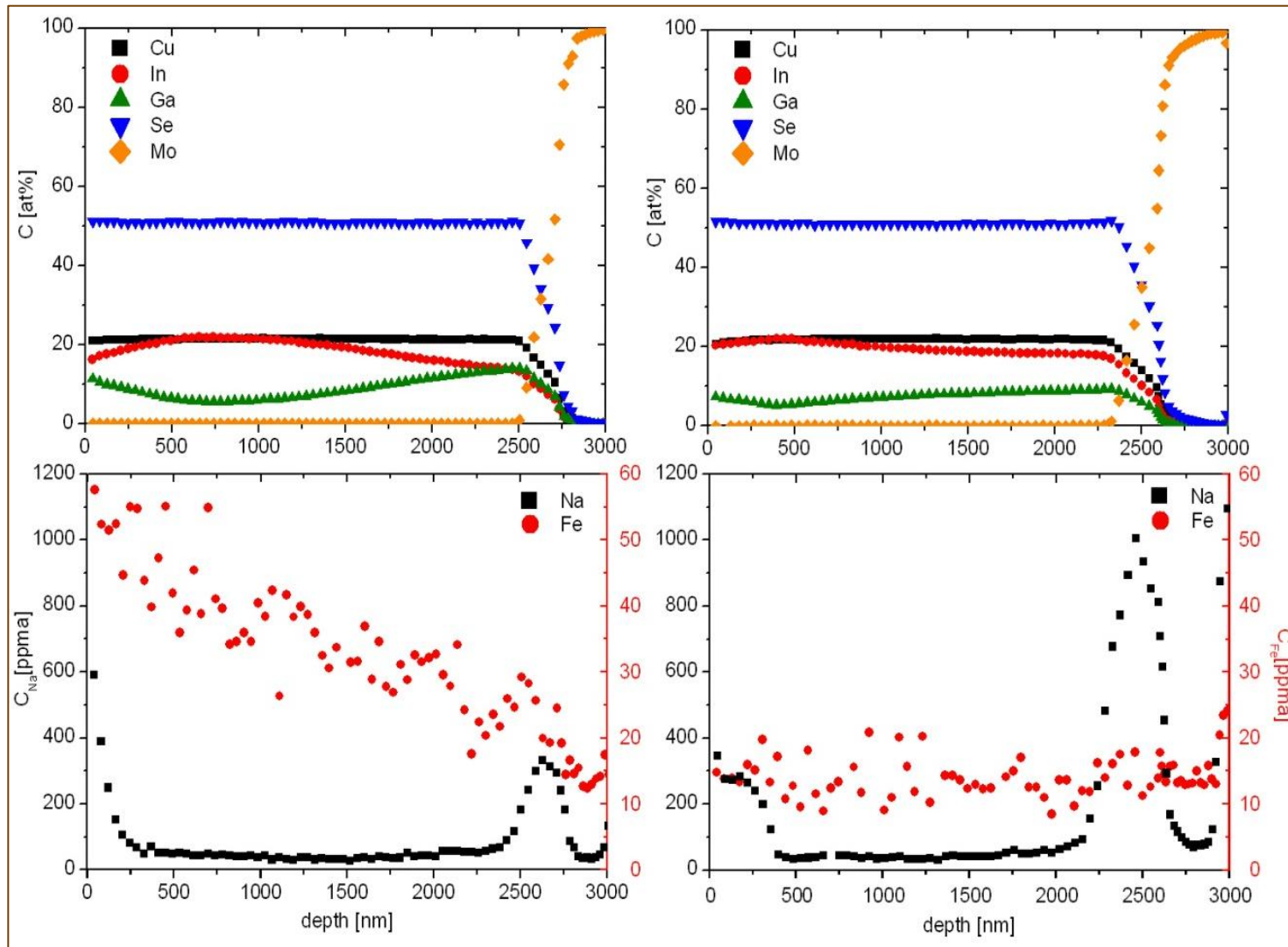


2 microns

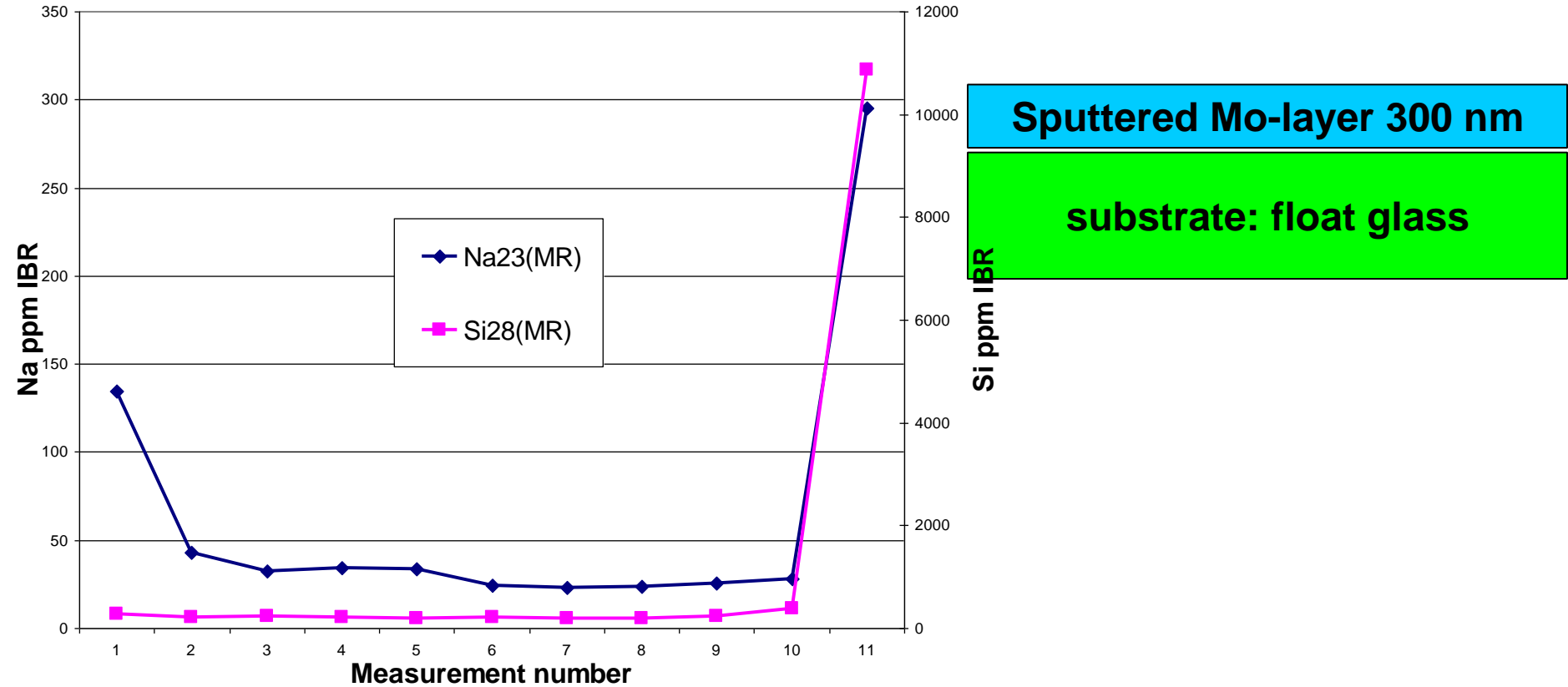


- Layer transition clearly visible in the right depth
- Good crater shape is preserved after 4 min of sputtering

Ergebnisse: CIGSe auf Glas

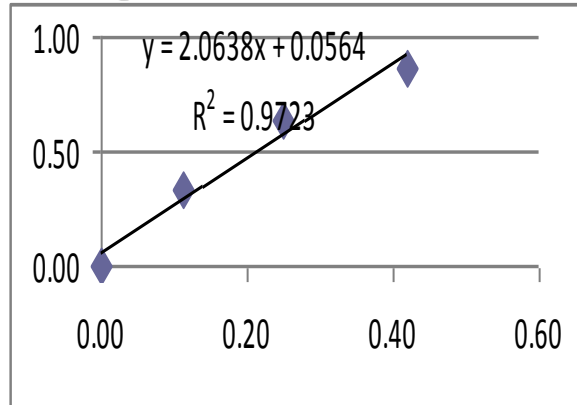


Ergebnisse: 300 nm Mo-Schicht auf Glas

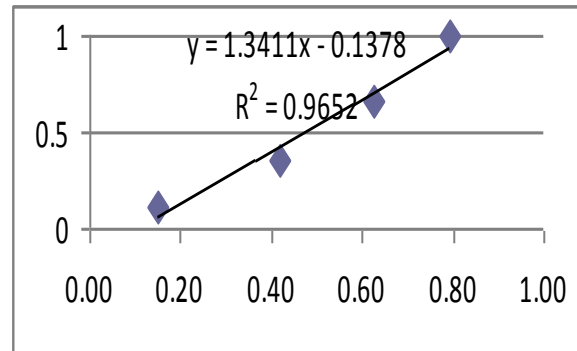
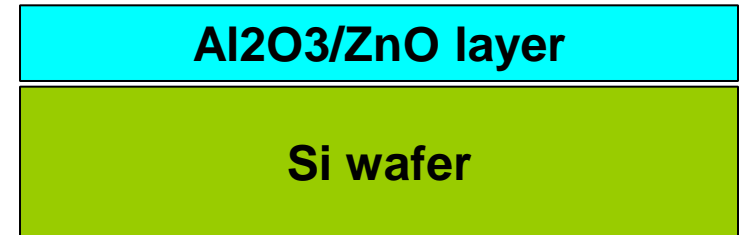


- Na and Si profile well visible
- Full scale multielement analysis to sub-ppm level also possible

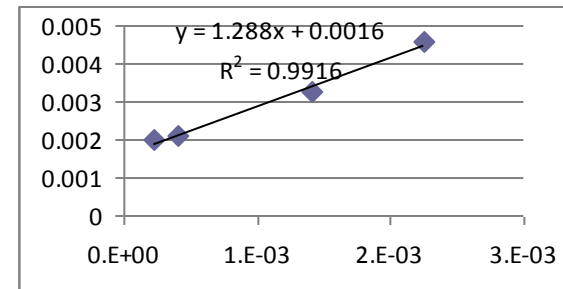
Ergebnisse: 1 µm AZO-Schichten auf Si-wafer



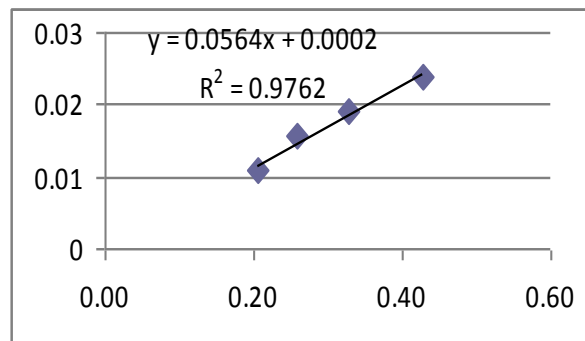
Al



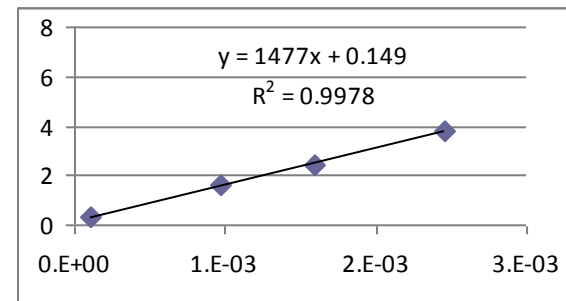
Zn



C



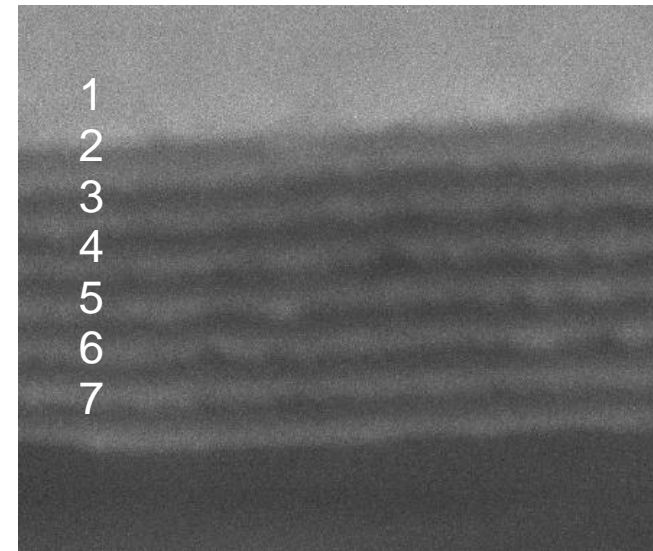
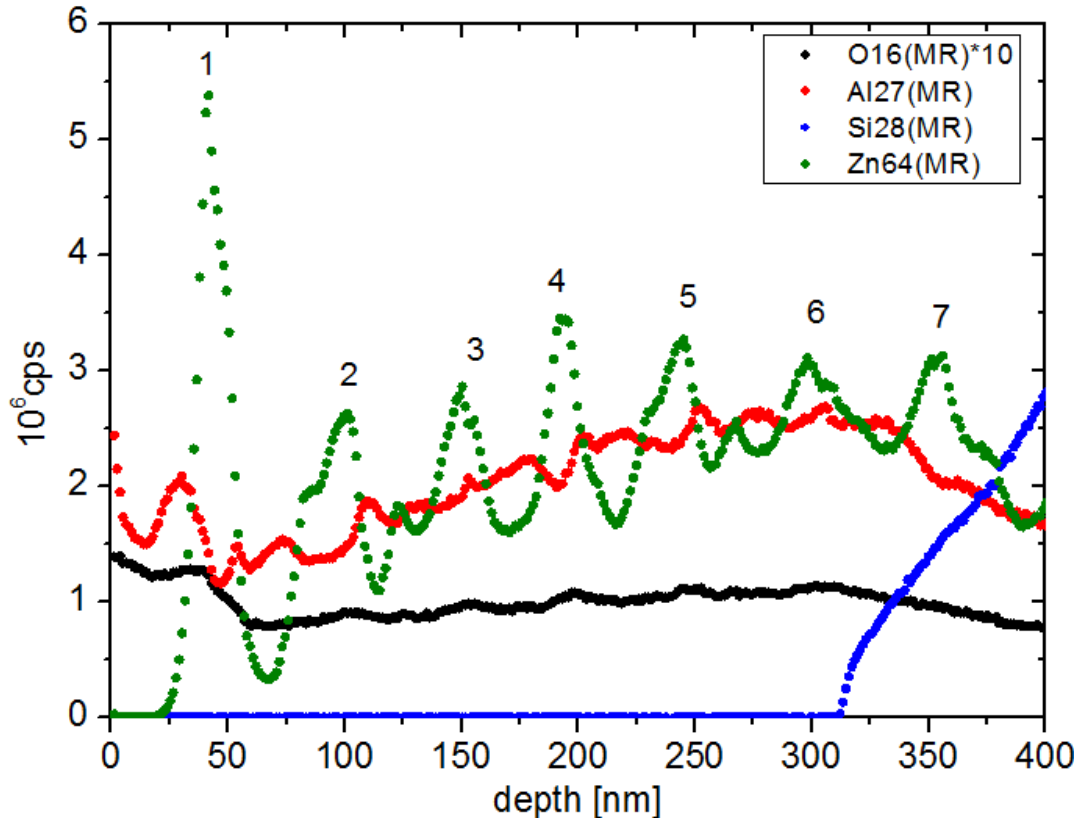
O



ArH

Grenzen: ZnO/Al₂O₃ multi-layer ALD film on Silicon

- 900V, 260sccm, 1.5% duty cycle, sputtering time 48min



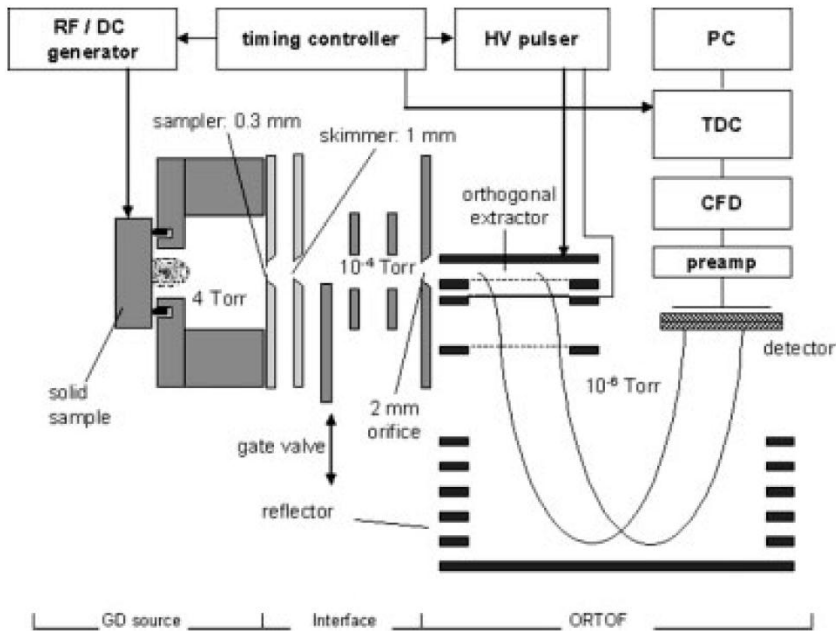
SEM picture of the multi-layer
20nm per layer

- **All seven ZnO layers can be clearly distinguished!!!**
- Unfortunately cratershape not measurable due to deformed sample
- Sample surface very rough after measurement, due to Al₂O₃-layers

rf-GD-TOF

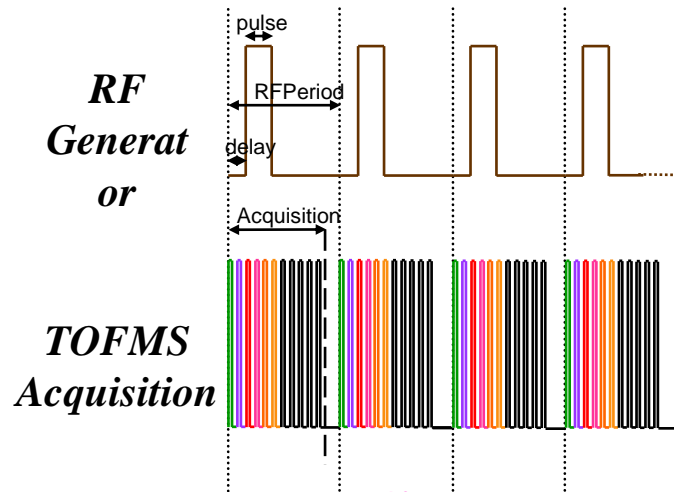
GD-TOF-MS instrument at EMPA Thun, Switzerland:

- ⊗ RF pulsed GD source with a fixed frequency matched RF system (13.56 MHz) – **Horiba JY**
- ⊗ Orthogonal TOF MS – mass spectrum up to 300 Da at 50 kHz extraction rate – **Tofwerk AG**
- ⊗ **Commercialisation 2012: Horiba Jobin Yvon**



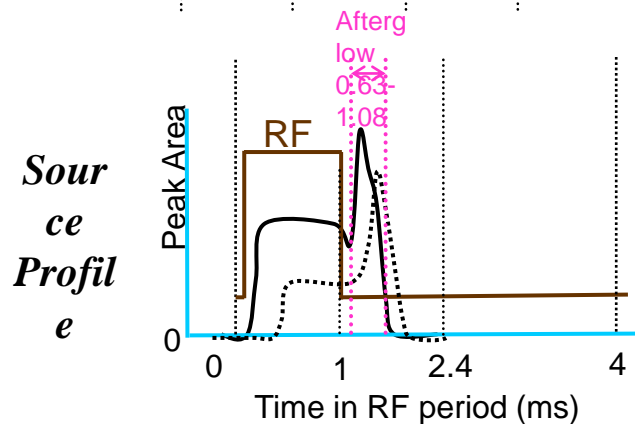
M. Hohl, A. Kanzari, J. Michler, T. Nelis, K. Fuhrer and M. Gonin, *Surf. Interface Anal.*, 2006, **38**, 292–295.

rf-GD-TOF



60 W
250 Hz
1 ms pulse / 4 ms period

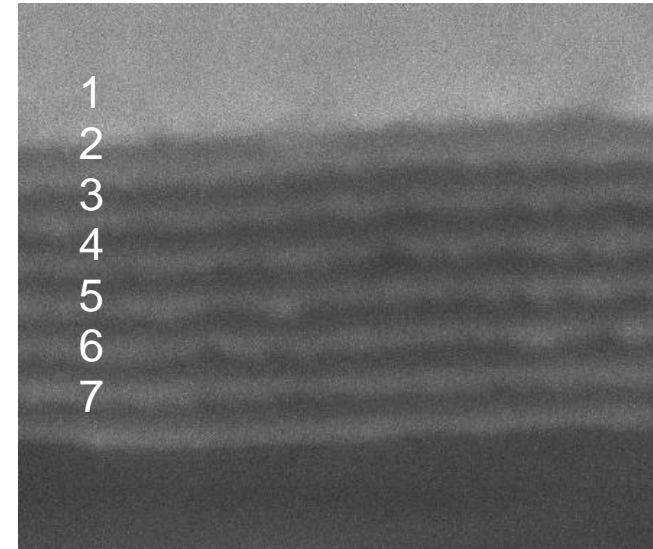
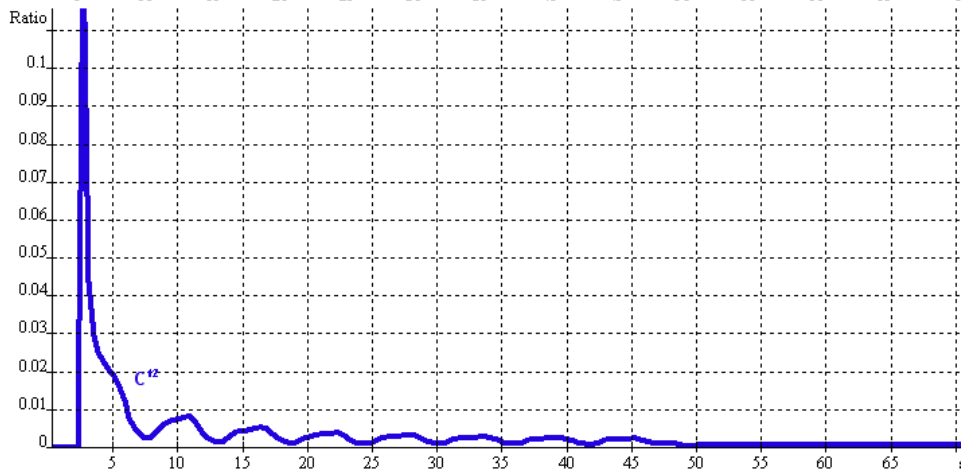
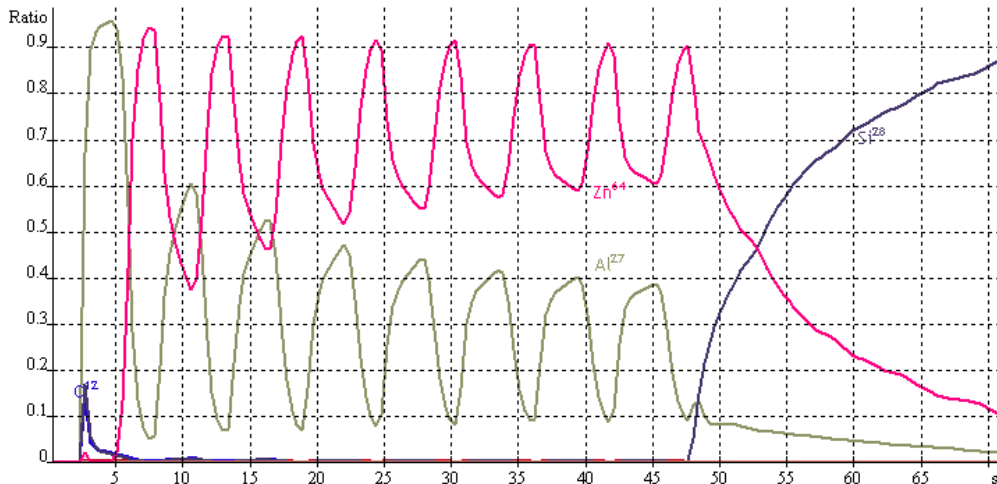
30 kHz
3 ms acq. / 4 ms RF full period
90 Mass Spectra



Use of enhanced
afterglow signal to
generate depth
profiles

rf-GD-TOF: ZnO/Al₂O₃ multi-layer ALD film on Si

- Sputtering time **70s**



SEM picture of the multi-layer
20nm per layer

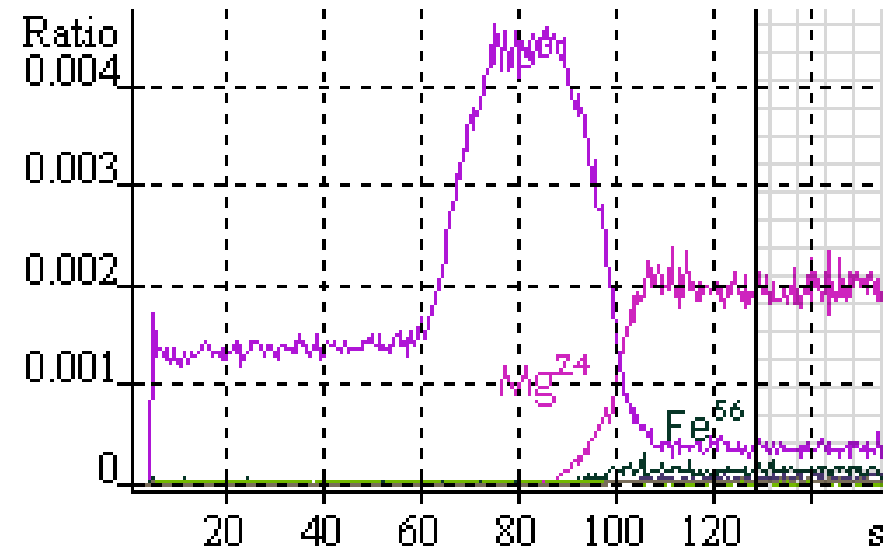
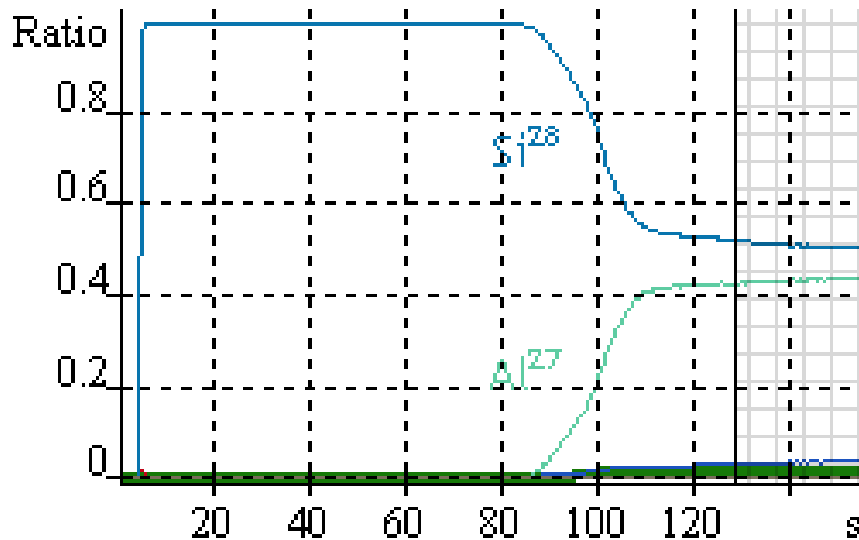
rf-GDTOF

170nm Si on glass

Si-layer 1: P-doped approx. 100 nm

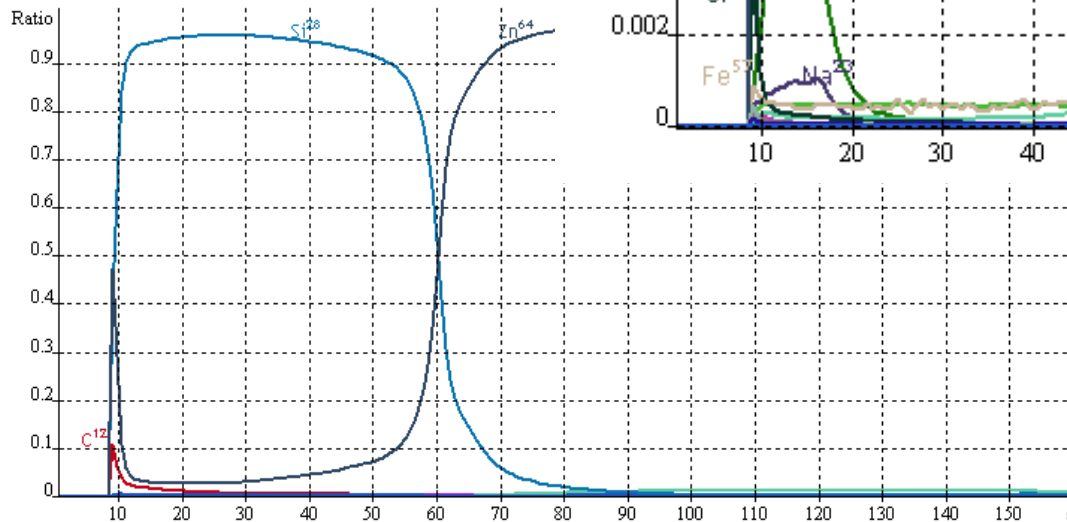
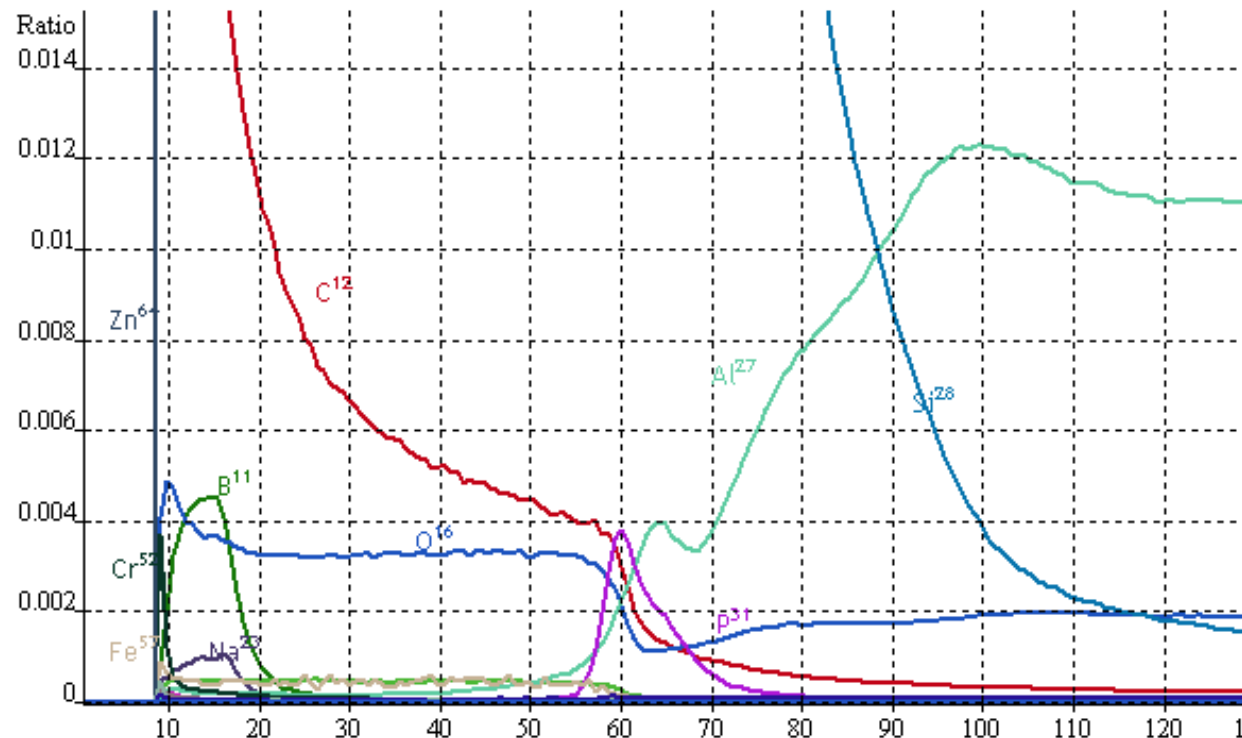
Si-layer 2: P-doped approx. 70 nm

substrate: float glass



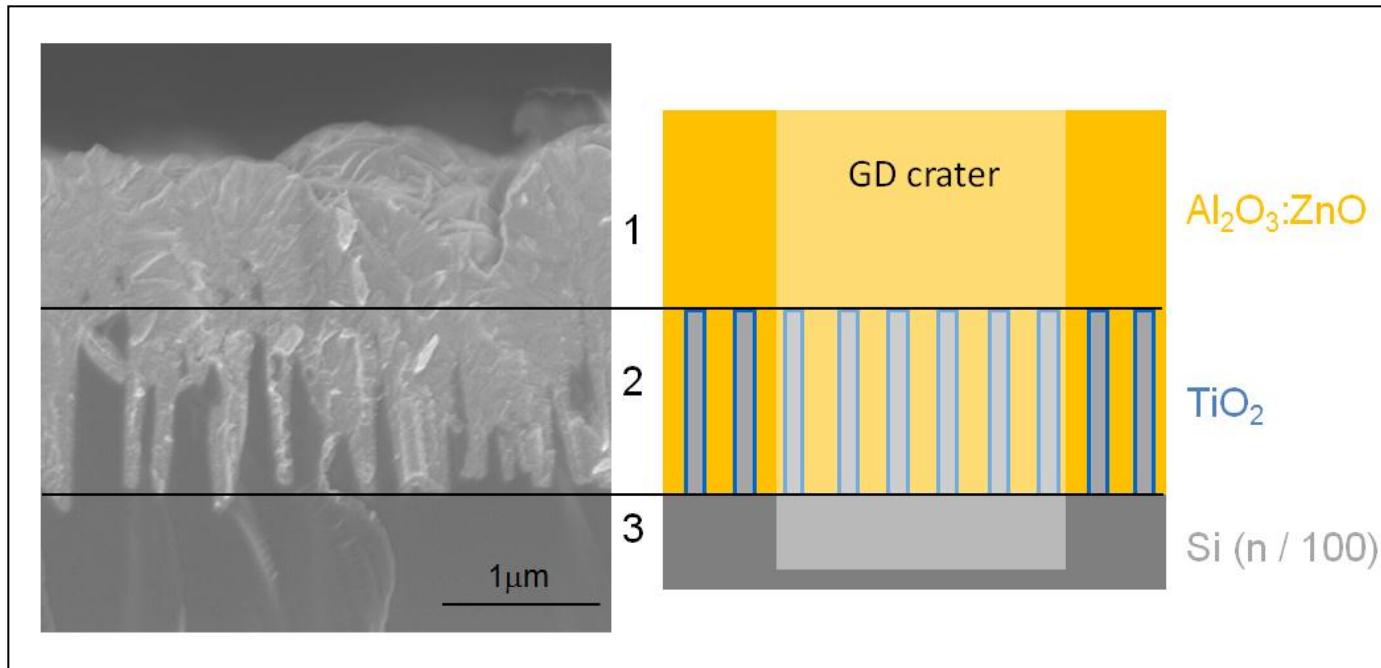
Rf-GD-TOF: (nm Si Schichten auf ZnO)

Layer 1: ca. 10 nm
Layer 2: ca. 100 nm
Layer 3: ca. 10 nm
Al:ZnO



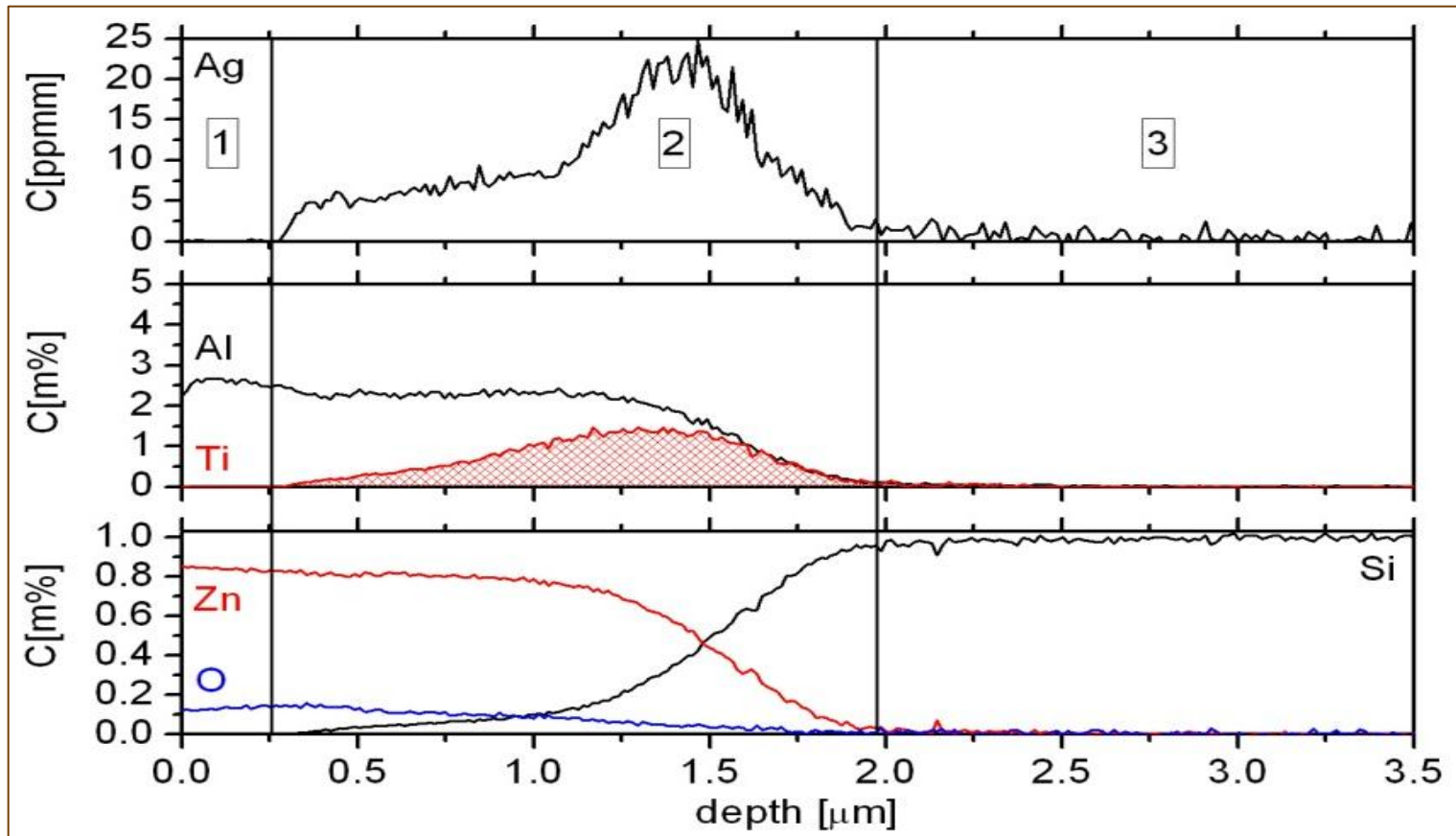
GD-OES: 3. Generation PV

Silicon nanowire solar cell



GD-OES: 3. Generation PV

Silicon nanowire solar cell



Zusammenfassung

- ⊗ **DC μ s pGD in Kombination mit einem kommerziellen Sector Feld Massenspektrometer ist ein wertvolles Instrument für Analysen von Schichtsystemen der Dünnschicht-Photovoltaik**
- ⊗ **Die Eignung für Tiefenprofilanalysen an CIS- und CIGSe im Schichtdickenbereich von einigen 100nm bis μ m wurde dargestellt**
- ⊗ **Grenzen: Wenn nichtleitende Schichten vorliegen und dünnere Schichten im Bereich von 100nm und darunter**
- ⊗ **rf-GD-TOF kann diese Grenzen überschreiten, kommerzielle Gerätetechnik ist erst in der Entwicklung**

Dank

- ❁ **EC funded Research Training Network GLADNET, contract no. MRTN-CT-2006-035459**
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- ❁ **Kooperation GD-TOF: A. Tempez, Horiba JobinYvon**

Dank

Für Ihre Aufmerksamkeit

