

**Oberflächenphysik**

**Grenzflächenphysik**

**Spurenanalyse**

# Oberflächen- und Grenzflächenphysik, Inhalt

## Grundlagen:

Reine Oberflächen - Wiederbelegung - UHV

Oberflächenstrukturen, Relaxation, Rekonstruktion

Elektron. Austrittsarbeit

Adsorption

## Erzeugung UHV

Dichtungen, Materialien

Vorpumpen

Ionenpumpe

Turbomolekularpumpe

Messung: Bayard - Alpert

Rollkugelmanometer

Sputtergun

## Messmethoden

GDOS Glow Discharge Optical Spectroscopy

SIMS Secondary Ion Mass Spectroscopy

Typen von Analysatoren

SEV - Secondary Electron Multiplier, Channelplate

AES Auger Electron Spectroscopy, el. Austrittstiefe

ESCA - UPS Ultraviolet Photoelectron Spectroscopy

XPS X-Ray Photoelectron Spectroscopy

Grenzflächenanalyse mit TEM

FEM - FIM Field Electron Microscope, Field Ion Microscope

Atomsonde, ToF Time of Flight Spectrometer

LEED Low Energy Electron Diffraction

HAS Helium Atom Scattering

PES Photoelectron Spectroscopy

STM Scanning Tunneling Microscope

AFM Atomic Force Microscope

Nanoindenter

## Oberflächenphysik in anderen Wissenschaften

Mit Vakuum: Nachweis schwerer Moleküle

Ausserhalb Vakuum:

Differentiell gepumpte Ionenschleuse

MALDI Matrix Assisted Laser Desorption Ionization

Laser Ablation

ESI - ESD Electro Spray Ionization, -Desorption

Imaging Ion Microscopy

LIBS Laser Induced Breakdown Spectroscopy

PIXE - PIGE Particle Induces X-Ray (Gamma) Emission

## Warum Oberflächen- und Grenzflächenphysik?

**Oberflächen:** Reibung und Verschleiss, Korrosion, Einbringen von Materie (Aufkohlen, Nitrieren...), Emission und Absorption von Licht, **Katalyse**

**Grenzflächen:** Korn- und Phasengrenzen: Plastizität und Versprödung, Keimbildung und Wachstum

Studium von reinen Oberflächen erst seit etwa 1970 ( $\pm$ )

Probleme:

1 cm<sup>3</sup> bulk (Volumen)  $\sim$  ca.  $10^{23}$  Atome, 1 cm<sup>2</sup> Oberfläche  $\sim$  ca.  $10^{15}$  Atome !

Wiederbelegung von Oberflächen mit reaktiven Gasen (O<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, ..)

daher Ultrahochvakuum (UHV)  $\sim 10^{-10}$  torr  $\sim 10^{-10}$  mbar

## Warum UHV ? Wiederbelegung!

$$j = \rho \bar{v}$$

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT$$

$$\rho = \frac{L}{V_{\text{mol}}} \frac{p}{p_0}$$

$$p_0 V_{\text{mol}} = RT$$

$$N \left[ \frac{1}{\text{cm}^2 \text{ sec}} \right] = 3,52 \cdot 10^{22} \frac{p}{\sqrt{MT}}$$

P in torr, M = Massenzahl  
(dimensionslos), T in Kelvin

Faustregel: Einheit „Langmuir“ L : 1 L entspricht  $10^{-6}$  torr x 1 sec Begasung, ergibt etwa 1 Monolage (ML) Gasbedeckung

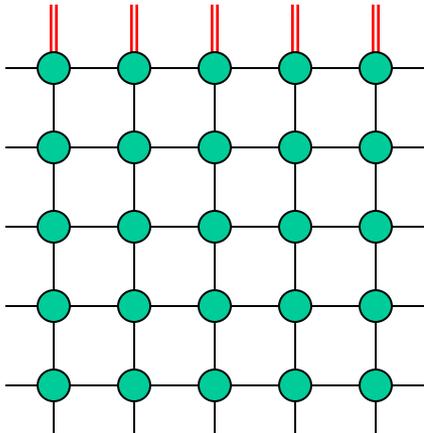


einige % Verunreinigung toleriert:  $10^{-10}$  torr, 1 Stunde

$$1 \text{ torr} = 133 \text{ Pa} \approx 1 \text{ mBar}$$

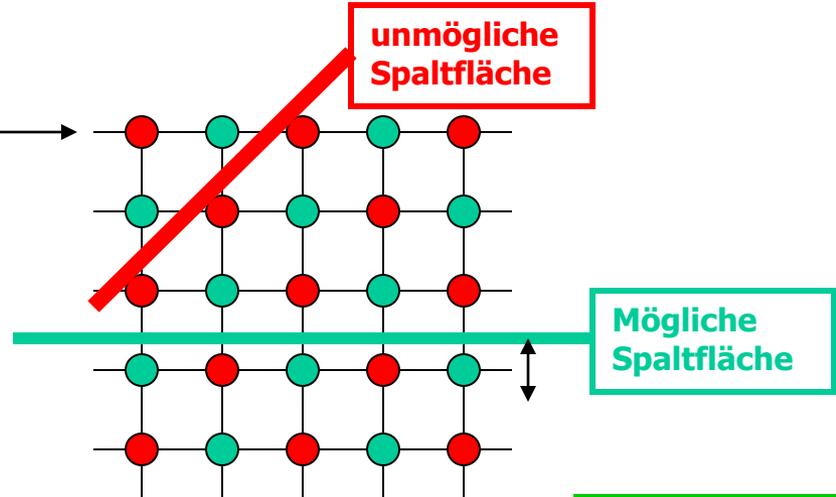
Oberfläche = Bruch der Translationssymmetrie des Kristalls

Broken bond model

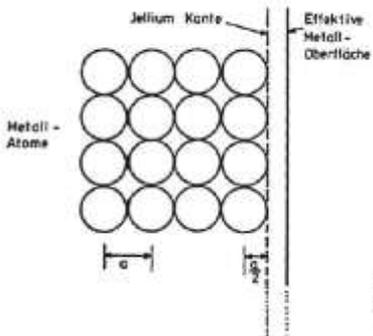


Oberfläche

Ionenkristall



Metallbindung - Jelliumnäherung

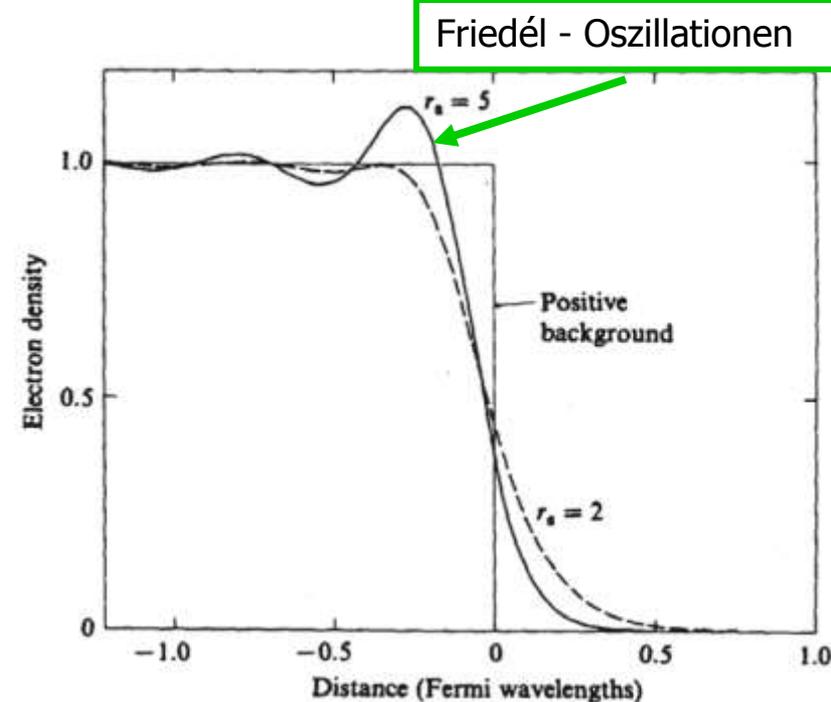


- Ionenrümpfe werden als gleichförmige Hintergrundladungsdichte betrachtet
- Ladungsdichte:

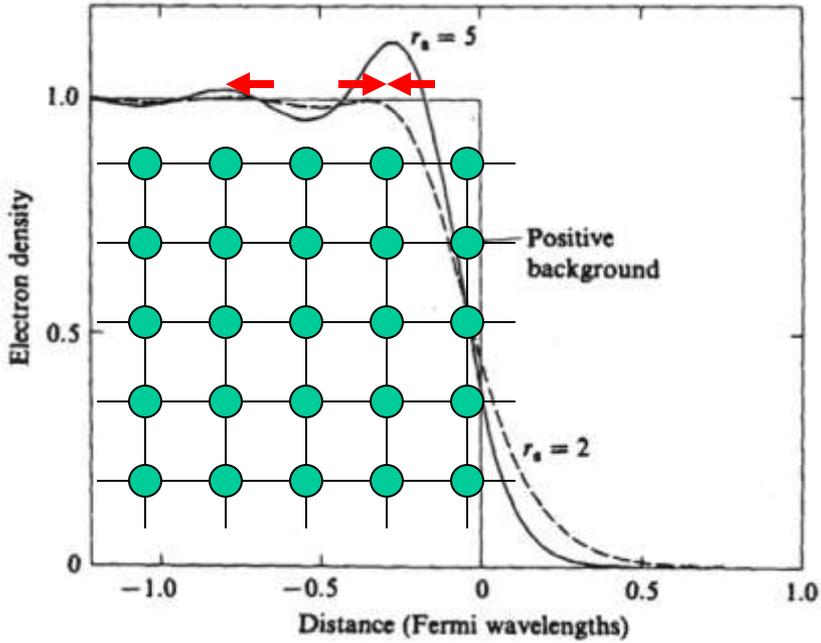
$$n_+(r) = \begin{cases} \bar{n} & , z < 0 \\ 0 & , z > 0 \end{cases}$$

mit:  $1/\bar{n} = (4\pi/3) \cdot r_s^3$

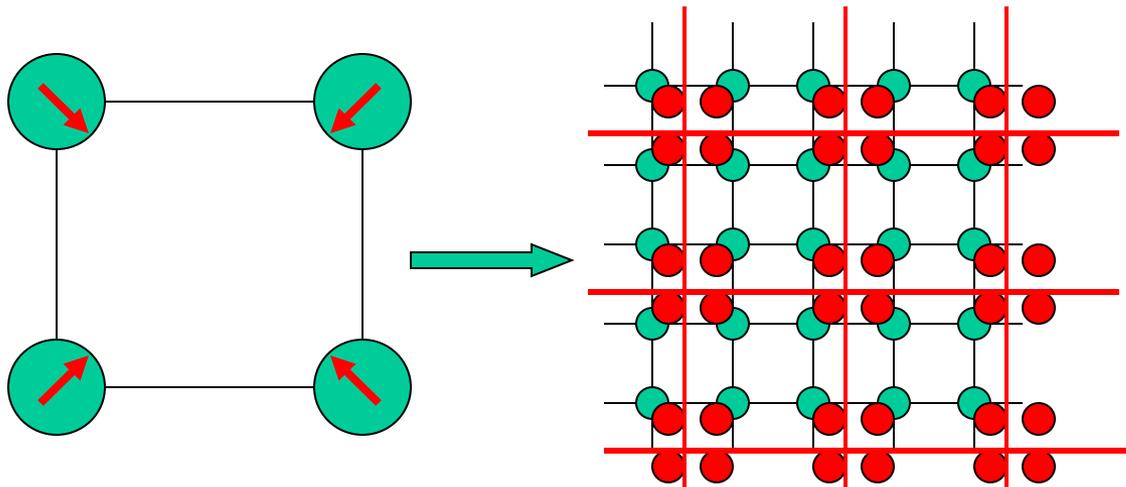
$r_s$  ist der Wigner-Seitz-Radius im Jellium-Modell, Werte liegen zwischen 2 und 5



# Surface reconstruction



a) normal zur Oberfläche

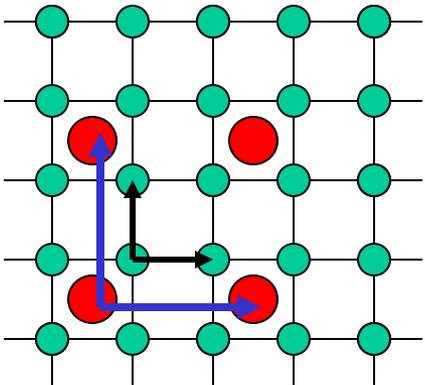


In Oberfläche -> Überstruktur

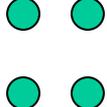
# Bezeichnung kohärenter Überstrukturen

Basisvektoren des Übergitters sind (a,b)-mal länger, als Basisvektoren des Grundgitters:

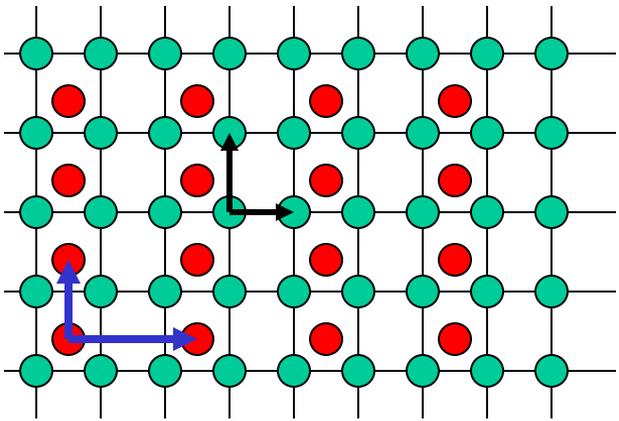
(a x b) - Struktur



Beispiel: (2x2)-Struktur

-  Atom des Grundgitters
-  Adsorptionsplatz
-  Adsorbiertes Atom

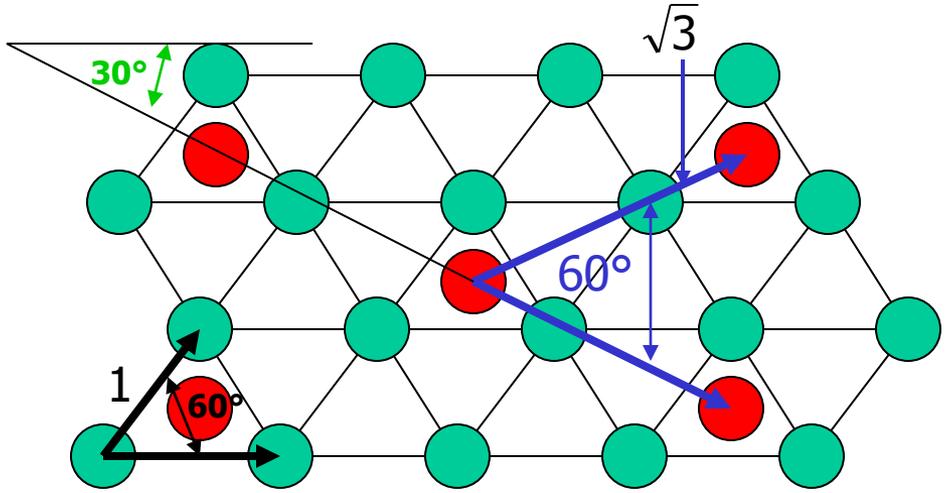
Beispiel: (2x1)-Struktur



# Bezeichnung kohärenter Überstrukturen 2

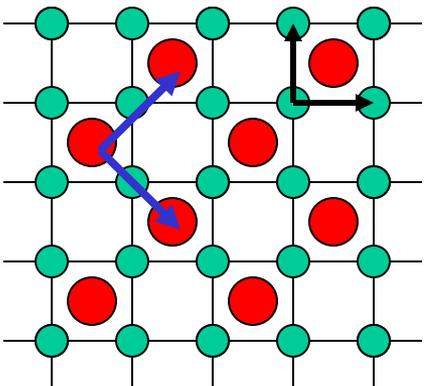
Sind die Basisvektoren des Übergitters zusätzlich um  $\alpha^\circ$  gegen das Grundgitter gedreht, kommt das Symbol  $R \alpha^\circ$  dazu.

Beispiel:  $(\sqrt{3} \times \sqrt{3})R30^\circ$  - Struktur

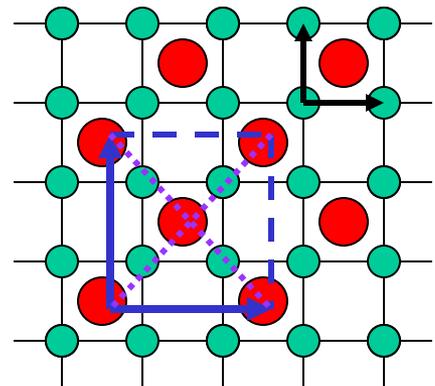


Ausnahme: bei quadratischen Gittern statt

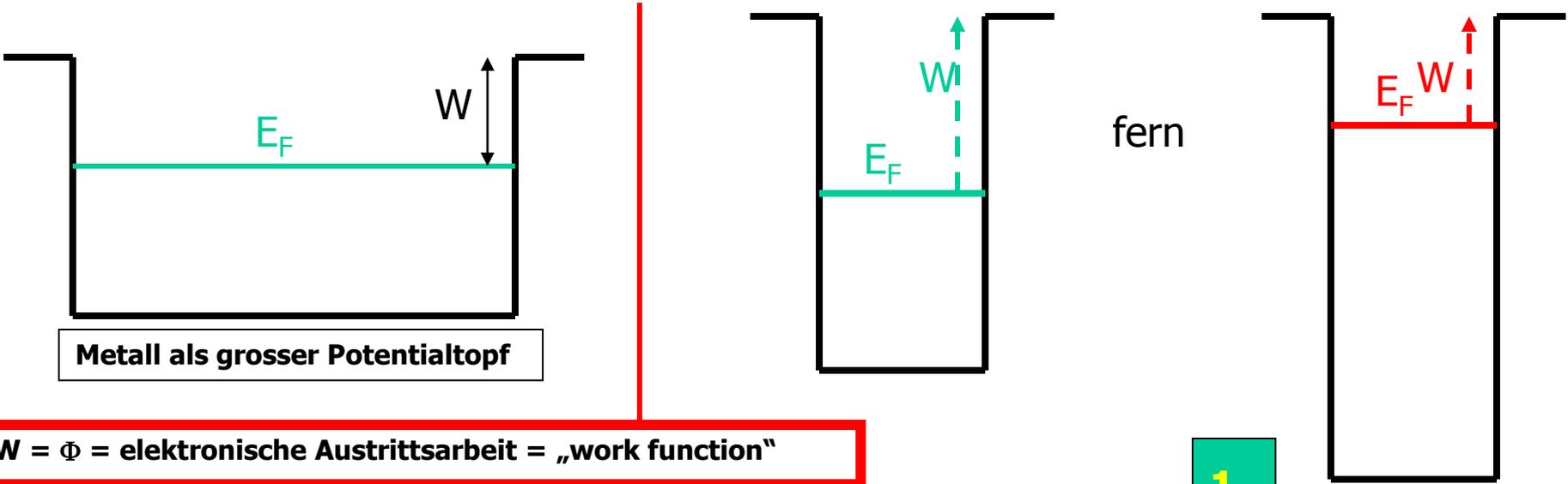
$(\sqrt{2} \times \sqrt{2})R45^\circ$



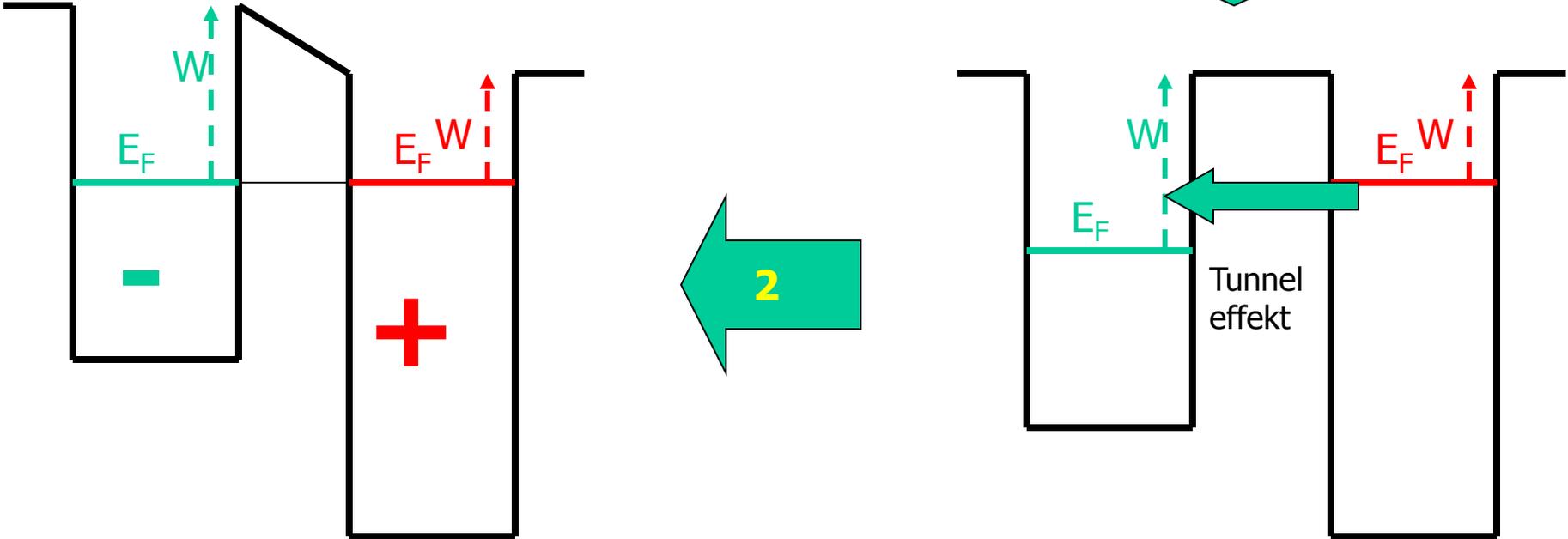
$c(2 \times 2)$ , c für centered



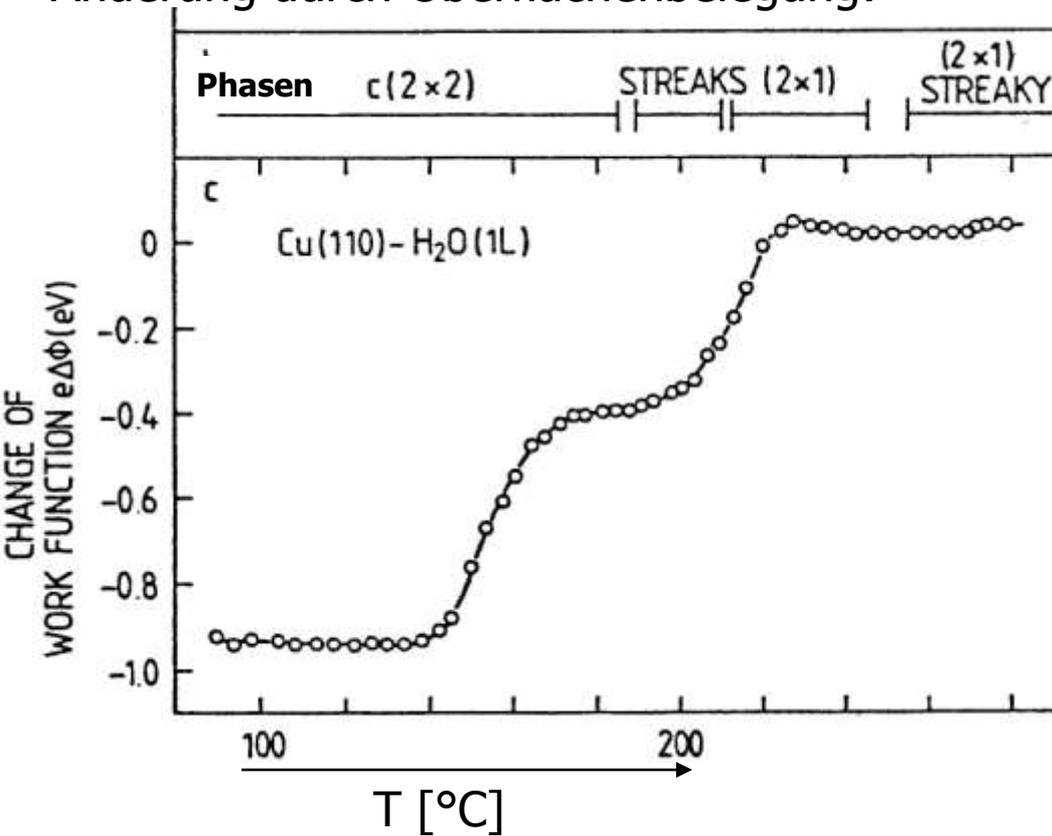
# Elektronenaustritt aus Festkörpern: Änderung durch Oberflächenbelegung:



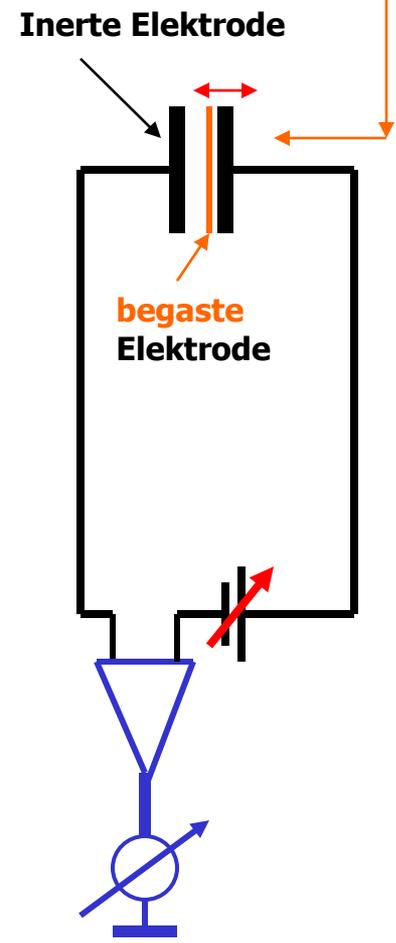
Annäherung **1**



# Änderung durch Oberflächenbelegung:



## Kelvin - Schwingkondensatormethode



$$d = d_0 + \Delta d \cos \omega t \Rightarrow C \approx C_0 - \Delta C \cos \omega t$$

$$I_{\approx} = \Delta \Phi \frac{dC}{dt} = \Delta \Phi \Delta C \omega \sin \omega t$$

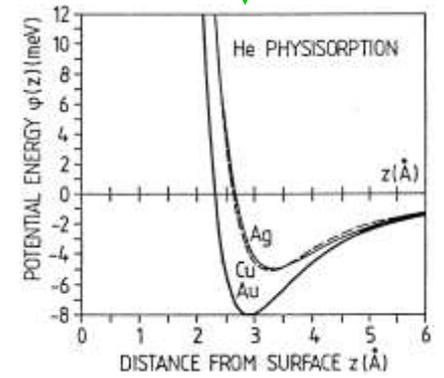
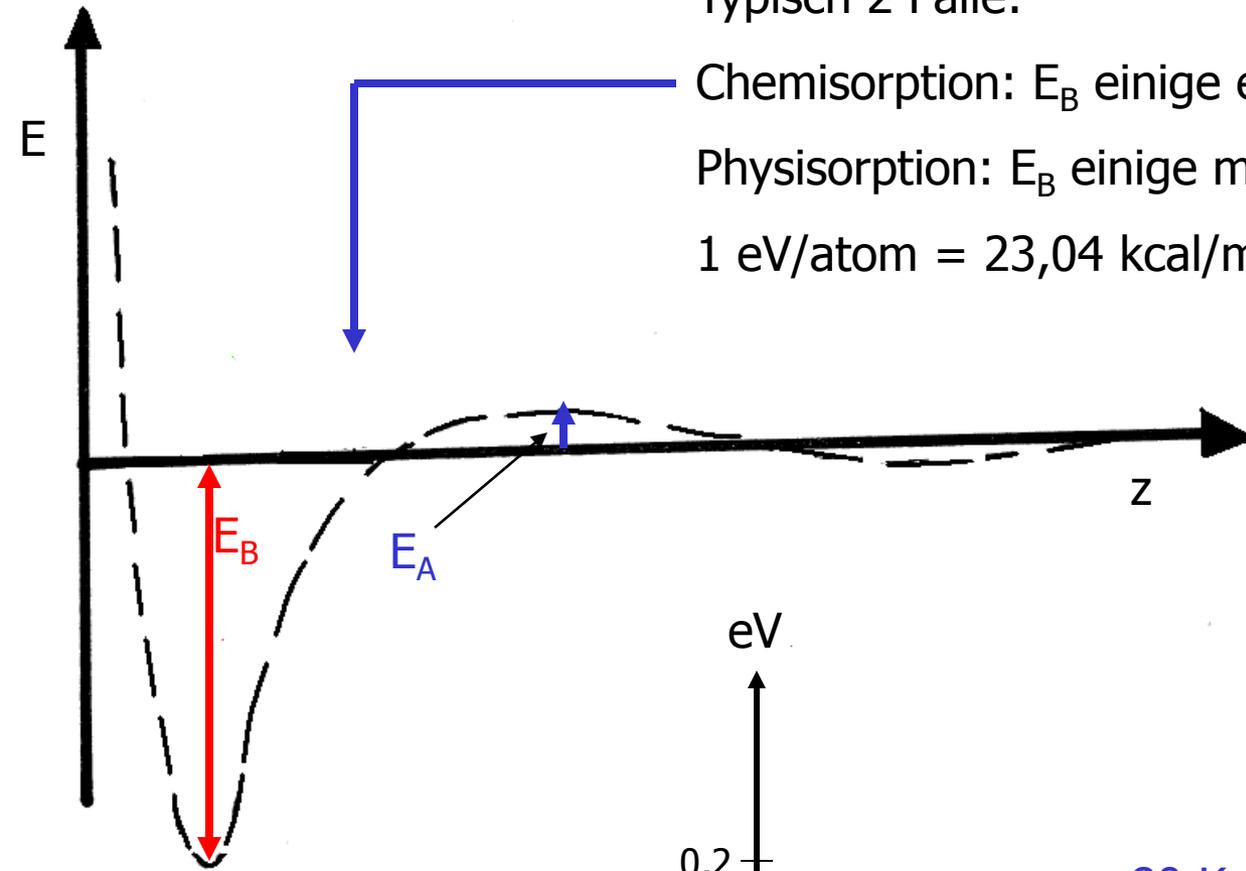
# Adsorption 1

Typisch 2 Fälle:

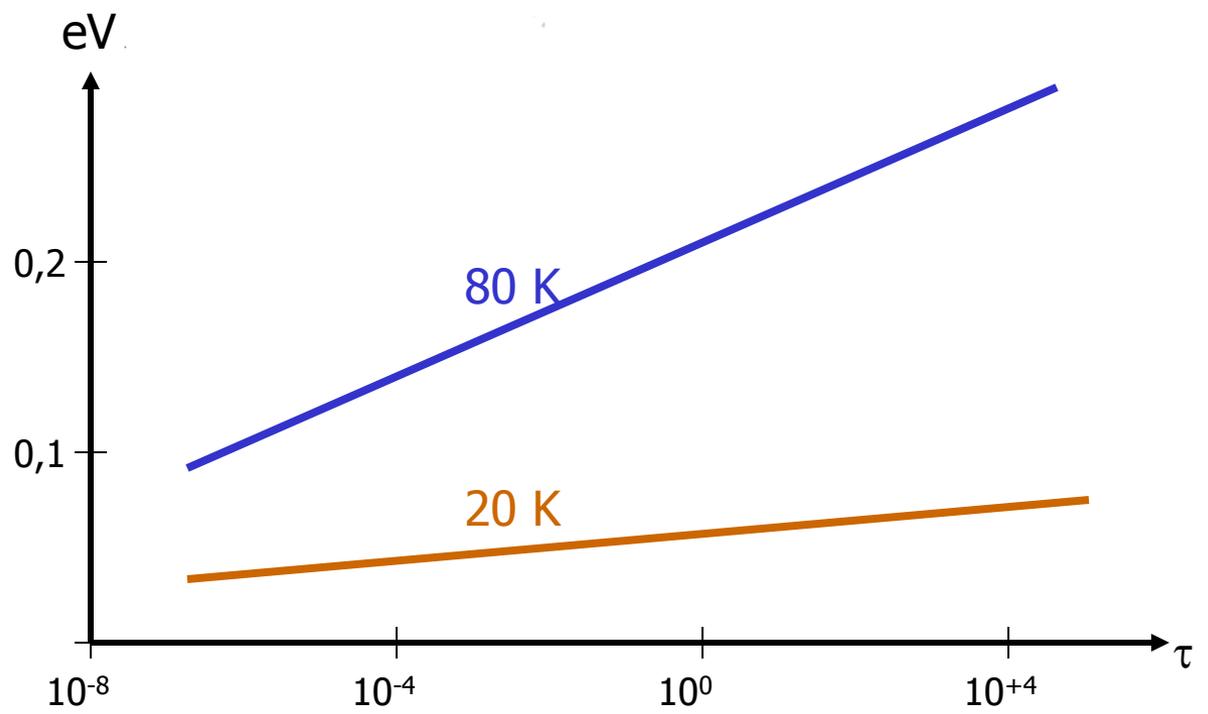
Chemisorption:  $E_B$  einige eV/atom

Physisorption:  $E_B$  einige milli-eV/atom

1 eV/atom = 23,04 kcal/mol



$$\tau = \frac{1}{\nu_0} e^{+\frac{E_B + E_A}{RT}}$$



# FLASH - Desorption

Aufheizen mit konstantem  $\dot{T} = \beta$

Redheadformel:

$$T(t) = T_0 + \beta t$$

Temperatur bei Peak:  $T_p$

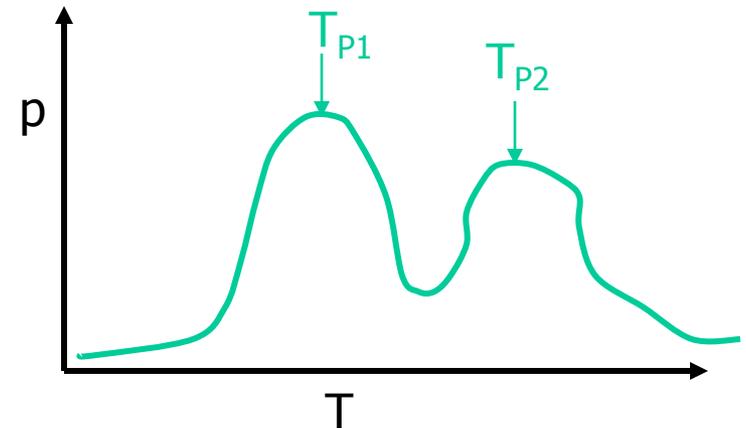
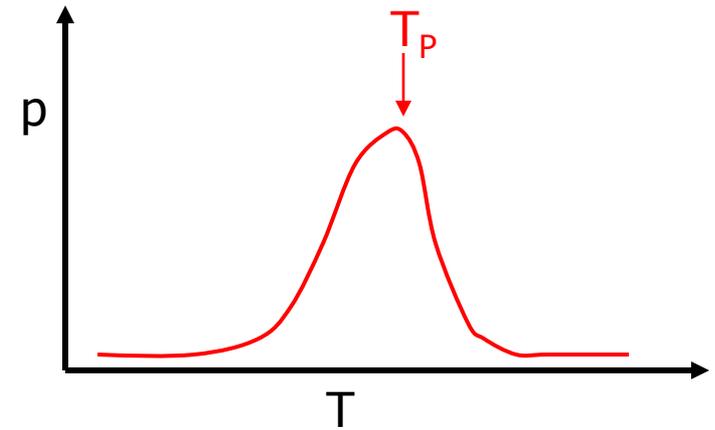
$$\frac{E_B}{RT_p} = \ln \frac{\nu_0}{\beta} - 3,64$$

$\nu_0$  := Debye - Frequenz,  $\approx 10^{13}$  Hz

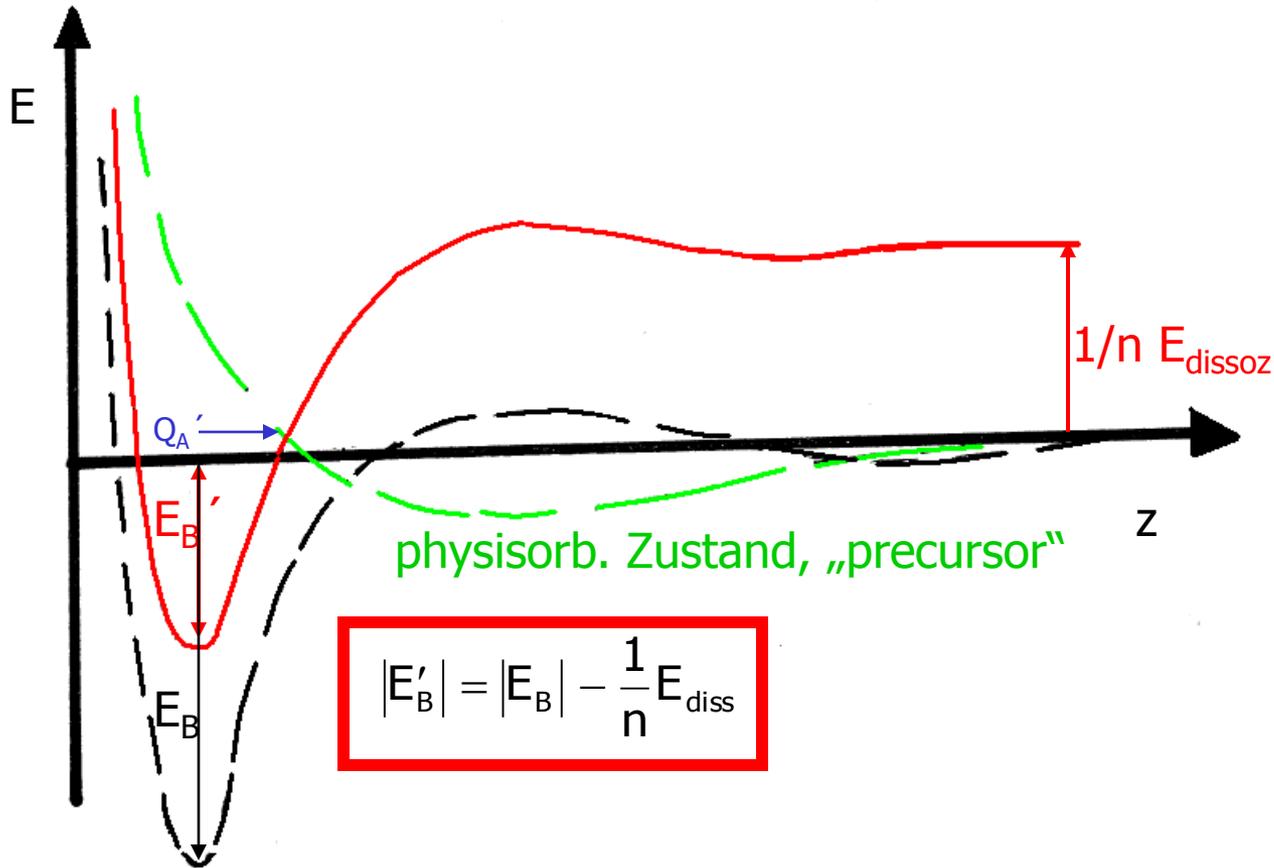
$$\nu_0 := 0,55 (0,70) \sqrt{\frac{E}{\rho(1 + \mu)}} \frac{1}{a} \quad \text{für bcc (fcc)}$$

Beispiele für Debyefrequenz:

W:  $7,3 \times 10^{12}$ , Ni:  $8,3 \times 10^{12}$



# Adsorption mit Precursor, Katalyse



Warum Katalysator?

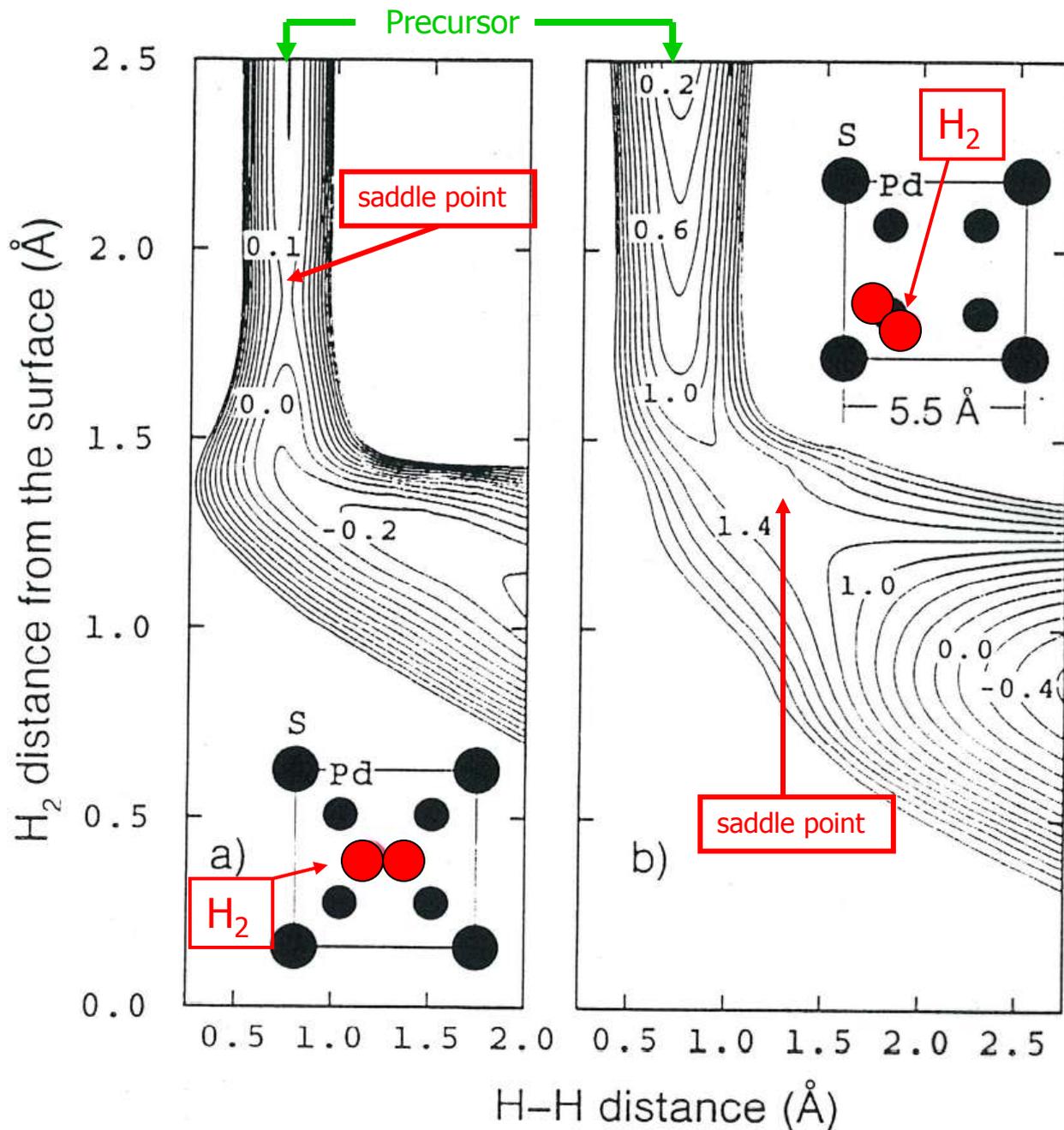
Ohne: Probleme

Dissoziation der  
Ausgangsmoleküle ( $N_2$ ,  
 $H_2$ ,  $O_2$ , ...)

Zusammenfinden der  
erwünschten  
Reaktionspartner

unerwünschte  
Dissoziation des  
Reaktionsproduktes

# Adsorption mit Precursor, Katalyse

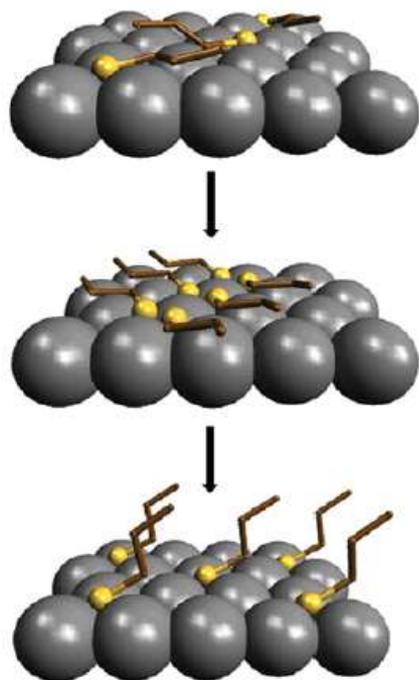


Potential Energy  
Surface of H<sub>2</sub>  
approaching Pd/(2x2)S

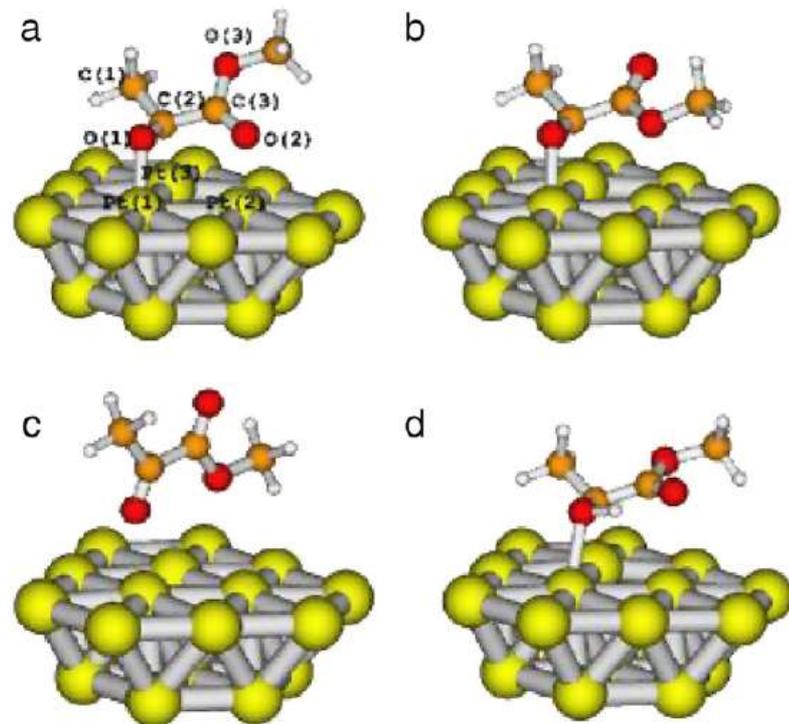
# Surface-level mechanistic studies of adsorbate-adsorbate interactions in heterogeneous catalysis by metals

Stephen T. Marshall, J. William Medlin

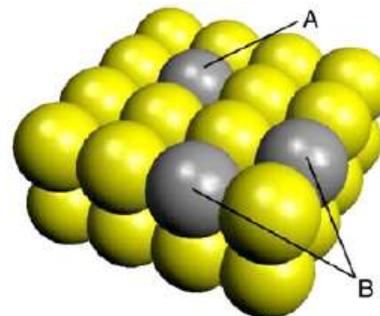
Surface Science Reports 66 (2011) 173–184



Three phases of self-assembled monolayer formation on fcc(111) metals. A: disordered thiols, B: striped phase, C: full monolayer. Sulfur is shown in yellow and carbon is shown in brown.



Adsorption modes of ethyl pyruvate on Pt surfaces from Ref. [77]. (a)  $\eta^2$ -cis, (b)  $\eta^2$ -trans, (c)  $\eta^1$ -trans, (d) semihydrogenated  $\eta^2$ -cis.



Pd metal ensembles observed on Au(100) for vinyl acetate synthesis. A: less active Pd monomer, B: more active Pd monomer pair.

# Kinetik der Adsorption und Desorption

Von  $N_a$  Atomen (Molekülen), die pro sec  $\text{cm}^2$  auf die Oberfläche auftreffen bleiben nur  $S \cdot N_a$  haften.  $S$  = „Haftkoeffizient“.

Überwinden der Aktivierungsenergie:

$$\longrightarrow e^{-\frac{E_A}{RT}}$$

Thermische Akkomodation – Abführen der Überschussenergie:  $\longrightarrow C$

Wenn Oberfläche zu %-Satz  $\theta$  vorbedeckt ist, bleibt Wahrscheinlichkeit eines freien Platzes:  $f(\theta) \longrightarrow$

$$S = C e^{-\frac{E_A}{RT}} f(\theta)$$

„Anfangshaftkoeffizient“  $S_0 := S(\theta=0)$

$$S_0 := S(\theta = 0) = C e^{-\frac{E_A}{RT}}$$

$$f(\theta) = (1 - \theta)^n \quad n = \text{„Ordnung der Adsorption“}$$

# Kinetik der Adsorption und Desorption 2

## Desorptionswahrscheinlichkeit

$$P_{\text{des}} = C_2 e^{-\frac{|E_B|+E_A}{RT}} g(\theta)$$

$$g(\theta) = \theta^n \quad n = \text{„Ordnung der Desorption“}$$

„rate equation“:

$$\frac{d\theta}{dt} = K_1 p S_0 f(\theta) - K_2 g(\theta) e^{-\frac{|E_B|+E_A}{RT}}$$

im Gleichgewicht:  $\frac{d\theta}{dt} = 0$

$$\frac{\Theta}{1 - \Theta} = \frac{p}{p_0} e^{-\frac{|E_B|}{RT}}$$

Langmuir - Isotherme

Versuche:

Reine Adsorption (ab reiner Oberfläche)

$S_0, f(\theta)$

reine Desorption (ab voll belegter Oberfläche)

$E_{\text{des}}, g(\theta)$

Gleichgewicht

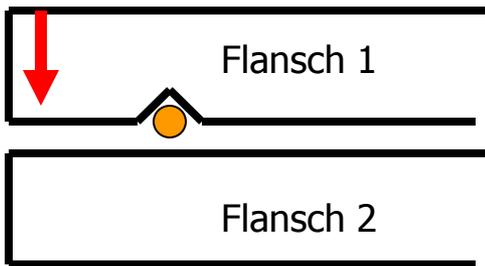
$E_B$

# UHV - Grundlagen

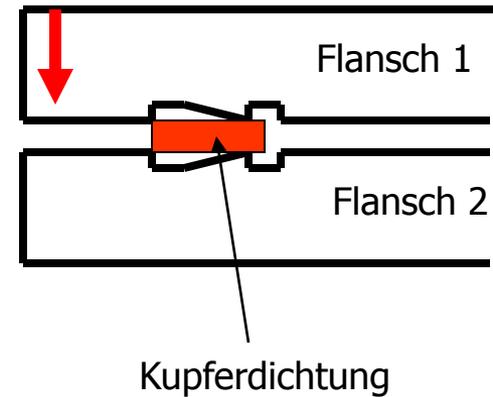
Dichtungen:

Plastische Verformung von Metall

a) Golddraht



b) „Torr-Seal“



Erzeugung:

1) von freier Atmosphäre (760 torr) -> 1 ... 10 mTorr: Sorptionspumpen

2) von 1 ... 10 mTorr -> 10<sup>-10</sup> Torr:

a) Ohne bewegte Teile

Ionenpumpe (Triodenpumpe)

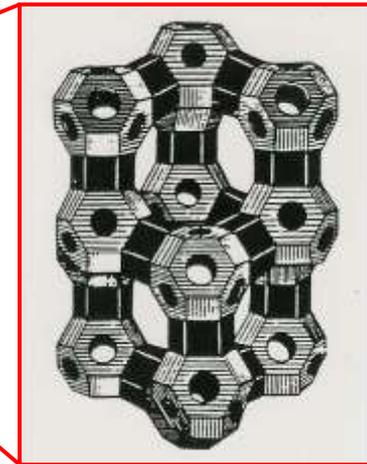
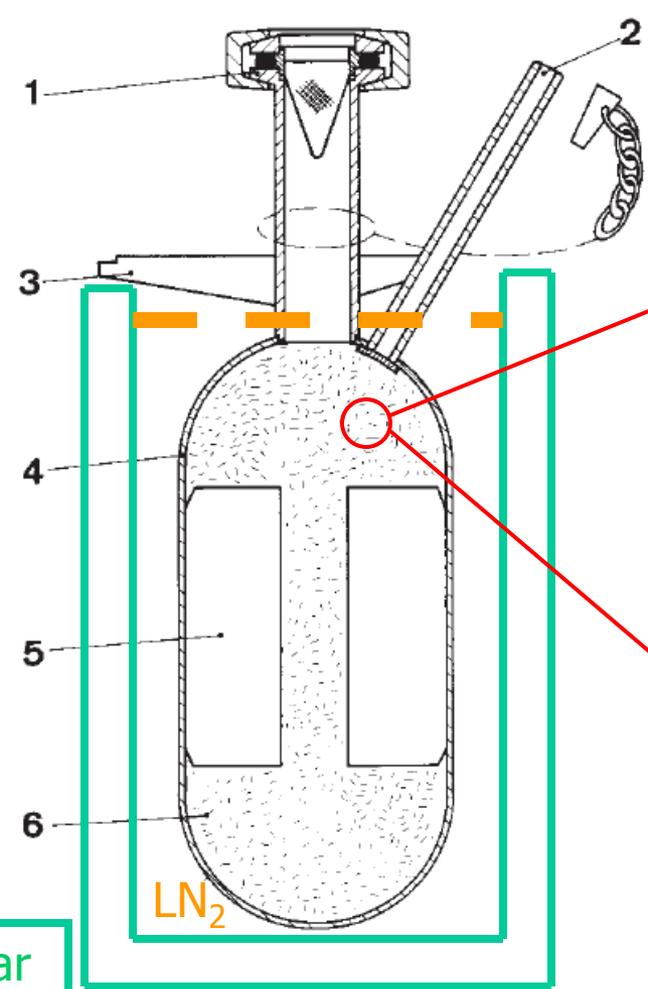
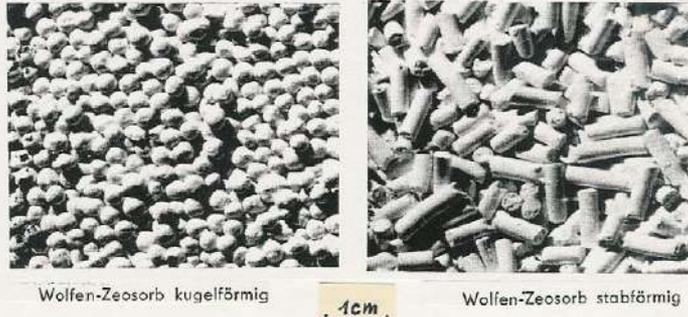
b) rotierend

Turbomolekularpumpe

# UHV - Grundlagen

## Erzeugung:

1) von freier Atmosphäre (760 torr) -> 1 ... 10 mTorr: Sorptionspumpen

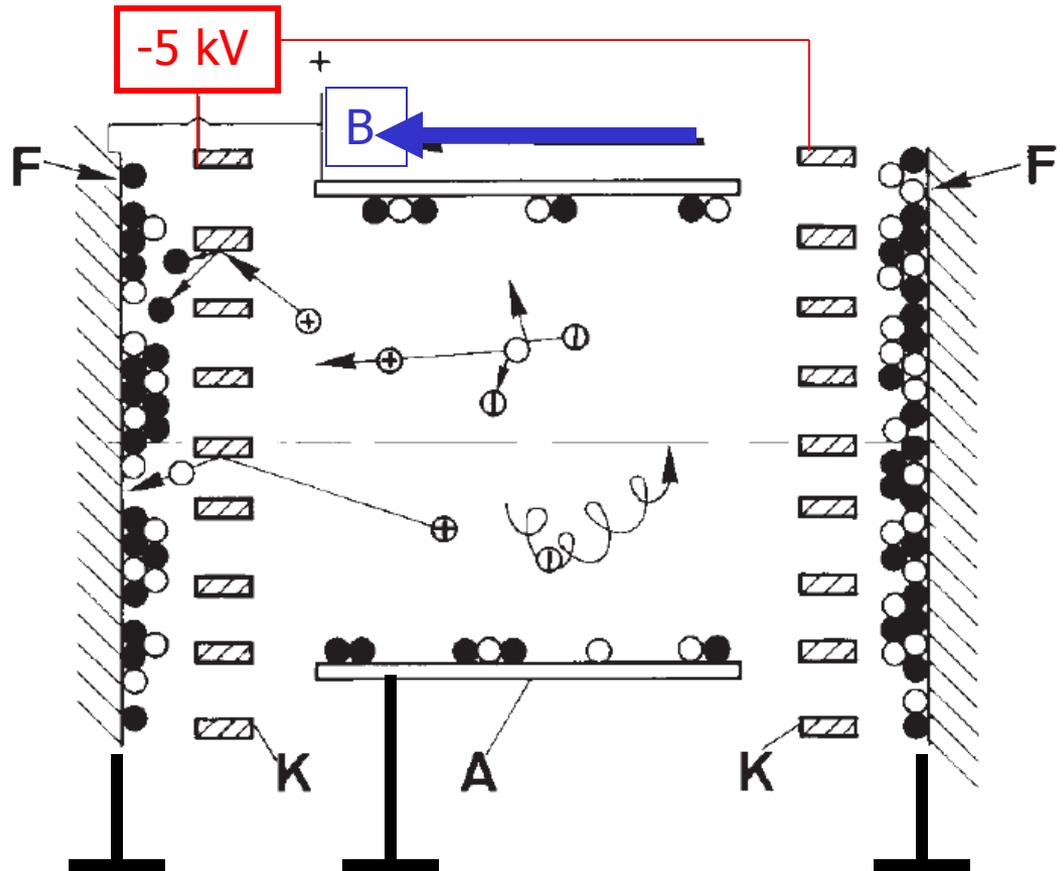


Zeolith

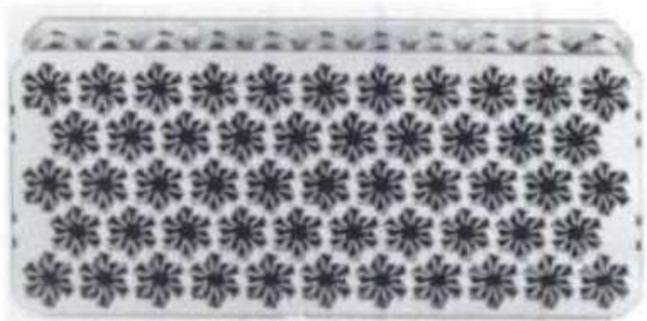
Dewar

- |                      |                                    |
|----------------------|------------------------------------|
| 1 Ansaugstutzen;     | 4 Pumpenkörper;                    |
| 2 Entgasungsstutzen; | 5 Wärmeleitbleche;                 |
| 3 Haltestreben;      | 6 Adsorptionsmittel (z.B. Zeolith) |

# UHV – Grundlagen: Ohne bewegte Teile: Ionenpumpe (Triodenpumpe)

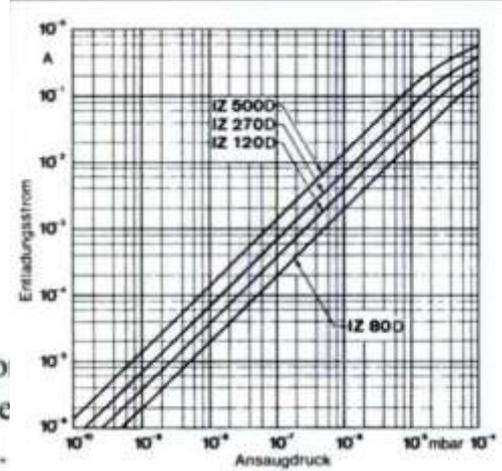


- Titanatome
- Gasteilchen
- ⊕ Ionen
- ⊖ Elektronen
- A Anodenzylinder  
(wie bei der Diodenpumpe)
- B Magnetfeld
- F Auffänger  
(Pumpengehäuse) als dritte Elektrode
- K Kathodengitter Titan



Nachteil: starkes Magnetfeld

**Bild 10.27**  
Kathode der StarCell®-Triodenpumpe von Varian. StarCell® ist ein Patent und geschützter Handelsname der Firma Varian.



# UHV - Grundlagen

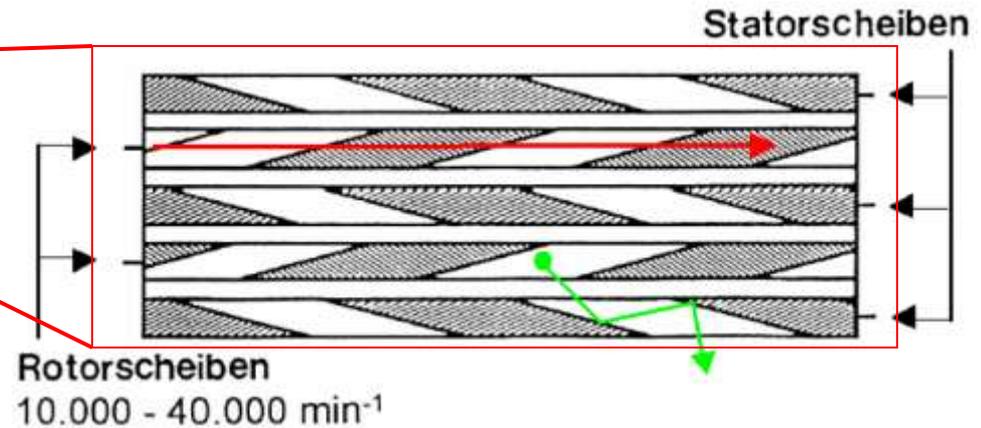
Rotierend: Turbomolekularpumpe



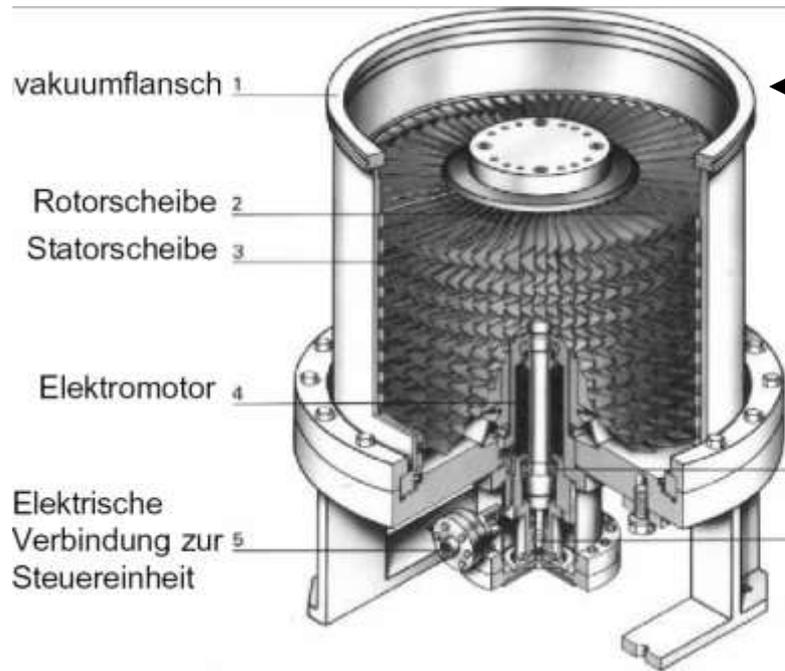
Kompressionsfaktor eines Rotor-Stator-Paares K:

$$K \propto e^{Gu\sqrt{M}}$$

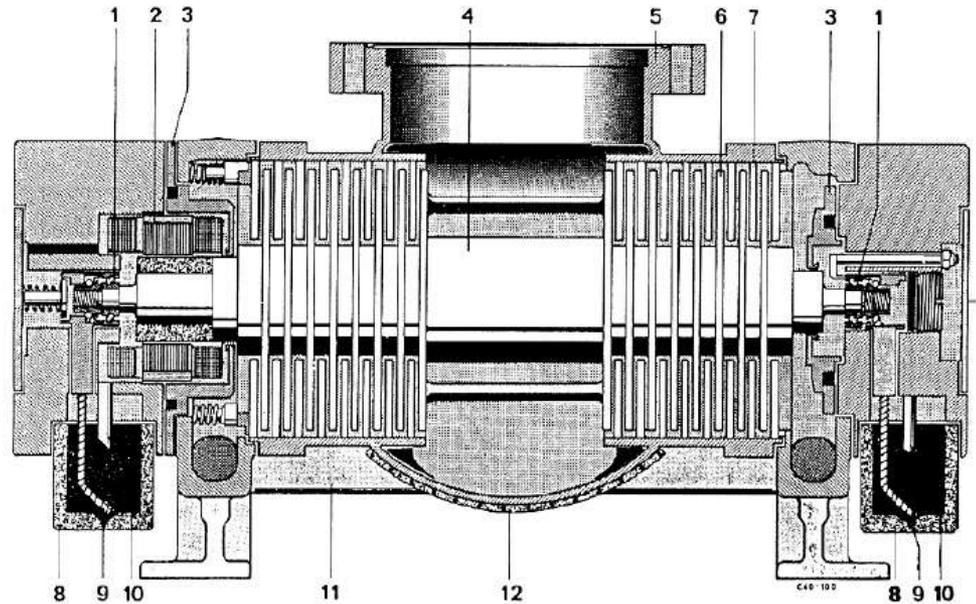
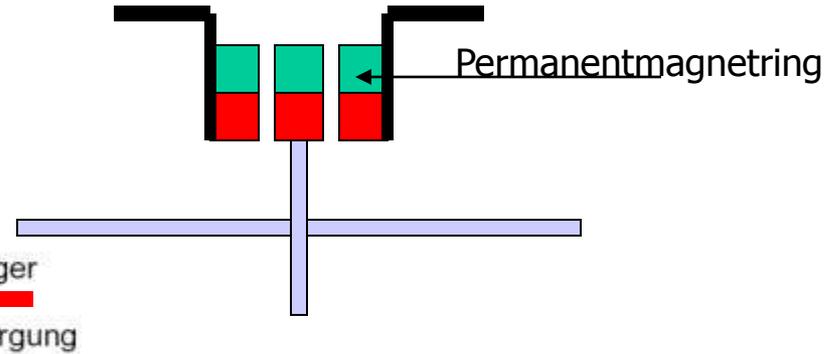
Kompressionsfaktor gesamt =  $K^m$   
(für m Stufen)



Während die Gasartabhängigkeit des Saugvermögens verhältnismäßig gering ist, ( $S \sim \bar{c} \sim 1/\sqrt{M}$ ), ist die Gasartabhängigkeit der Kompression  $k_0$  bei Nullförderung und damit auch die Kompression  $k$  wegen  $k_0 \sim e^{\sqrt{M}}$  oder  $\log k_0 \sim \sqrt{M}$  sehr hoch.



← Darf nur aufrecht betrieben werden!  
Stossempfindlich! (Magnetlager uhv-seitig)



- Allgemein:
- Kurze UHV-Wege !!
- Eventuell Faltenbalg (Vibrationsisolation)
- Vorvakuumpumpe nötig
- Absperrschieber zu UHV günstig

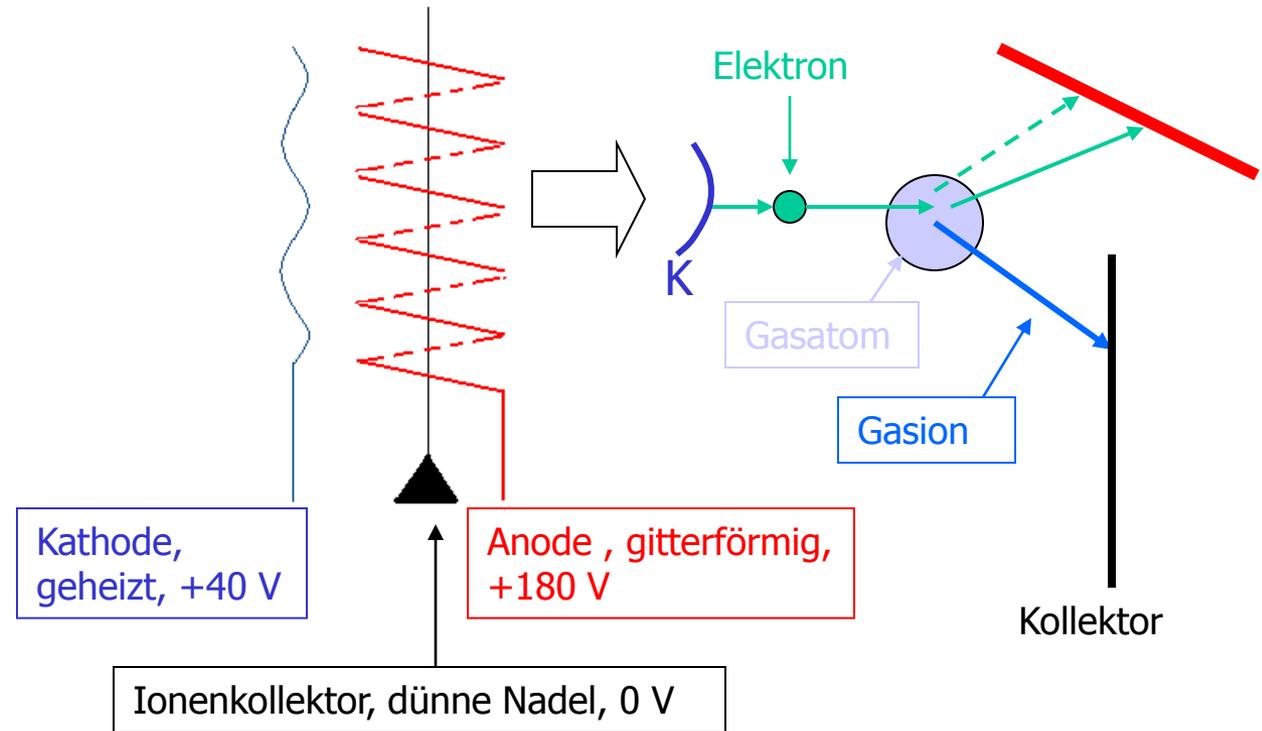
Bild 7.7 Schnittdarstellung der zweiflutigen Turbomolekularpumpe TPU 200 nach Becker. 1 Lager, 2 Motor, 3 Labyrinthkammern, 4 Rotor, 5 Hochvakuumschluß, 6 Rotorscheibe, 7 Statorscheibe, 8 Ölbehälter, 9 Ölzufuhr zum Lager, 10 Ölrücklauf, 11 Vorvakuumkanal, 12 Heizung.

# UHV – Grundlagen: Druckmessung

- 1) Pirani
- 2) Bayard-Alpert
- 3) Rollkugel

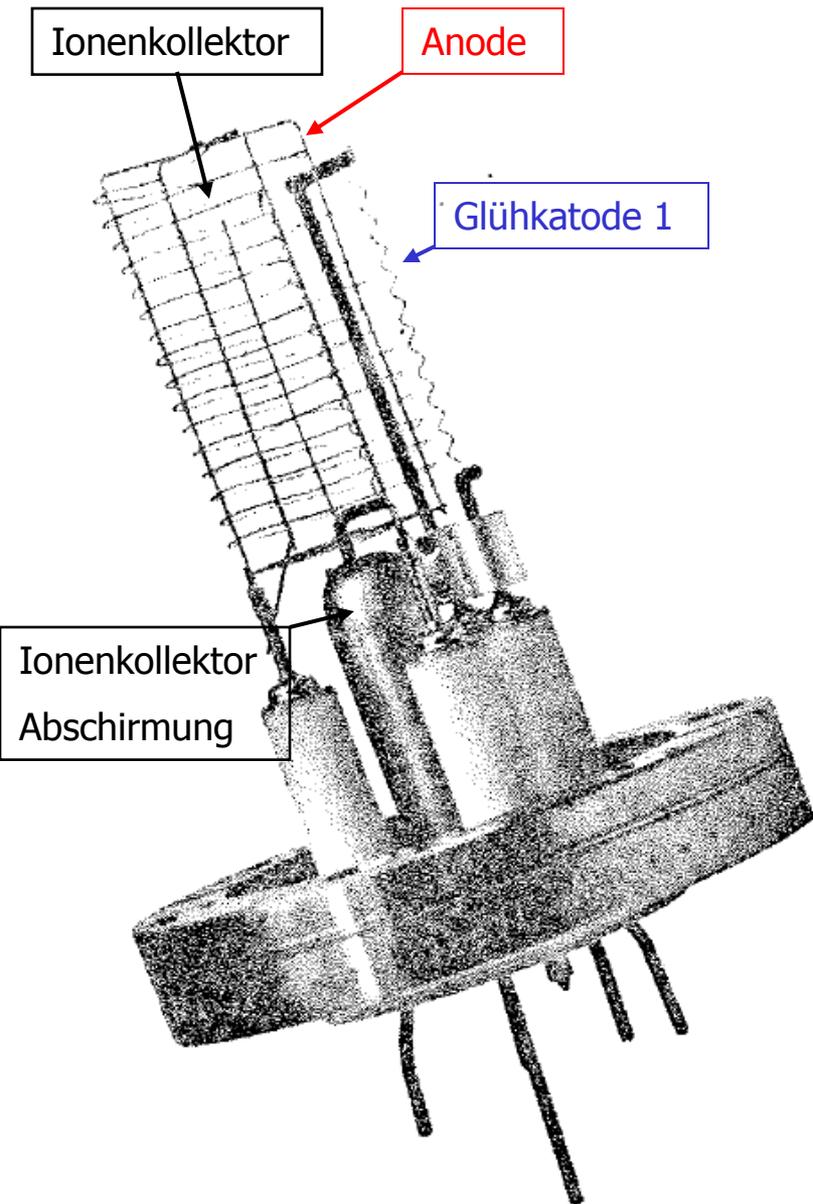
1) Pirani  
Eigentlich kleine  
Ionenpumpe  
(Diodenpumpe,  
ohne Ti-Gitter)

## 2) Bayard-Alpert

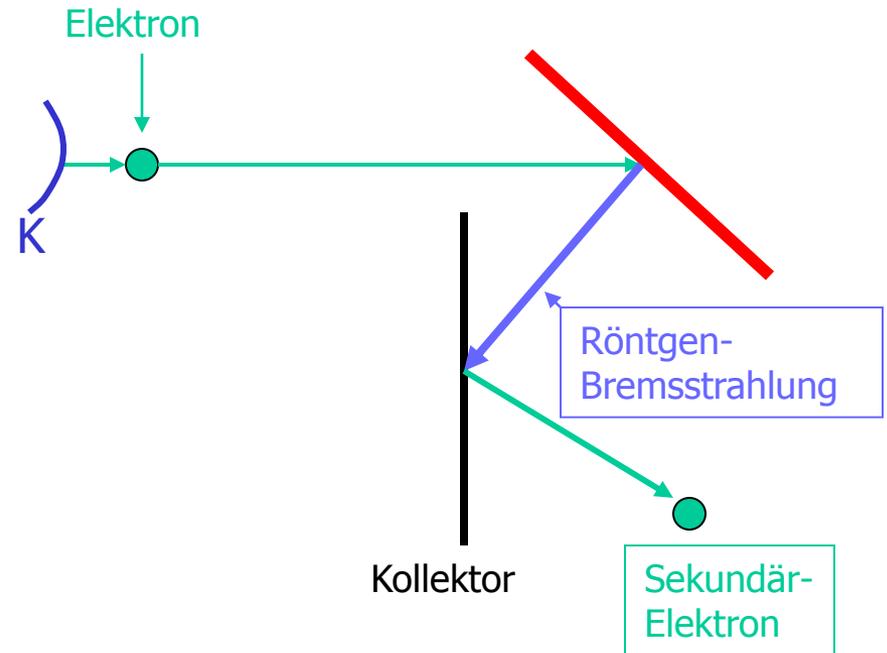


$$I_{\text{ion}} = \text{const.} \cdot I_{\text{elektron}} \cdot p_{\text{Gas}}$$

# UHV – Grundlagen: Druckmessung



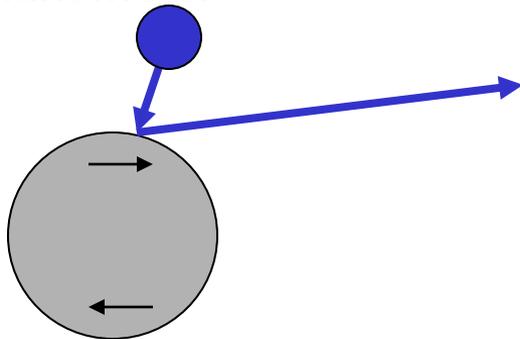
## Bayard-Alpert: Röntgengrenze



Jedes Sekundärelektron zählt  
wie ein auftreffendes Gasion !

Röntgengrenze:  $10^{-11}$  Torr

## 3) Rollkugelmanometer



Der Gasdruck wird aus der relativen Abnahme der Drehzahl  $\dot{f}$  (Abbremsung) aus folgender Gleichung abgeleitet:

$$-f \cdot \frac{df}{dt} = \frac{10}{\pi} \cdot \frac{p \cdot \sigma}{\bar{c} \cdot r \cdot \rho}$$

$p$  = Gasdruck

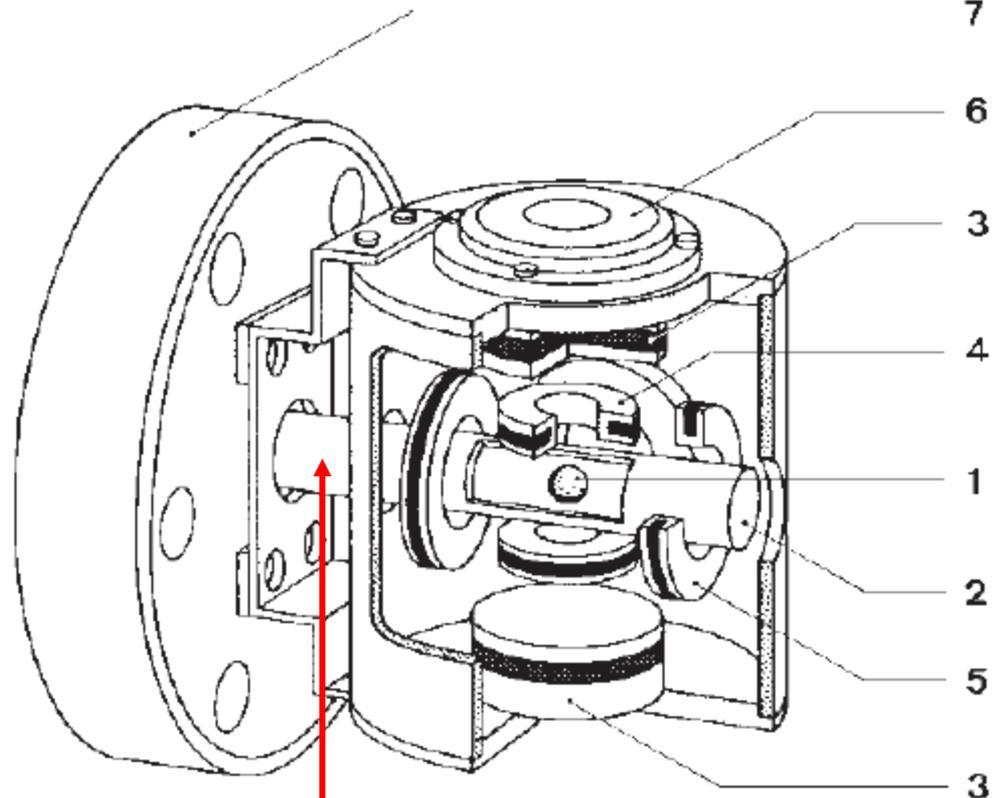
$r$  = Radius der Kugel

$\rho$  = Dichte des Kugelmateri als

$\bar{c}$  = mittlere Geschwindigkeit der Gasteilchen, gasartabhängig

$\sigma$  = Reibungskoeffizient der Kugel, gasartunabhängig, nahezu 1.

**Absolutmessung des Gasdruckes !**

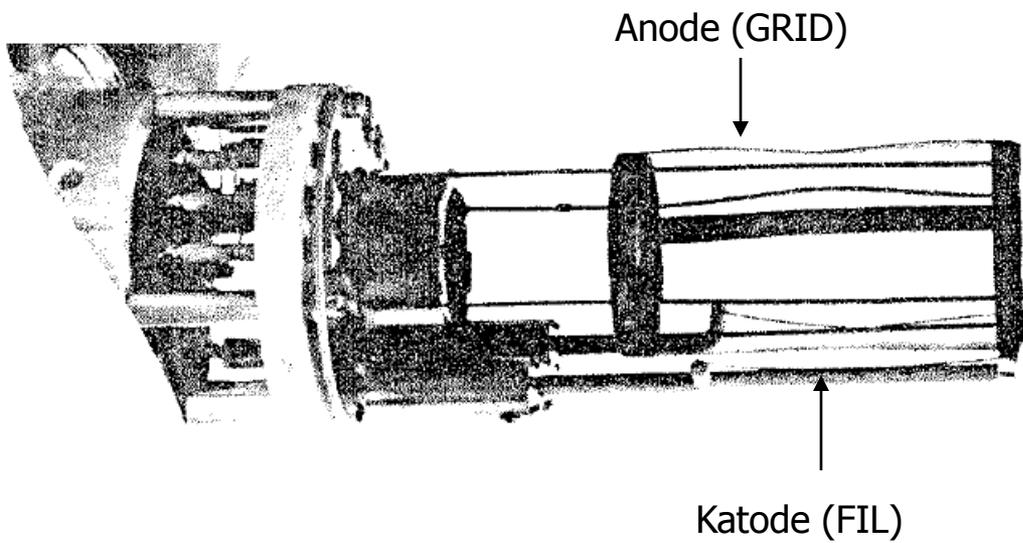
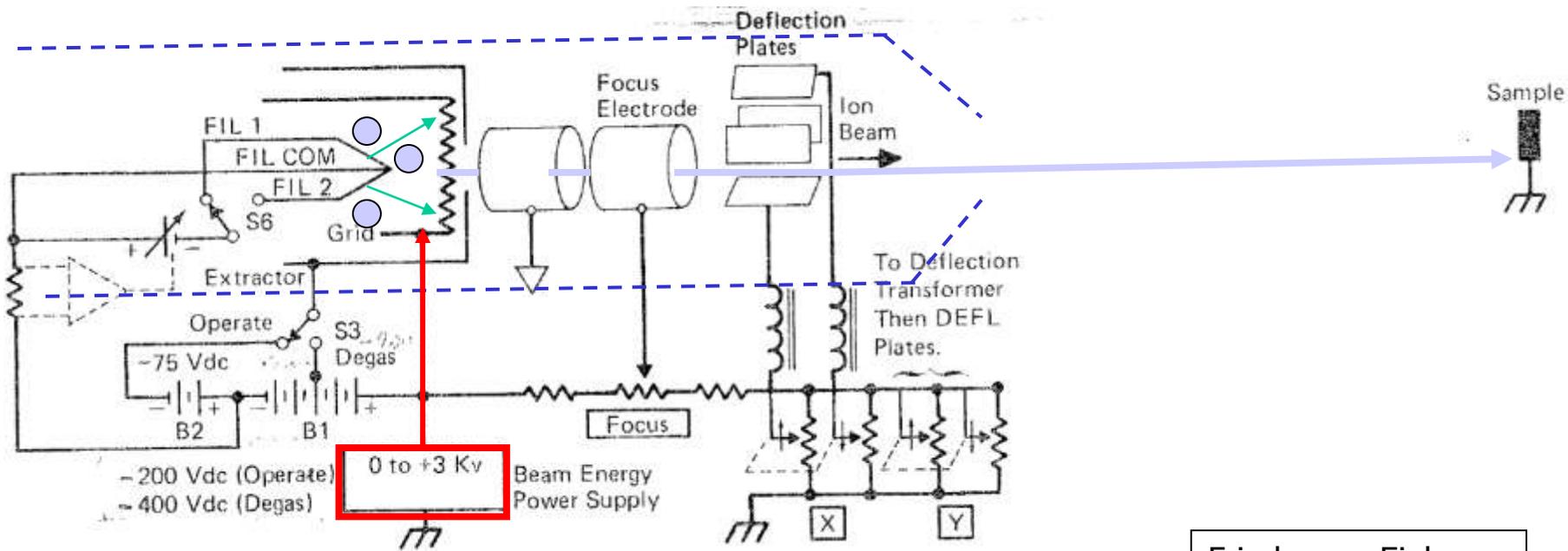


Ventil zweckmässig !

- 1 Kugel,
- 2 Meßrohr, einseitig geschlossen, in den Anschlußflansch 7 eingeschweißt,
- 3 Permanentmagnete,

- 4 Stabilisierungsspulen,
- 5 vier Antriebsspulen,
- 6 Libelle,
- 7 Anschlußflansch

# Erzeugung reiner Oberflächen - Sputtern



Frischgas – Einlass



Frischgas – Sputter - Gun

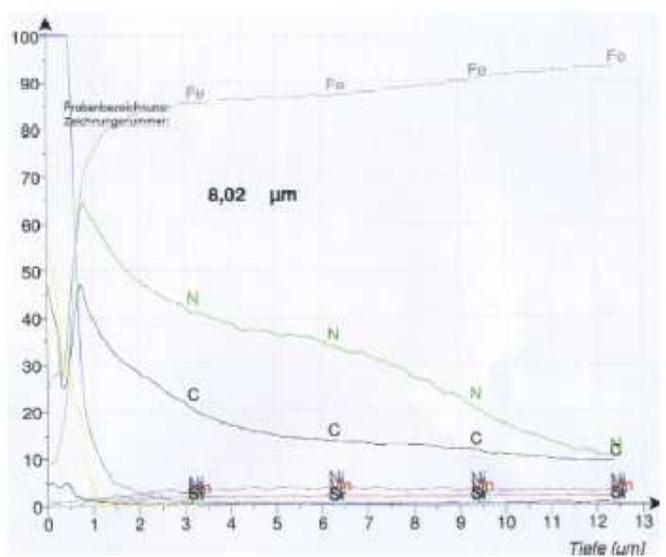
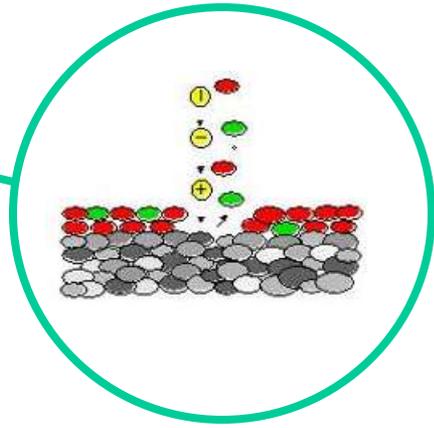
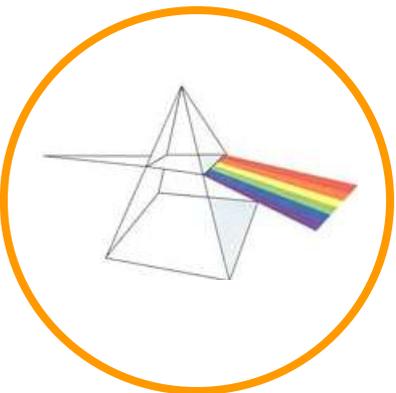
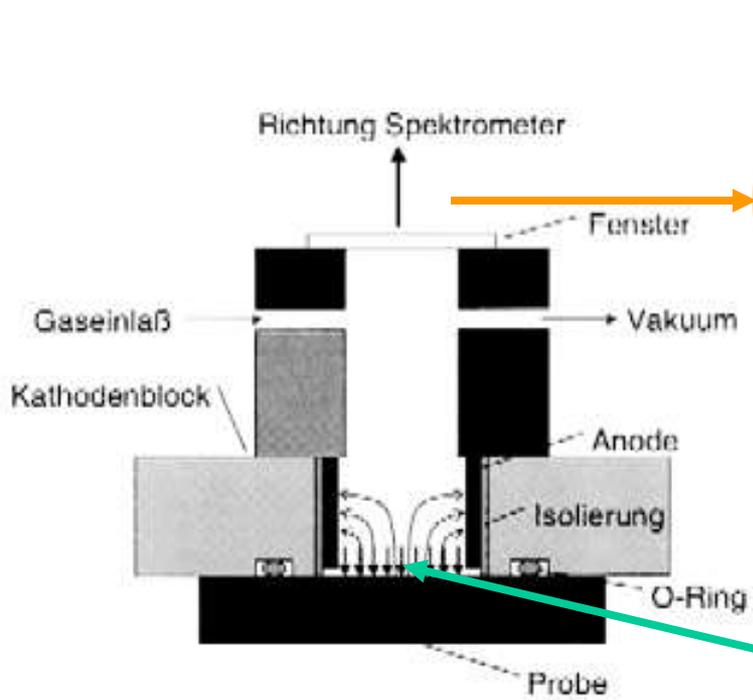
# Übersicht über einige Untersuchungsmethoden

Ein Aus		Elektronen	Ionen, Neutralteilchen	Photonen	E-Feld
		Elektronen	AES, EELS LEED, SEM	IMMA	ESCA UPS, XPS PES (XPD)
Ionen	EIID ESD	ISS SIMS Sputtern		FIM	
Neutrale Teilchen	ESD	Sputtern, HAS	Photodesorption		
Photonen	EPMA, EDX	PIXE, PIGE	LIBS	GDOS	

# GDOS - glow discharge optical spectroscopy

## Messprinzip

Das GDA 750 besteht im wesentlichen aus einer Glimmentladungsquelle (**Skizze rechts**). Charakteristisch für diese Art von Quelle ist, daß die zu untersuchende Probe einen Teil der Glimmentladungsquelle bildet. Zwischen der Anode und der Probe, die auf dem Kathodenblock aufliegt, liegt eine Spannung von wahlweise 500 bis 2000 V an. Bei einem Abstand von wenigen Millimetern zwischen Anode und Probe bildet sich in einer Argonatmosphäre von 3 bis 5 mbar ein leuchtendes Plasma, die Glimmentladung, aus. Die Argonionen werden auf die Probe beschleunigt und zerstäuben diese gleichmäßig über den ganzen Durchmesser der ringförmigen Anode. Die abgetragenen Probenatome werden in der Glimmentladung durch Stöße mit freien Elektronen zur Lichtemission angeregt. Dieses Licht wird im Gitterspektrometer in seine spektralen Anteile zerlegt und von den Photomultipliern registriert. Die Software berechnet unter Berücksichtigung der gemessenen Intensitäten und den Kalibrationsdaten die absoluten Elementkonzentrationen.



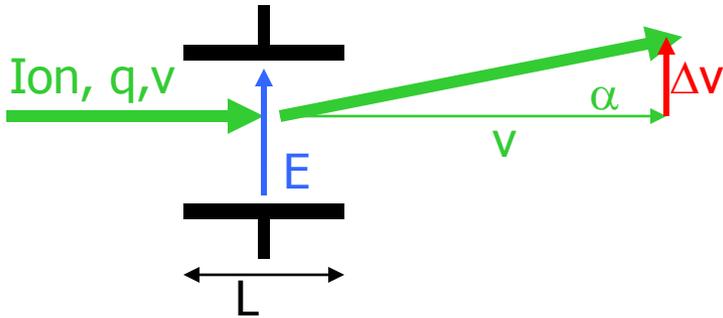
„Oberflächenphysik des armen Mannes“

- Fe - s(100%)
- N - s(20%)
- Mn - s(50%)
- S - s(1%)
- Si - s(100%)
- C - s(6%)
- Cr - s(5%)
- Ni - s(100%)
- O - s(50%)

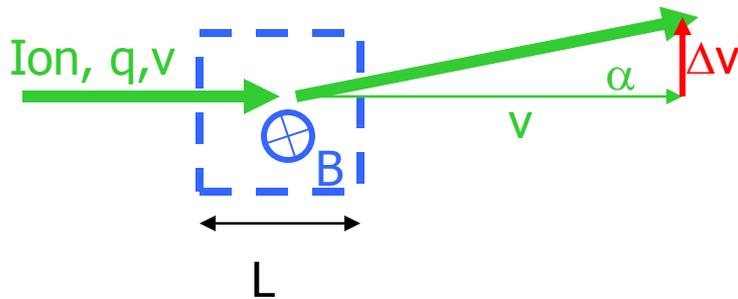
Beachte Tiefenskala µm !

# Massenspektroskopie

## Ablenkung von Ionen im elektrostatischen und magnetischen Feld 1



$$F = q \cdot E \rightarrow a = \frac{q}{m} E$$
$$t = \frac{L}{v} \rightarrow \Delta v = \frac{qE}{m} \frac{L}{v}$$
$$\tan \alpha = \frac{\Delta v}{v} = \frac{q}{m} \frac{L E}{v^2}$$

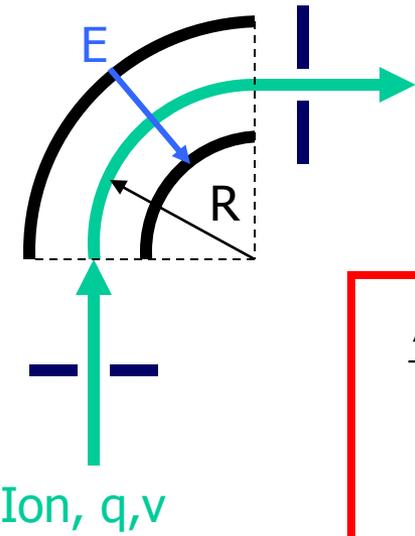


$$F = q \cdot v \cdot B \rightarrow a = \frac{q}{m} v \cdot B$$
$$t = \frac{L}{v} \rightarrow \Delta v = \frac{q}{m} L \cdot B$$
$$\tan \alpha = \frac{\Delta v}{v} = \frac{q}{m} \frac{L B}{v}$$

verschiedene Abhängigkeit des  $\tan \alpha$  von  $v$  !

# Ablenkung von Ionen im elektrostatischen und magnetischen Feld 2

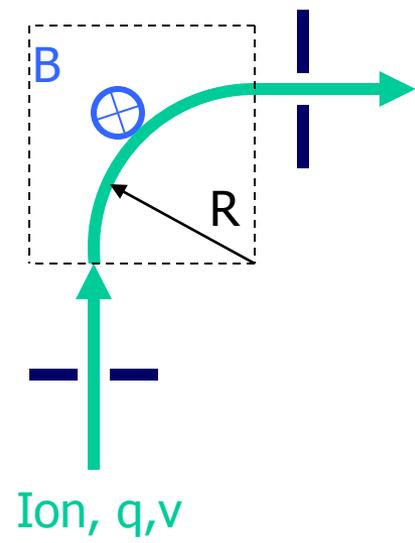
## stabile Kreisbahn



$$F_z = \frac{mv^2}{R} \quad F_E = q \cdot E \quad \rightarrow \quad \frac{mv^2}{R} = q \cdot E \quad \text{stabile Kreisbahn}$$

$$E = \frac{m v^2}{q R} \quad \rightarrow \quad \frac{m}{q} = \frac{ER}{v^2} \quad \star \quad \rightarrow \quad \frac{\Delta m}{m} = \frac{\Delta R}{R}$$

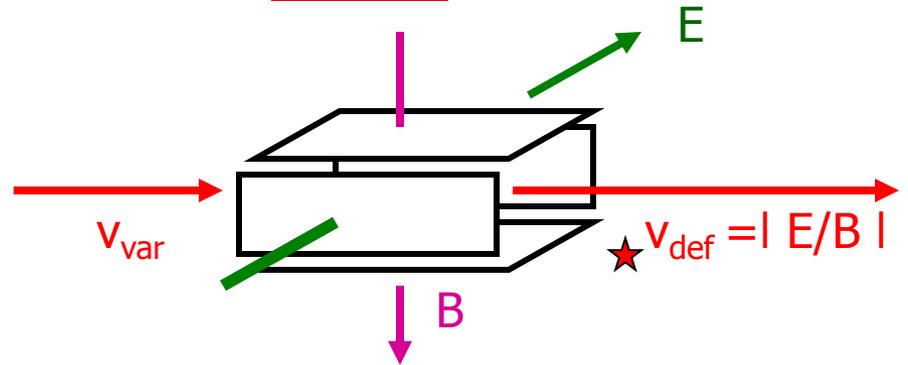
$\frac{\Delta m}{m}$  = Massenauflösung  
 meist wird der Kehrwert als „Auflösung“ angegeben  $\frac{m}{\Delta m}$



$$F_z = \frac{mv^2}{R} \quad F_B = q \cdot v \cdot B \quad \rightarrow \quad \frac{mv^2}{R} = q \cdot v \cdot B \quad \text{stabile Kreisbahn}$$

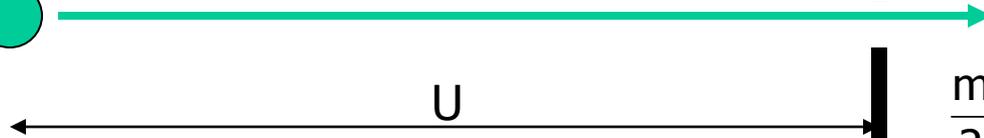
$$B = \frac{m v}{q R} \quad \rightarrow \quad \frac{m}{q} = \frac{BR}{v} \quad \star \quad \rightarrow \quad \frac{\Delta m}{m} = \frac{\Delta R}{R}$$

Anwendung:  
 „Wien-Filter“  
 Reines  
 Geschwindigkeitsfilter,  
 unabhängig von m/q



## Beschleunigung von Ionen im elektrostatischen und magnetischen Feld

Ion,  $q, v=0$



Ion,  $q, v$

$$\frac{m}{2} v^2 = q \cdot U \quad \rightarrow \quad v = \sqrt{\frac{2 q U}{m}}$$

Keine Beschleunigung „aus dem Stand“ durch magnetische Felder

In allen Formeln taucht der Faktor  $m/q$  auf. Misst man  $m$  in AMU und  $q$  in Elementarladungen, dann ist das äquivalent zu  $M/z$  ( $M$ : =Molekulargewicht,  $z$ : = Ladungszahl).

Eine unabhängige Messung von  $M$  oder  $z$  ist nicht möglich.

Neue Quelle der Vieldeutigkeit: Positive und negative Ionen, dieselbe Massenzahl  $M$  zeigt sich bei  $M, M/2, M/3, M/4 \dots$

Abhilfe: oft möglich durch Vergleich.

Beispiel: zweifach geladenes  $^{56}\text{Fe}^{2+}$  zeigt sich bei  $M/z = 28$ , ebenso wie einfach geladenes  $\text{CO}^+$  ! Aber  $^{56}\text{Fe}$  zeigt sich auch bei  $M/z = 56$ , nicht jedoch  $\text{CO}$ .

Massenspektroskopie besteht also darin, von den Ingredienzien der Probe

- a) Ionen zu erzeugen
- b) die Ionen nach M/z zu sortieren
- c) sie nach Klassen getrennt zu zählen
- d) die Zählresultate richtig zu interpretieren

Generelles Problem:

Freifliegende Ionen brauchen ein Vakuum, um Wechselwirkungen mit den Gasatomen zu minimieren.  $10^{-6}$  bis  $10^{-7}$  torr ausreichend.

Nicht alle Proben sind vakuumtauglich (flüssige, gasförmige, biologische, ...)

## Erzeugung von Ionen

Energie-Eintrag in die Oberfläche durch Beschuss mit

1) Ionen -> SIMS = Secondary Ion Mass Spectroscopy

2) Laserstrahlung -> Laser Desorption Ionization -> Spurenanalyse

### Vorteil von SIMS:

die meisten (60 – 70%) Ionen kommen aus der ersten Atomlage

Auftreten von Komplex-Ionen (z.B. Metall-Karbide, -Nitride, ...)

Abrastern einer Oberfläche leicht

### Nachteile:

Ionenausbeute sehr gering und unvorhersagbar, denn

Sputterprozess elementspezifisch (Masse, Bindungsenergie)

Ionisierungswahrscheinlichkeit extrem von Umgebung etc abhängig

Abhilfe: Nachionisierung der weggesputterten Neutralteilchen

Ionen fliegen nach allen Richtungen und mit sehr verschiedenen Geschwindigkeiten weg

Ausbeute für schwere (Molekül-) Ionen extrem gering

Problem der Aufladung nichtleitender Proben

Vakuum

# SIMS – Secondary Ion Mass Spectrometry

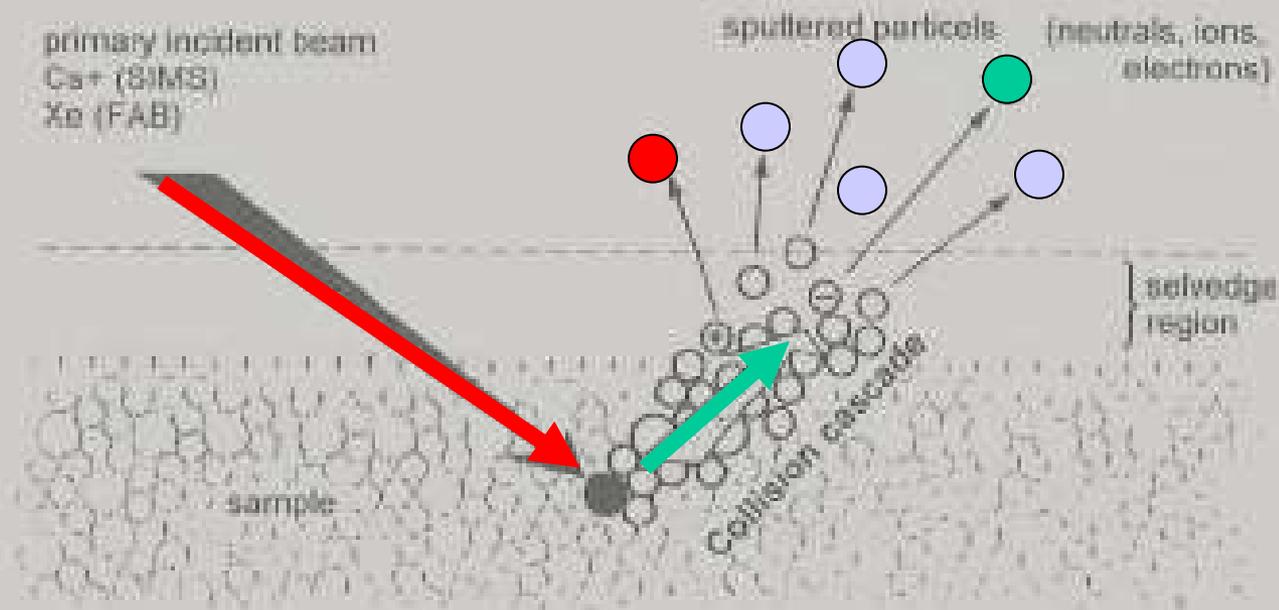


Fig. 9.4. Simple illustration of an instantaneous collision cascade generated as a result of primary particle impact in desorption/ionization mass spectrometry. Adapted from Ref. [24] by permission. © John Wiley & Sons, 1995.

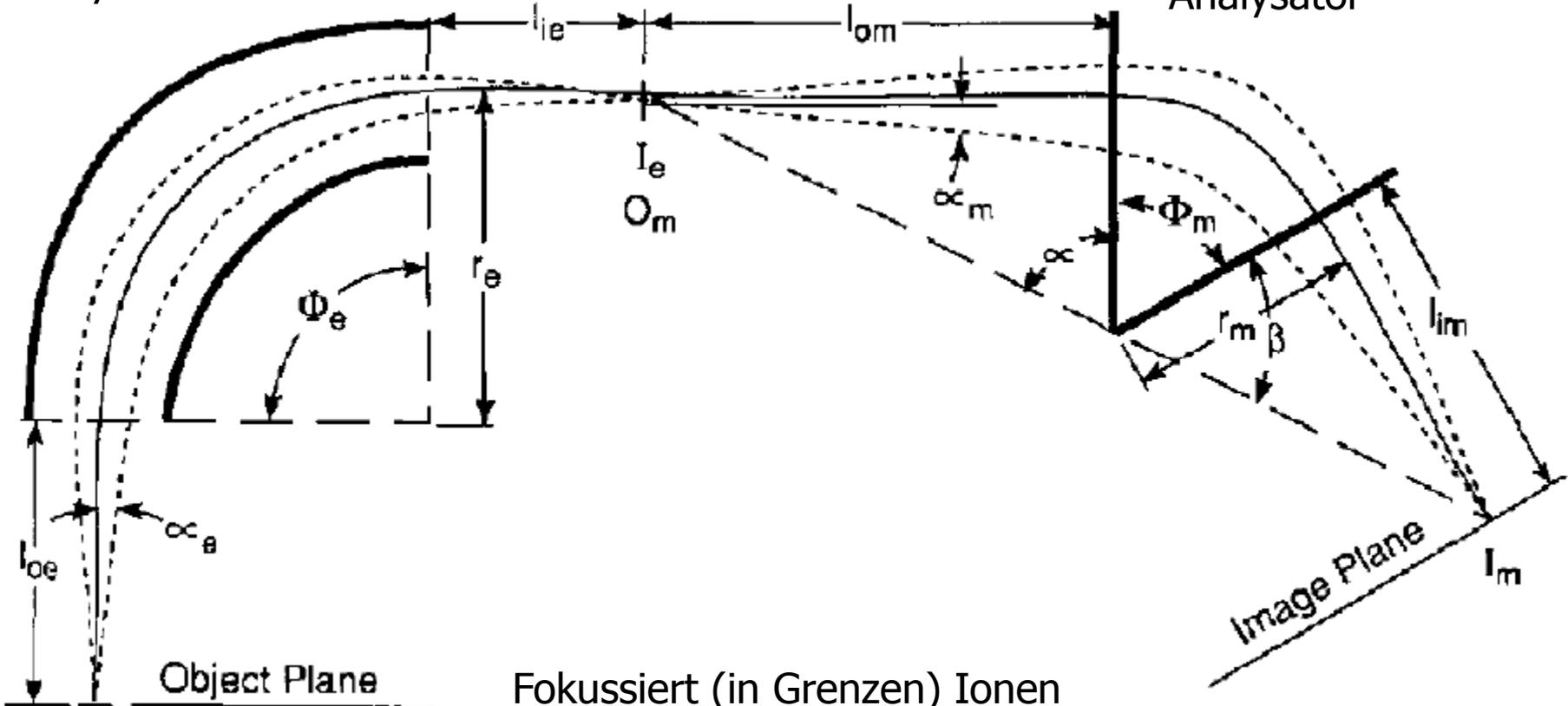
## *SIMS schematisch*

Wegfliegende Atome (Ionen) kommen fast nur (60-70%) aus der ersten Atomlage.

# SIMS: Doppeltfokussierendes Massenspektrometer

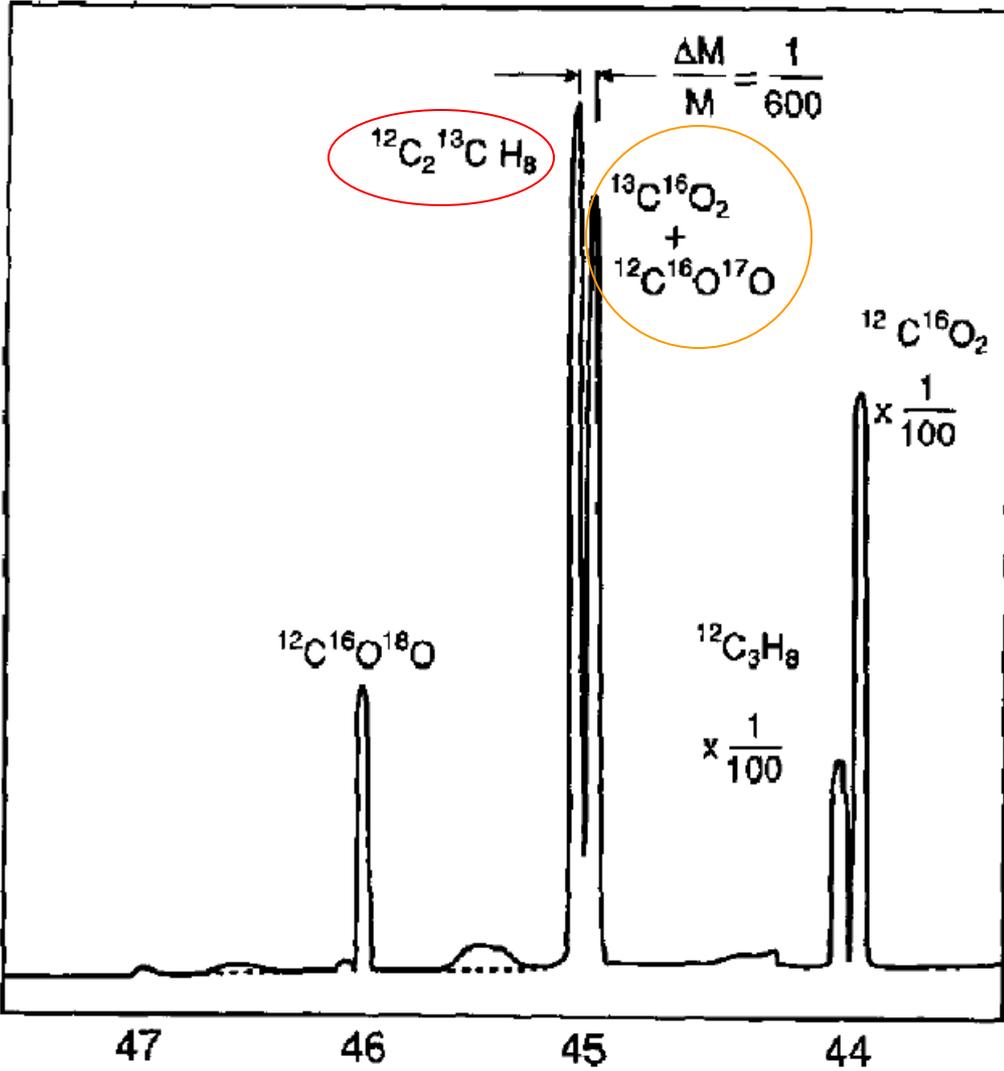
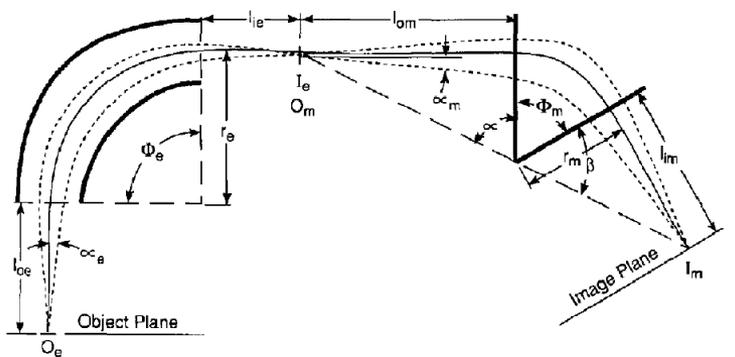
Elektrischer  
Analysator

Magnetischer  
Analysator

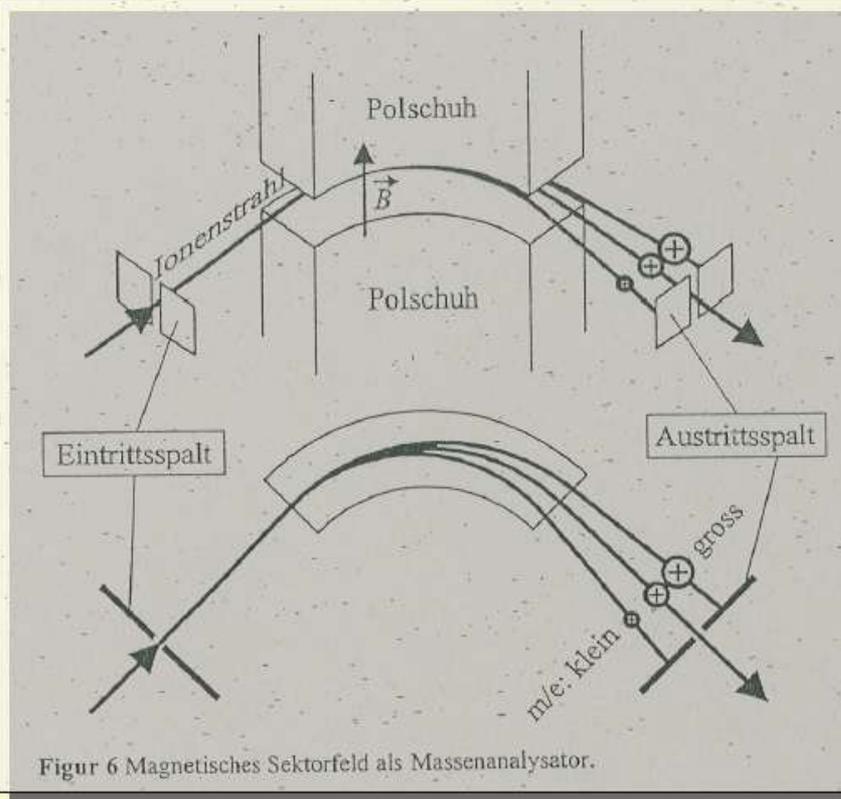


Fokussiert (in Grenzen) Ionen  
verschiedener  
Anfangsgeschwindigkeiten und  
Austrittsrichtungen

# Doppeltfokussierendes Massenspektrometer, Spektrum



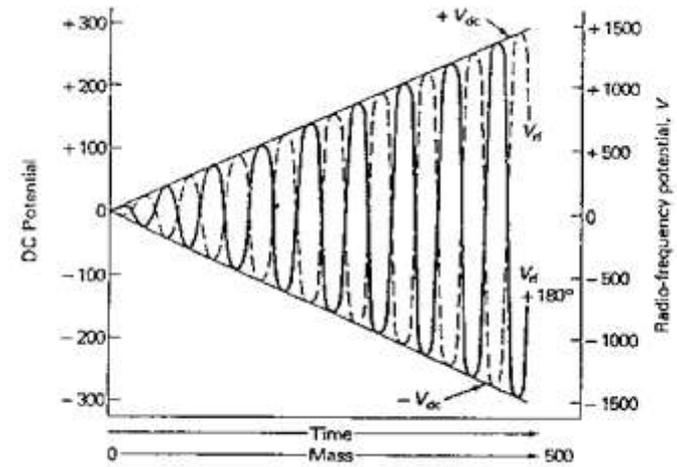
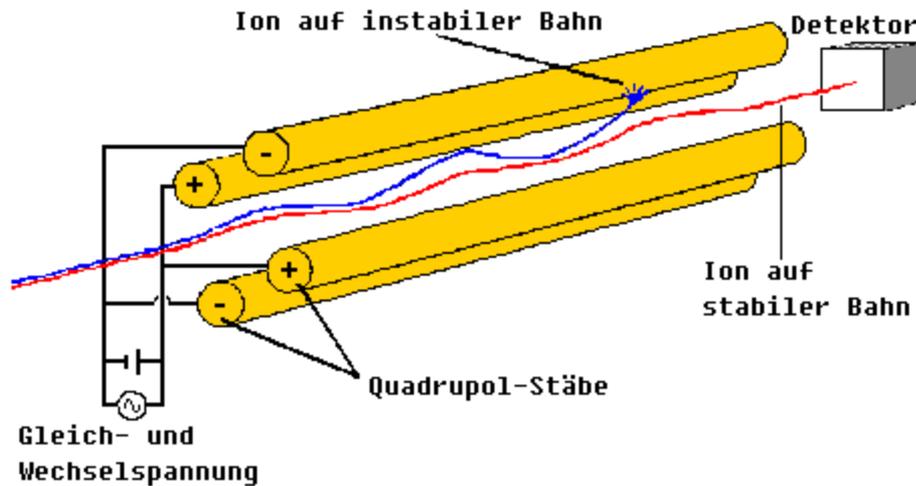
**Figure 3.** Mass spectrum over the 44-47 mass region when a mixture of  $\text{CO}_2$  and  $\text{C}_3\text{H}_8$  was introduced into the instrument shown in Figure 1. When this spectrum was run, the source-defining slit that served as  $O_e$  had a width of 0.125 mm, and the final image slit at  $I_m$  a width of 0.150 mm.



Figur 6 Magnetisches Sektorfeld als Massenanalysator.

Prinzipieller Aufbau eines Sektorfeld-MS

# Quadrupol-Massenfilter



Zeitlicher Verlauf von Gleichspannung  $V_{DC}$  und Wechselspannung  $V_{RF} \cdot \cos \omega t$  beim Durchfahren eines Massenspektrums

- Für ein konstantes Potential wird die Bahn in der  $xz$ -Ebene stabil für alle Ionen. In der  $yz$ -Ebene dagegen divergieren alle Bahnen und treffen früher oder später die Elektroden, verlieren ihre Ladung und gehen damit verloren.
- Wählt man ein periodisches Potential so werden die Ionen in beiden Ebenen abwechselnd in die eine oder andere Richtung beschleunigt. Schwere Ionen reagieren dabei schwächer auf diese Defokussierung.
- Kombiniert man nun diese beiden Potentiale, wählt also  $\Phi_0 = U + V \cos \omega t$  so werden die Flugbahnen in der  $xz$ -Ebene für schwere Ionen stabil (Hochpaß-Massenfilter) und in der  $yz$ -Ebene für leichte Ionen (Tiefpaß-Massenfilter).

Nachteil: braucht Ionen mit bestimmter Energie (Geschwindigkeit)

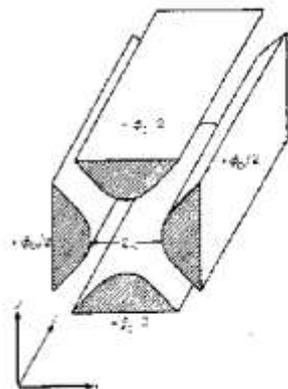
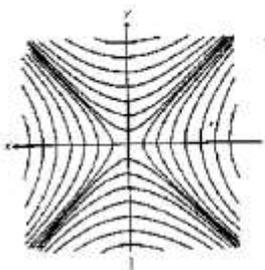


Abbildung: Äquipotentiallinien eines Quadrupolfeldes und Elektrodenanordnung um ein solches Feld zu erzeugen

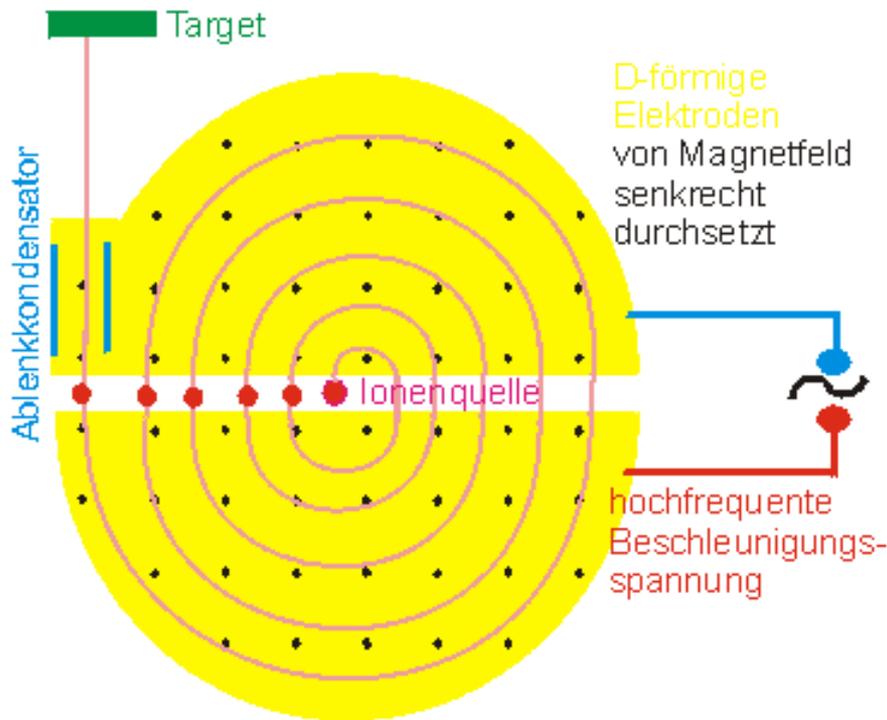


# Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: A Primer

Peter Abraham and Alex Huffman

Mass Spectrometry Reviews, **1998**, 17, 1-35

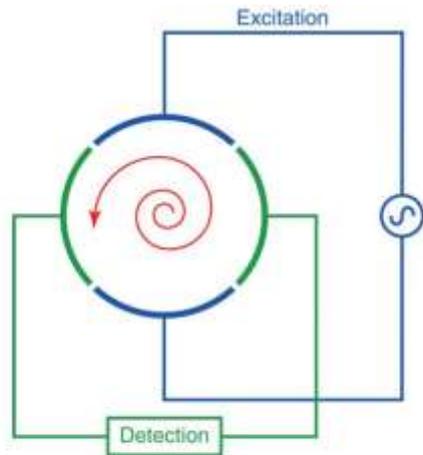
Zyklotron: ursprünglich als Teilchenbeschleuniger für Kernphysik von E. O. Lawrence 1930 erfunden



$$\mathbf{F} = z\mathbf{v} \times \mathbf{B}$$
$$\omega_c = \frac{zB}{2\pi m}$$
$$m/z = \frac{B}{2\pi\omega_c}$$

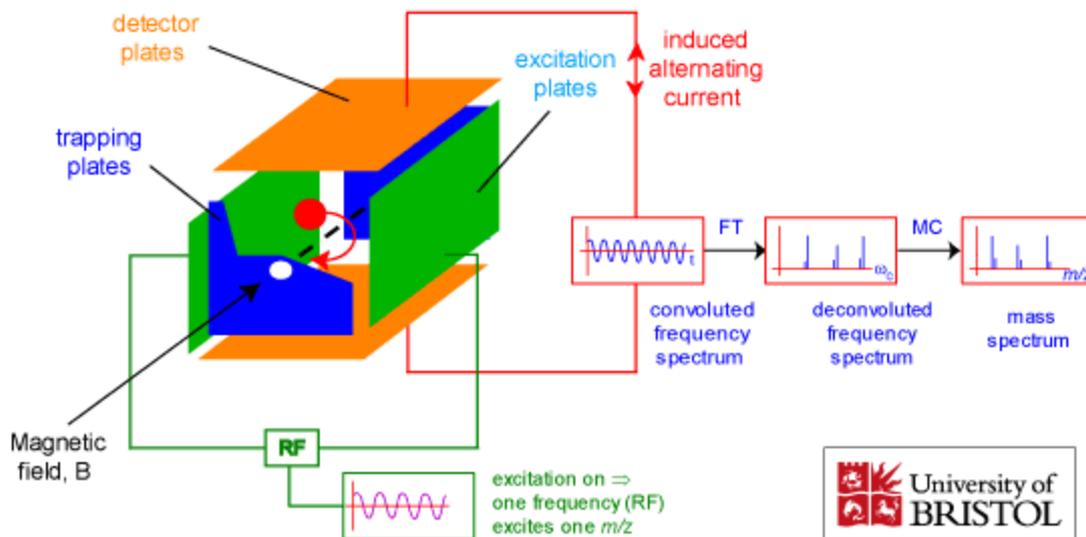
- $\mathbf{F}$  is the Lorentz Force observed by the ion when entering the magnetic field
- $\mathbf{B}$  is the magnetic field strength (constant)
- $\mathbf{v}$  is the incident velocity of the ion
- $\omega_c$  is the induced cyclotron frequency
- $m$  is the mass of the ion
- $z$  is the charge on the ion

**Daher für Massen-Analyse brauchbar!**  
**Ursprüngliche Geschwindigkeit kommt nicht vor !**



A cross section of a cylindrical FT-ICR analyzer cell, depicting excitation of ions (in red) through the application of an RF potential to the excitation electrodes. Once the ions have been excited to a cyclotron motion of suitable radius, the image current of the orbiting ions can be detected on the detection plates.

A Schematic of FT-ICR-MS showing the ion trapping, detection and signal generation.



## Fourier Transform Aspects

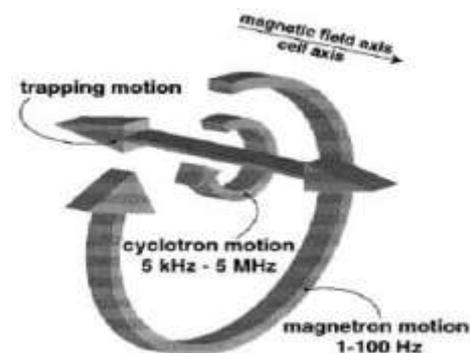
Frequency can be measured much more accurately

- Resolution, Speed increase x10,000
- Mass Range x500
- Sensitivity in attomole range ( $10^{-18}$ )
- Advantage of fixed magnetic field

Most instruments use an RF sweep that covers the range between several kilohertz and the lower megahertz range to accelerate the ions trapped inside the cell. This sweep pulse is called a chirp

Trapping führt zur „Magnetron-Korrektur“

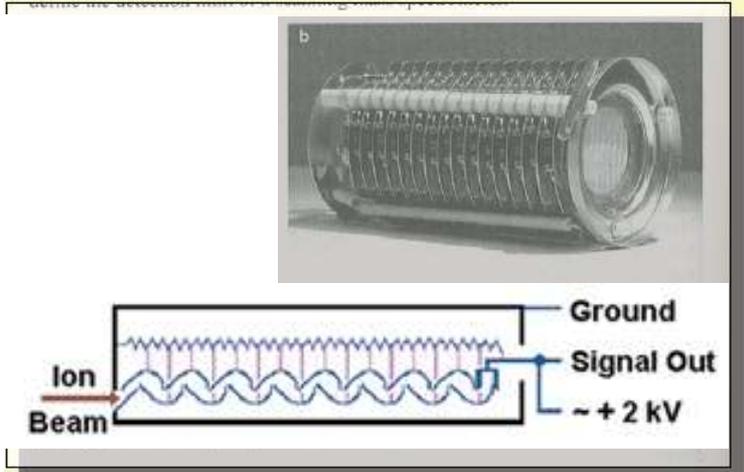
$$\omega_{\pm} = \frac{\omega_c}{2} \pm \sqrt{\left(\frac{\omega_c}{2}\right)^2 - \left(\frac{\omega_t}{2}\right)^2}$$



Scheme of the three ion motions in the analyzer cell.

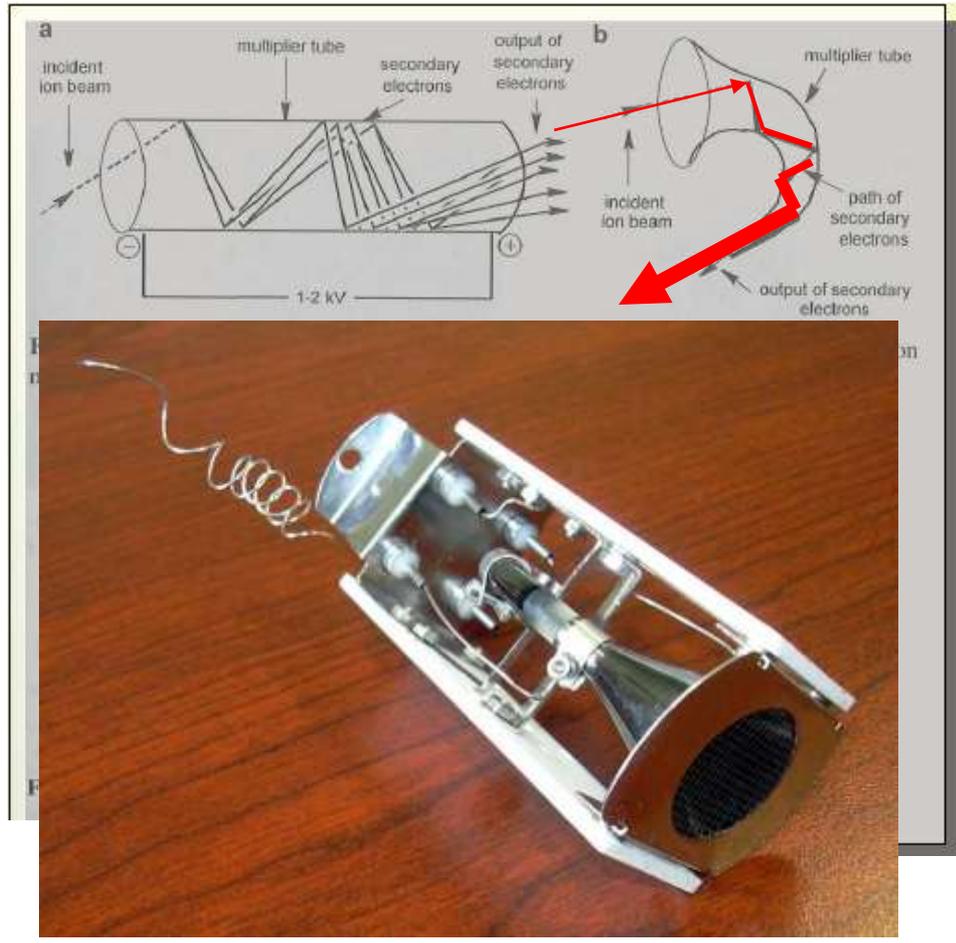
FTICR instruments afford high resolution ( $\sim 150,000$ ) and accurate ( $\sim 2$  ppm) mass spectra on a routine basis. The reason for this performance lies in the unique technique used for mass analysis. Whereas in other mass spectrometers ions are filtered in a magnetic or electric field or selected by flight time, in FTICR instruments ions are detected by their resonance frequency; this can be measured accurately with today's electronics and, therefore, accurate results can be obtained.

# Zählen von Ionen: SEV - Sekundärelektronenverstärker

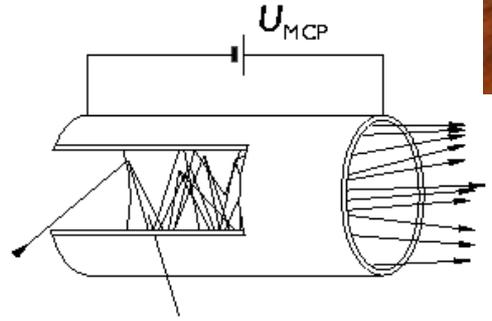
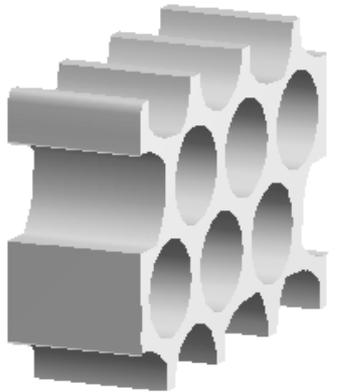


Old-fashioned discrete dynode multiplier

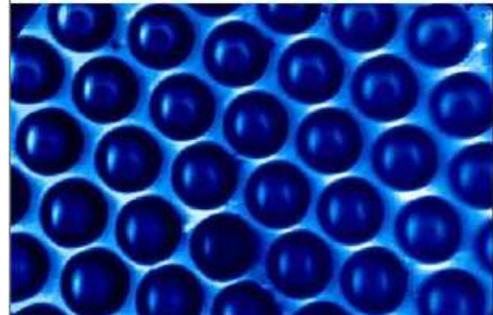
# Kontinuierlicher SEV



# Channelplate



Sekundärelektronen

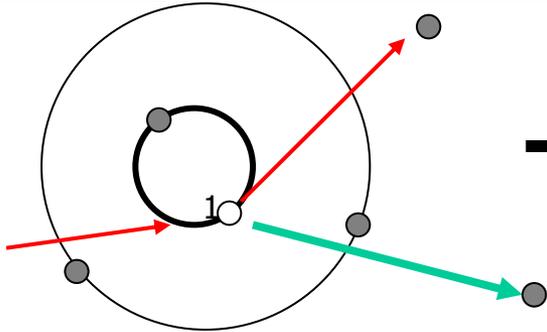


Ansicht  
Kanal-  
durch-  
messer ca.  
10  $\mu\text{m}$

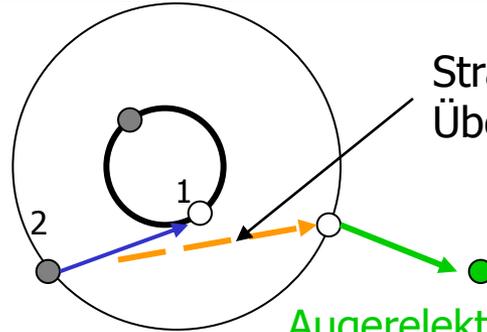
Abbildung 2.16: Das Channelplate. Links Querschnitt durch einen Teil des Plates, rechts Einzelansicht eines Kanals mit einfallendem Elektron, Sekundärelektronen und austretenden Elektronen.

# Augerelektronenspektroskopie (AES)

Augerprozess ist Atomprozess, ziemlich unabhängig von Umgebung



Primärelektron ionisiert ein Atom

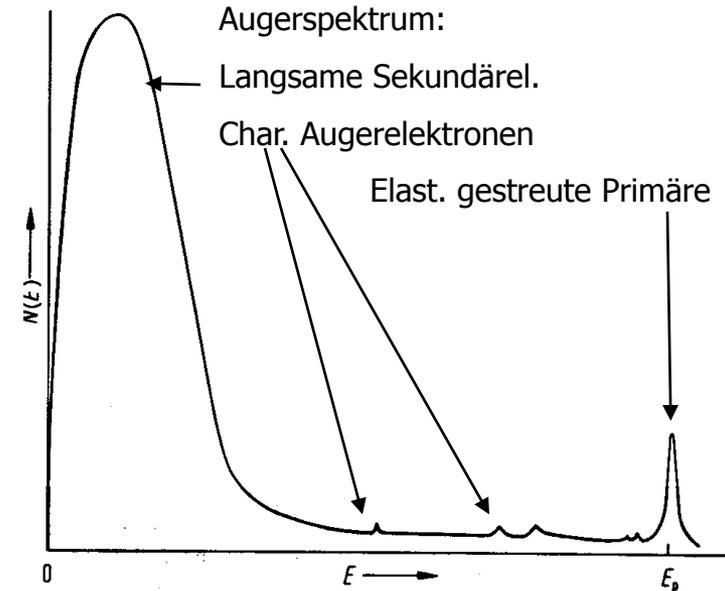
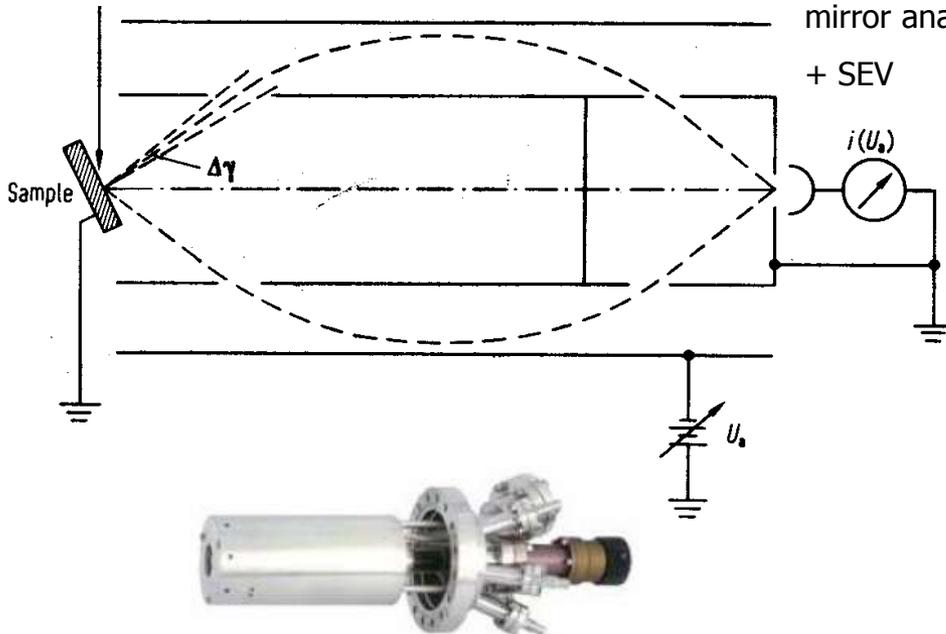


Strahlungsloser Übergang

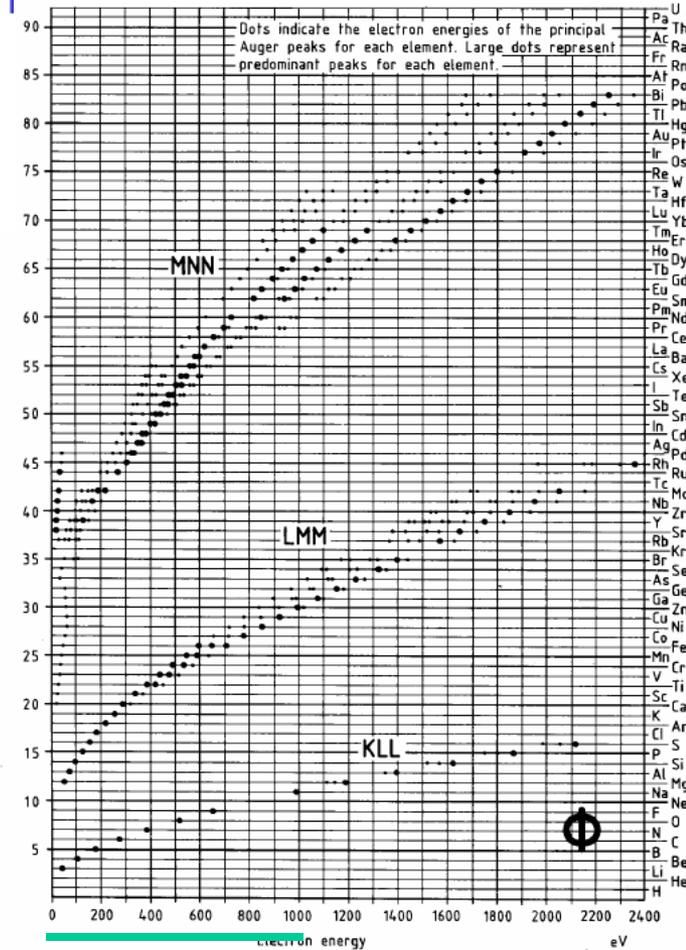
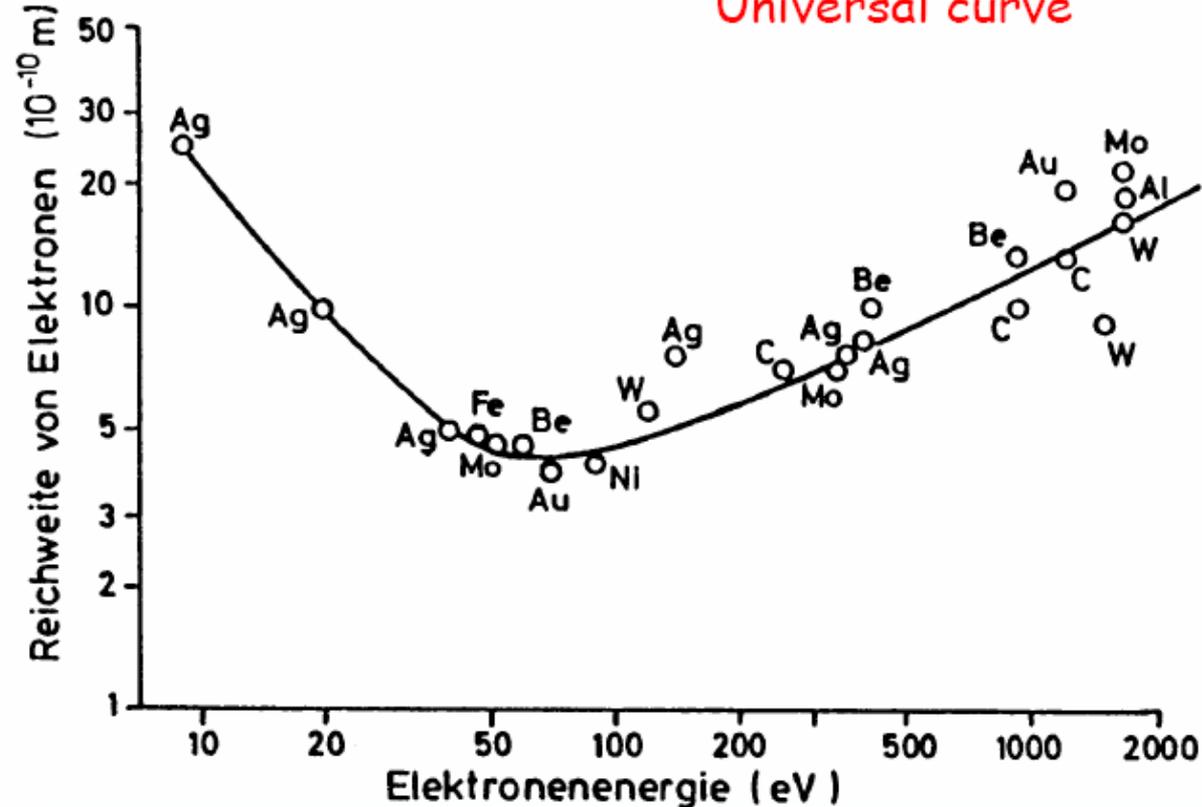
Augerelektron:

$$|E_b(1)| - |E_b(2)| = E_{kin} + |E_b(2)|$$

Analyse der Elektronenenergie:  
meist mit CMA: (cylindrical mirror analyzer)

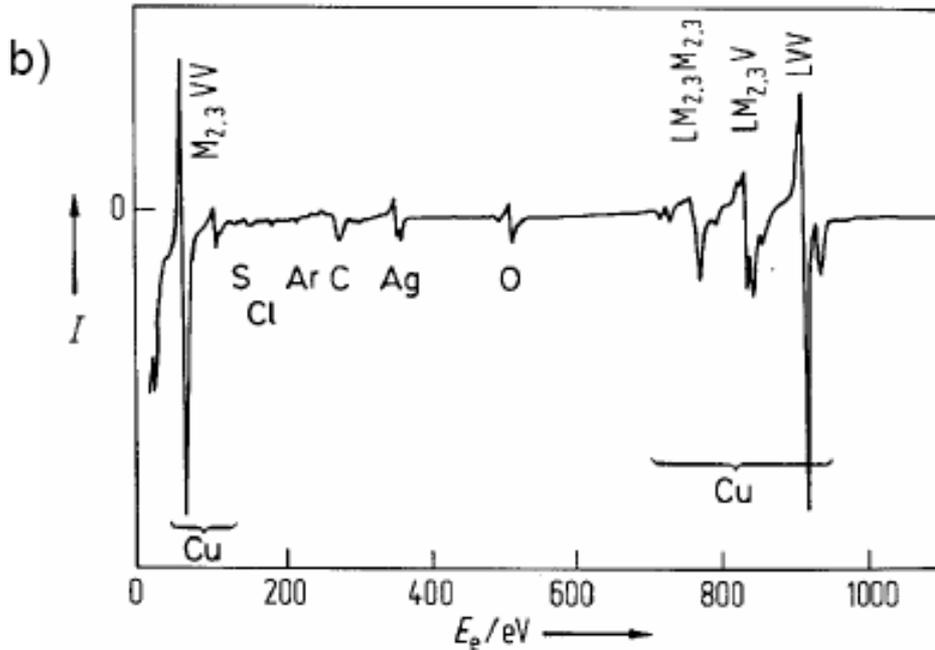
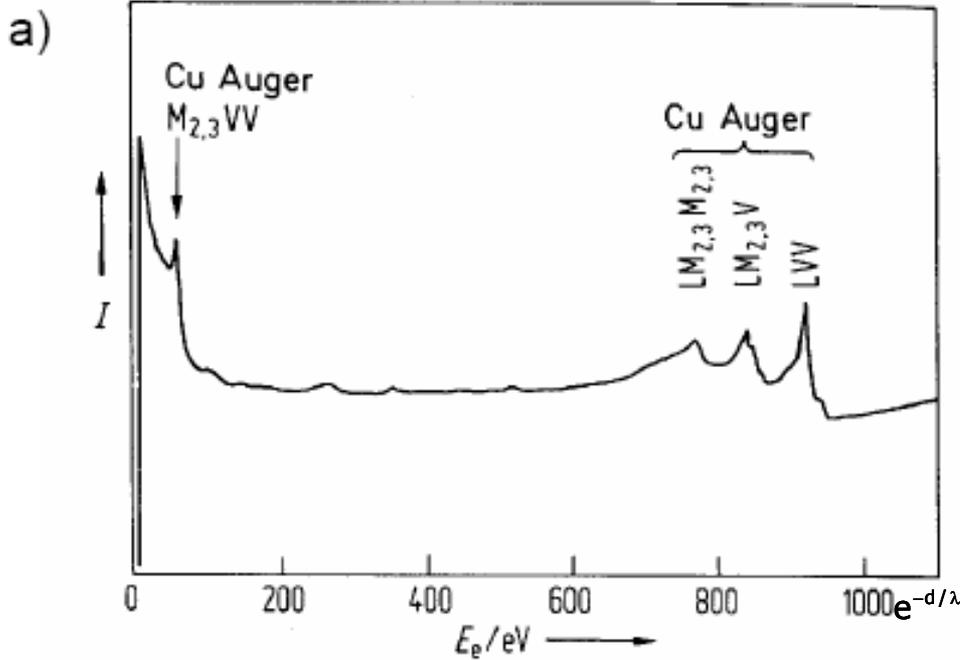


## Mittlere freie Weglänge von Elektronen



Bezeichnung von Auger-Linien: 3 Buchstaben: 1) Zustand des zuerst herausgestossenen  $e^-$   
 2) Zustand des nachspringenden  $e^-$ , 3) Zustand des Augerelektrons  
 Beispiel: KLL, LMM - genauer etwa  $LM_1M_2$ , oder LVV

# Augerspektrum von Cu: a) integral, b) differenziert



## Auger – Quantifizierung

trivial:  $\frac{(\text{ppH})_i}{S_i} = k c_i$   $k$  aus  $\sum_i c_i = 1$

$S_i$  = Sensitivity der i-ten Atomsorte

komplizierter: Signal aus Tiefe  $d$  wird mit  $e^{-d/\lambda}$  abgeschwächt:

$\lambda$  = Ausdringtiefe

$$(\text{ppH})_i = k_i \int_0^{\infty} c_i(z) e^{-z/\lambda_i} dz \quad \text{mit } k_i \text{ aus}$$

$$S_i = k_i \int_0^{\infty} 1 \cdot e^{-z/\lambda_i} dz$$

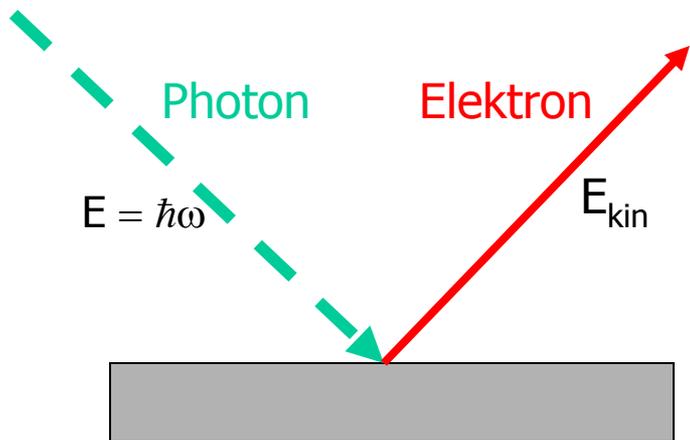
# ESCA - UPS - XPS

## X-ray Photoelectron Spectroscopy (XPS)

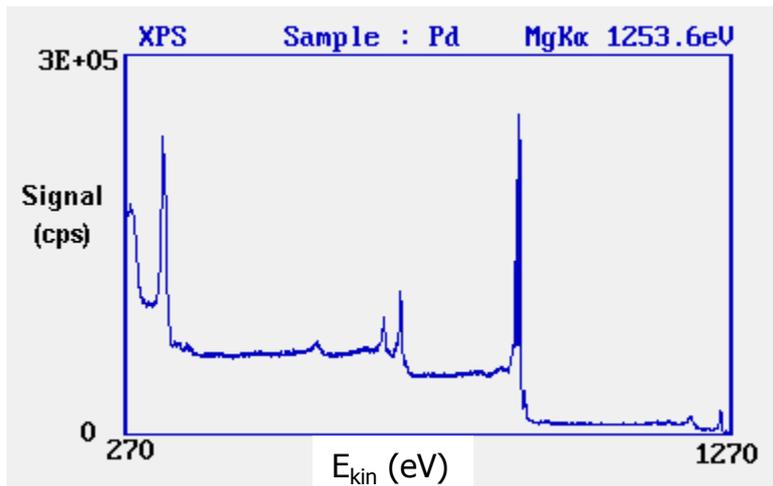
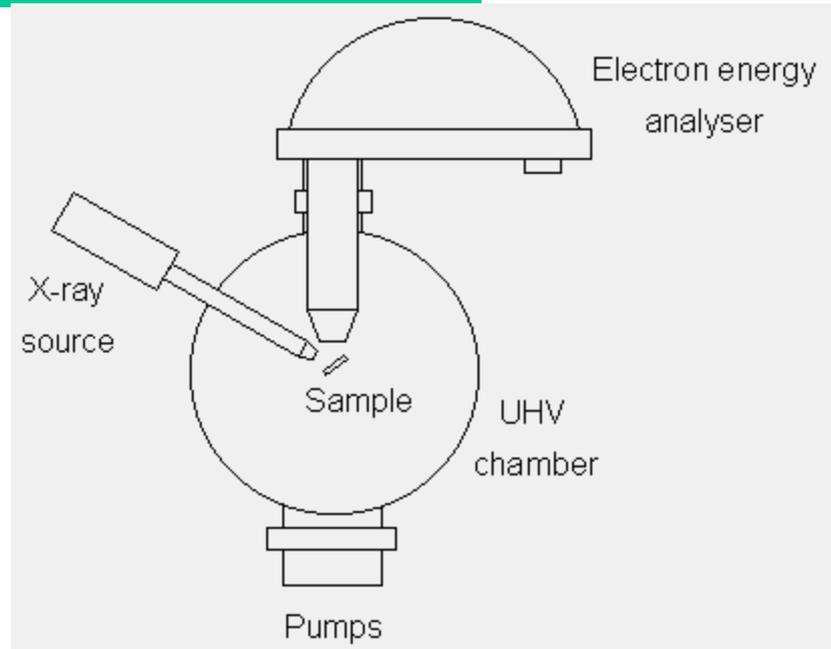
- using soft x-rays (with a photon energy of 200-2000 eV) to examine core-levels.

## Ultraviolet Photoelectron Spectroscopy (UPS)

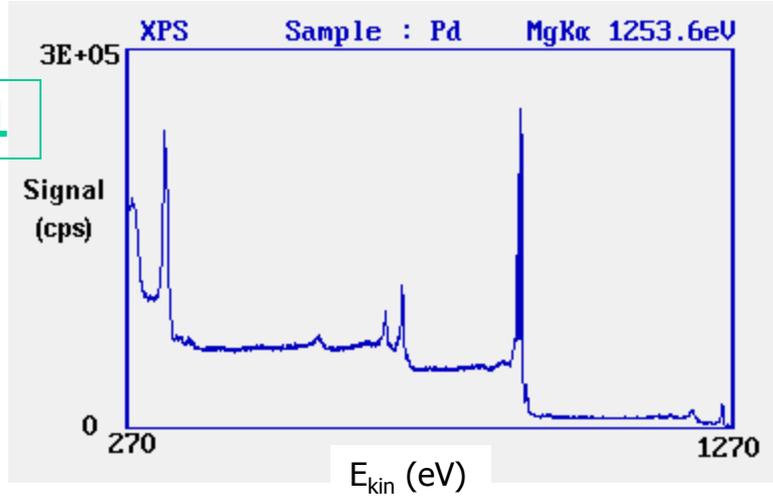
- using vacuum UV radiation (with a photon energy of 10-45 eV) to examine valence levels.



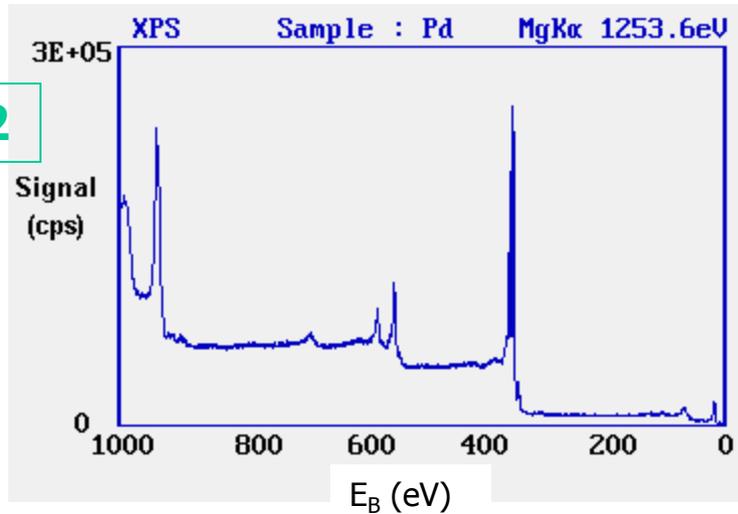
$$\hbar\omega = E_B + E_{kin} + \Phi_P$$



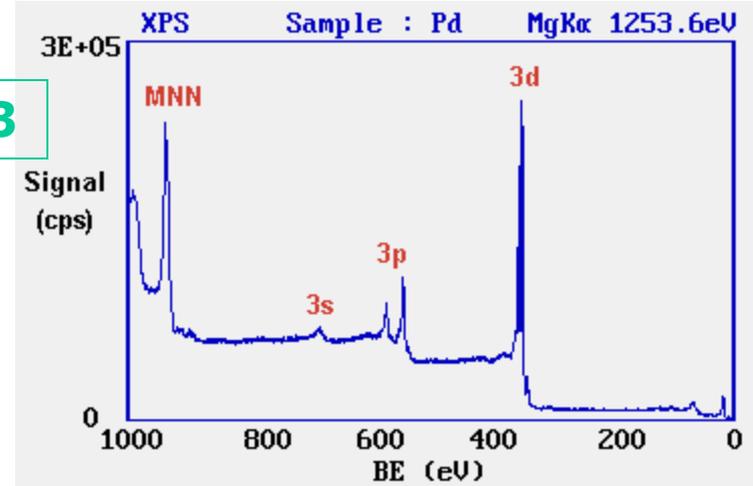
# ESCA - UPS - XPS: Arbeitsschritte



- the main peaks occur at kinetic energies of ca. 330, 690, 720, 910 and 920 eV.

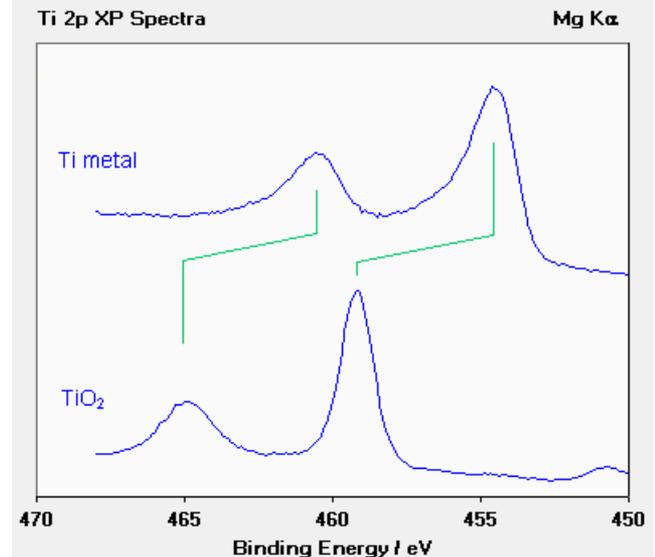


The most intense peak is now seen to occur at a binding energy of ca. 335 eV



Zuordnung und Identifikation

## Chemical shift



# Eine Alternative für Grenzflächen: STEM/EDX

## QUANTITATIVE COMPOSITIONAL MAPPING OF Bi SEGREGATION TO GRAIN BOUNDARIES IN Cu

V. J. KEAST and D. B. WILLIAMS

Acta Metall. Vol. 41, No. 12, pp. 3000-3008, 1993

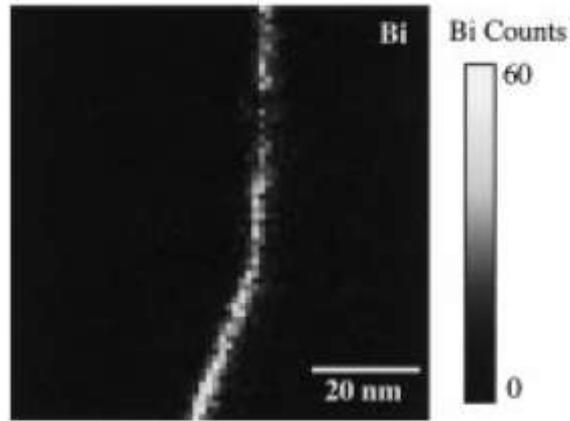
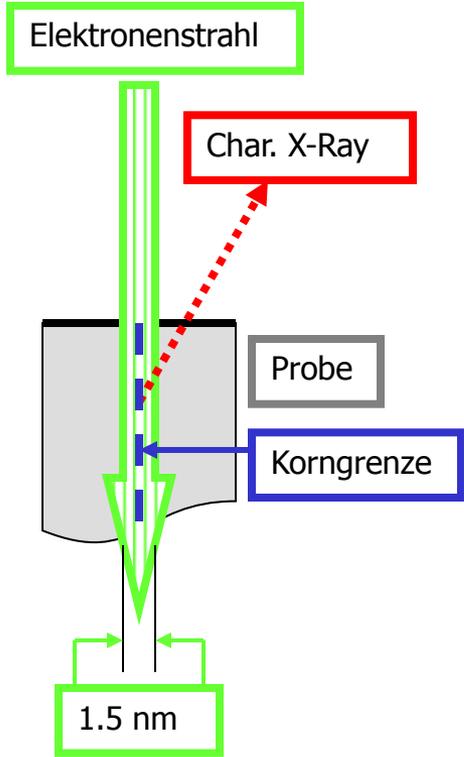
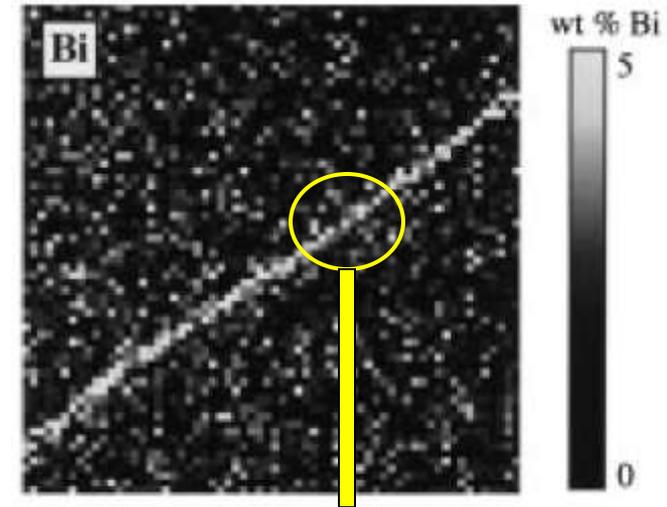
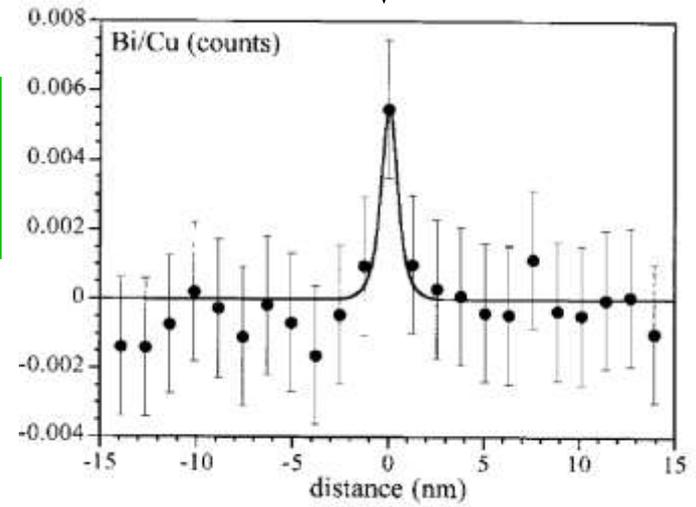


Fig. 1. Map of Bi  $L_{\alpha}$  counts on a faceted grain boundary in Bi-doped Cu. The upper and lower facets have grain boundary coverage of  $10.8 \pm 1.1$  atoms/nm<sup>2</sup> (1.2 monolayers) and  $12.8 \pm 1.3$  atoms/nm<sup>2</sup> (1.4 monolayers), respectively.

For compositional mapping, energy windows corresponding to the elemental peaks (the Cu  $K_{\alpha}$  at 8.047 keV and the Bi  $L_{\alpha}$  at 10.836 keV), and background windows for each characteristic peak were also collected.



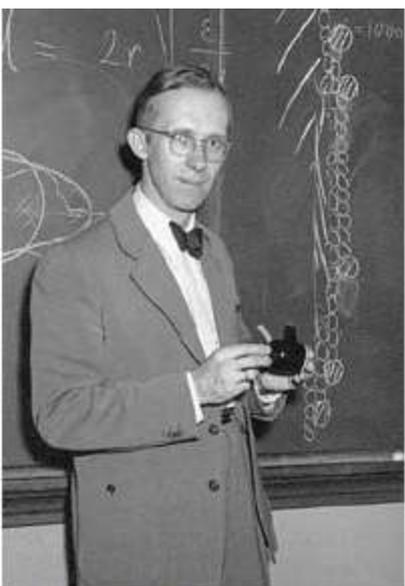
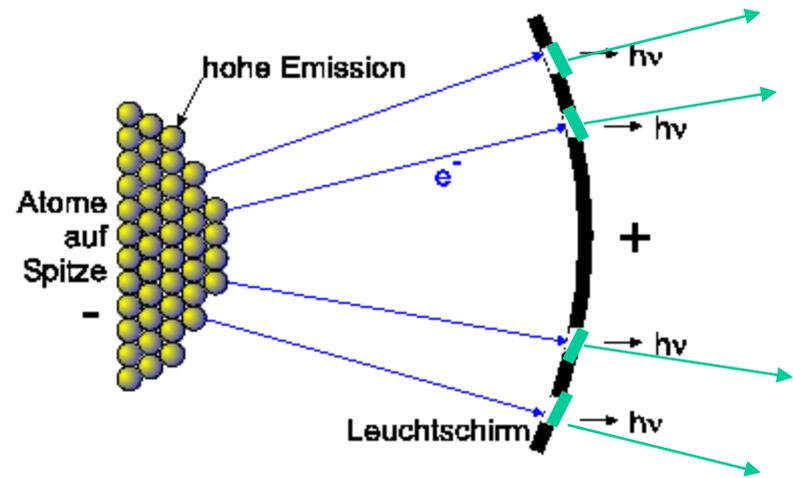
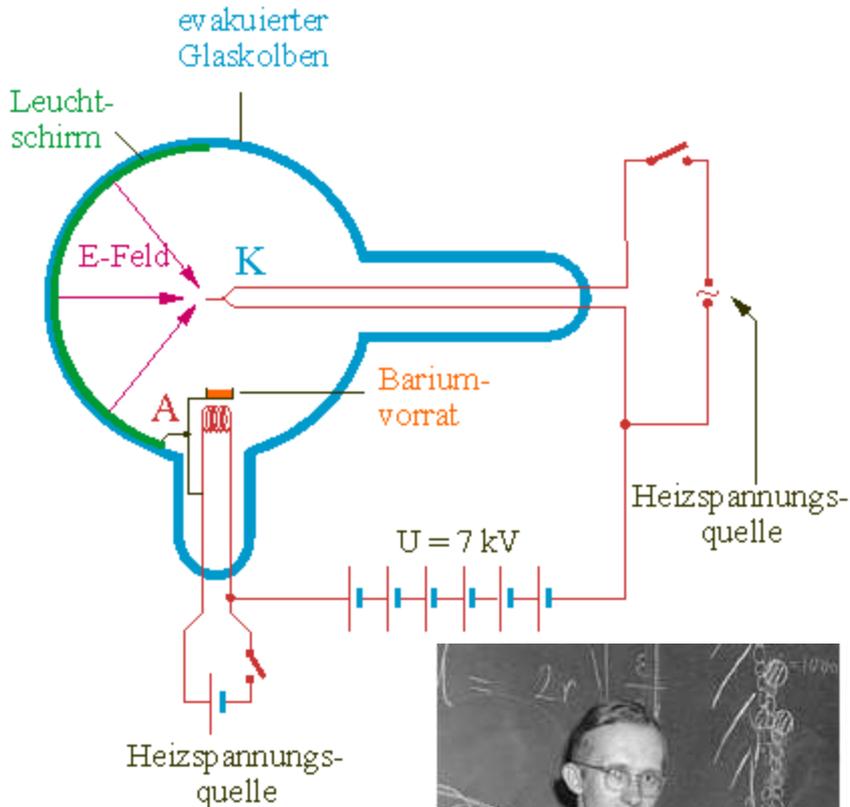
compositional map of Bi content at a grain boundary Bi-doped specimen showing a spatial resolution < 2 nm.



Bi segregation profile extracted from the map

The main limitation with AES for grain boundary segregation studies is the requirement that the sample be fractured intergranularly. This is a disadvantage if one wishes to study differences between strongly and weakly embrittled boundaries or alternatively some other grain boundary phenomenon. It may also lead to erroneous results for segregation levels. The fracture path will most likely follow the most embrittled grain boundaries, which will be those containing the most amount of segregant, so the measured distribution of segregant with AES will be biased towards those boundaries with high segregation levels.

# FEM – Feldelektronenmikroskop (E.W. Müller, 1935)

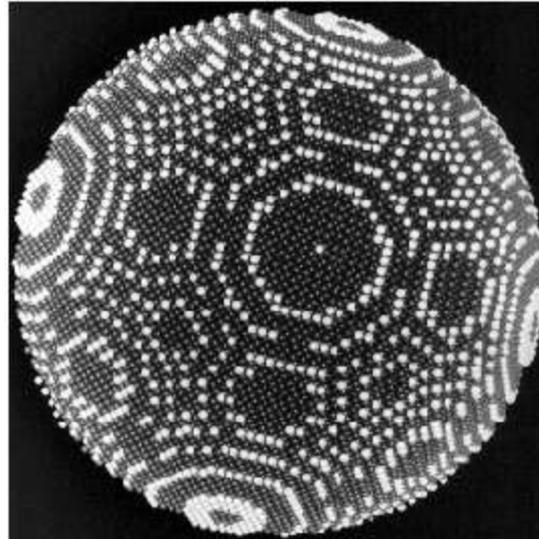
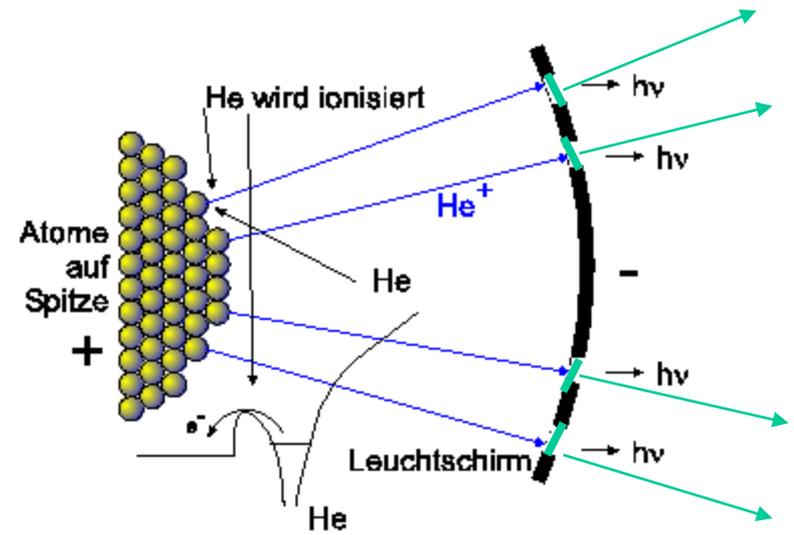
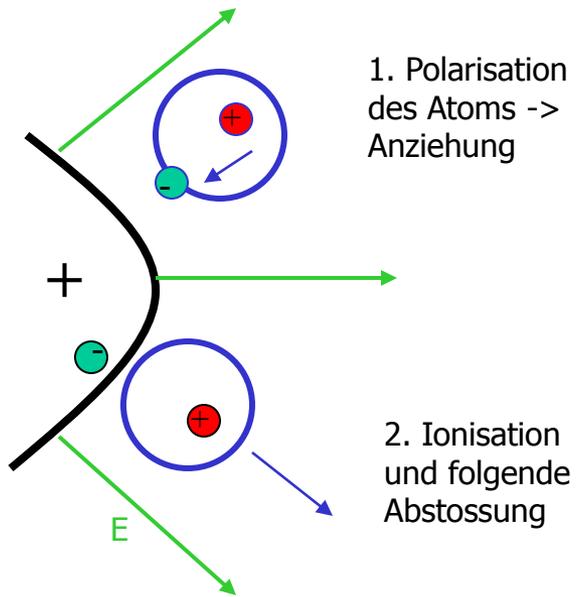


Erwin Müller präsentiert ein Miniatur Feldelektronenmikroskop

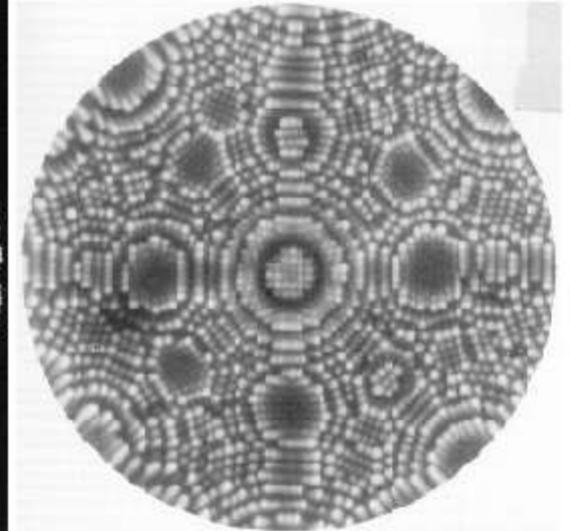


Montage des Versuchsaufbaus vom Bundes-Gymnasium Klagenfurt (Leuchtschirm um 90° geklappt)

# FIM – Feldionenmikroskop



Modell einer Spitze



FIM-Bild

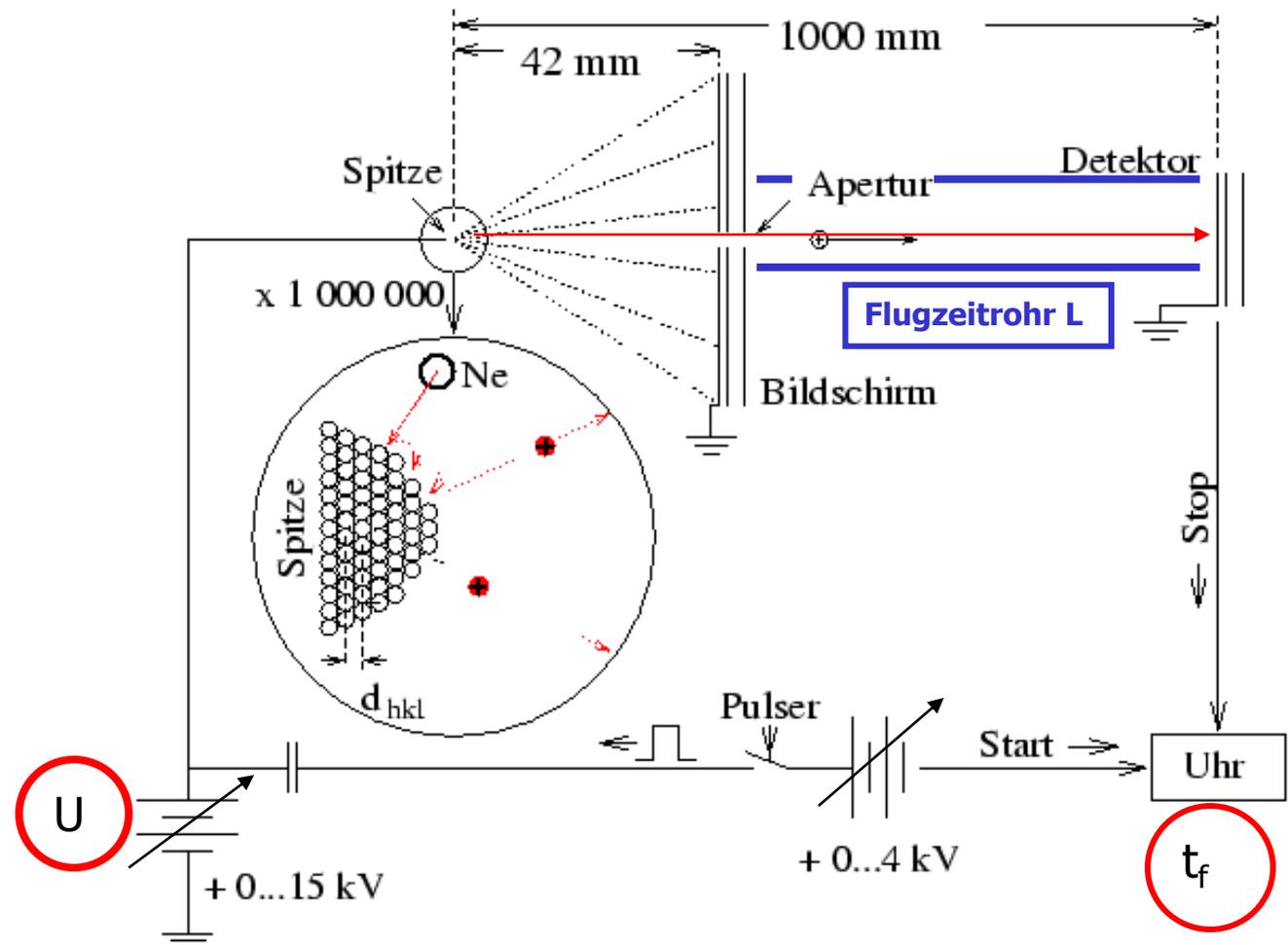
# FIM (Feldionenmikroskop) – Atomsonde

Abbildung auf atomarem Massstab (FIM) und chemische Identifikation einzelner Atome (Atomsonde) durch Flugzeitspektroskopie

$$e U = \frac{1}{2} m v^2$$

$$t_f = \frac{L}{v}$$

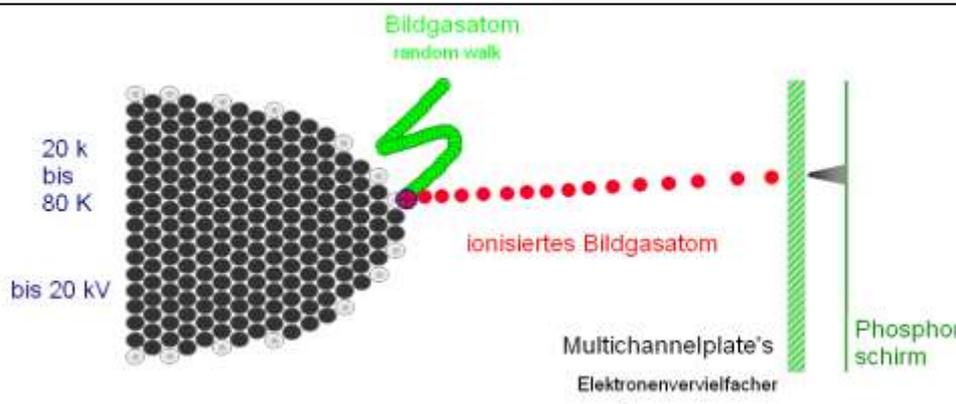
$$m = \frac{2e U}{L^2} t_f^2$$



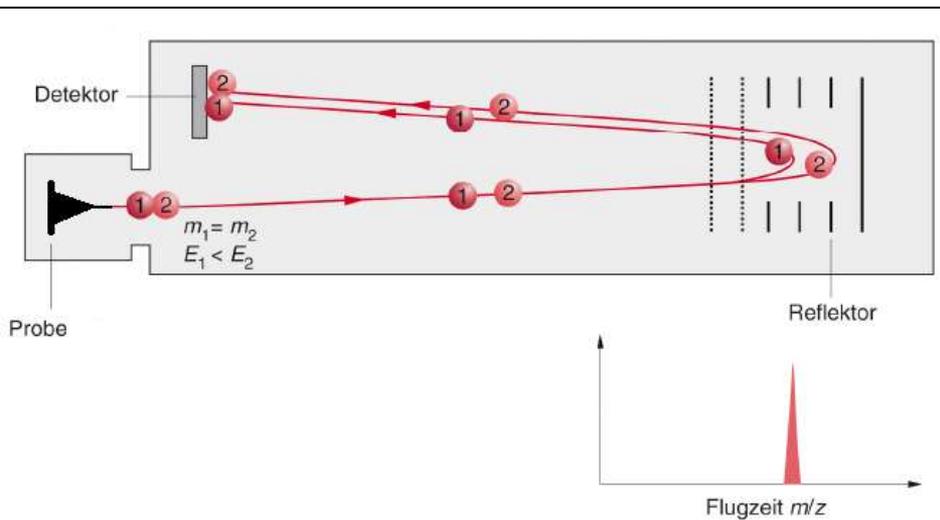
**Abbildung:** Aufbau eines Feldionenmikroskops mit Atomsonde: an der Spitze werden entweder Bildgasionen (Ne) ionisiert und damit ein stark vergrößertes Bild auf dem Schirm erzeugt, oder es werden durch Hochspannungspulse Atome aus der Spitze herausgerissen und in einem Flugzeitmassenspektrometer analysiert.

# ATOMSONDE: Funktionsprinzip

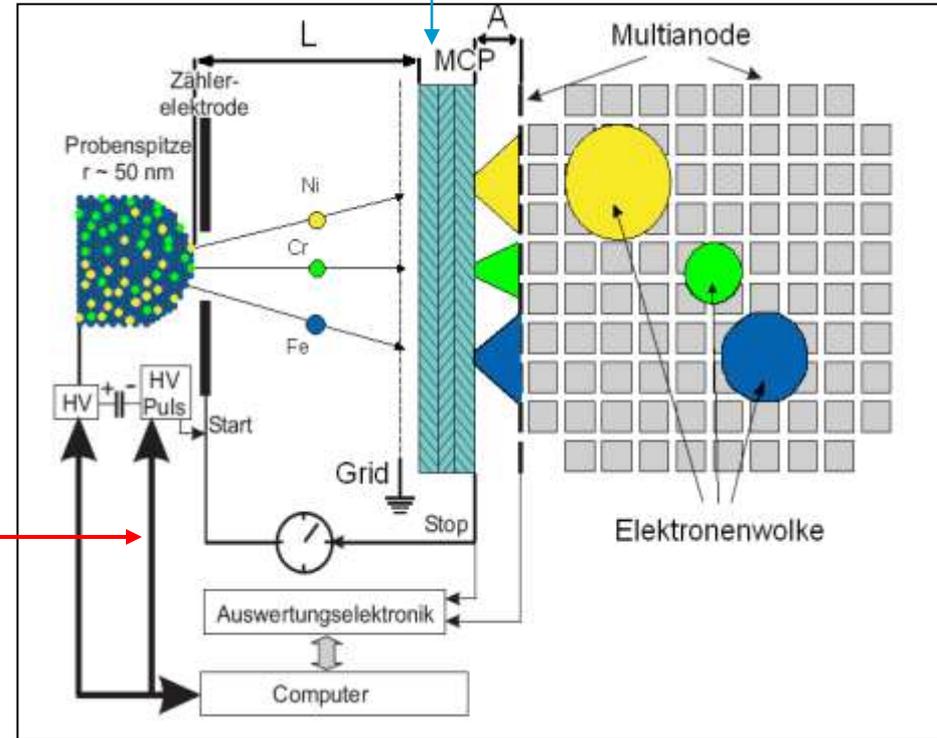
Funktionsprinzip des FIM mit channelplate



Reflektron: Korrektur der  $V_0$



Channelplate

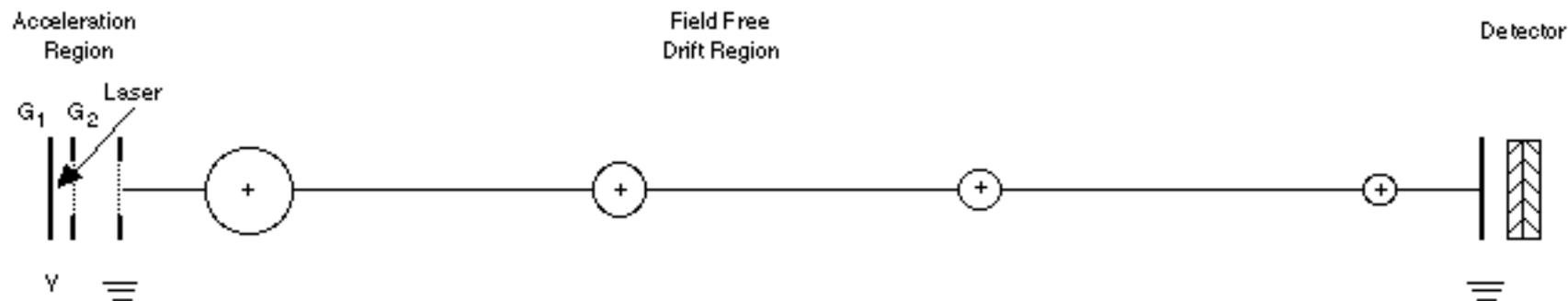


Funktionsprinzip der 3-D Atomsonde  
Flugzeitspektrometer =  
ToF - Spektrometer

Alternativ: Auslösung der Ionen durch  
Kurzzeit (fs-) Laserpuls

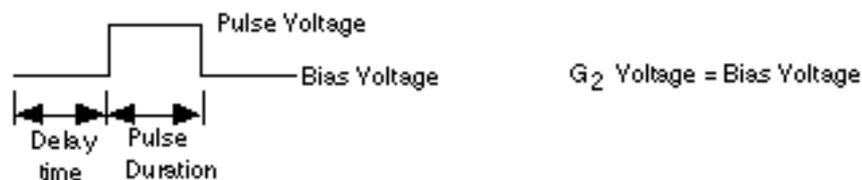
# Flugzeitspektrometer = ToF - Spektrometer

## Linear TOF mass spectrometer



For continuous ion extraction:  $G_1 > G_2$

For delayed ion extraction:  $G_1$  Voltage:



## Reflecting TOF mass spectrometer

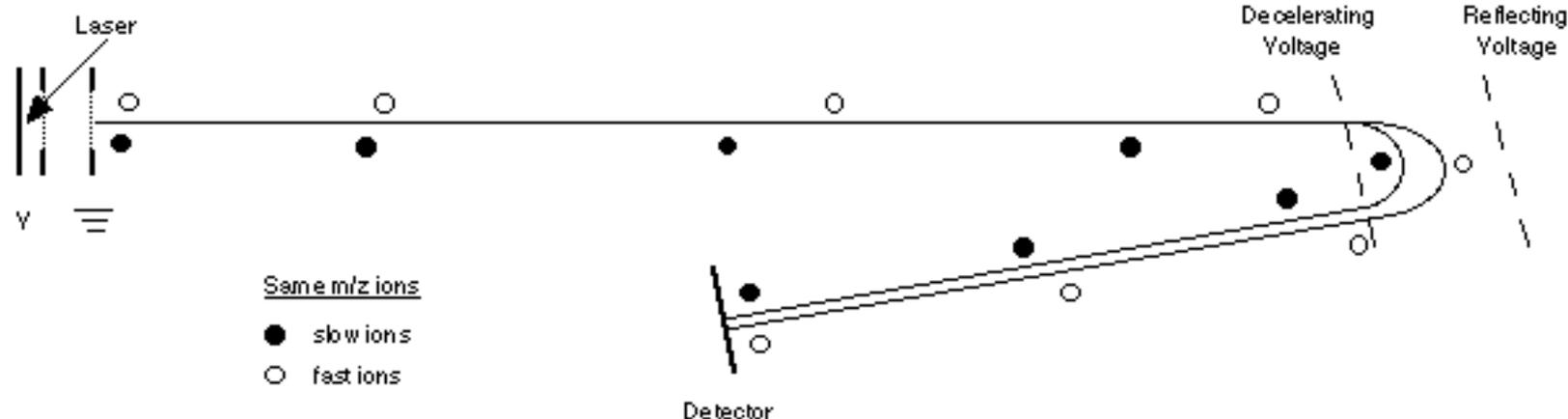
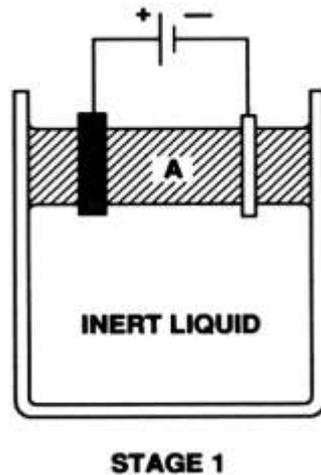
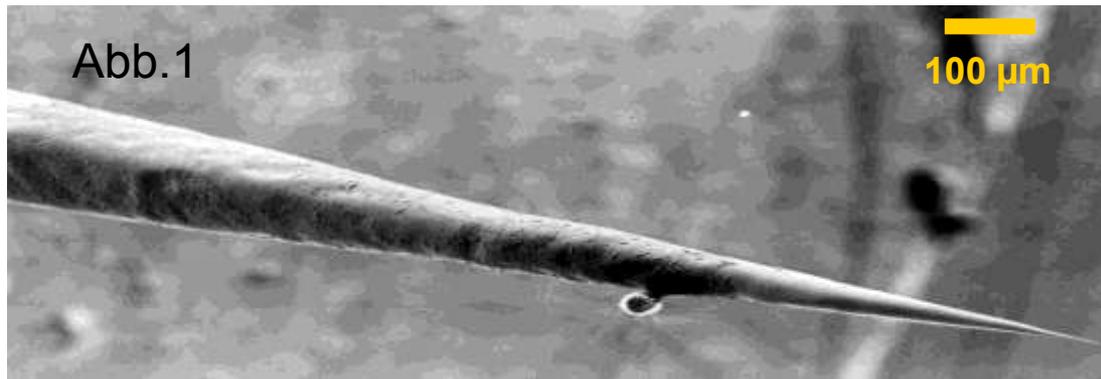
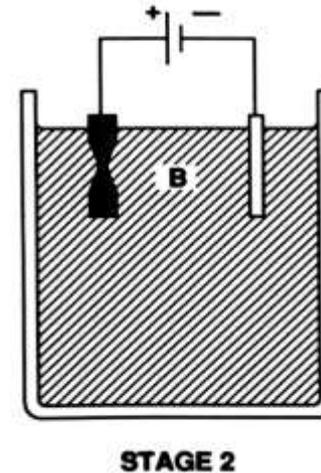


Figure 1. Basic components of a linear (upper) and reflecting (lower) TOF mass spectrometer.

# Spitzenpräparation



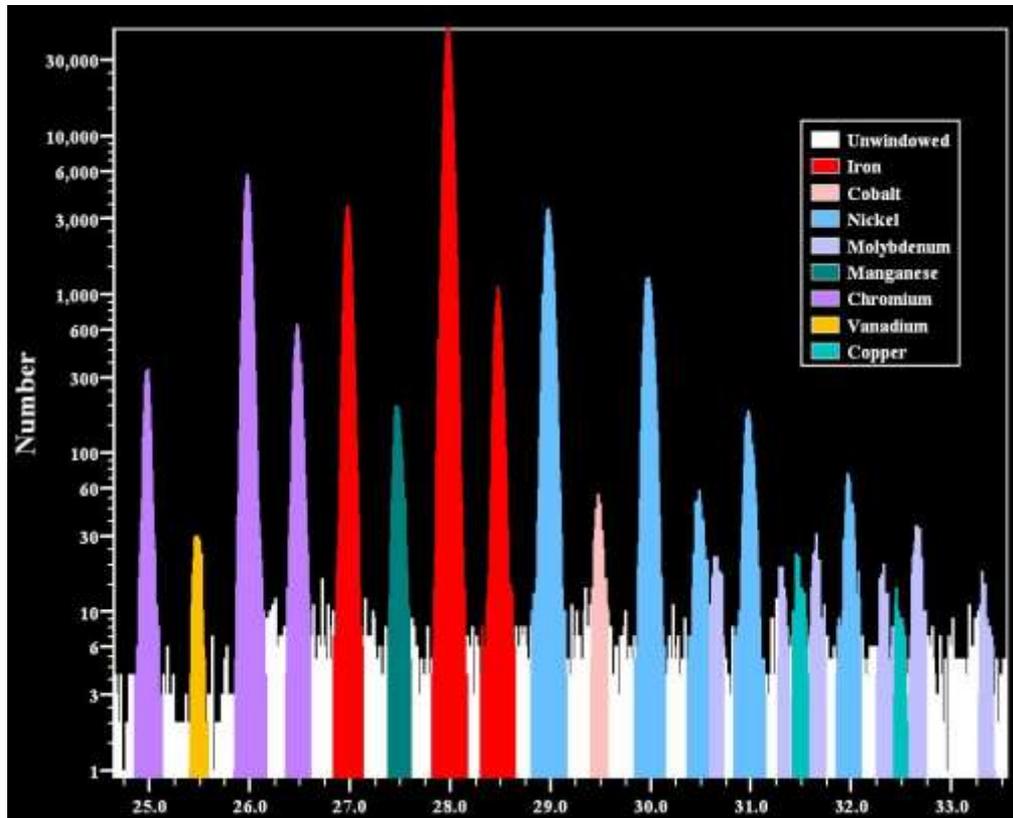
Die Präparation der benötigten Spitzen erfolgt mit Hilfe des elektrochemisches Ätzen in zwei Stufen. Der Erfolg der Präparation wird mit dem REM oder TEM kontrolliert. (siehe Abb.1)



Alternative: Ionendünner

# Ergebnisse von Atomsondenmessungen

## Massenspektrum



Fe

53.9396	5.8%
55.9349	91.72%
56.9354	2.1%
57.9333	0.28%

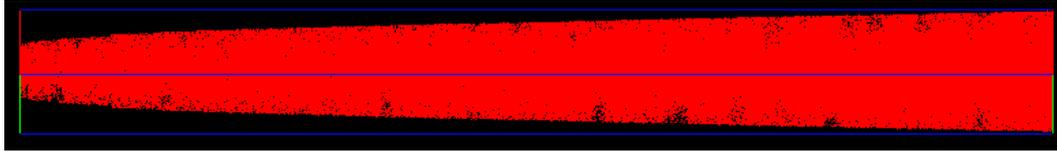
Ni

57.9353	68.27%
59.9306	26.10%
60.9311	1.13%
61.9283	3.59%
63.9280	0.91%

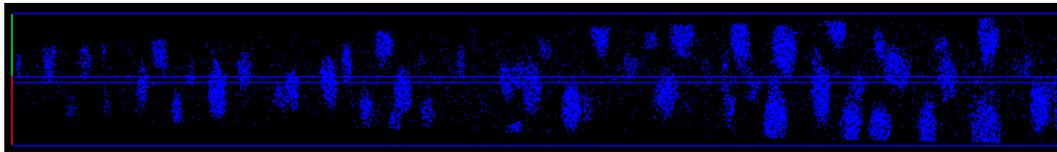
Massenspektrum eines korrosionsbeständigen Maragingstahles (Fe-12,8at.%Cr-8,52at.%Ni-3,4at.%Al-0,11at.%C). Die Massenauflösung bei diesem Gerät liegt bei  $m/\Delta m > 600$ .

# Ergebnisse von Atomsondenmessungen

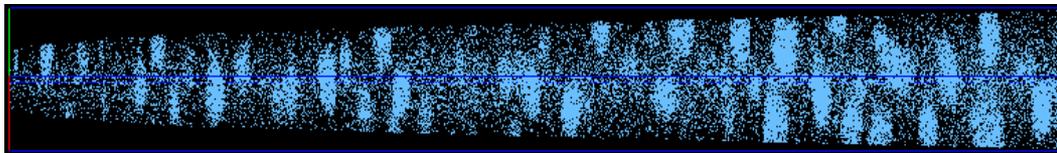
symbolisch: Spitze



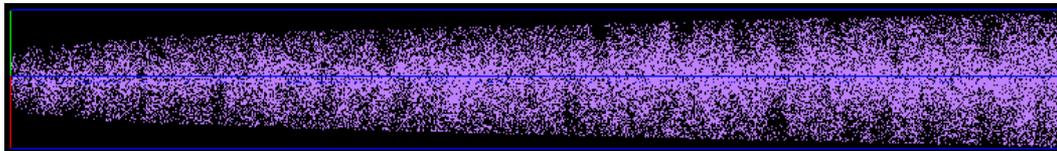
Eisen



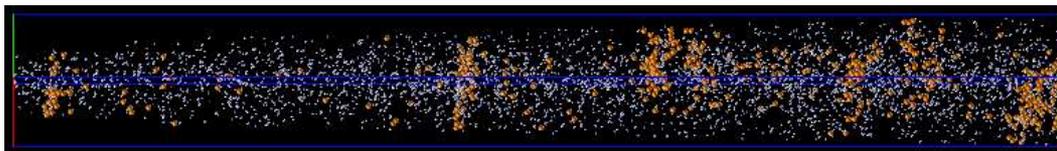
Aluminium



Nickel



Chrom



Kohlenstoff

Elementverteilungen  
des gemessenen  
Probenvolumen

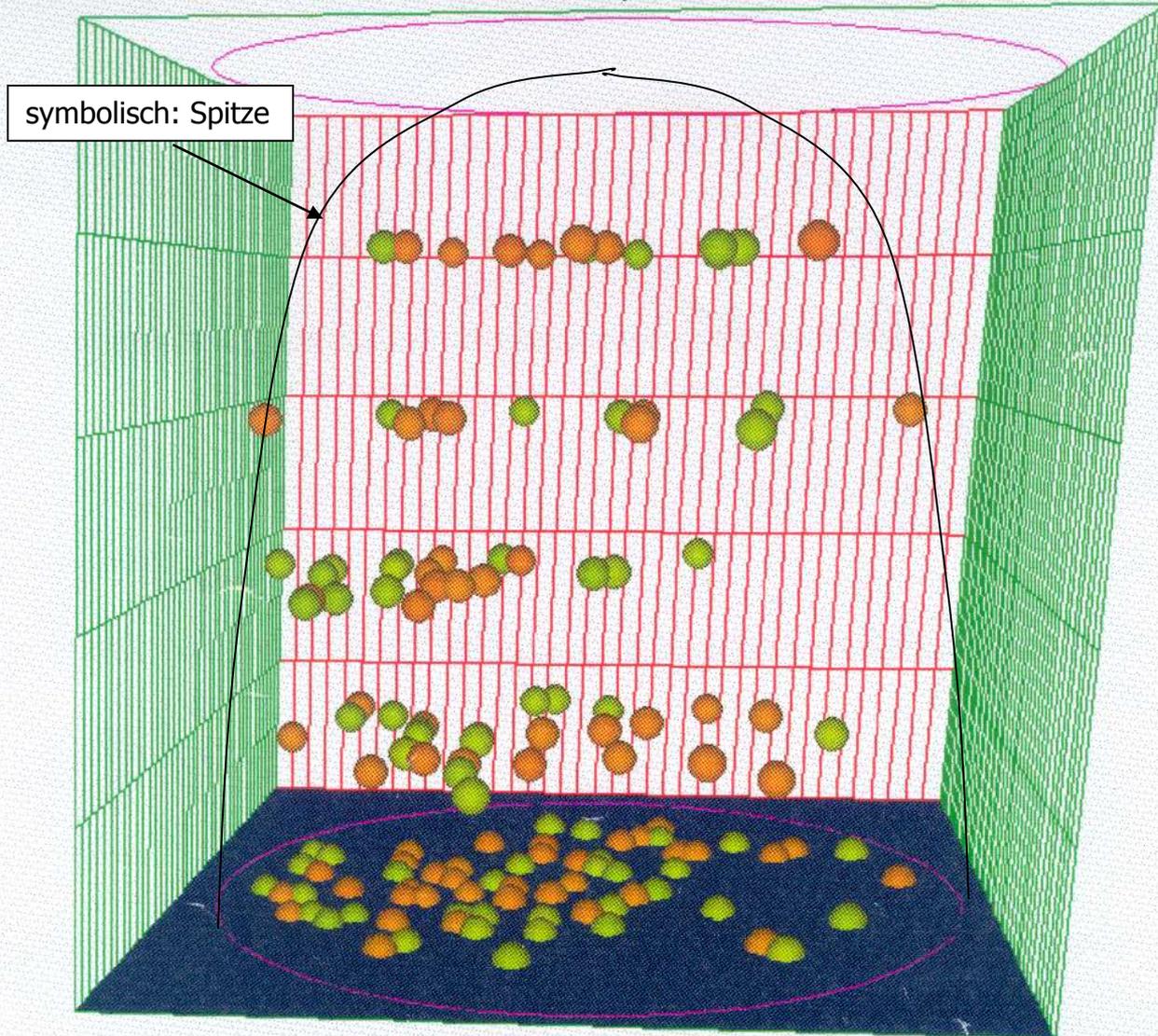
Korrelation!

Bei diesen Aufnahmen handelt es sich ebenfalls um den korrosionsbeständigen Maragingstahl, (Fe-12,8at.%Cr-8,52at.%Ni-3,4at.%Al-0,11at.%C), welcher bei 525°C für 10 Stunden ausgelagert wurde.

Computergenerierter Längsschnitt durch Spitze

# Pt4Cu nach Wärmebehandlung

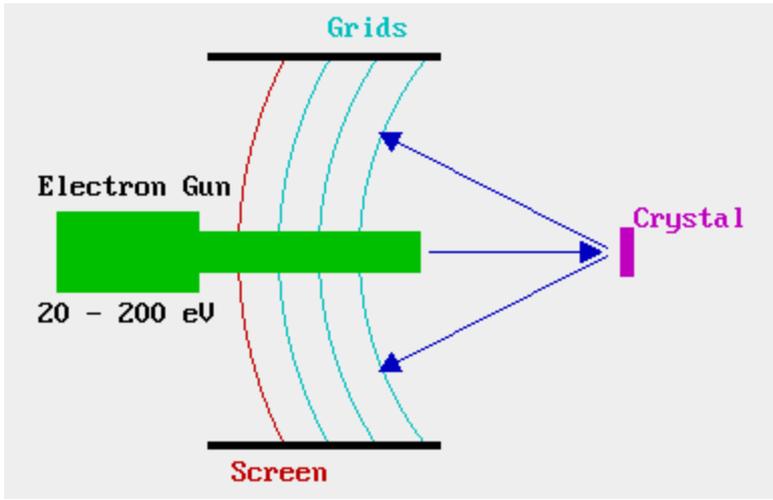
Cu<sup>+</sup>, Cu<sup>++</sup>



symbolisch: Spitze

Oberfläche

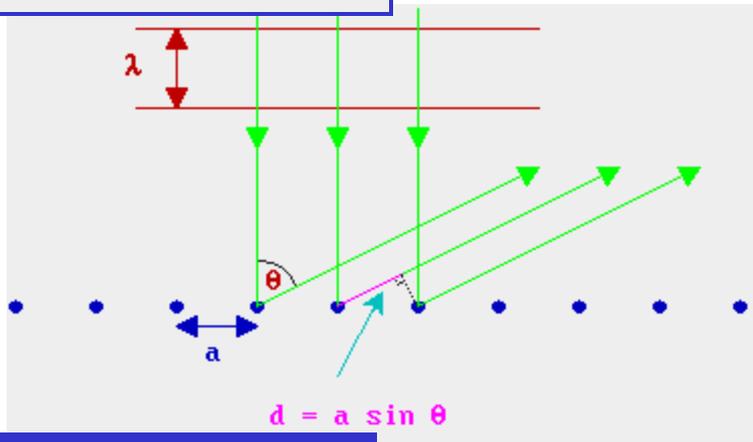
# LEED - Low Energy Electron Diffraction



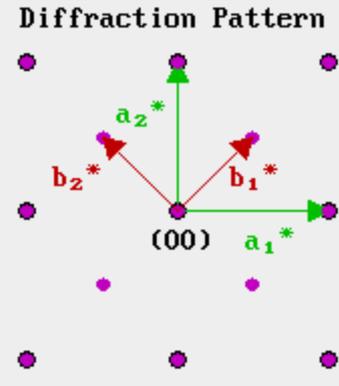
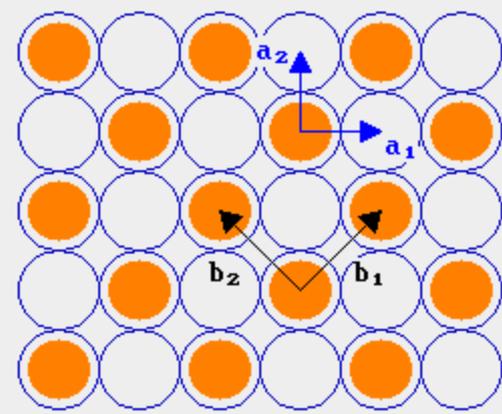
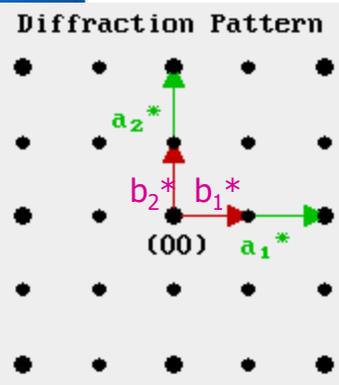
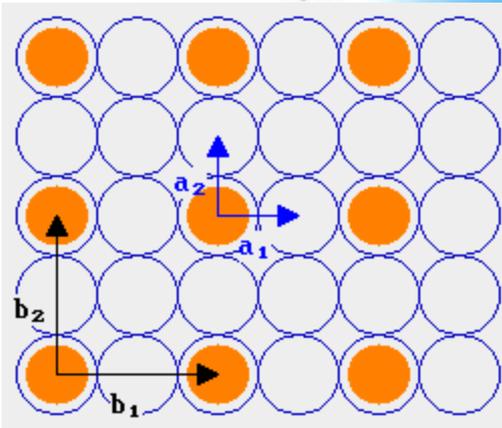
Grundgitter  
Übergitter

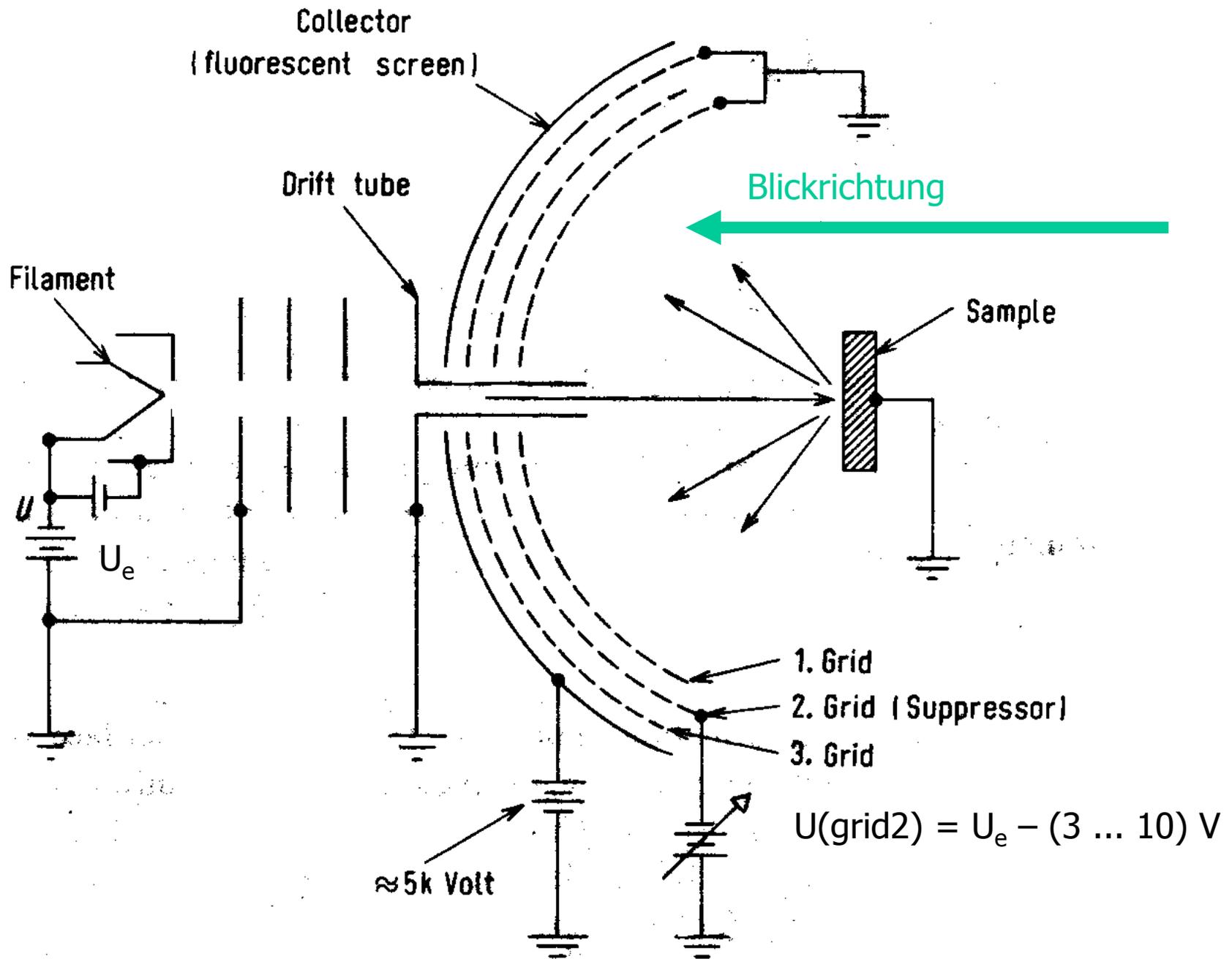
The wavelength of the electrons is given by the de Broglie relation:  
Wavelength,  $\lambda = h / p$  (where  $p$  - electron momentum)

Wavelength,  $\lambda = h / (2m.e.V)^{1/2}$



$d = a \sin \theta = n \cdot \lambda$





## Beispiele

a

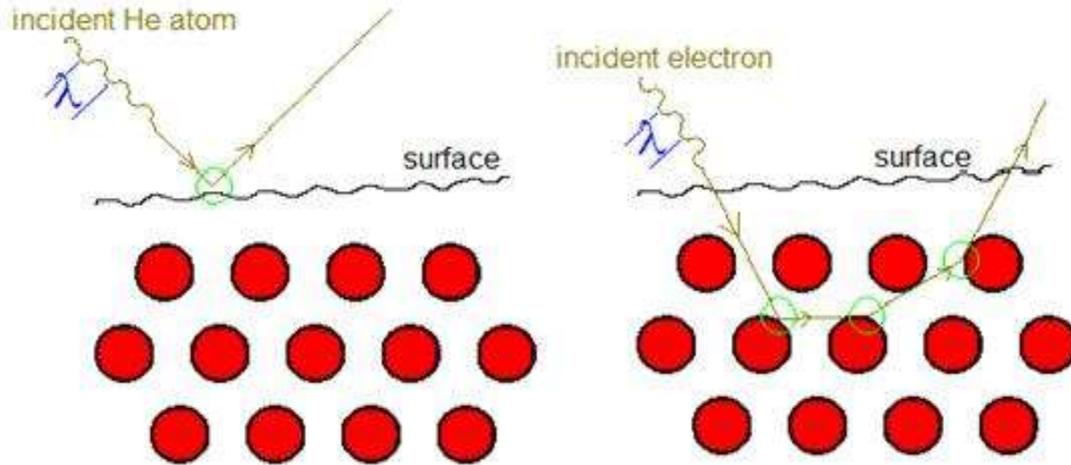


b



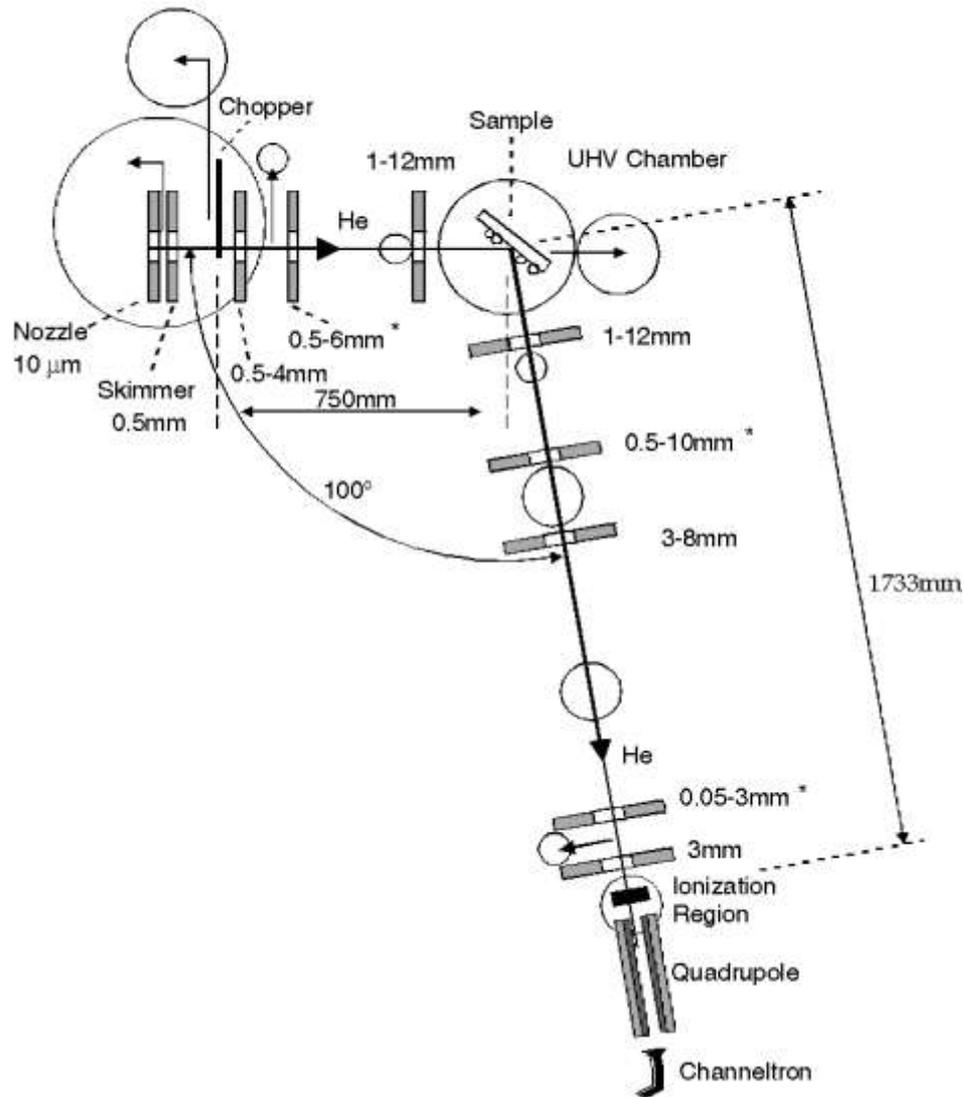
LEED images for sulfur adsorbed on Pd(111). A:  $(\sqrt{3} \times \sqrt{3})R30$  structure observed before heating and reconstruction, B :  $(\sqrt{7} \times \sqrt{7})R19.1$  surface reconstruction observed after heating.

# Helium atom scattering

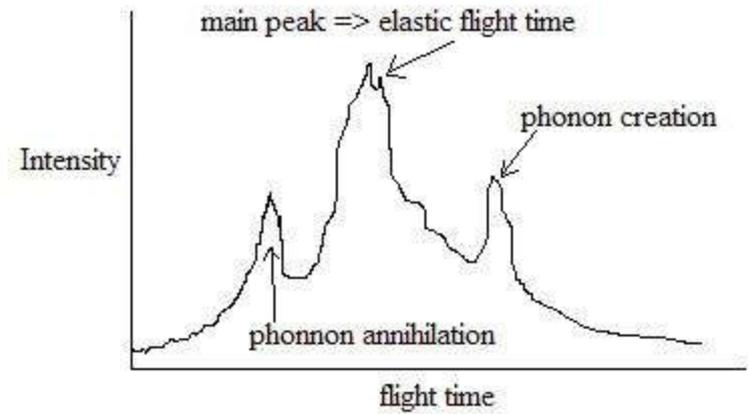


There are several advantages to using helium atoms as compared with x-rays, neutrons, and electrons to probe a surface and study its structures and phonon dynamics. As mentioned previously, the lightweight helium atoms at thermal energies do not penetrate into the bulk of the material being studied. This means that in addition to being strictly surface-sensitive they are truly non-destructive to the sample. Their de Broglie wavelength is also on the order of the interatomic spacing of materials, making them ideal probing particles. Since they are neutral, helium atoms are insensitive to surface charges. As a noble gas, the helium atoms are chemically inert. When used at thermal energies, as is the usual scenario, the helium atomic beam is an inert probe (chemically, electrically, magnetically, and mechanically). It is therefore capable of studying the surface structure and dynamics of a wide variety of materials, including those with reactive or metastable surfaces. A helium atom beam can even probe surfaces in the presence of electromagnetic fields and during ultra-high vacuum surface processing without interfering with the ongoing process.

# Messprinzip



# Ein Resultat



# *Photoelectron Diffraction Pattern* *Polar Scan*

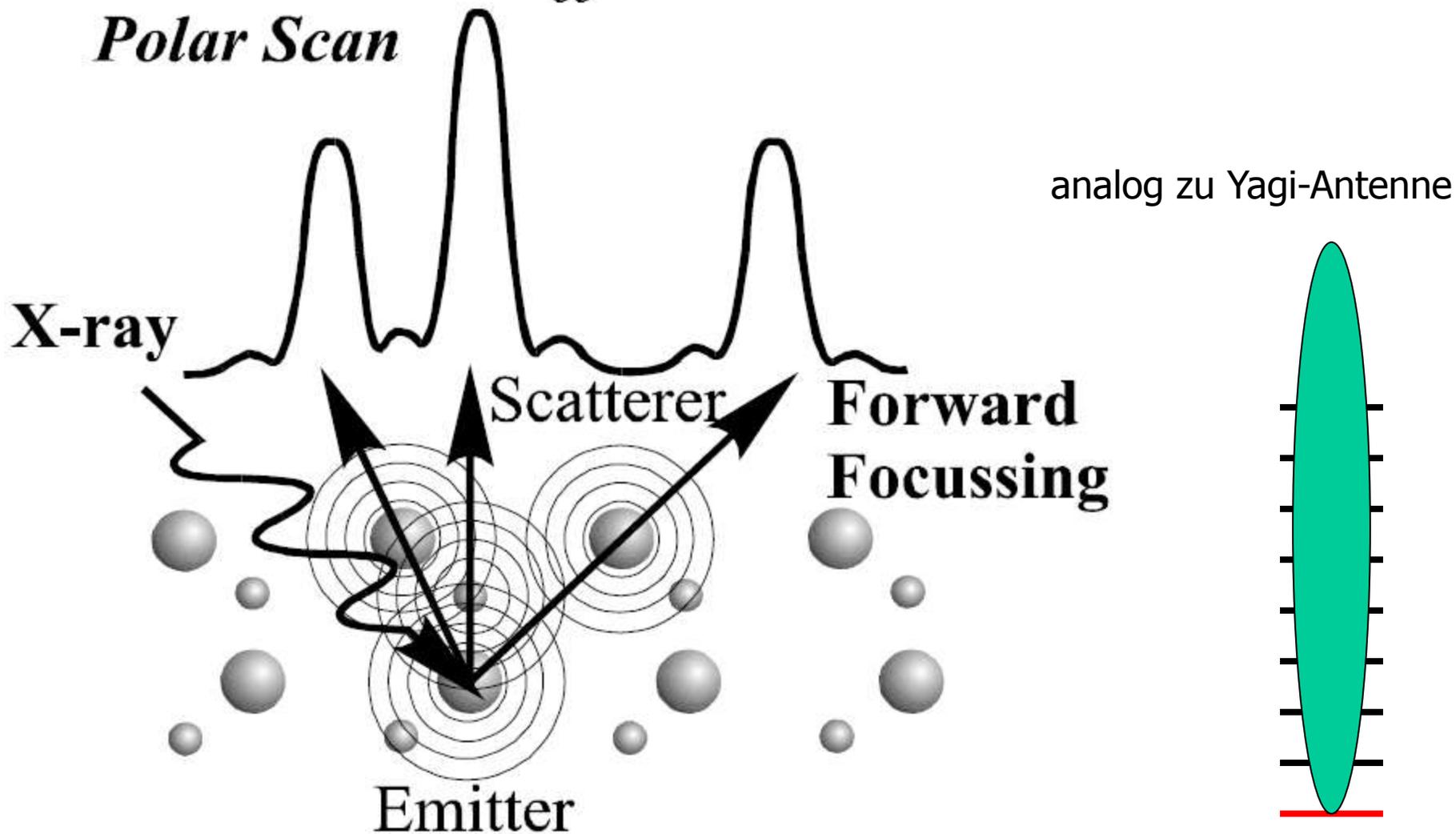
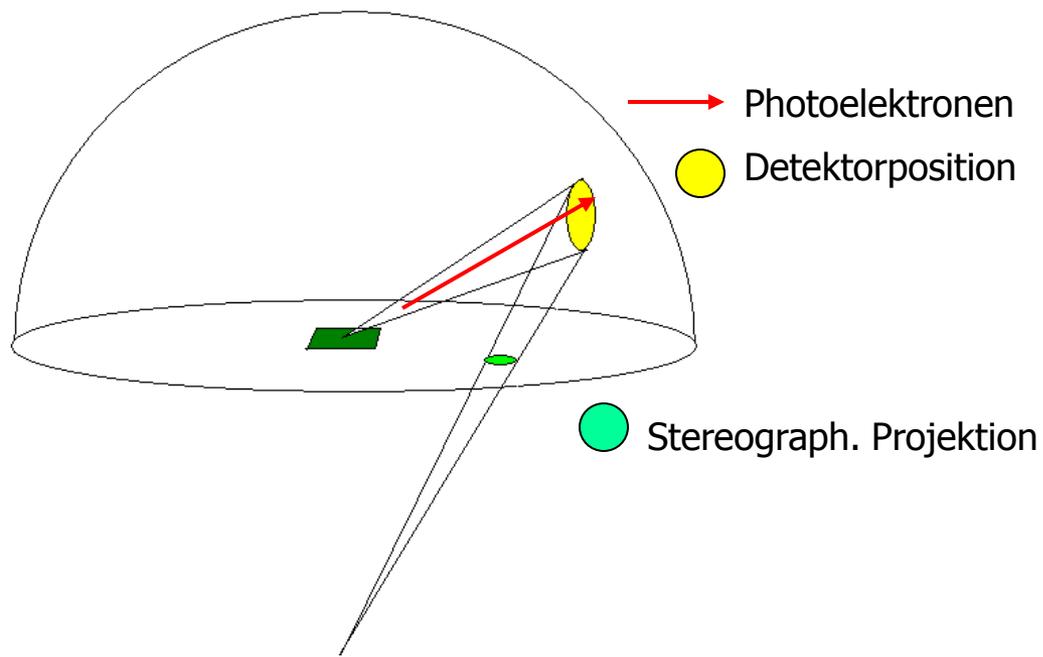
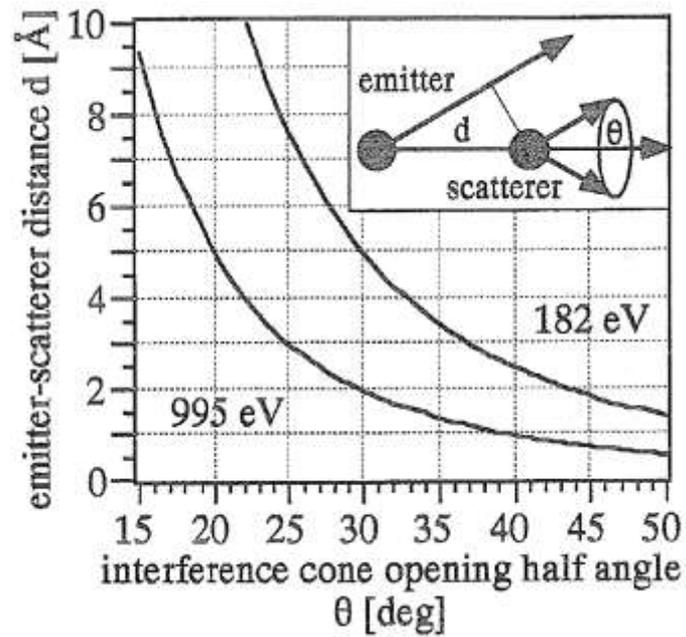


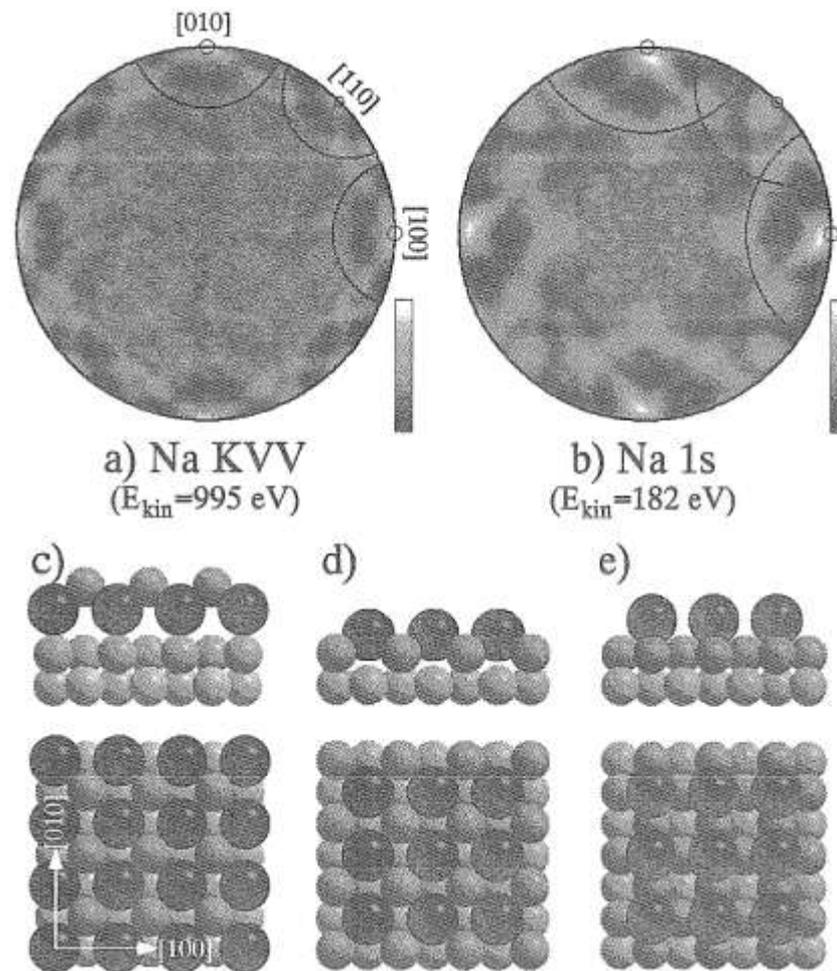
Fig. 1  
Principle of photoelectron diffraction

# XPD – X-Ray Photoelectron Diffraction



Direct structural information from X-ray photoelectron diffraction: intermixing and on-surface adsorption of Na on Al surfaces

R. Fasel \*, P. Aebi, J. Osterwalder, L. Schlapbach  
Surface Science 331–333 (1995) 80–87



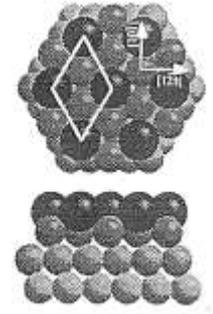
# XPD – X-Ray Photoelectron Diffraction

Table 1  
Quantitative results from the geometrical analysis of the  $c(2 \times 2)$ -Na/Al(001) and  $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na/Al(111) diffraction patterns

Structure	Symmetry	NN directions	$\theta_{NN}$	NN distance (Å)	NNN directions	$\theta_{NNN}$	NNN distance (Å)
$c(2 \times 2)$ -Na/Al(001)	4	$\langle 100 \rangle$	$33 \pm 1^\circ$	$4.0 \pm 0.3$	$\langle 110 \rangle$	$28.5 \pm 1^\circ$	$5.6 \pm 0.5$
$(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na/Al(111)	6	$\langle 1\bar{2}1 \rangle$	$30.5 \pm 1^\circ$	$4.8 \pm 0.4$	$\langle 1\bar{1}0 \rangle$	$23 \pm 1^\circ$	$9.2 \pm 0.9$

The in-plane NN and NNN distances are calculated from the respective interference cone opening half angles  $\theta_{NN}$  and  $\theta_{NNN}$  (Eq. (1)).

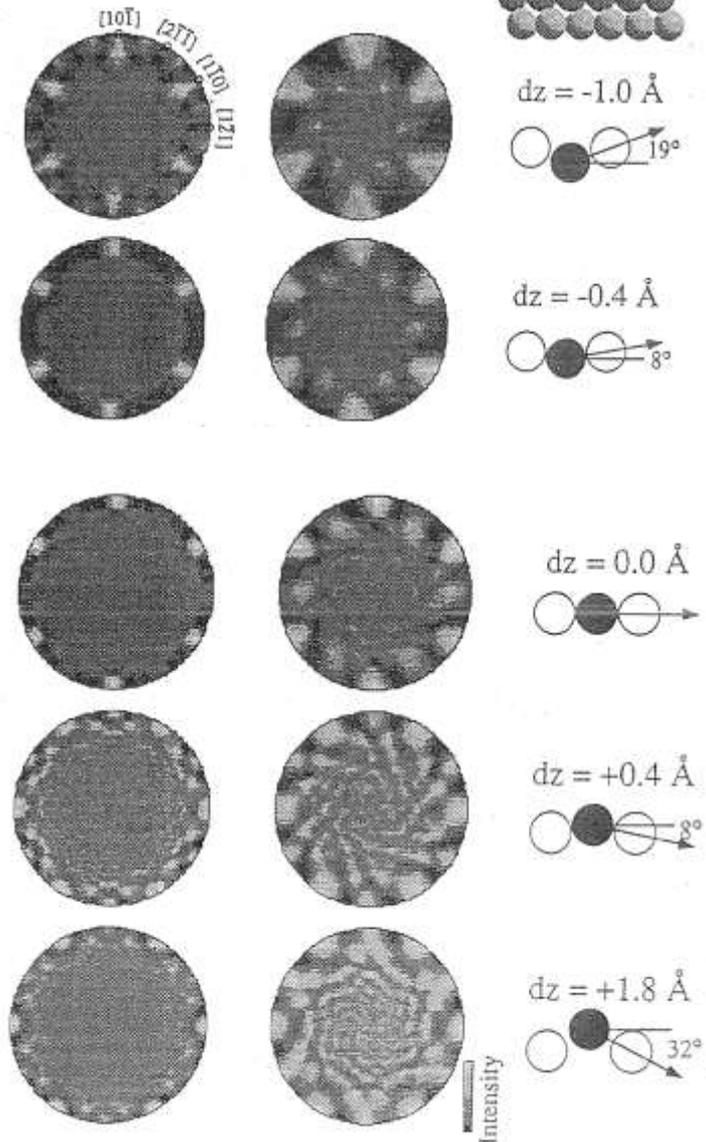
$(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na/Al(111)



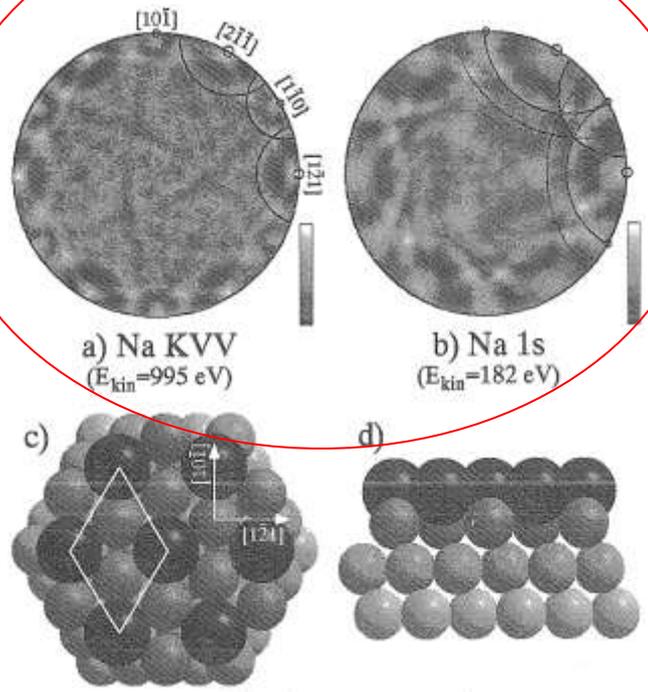
SSC calculations

Na KVV  
( $E_{kin}=1007$  eV)

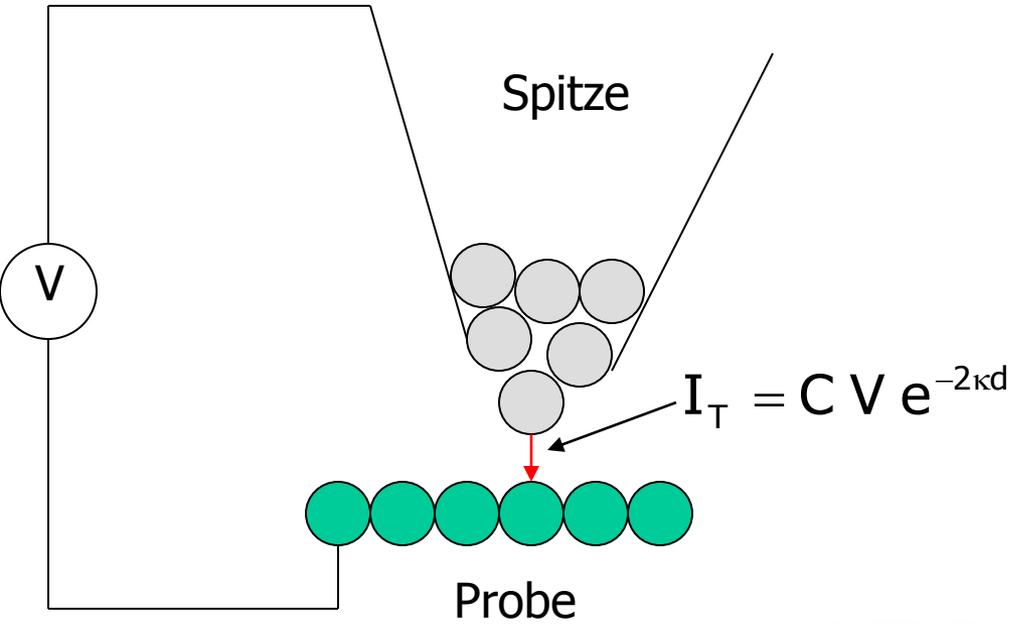
Na 1s  
( $E_{kin}=182$  eV)



## Experiment



# STM - Scanning Tunneling Microscope - Rastertunnelmikroskop

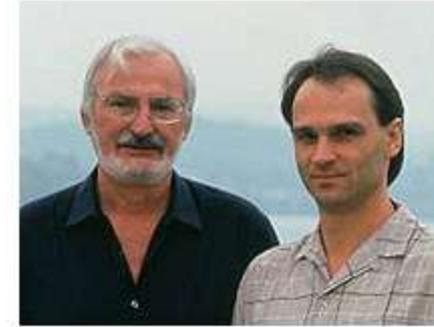


Probleme:

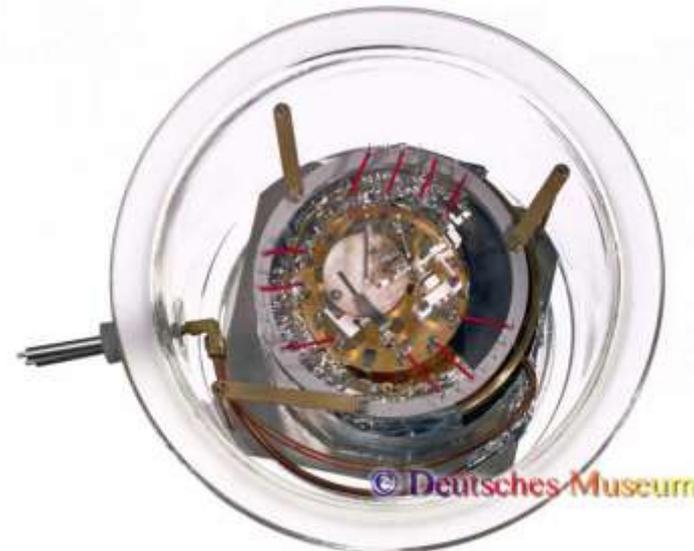
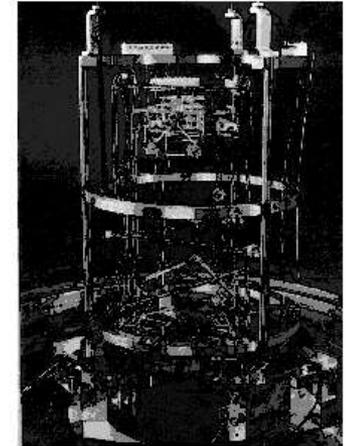
Tunnelstrom pA bis nA

Vibrationen

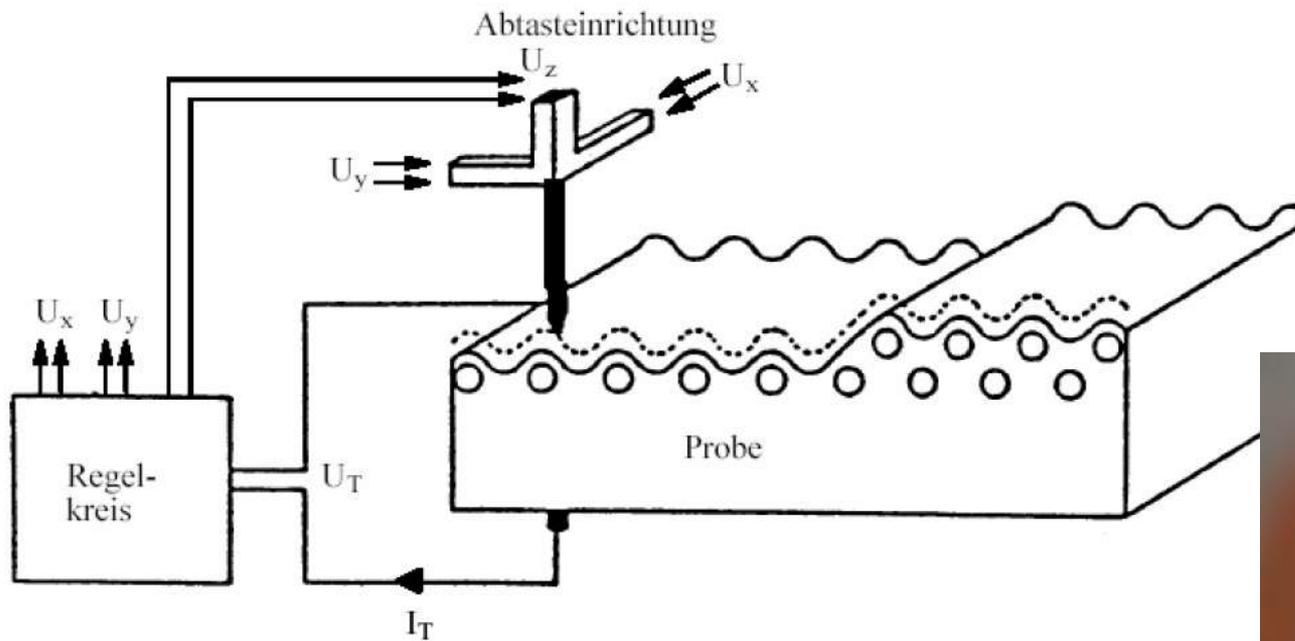
Nobelpreis für die Erfinder



Heinrich Rohrer (links) und Gerd Binnig



# STM - Scanning Tunneling Microscope - Rastertunnelmikroskop



2 Möglichkeiten:

Konstanter Abstand Spitze-Probe

Konstanter Tunnelstrom

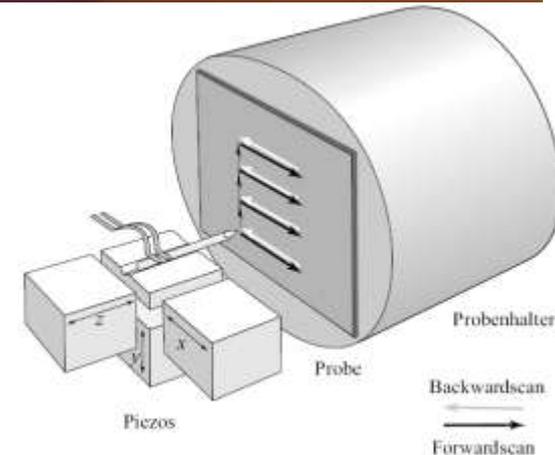
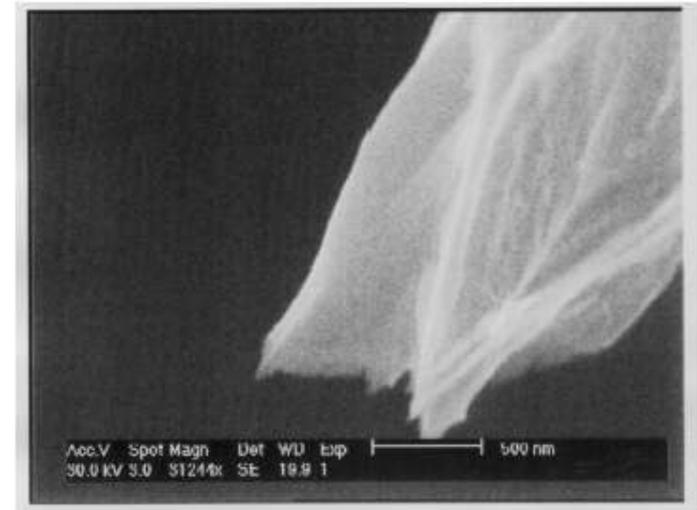
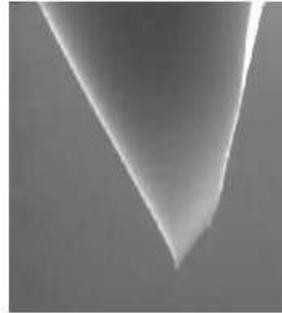


Abbildung 3: Scan-Bewegung

# STM - Scanning Tunneling Microscope - Rastertunnelmikroskop

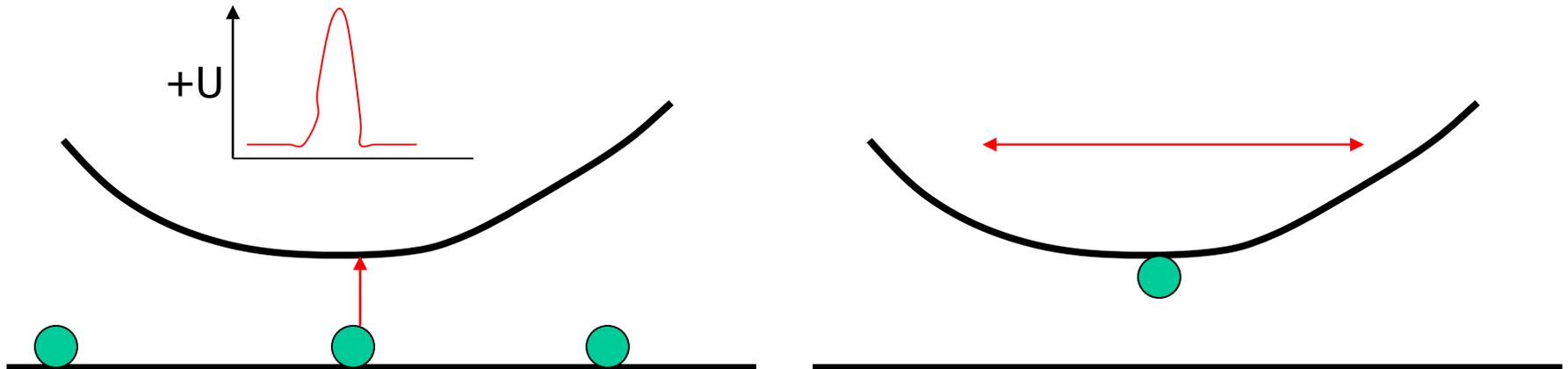
Spitze:

atomar scharf (ionengedünnt)



*Bild einer (mäßig guten) RTM Spitze*

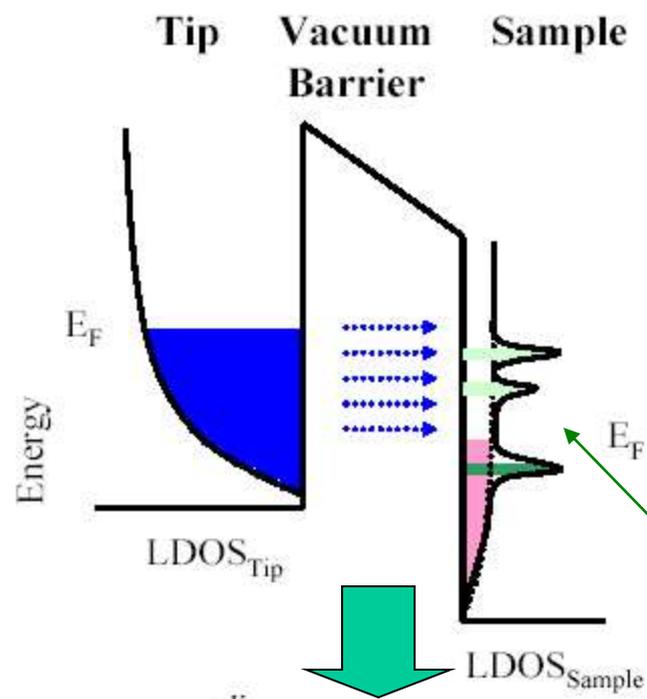
stumpf mit adsorbiertem Atom



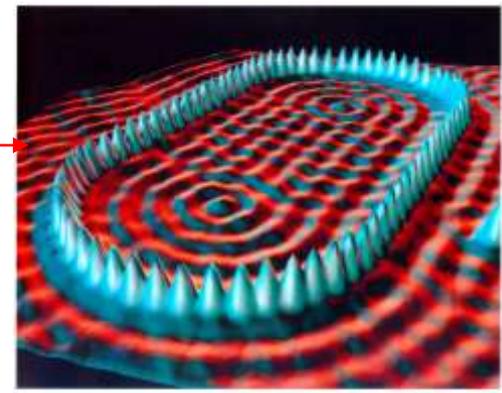
# STM - Scanning Tunneling Microscope - Rastertunnelmikroskop

## Spektroskopie:

Abbildung:  
z-Masstab  
stark überhöht!



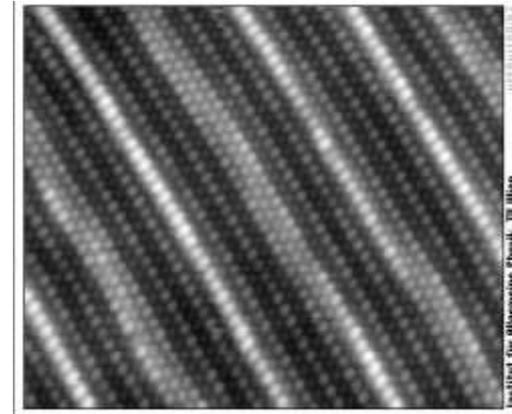
Das STM bildet die Elektronendichte nahe der Oberfläche ab!  
Quantenmechan. Interferenzen in und um den „corral“



Quantum corral

$$I \sim e^{-\kappa z} \int_0^{eV} dE \cdot LDOS_{Sample}(E_F + E)$$

$$\left. \frac{dI}{dV} \right|_V \sim LDOS_{Sample}(E_F + eV)$$



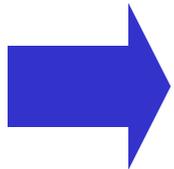
Surface reconstruction

Schwäche des Rastertunnelmikroskops:

Probe muss (minimal) elektrisch leitfähig sein

Atomare Auflösung braucht UHV

STM funktioniert *auch* in Luft, sogar in isolierenden Flüssigkeiten – aber mit geringerer Auflösung



AFM

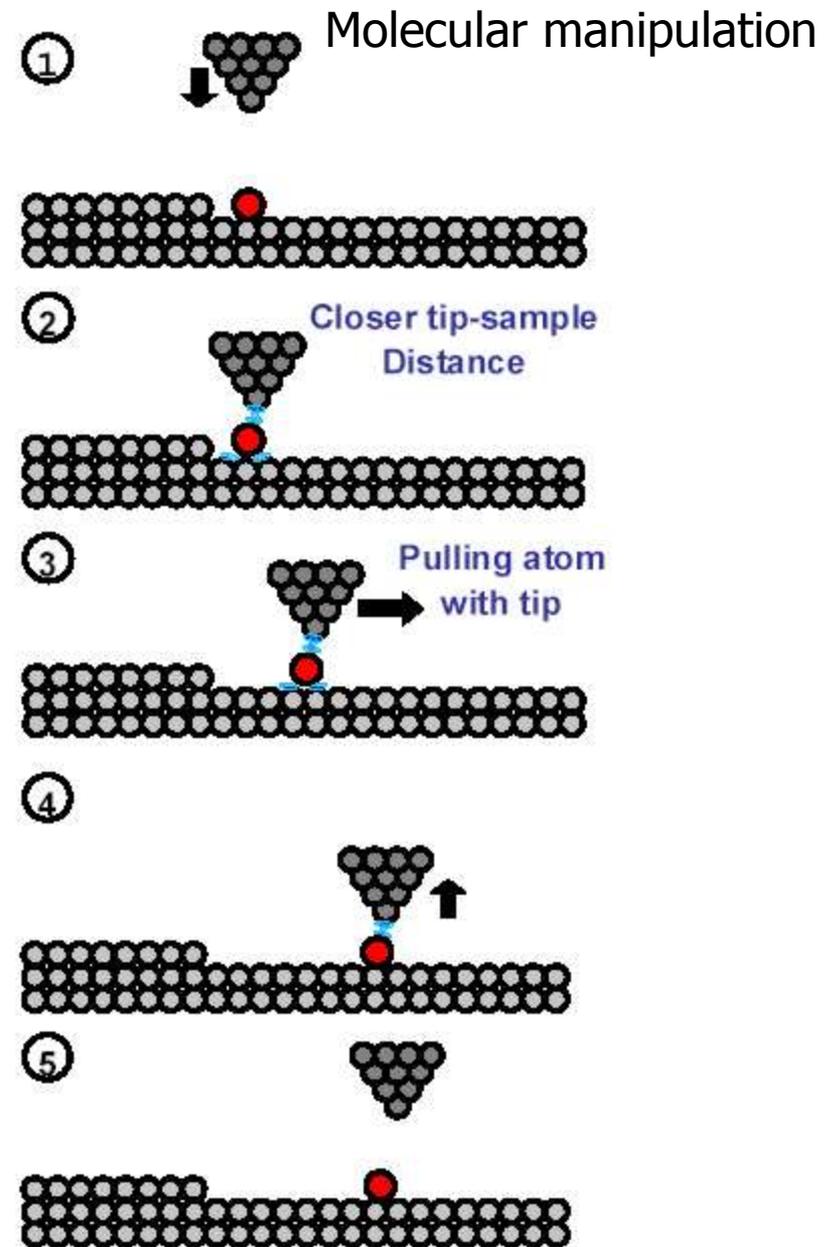
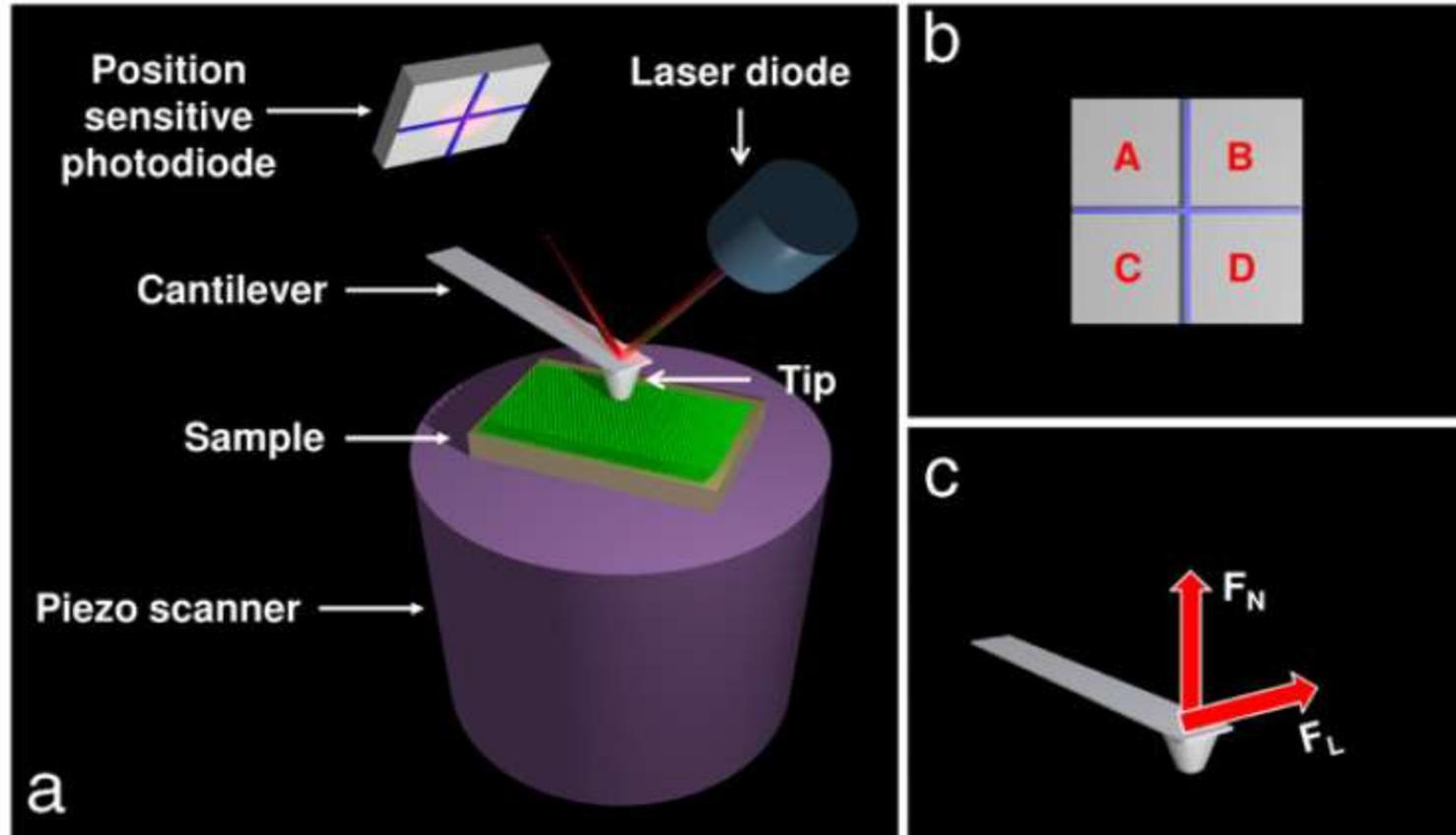


Figure 5: Schematic diagram of molecular manipulation with the STM

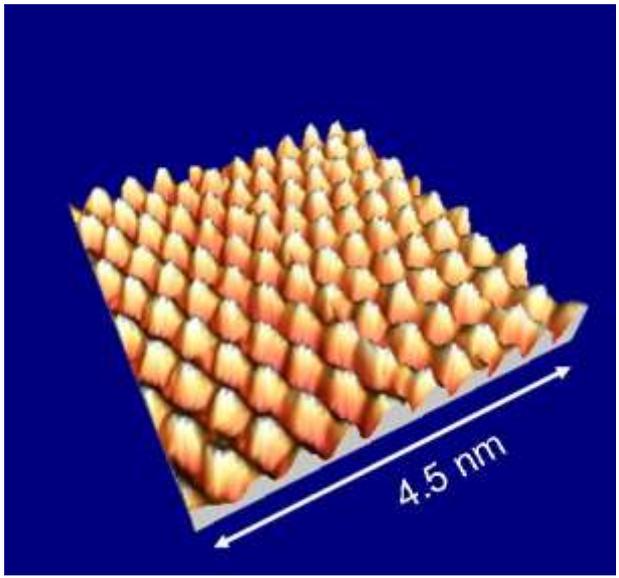
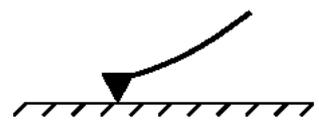
# AFM – Atomic Force Microscope - Rasterkraftmikroskop



Schematic representation of (a) the static mode AFM operation, (b) a four-quadrant position sensitive photodiode, and (c) forces exerted on the cantilever-tip assembly by the sample surface.

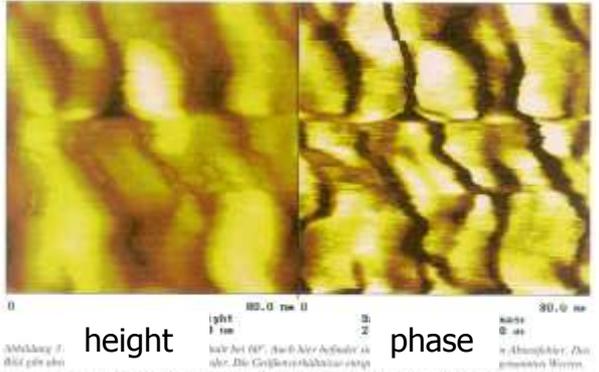
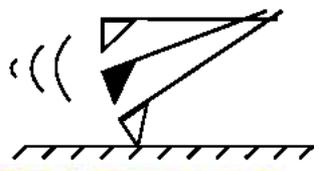
# AFM – Atomic Force Microscope - Rasterkraftmikroskop

Contact mode

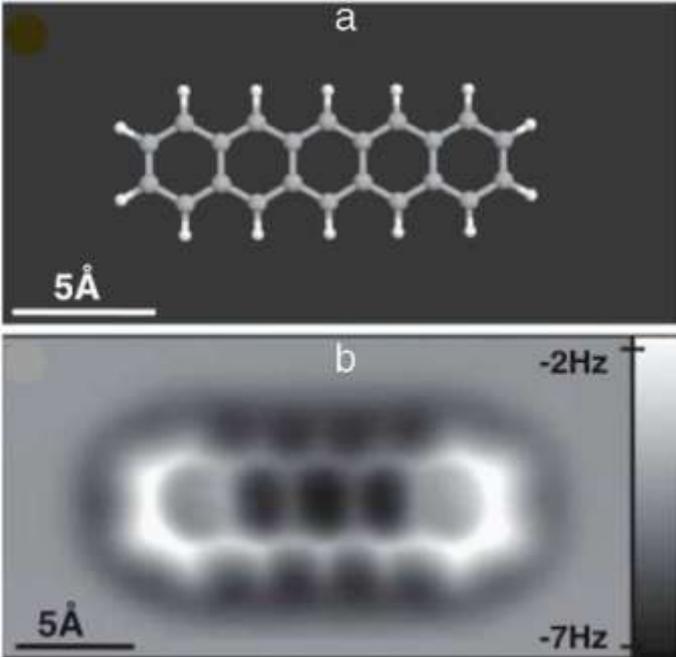


NaCl Oberfläche, atomare Auflösung

Tapping mode



Hein-Weisser,  
Mineralplättchen,  
AFM



Ball-and-stick model of the pentacene molecule.  
FM-AFM images of pentacene.

Investigation of organic films by atomic force microscopy: Structural, nanotribological and electrical properties  
Yabing Qi  
Surface Science Reports 66 (2011) 379–393

# AFM – Atomic Force Microscope - Rasterkraftmikroskop

Laterale Auflösung durch Spitzenradius und –aspect ratio gegeben, ->  
Spezialität: CNT als „Spitze“

*L. Guo et al. / Physica E 27 (2005) 240–244*

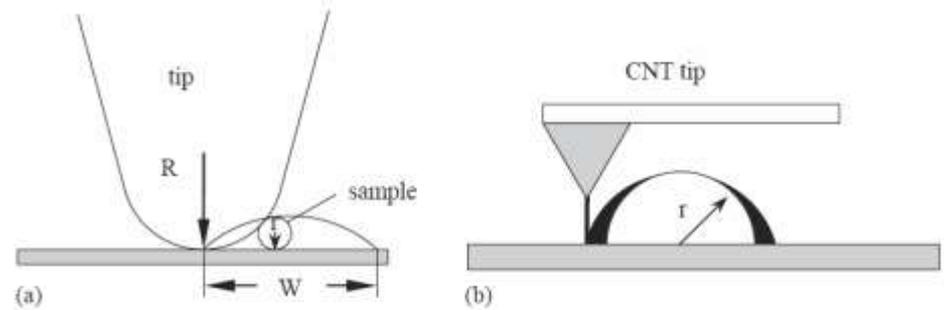
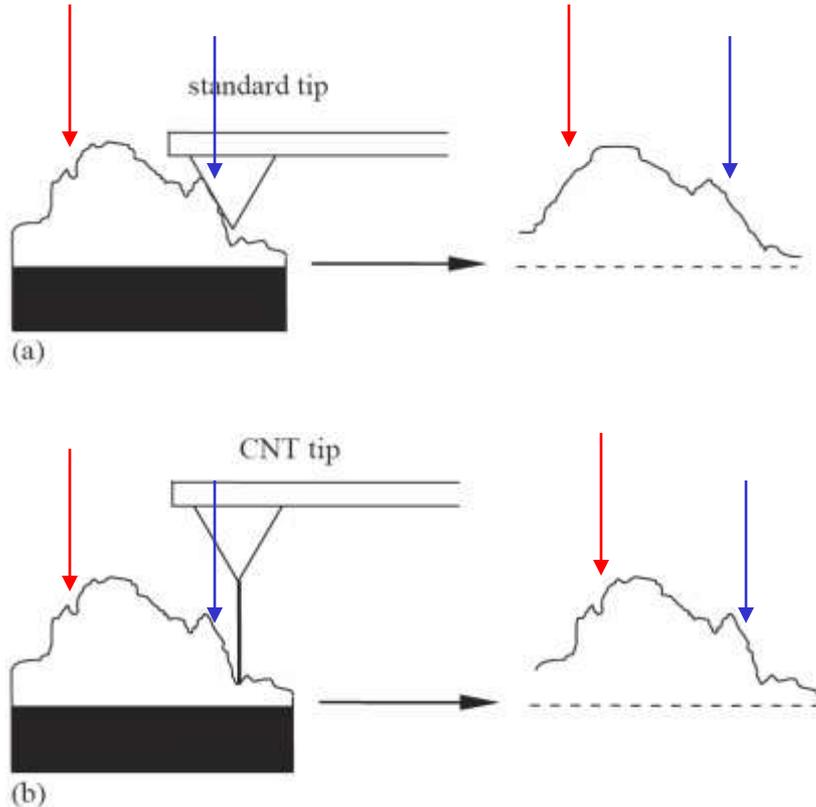


Fig. 4. Standard (a) and CNT tip (b) deconvolution model.

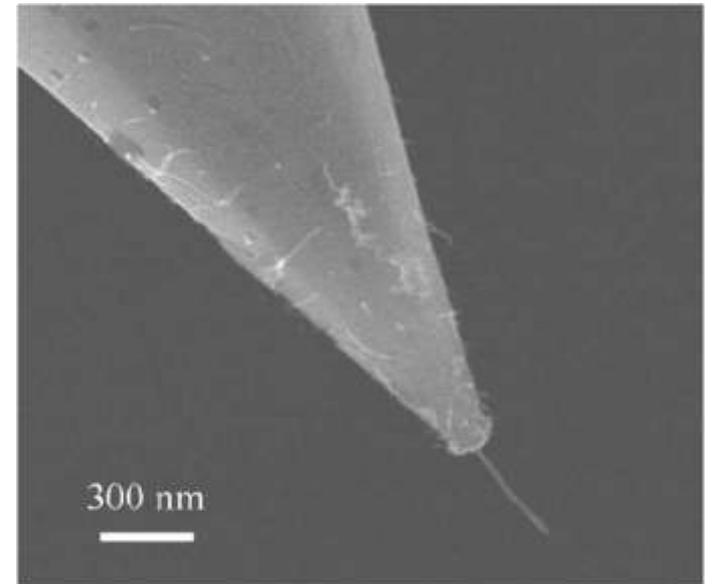
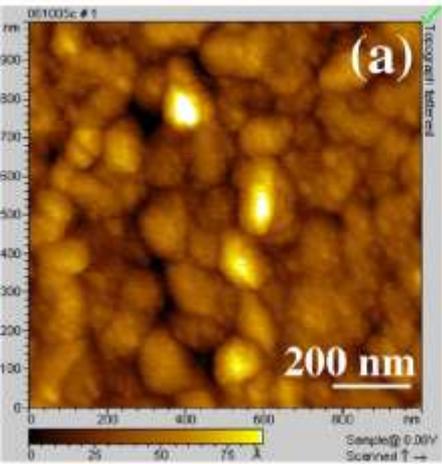


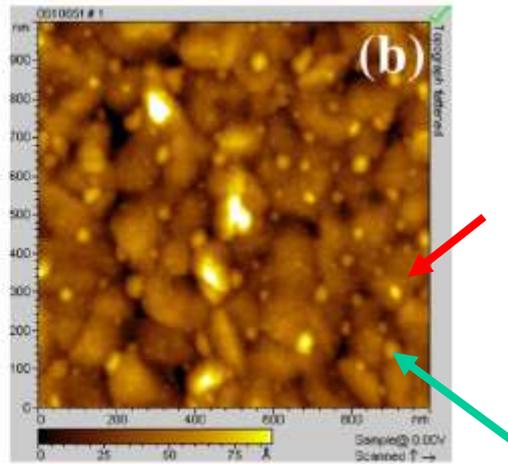
Fig. 1. SEM image of a CNT tip attached to a standard AFM

# Tapping mode AFM – Abbildung von Wassertropfen: Al<sub>2</sub>O<sub>3</sub> in Luft

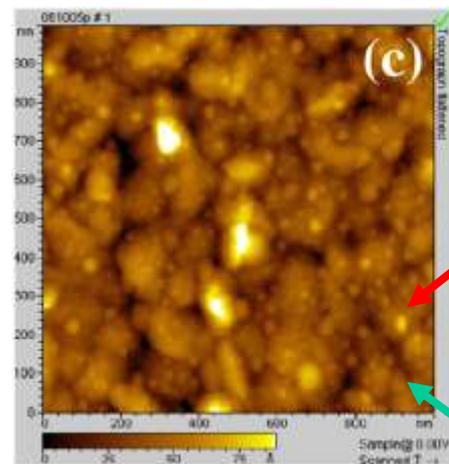
*N. Misserl, R.G. Copeland / Applied Surface Science 254 (2008) 1972–1976*



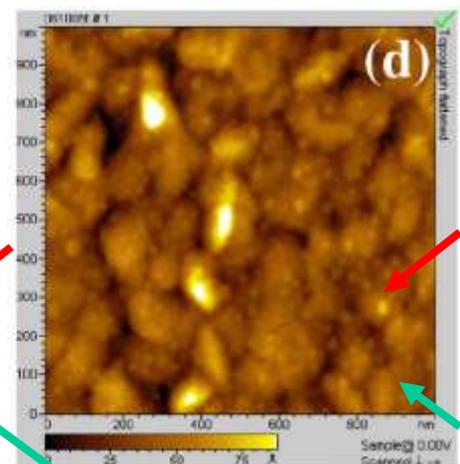
RH 54%



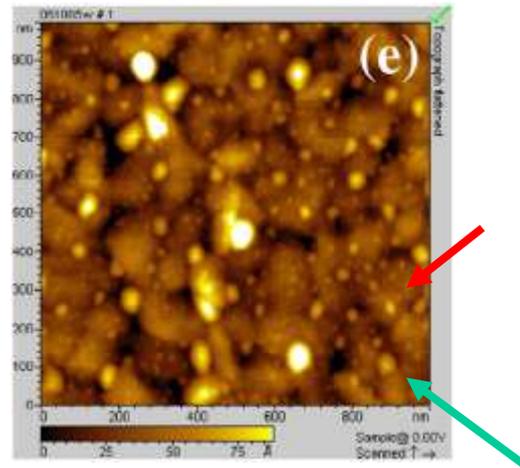
RH 77%



RH 53%



RH 7%



Substrat: Al<sub>2</sub>O<sub>3</sub> in Luft

RH 78%

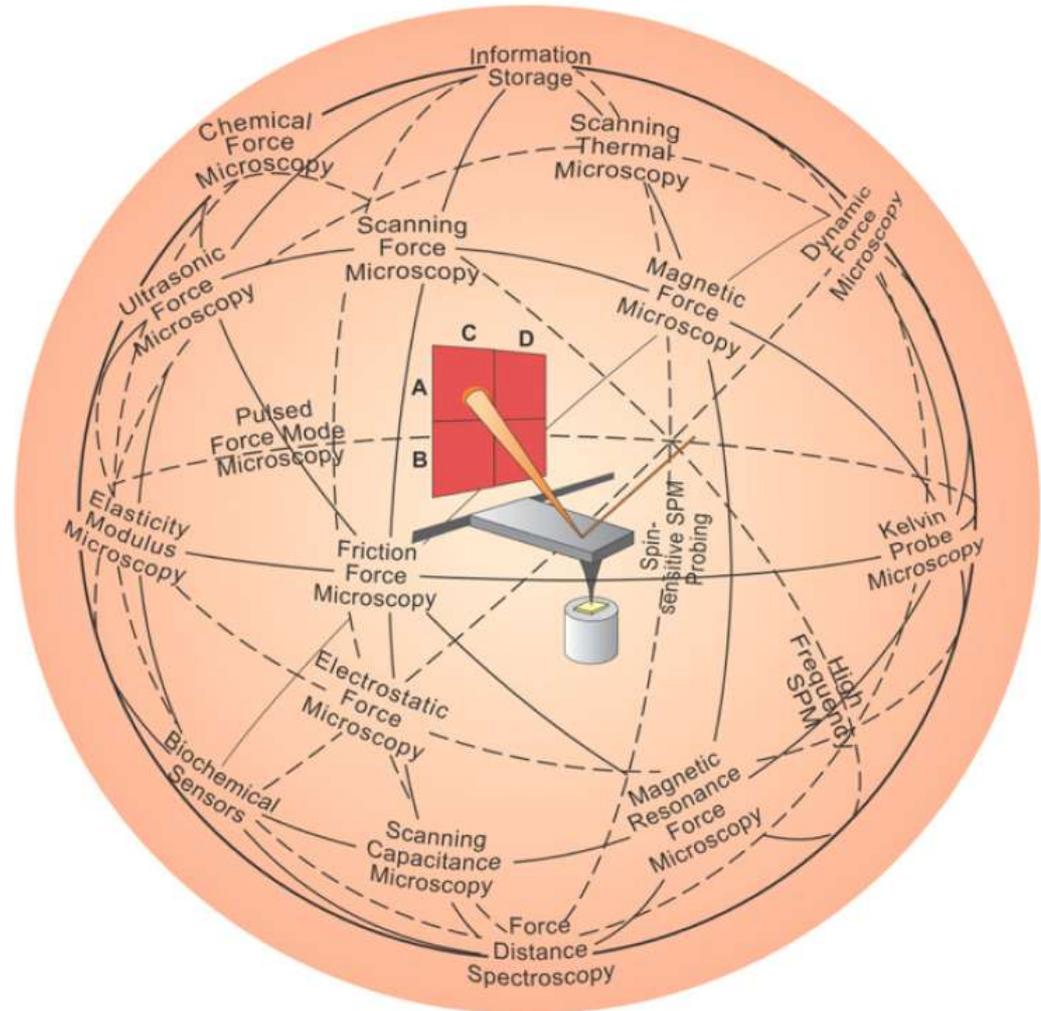
# AFM – Atomic Force Microscope - Rasterkraftmikroskop

## Weitere Betriebsarten:

Investigation of organic films by atomic force microscopy: Structural, nanotribological and electrical properties

Yabing Qi

Surface Science Reports 66 (2011) 379–393

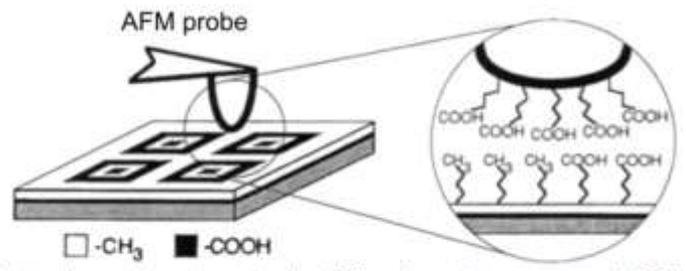


Offspring techniques inspired by AFM.

# AFM – Atomic Force Microscope - Rasterkraftmikroskop

Weitere Betriebsarten:

Lateralkraftmessung

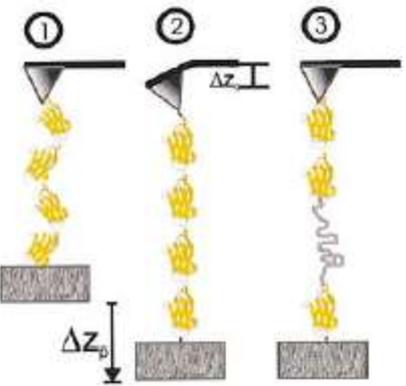


Schematic representation of using CFM to investigate a patterned SAM sample surface.

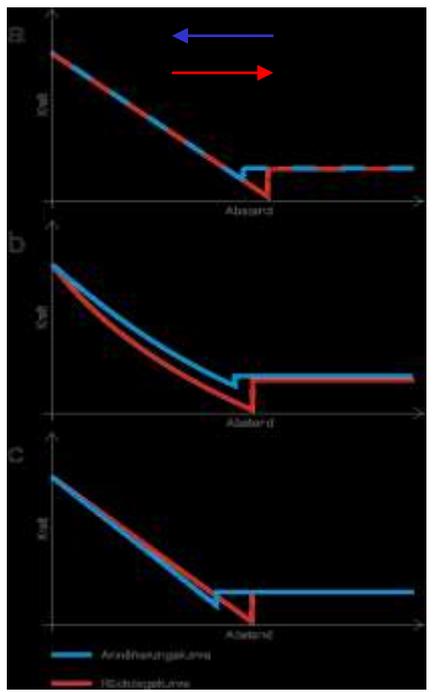
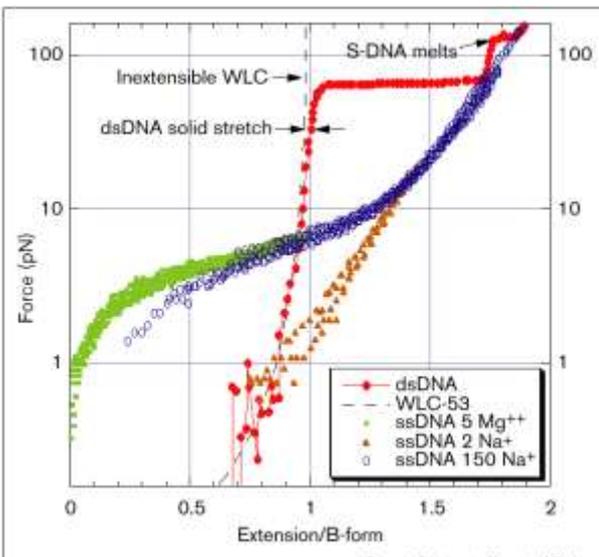
CFM - Chemical Force Microscope

Mechanische Spektroskopie

Single molecule force spectroscopy



Titin, Tenascin, ..



# Weitere Betriebsarten: MFM - Magnetic Force Microscope

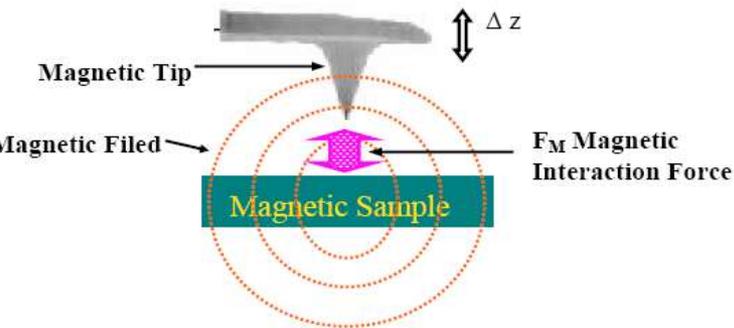


Figure 3.2.1. The operation principle of a MFM

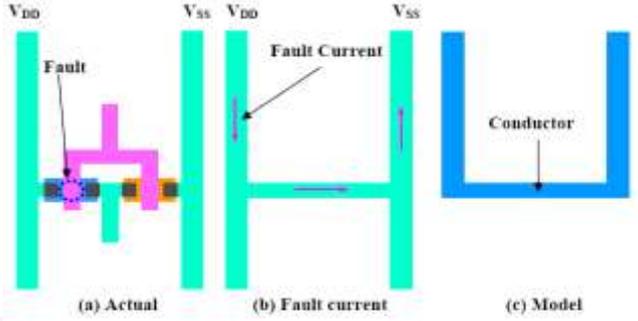
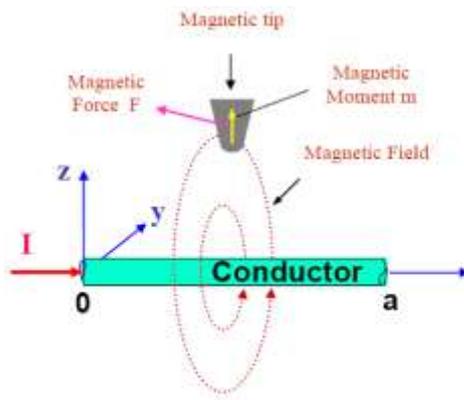
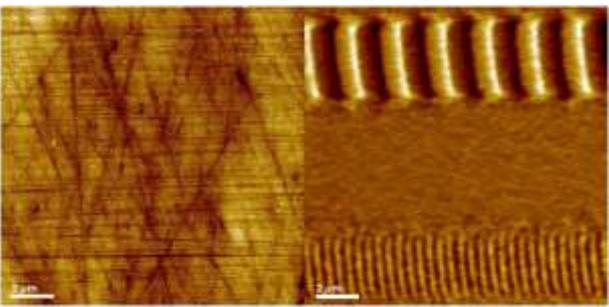


Figure 5.1.1. An experimental model for IC fault. (a) A CMOS inverter has a fault that produces the fault current in (b). (c) An experimental model used for sample design.



Experimental HD

bar = 2  $\mu m$

Possible resolution: ~ 10 nm

Magnetic interaction between the tip and the current-carrying conductor.

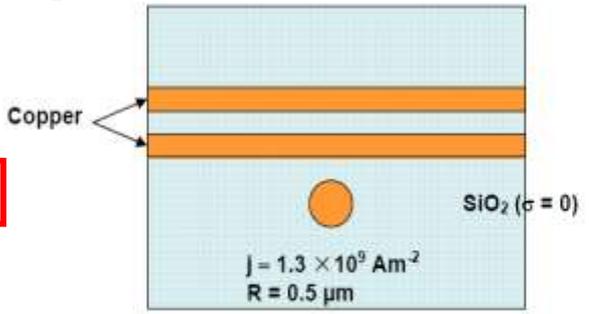
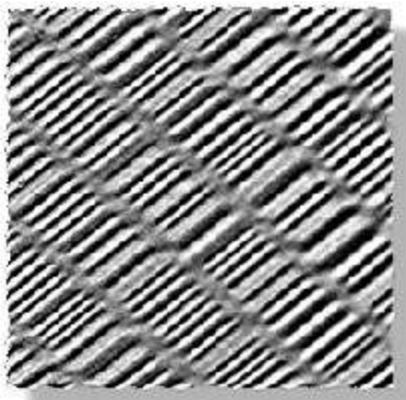
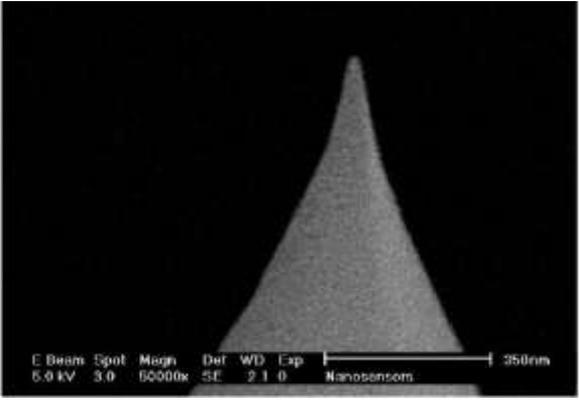


Figure 3.7.1. A current carrying conductor is buried under two copper layers. The conductor has a radius of 0.5  $\mu m$  and each copper has a thickness of 0.5  $\mu m$ .

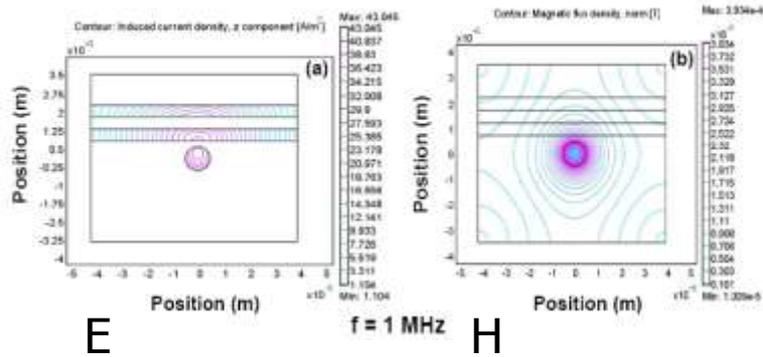


MFM image showing the bits of a hard disk.

Field of view 30  $\mu m$



MFM tip, bar=350nm



# Weitere Betriebsarten: SNOM – Scanning Near-Field Optical Microscopy

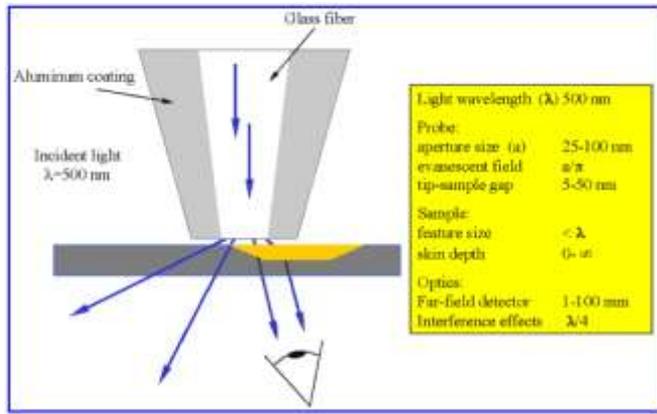


FIGURE 3: Schematic of near-field optical microscopy.

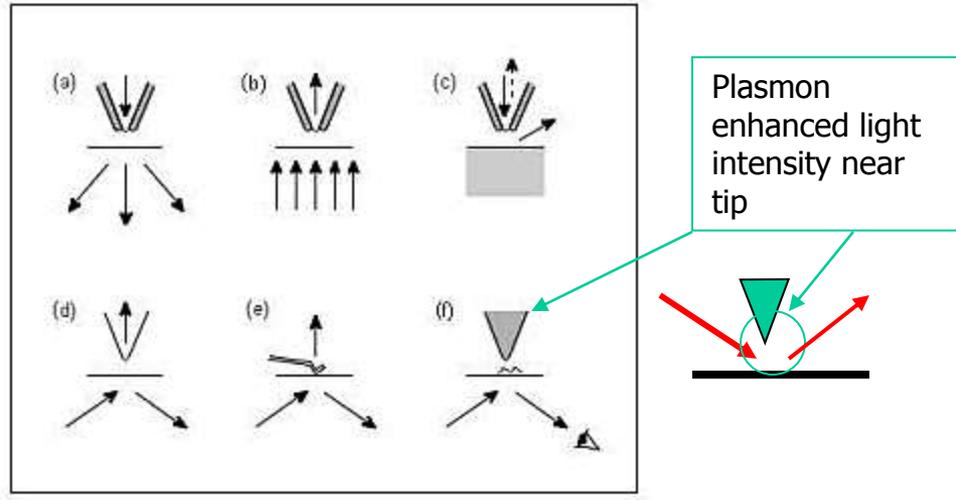


Diagram showing different methods of operation for Scanning Near-Field Optical Microscopy (SNOM).

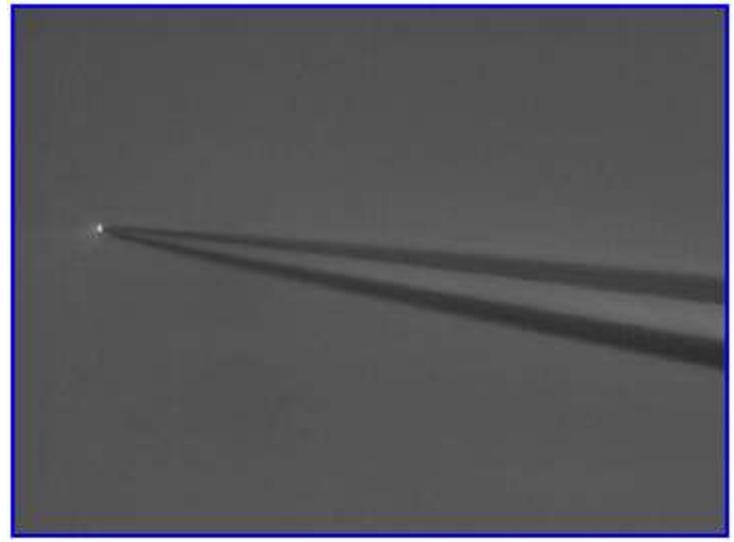
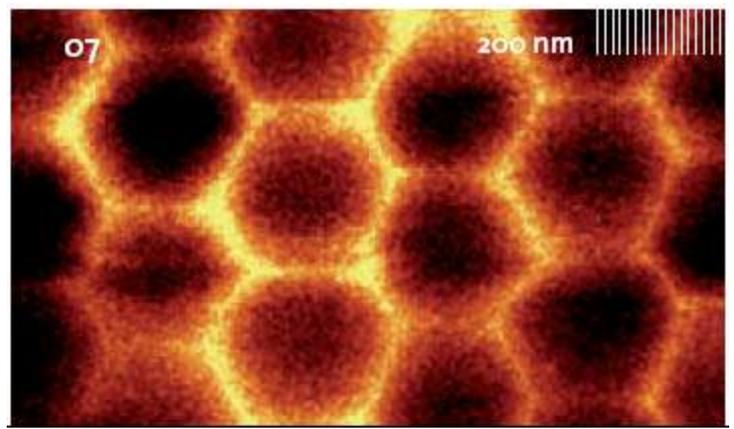


FIGURE 4: Optical microscope image of an NSOM tip.

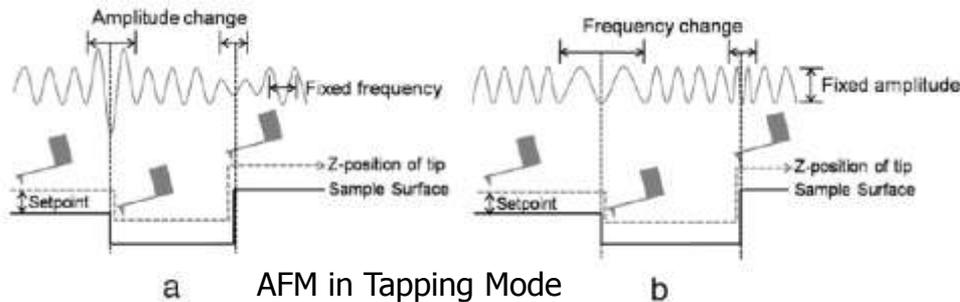


07. AC-Mode-SNOM of polystyrene spheres

# Kelvin probe force microscopy and its application

Wilhelm Melitz <sup>a,b</sup>, Jian Shen <sup>a,b</sup>, Andrew C. Kummel <sup>a</sup>, Sangyeob Lee <sup>a,\*</sup>

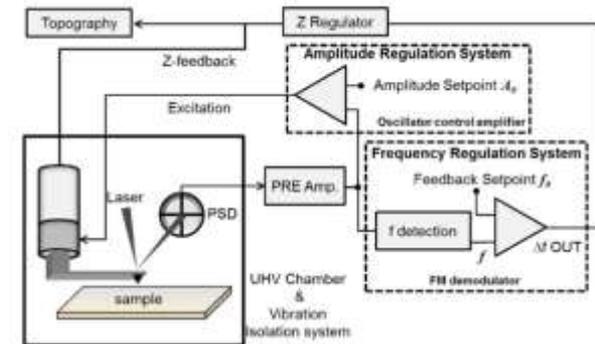
Surface Science Reports 66 (2011) 1–27



By applying an AC voltage ( $V_{AC}$ ) plus a DC voltage ( $V_{DC}$ ) to the AFM tip, KPFM measures the work function of the sample.  $V_{AC}$  generates oscillating electrical forces between the AFM tip and sample surface, and  $V_{DC}$  nullifies the oscillating electrical forces that originated from CPD between tip and sample surface. The electrostatic force ( $F_{es}$ ) between the AFM tip and sample is given by:

$$F_{es}(z) = -\frac{1}{2} \Delta V^2 \frac{dC(z)}{dz}, \quad (2.6)$$

where  $z$  is the direction normal to the sample surface,  $\Delta V$  is the potential difference between  $V_{CPD}$  and the voltage applied to the AFM tip, and  $dC/dz$  is the gradient of the capacitance between tip and sample surface.



**Fig. 2.** Block diagram of FM mode AFM system operated in UHV. The piezo scanner and the laser/PSD are enclosed in a UHV chamber system. The laser signal is amplified through the pre-amp and fed into two feedback systems for the amplitude and frequency regulation systems. The amplitude is set to a pre-determined setpoint  $A_0$ . The frequency shift ( $\Delta f$ ) is kept constant to acquire topographic images of the sample surface.

Resultat:

Ladungszustand  
adsorbierter  
Goldatome

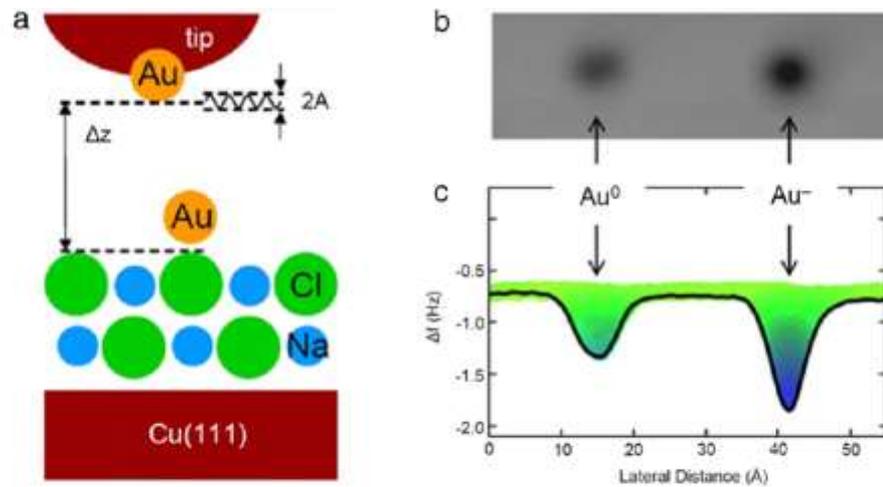


Fig. 15. A schematic diagram of AFM measurement and frequency shifts of Au adsorbed on NaCl/Cu(111). (a) Model geometry of the experimental setup for the AFM measurements of Au/NaCl. Au, Cl<sup>-</sup>, and Na<sup>+</sup> are colored gold, green, and light blue, respectively. (b) Frequency shifts recorded in a constant height mode ( $\Delta z = 5.0$  Å,  $V = -5$  mV, and  $I = 0.3$  Å). (c) Line scan of the frequency shift through the center of Au<sup>0</sup> and Au<sup>-</sup> atoms shown in (b). The color scale in (c) corresponds to the  $\Delta f$  values, in a three-dimensional representation of the cut along the line profile.

Resultat:

Goldatome  
adsorbiert auf  
KCl (100)

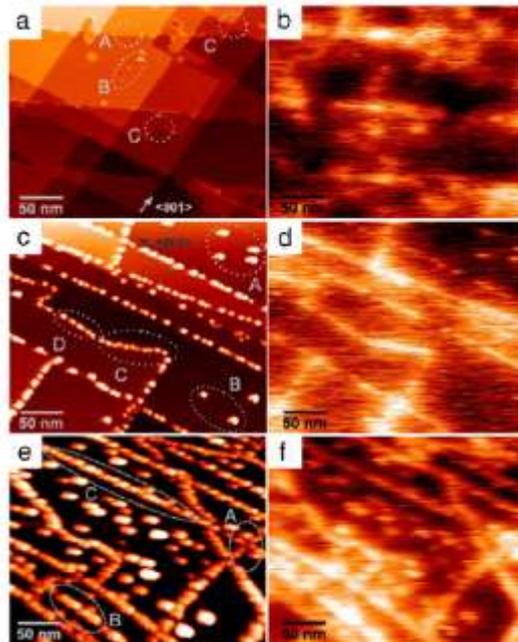
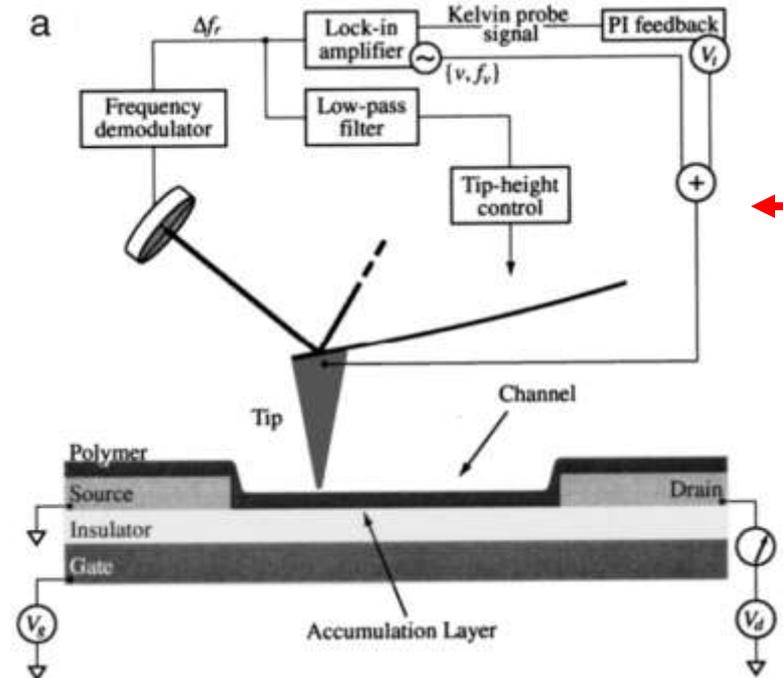


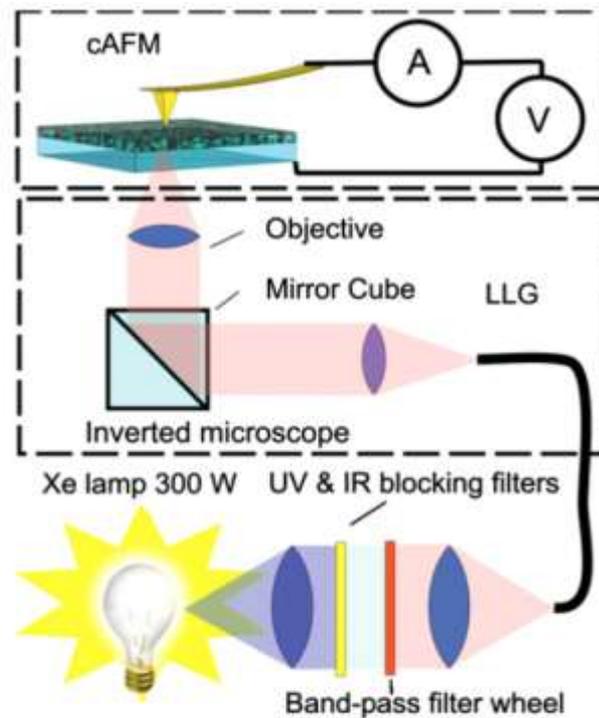
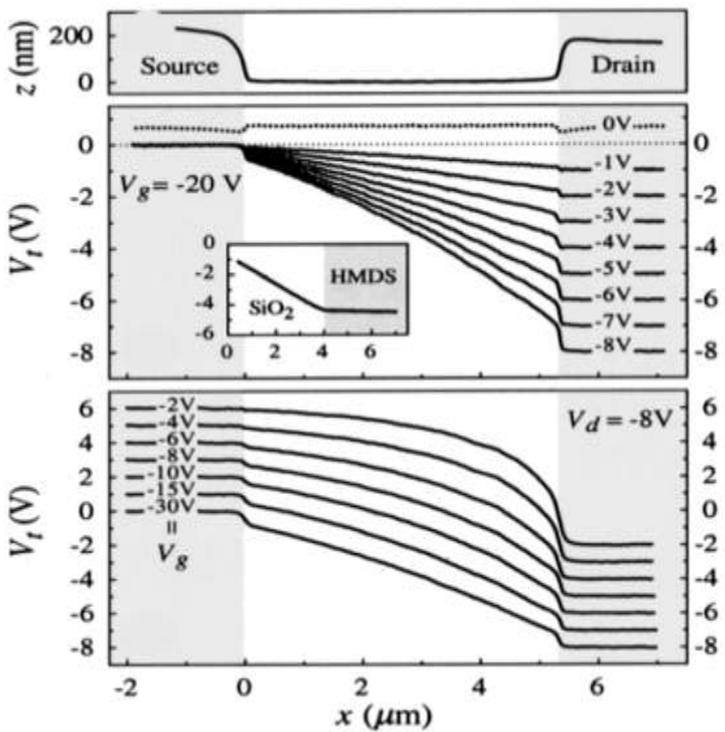
Fig. 14. The topography and work function images of UHV-cleaved KCl, surface with different coverages of Au. Topography, (a), (c), and (e), and simultaneously recorded surface potential images, (b), (d), and (f), of the clean KCl(001) surface, (a) and (b), the same surface after a deposition of 0.04 ML Au at room temperature, (c) and (d), and 1.44 ML of Au at 200 °C, (e) and (f). The clean surface was prepared by UHV cleaving and annealing at 120 °C for 2 h.

# Kelvin Probe Microscopy



Potentialverteilung in invertiertem O-FET

Lokale Untersuchung an Solarzellen



Schematic representation of PC-AFM.

## Quantitative Atomic Force Microscopy with Carbon Monoxide Terminated Tips

Zhixiang Sun (孙志祥), Mark P. Boneschanscher, Ingmar Swart, Daniël Vanmackelbergh, and Peter Liljeroth

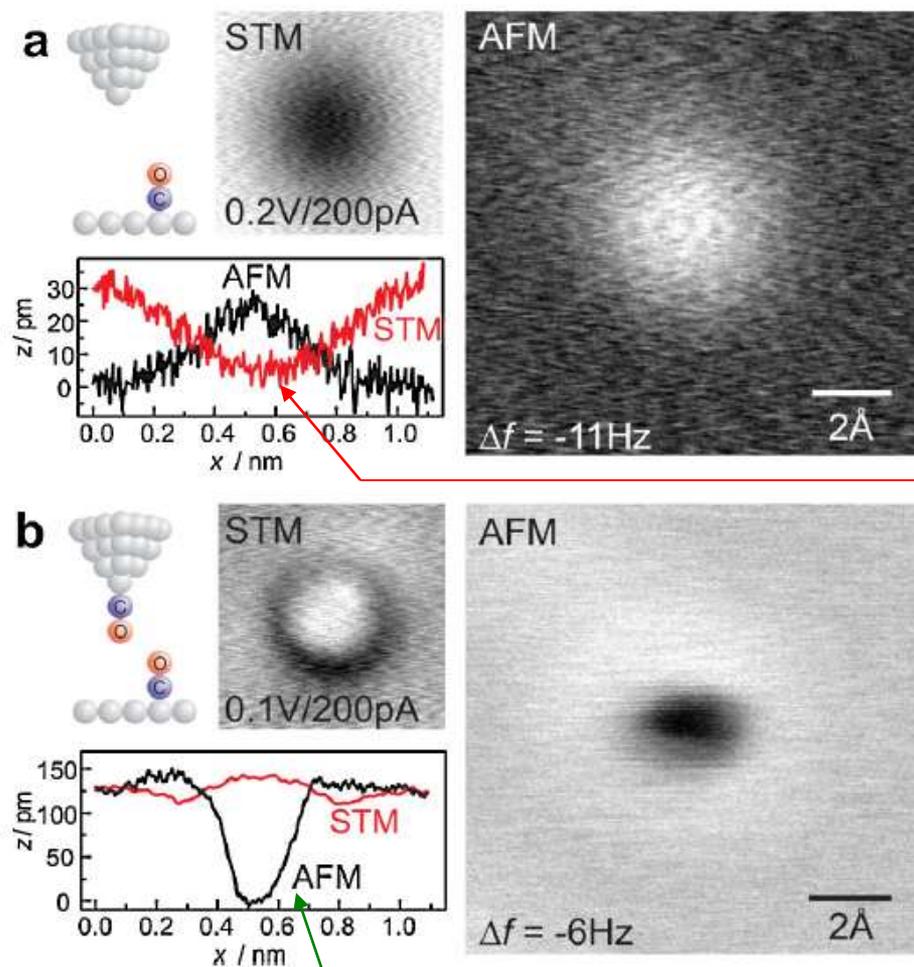


FIG. 1 STM and AFM images of a CO molecule adsorbed on Cu(111) surface acquired with (a) a clean metal tip and (b) a tip that is terminated by a CO molecule. The line profiles are taken from the images across the middle of the CO molecule. All images are  $11 \times 11 \text{ \AA}^2$ .

Beachte: STM-Artefakt !

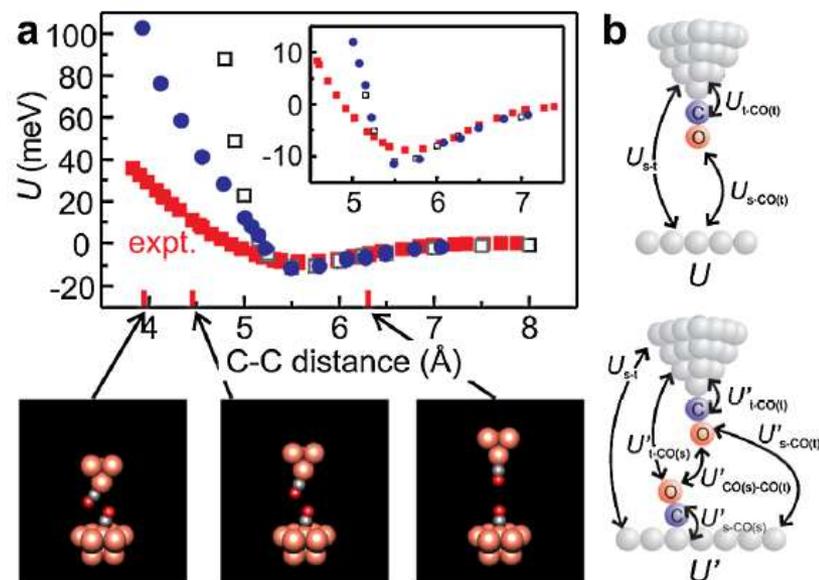


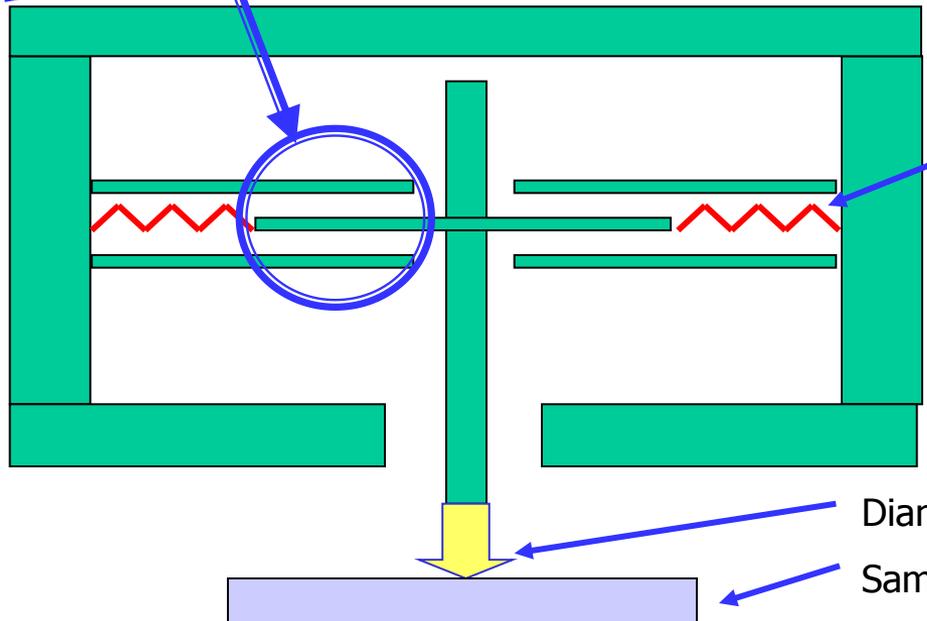
FIG. 4 (color online). Effect of relaxation on the force distance curves.

Beachte: AFM-Artefakt !

# Nanoindenter, Scheme

## Condenser:

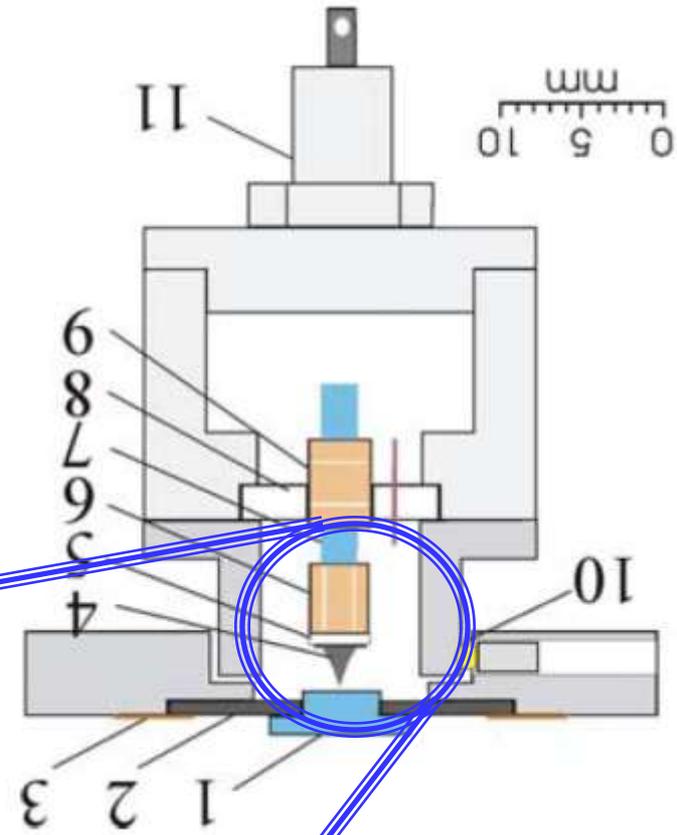
DC: applies force to indenter  
AC: measures capacity as a function of plate displacement: indentation depth



Springs

Diamond tip

Sample



11

10 μm  
0 5 10

6

8

7

9

5

4

10

3

2

1

# Evaluation of Nanoindenters

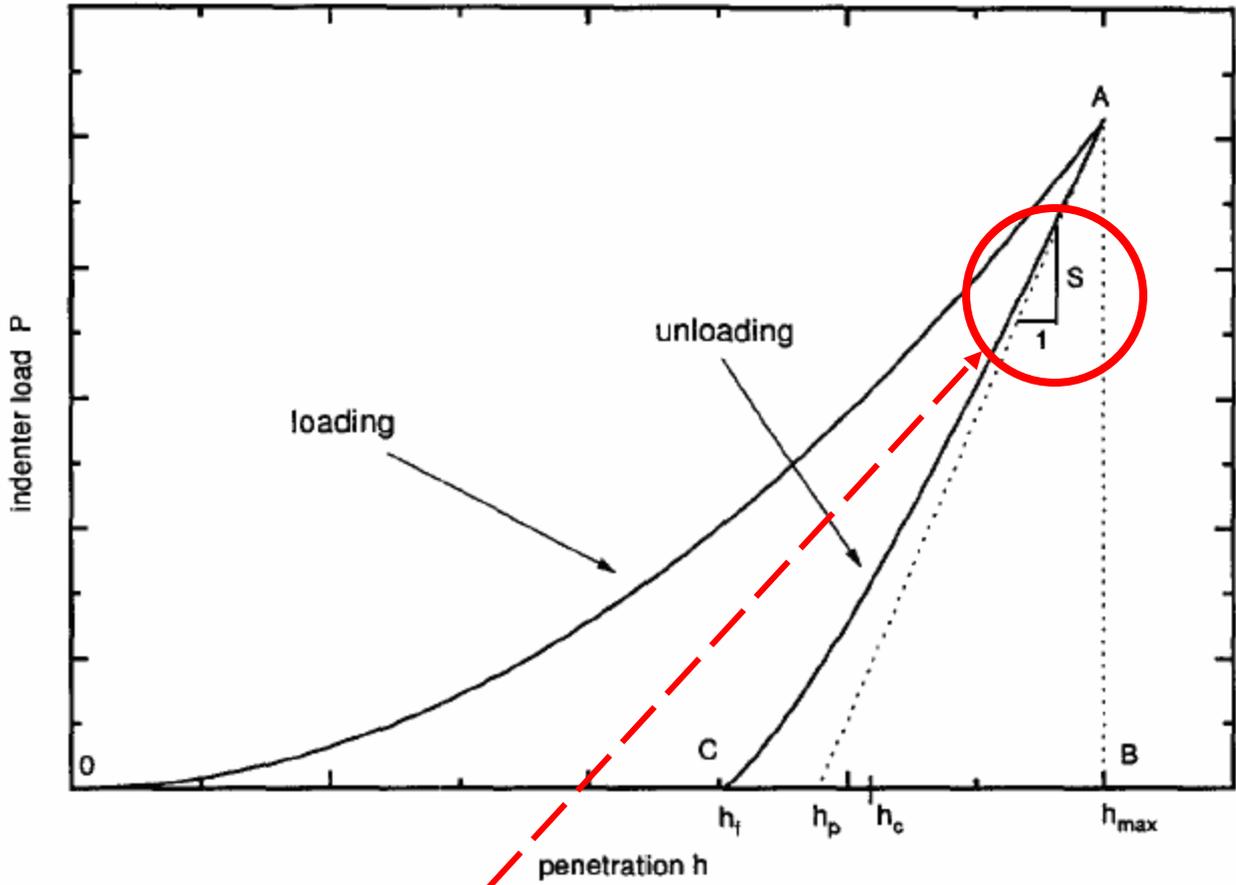


Fig. 2. General load penetration curve.

## Hardness $H = P/A$

$P$  = max. force,  $A$  = projected area of indent at max. force,  
 for metals  $H \approx (2.5 \dots 3) \cdot \sigma_y$  (Tabor, 1951)

## Elastic modulus $E_s$ from gradient of the beginning of the unloading curve

(Method of Oliver & Pharr, 1992):

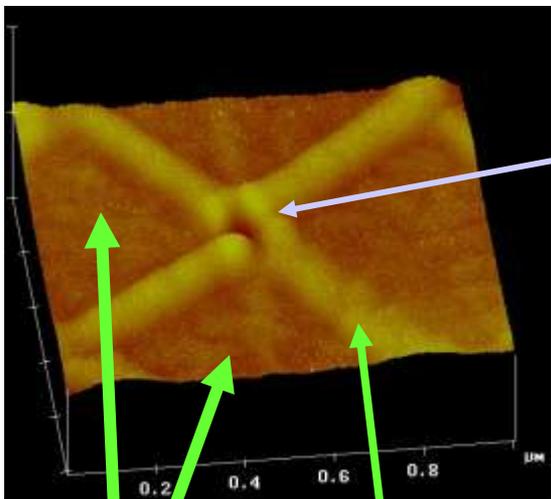
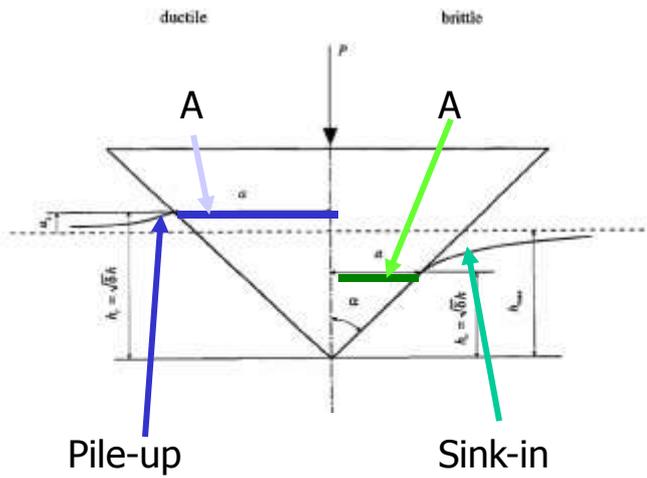
$$\frac{dP}{dh} = S = \beta \frac{2}{\sqrt{\pi}} \sqrt{AE_r}$$

with  $\beta$  = empirical indenter shape factor  $\approx 1$ , and

$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i}$$

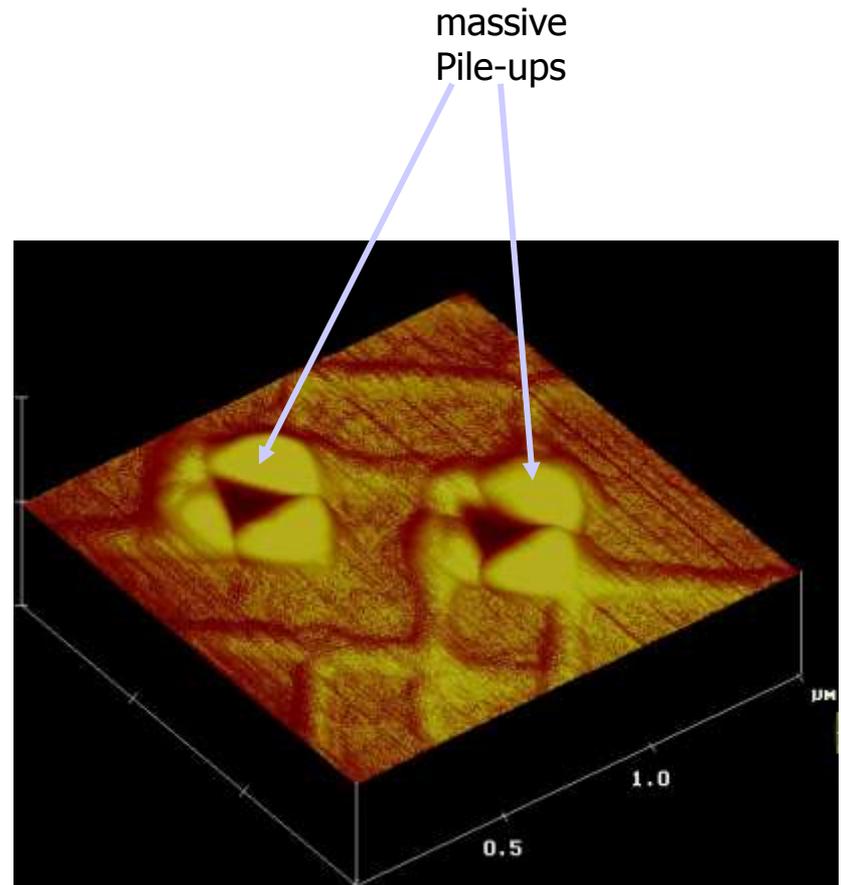
- indices:
- r = reduced,
- s = sample,
- i = indenter

**Special problems with projected area: Pile-up and Sink-in**

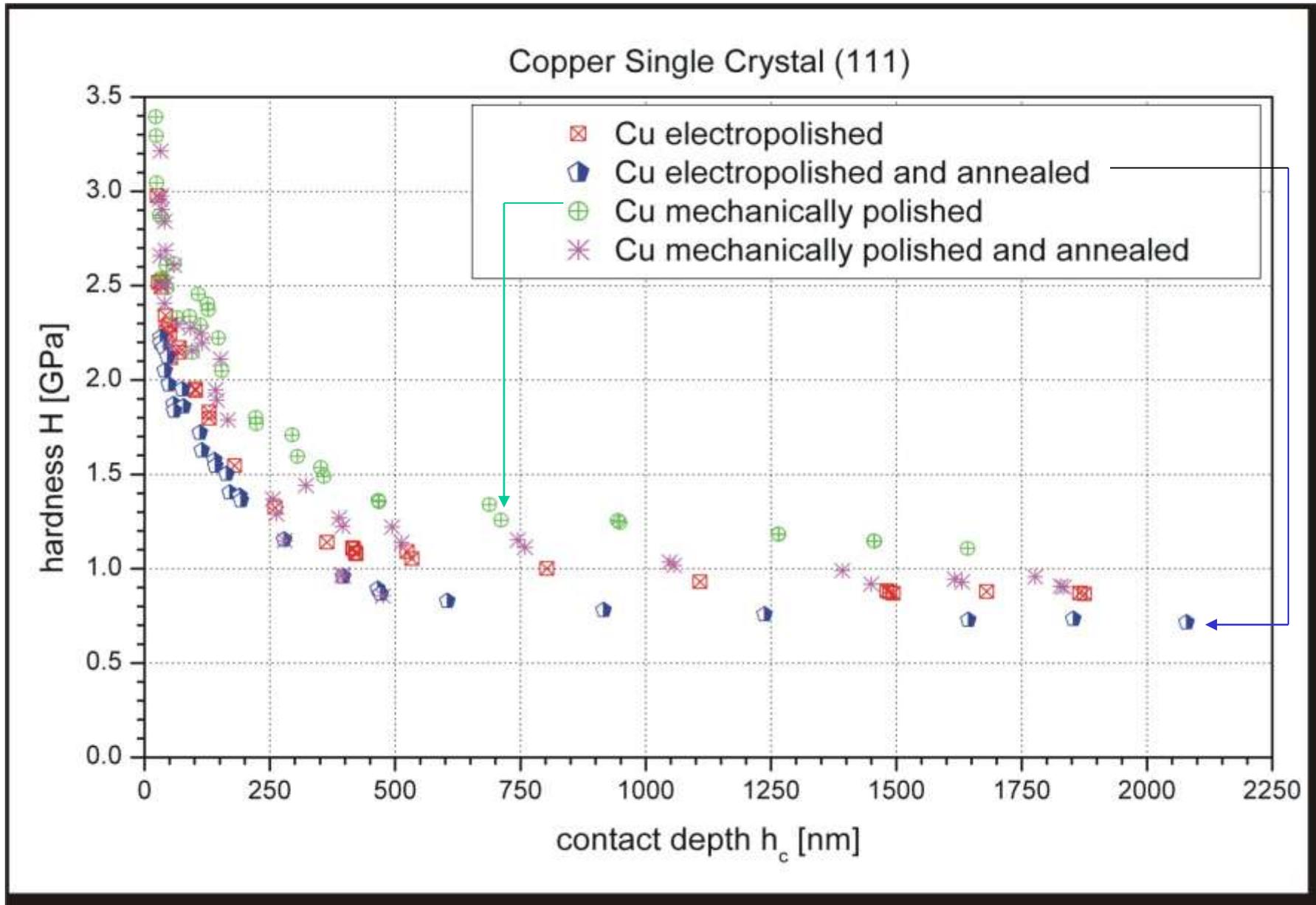


Indent in matrix with slight pile-up

Precipitations in a matrix:  
typical AFM-picture

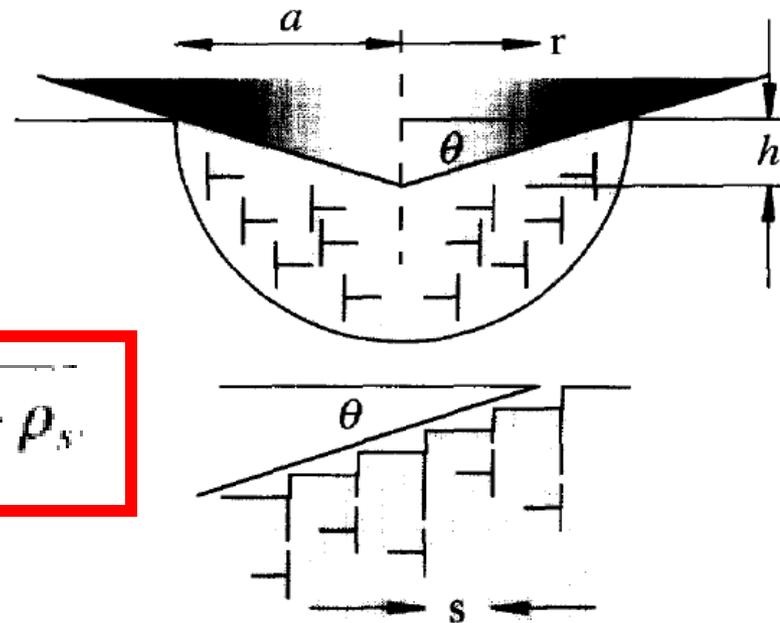


# Indentation size effect



Erklärungen: Oberflächenoxyde, Polierschichten, Erzeugung von GNDs (geometrically necessary dislocations)

## Geometrically Necessary Dislocations



Geometrically necessary dislocations created by a rigid conical indentation. The dislocation structure is idealized as circular dislocation loops.

We

assume that the von Mises flow rule applies and that Tabor's factor of 3 can be used to convert the equivalent flow stress to hardness:

$$\sigma = \sqrt{3}\tau, \quad H = 3\sigma$$

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}}$$

$$H_0 = 3\sqrt{3}\alpha\mu b\sqrt{\rho_s}$$

$$h^* = \frac{81}{2} b\alpha^2 \tan^2 \theta \left( \frac{\mu}{H_0} \right)^2$$

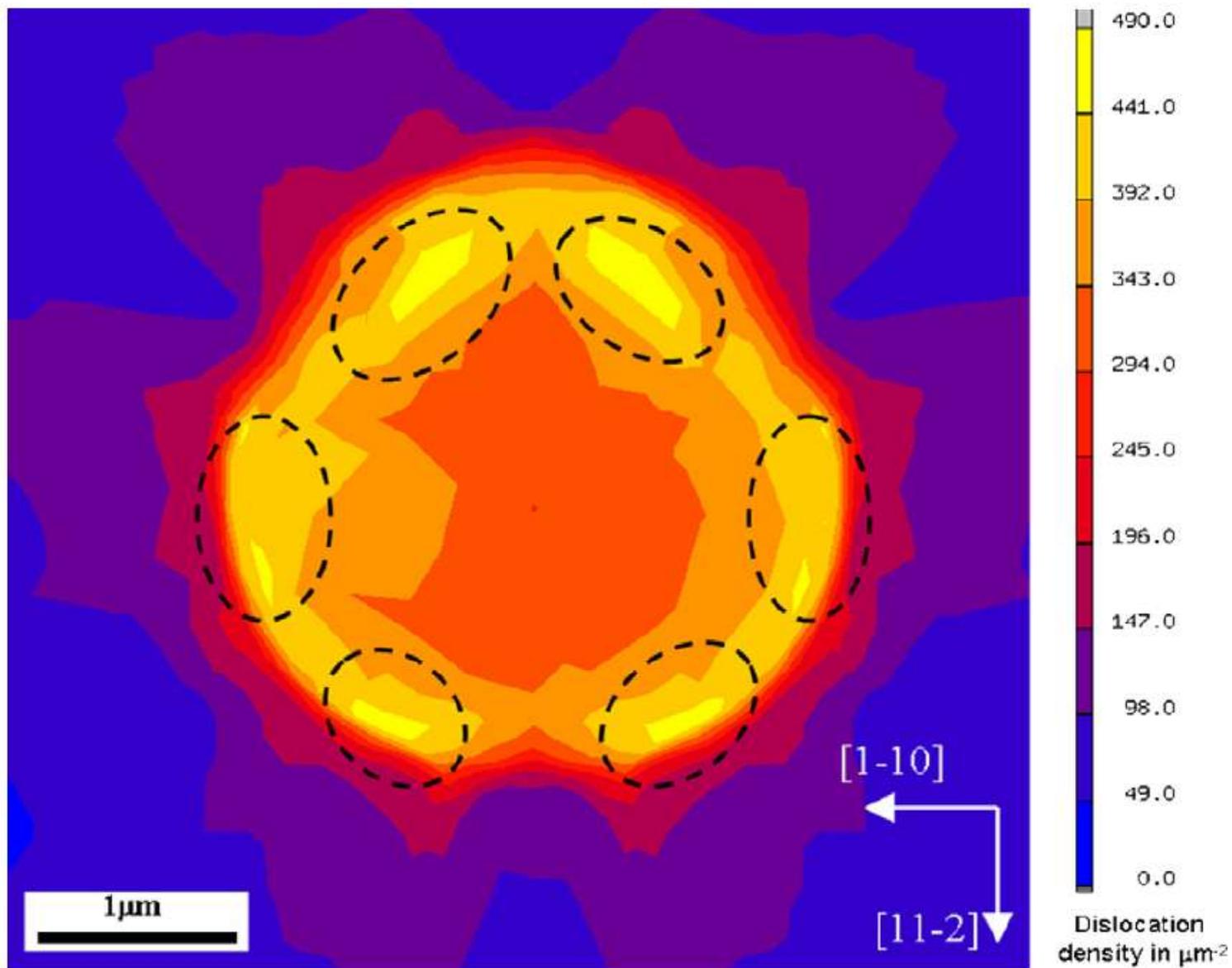
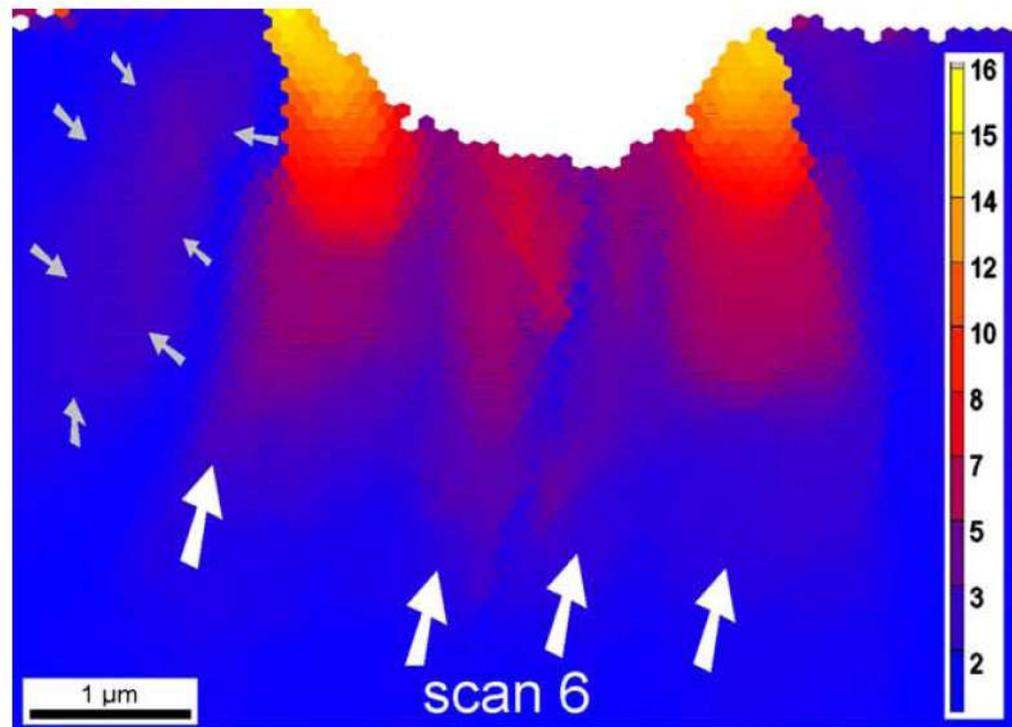
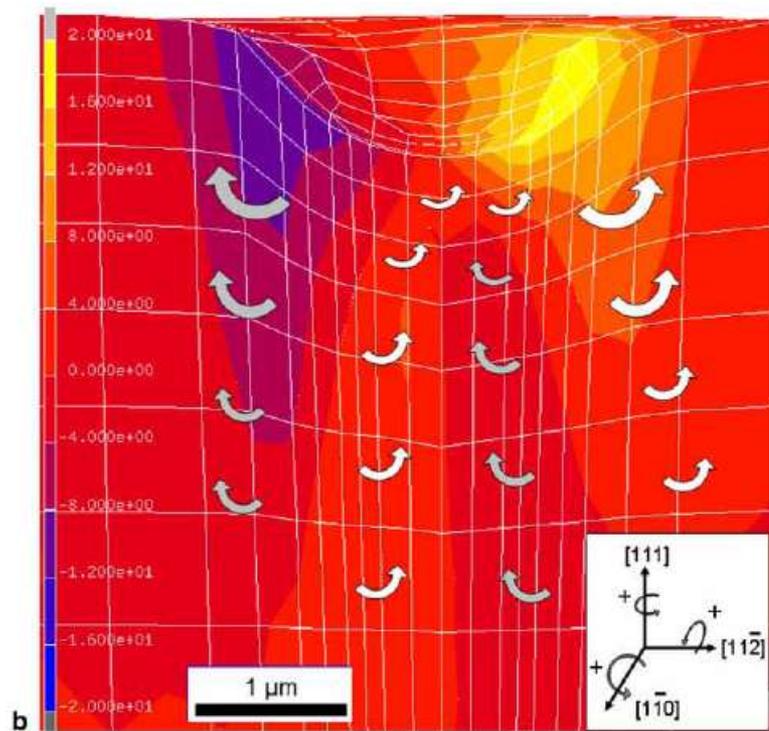
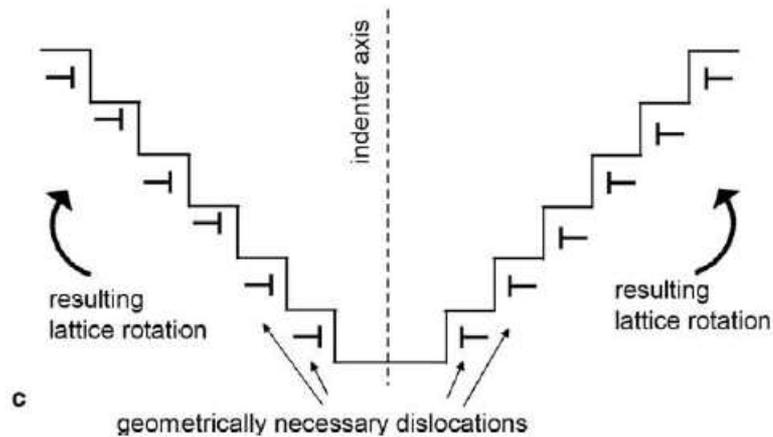


Fig. 9. Distribution of the mobile dislocation density close to the surface.



Experiment, EBSD



3D presentation of the simulated rotations (crystal plasticity finite element model) about the crystallographic  $[1\bar{1}0]$  axis presented in the  $(1\bar{1}0)$  plane.

# Alternatives Modell: Erzeugung der ersten Versetzungen



Contents lists available at ScienceDirect

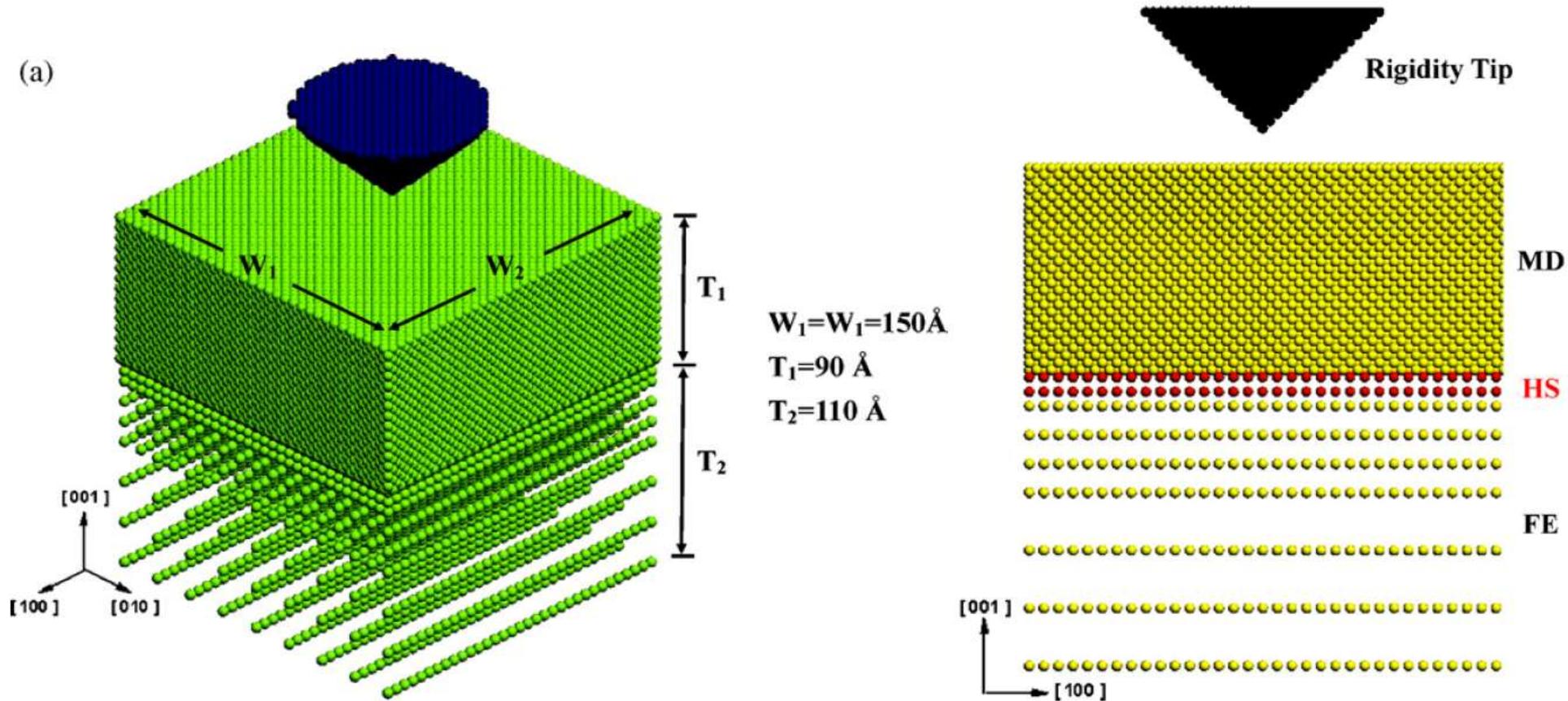
Applied Surface Science

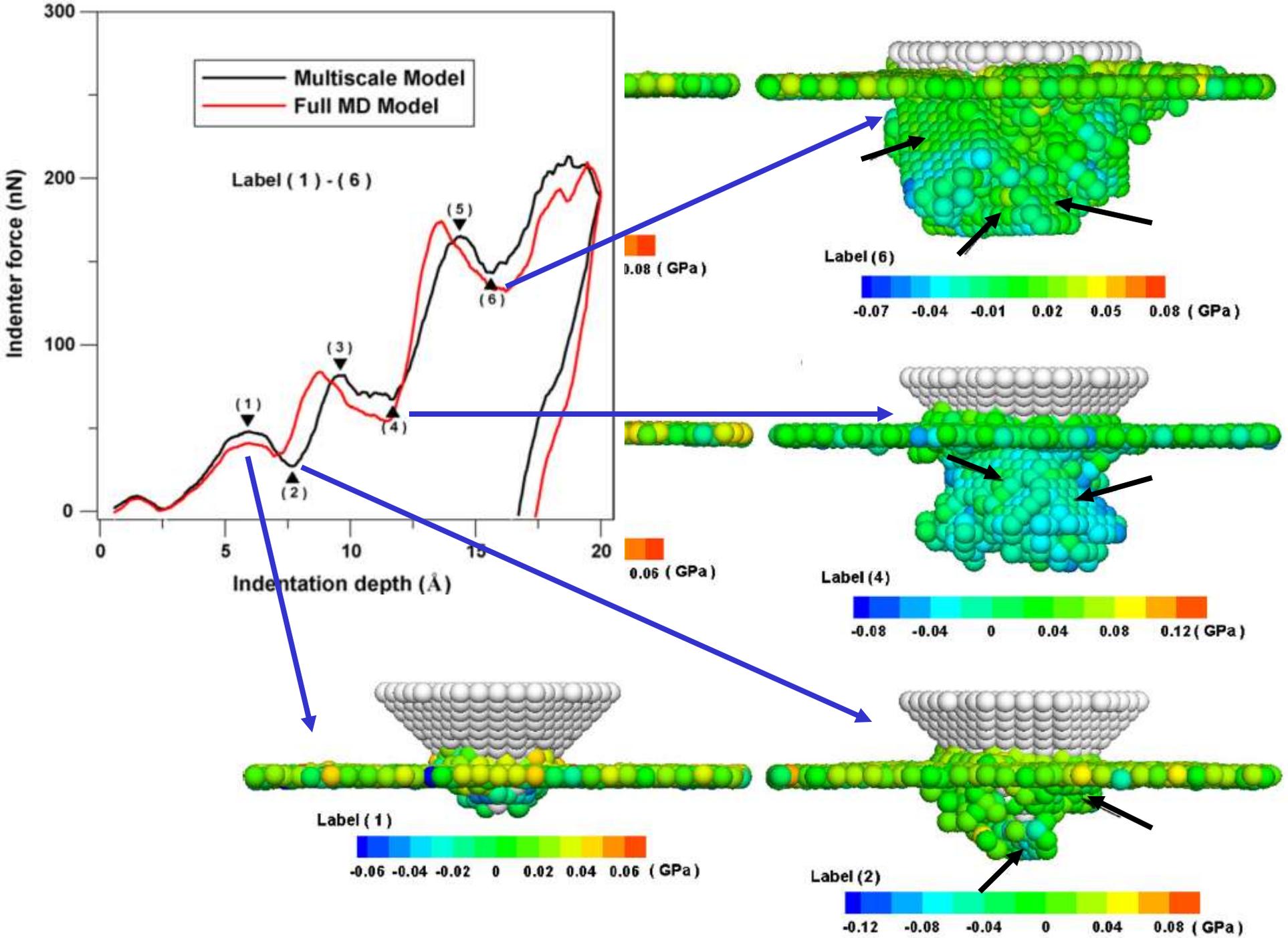
Journal homepage: [www.elsevier.com/locate/apsusc](http://www.elsevier.com/locate/apsusc)

Applied Surface Science 255 (2008) 3240–3250

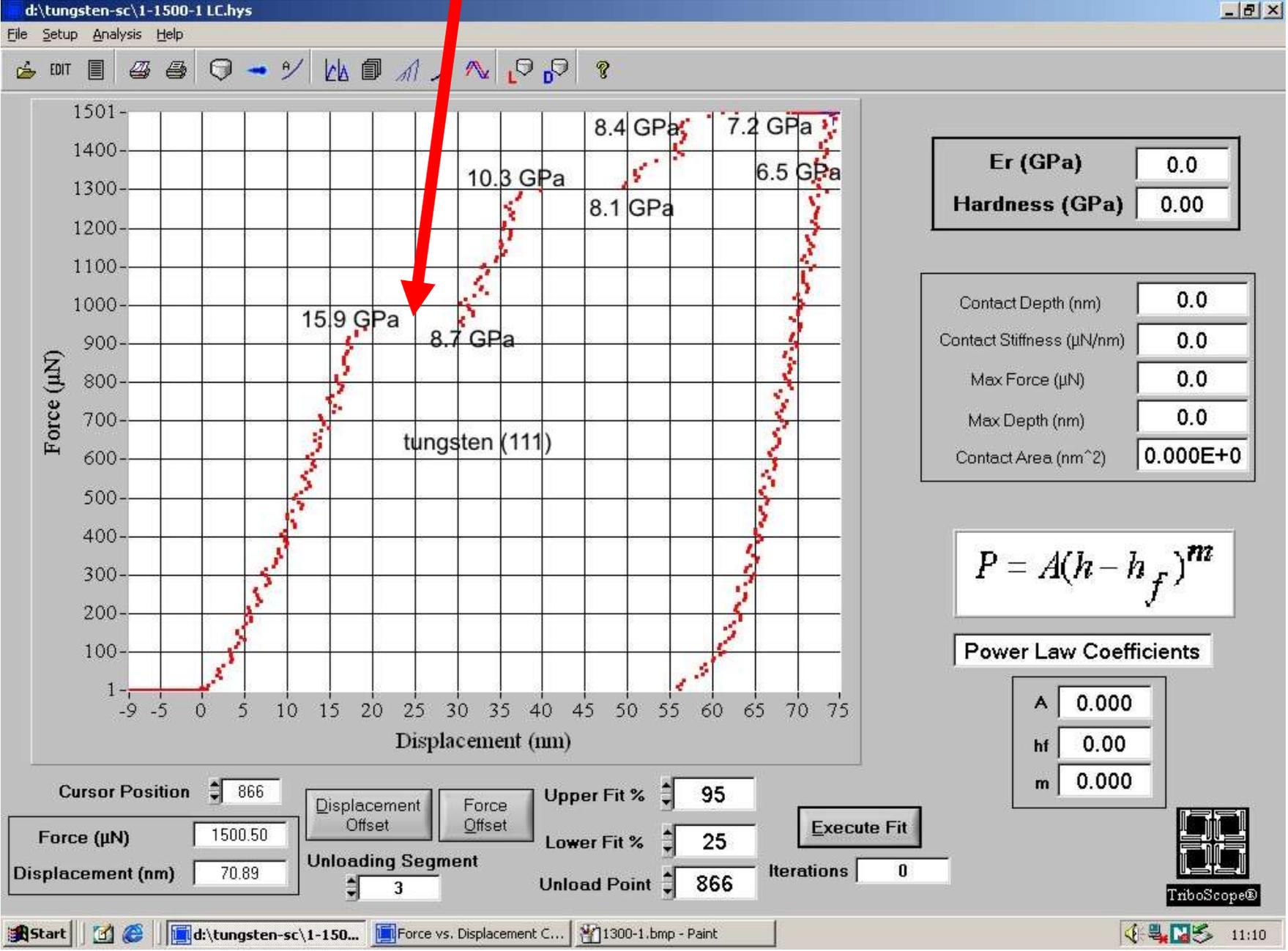
## Multiscale simulation of nanoindentation on Ni (100) thin film

Chung-Ting Wang<sup>a</sup>, Sheng-Rui Jian<sup>b</sup>, Jason Shian-Ching Jang<sup>b</sup>, Yi-Shao Lai<sup>a,\*</sup>, Ping-Feng Yang<sup>a</sup>

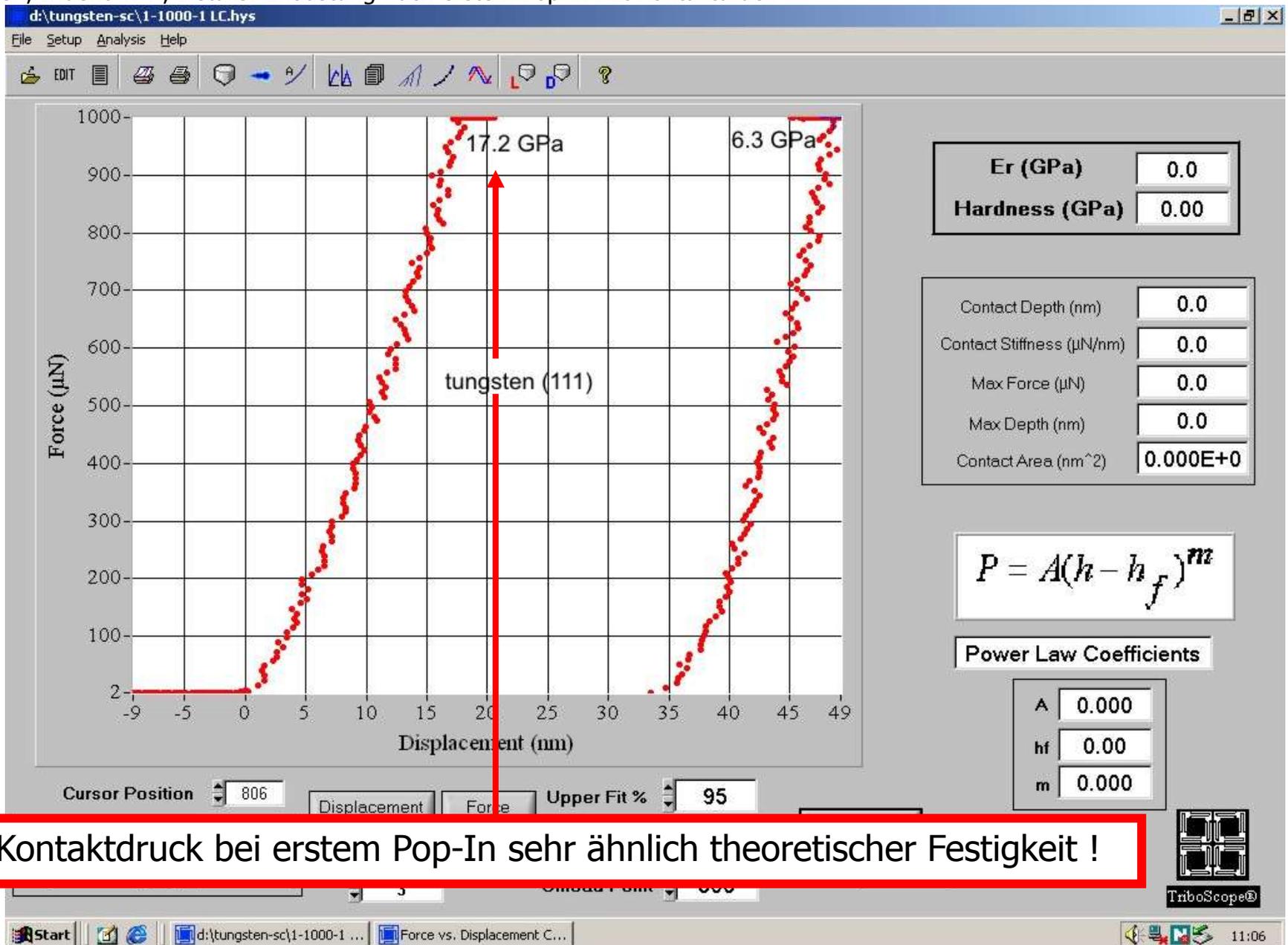




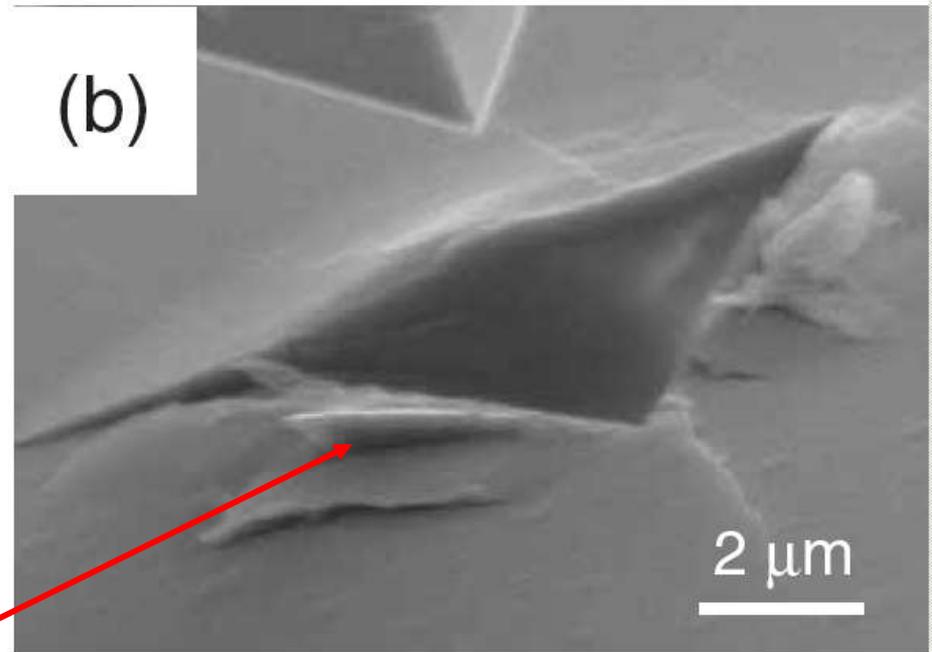
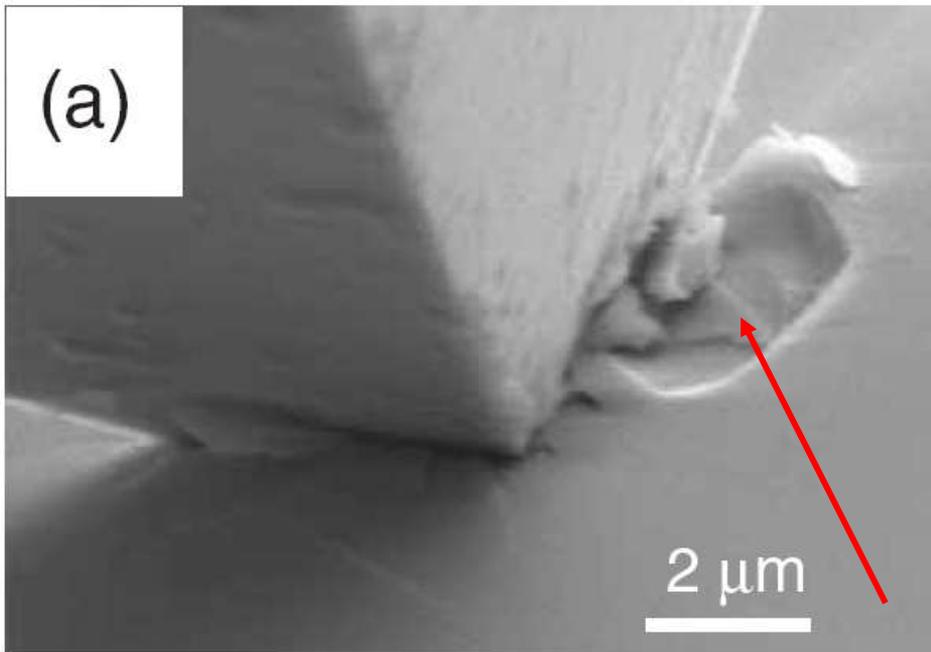
# Schöberl, Indent in W, Details: Pop-in mit Kontaktdruck



TriboScope®

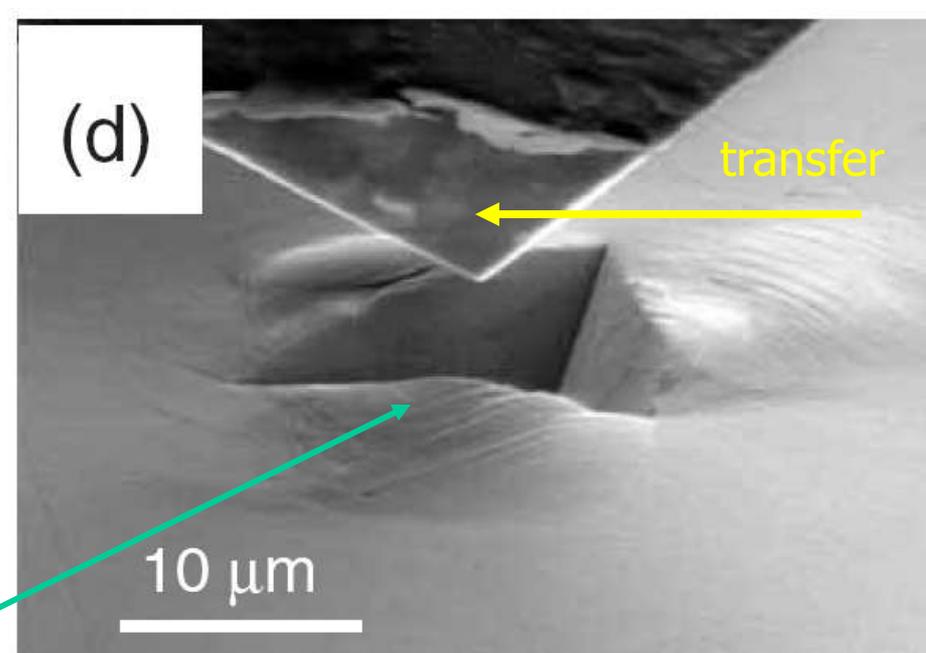
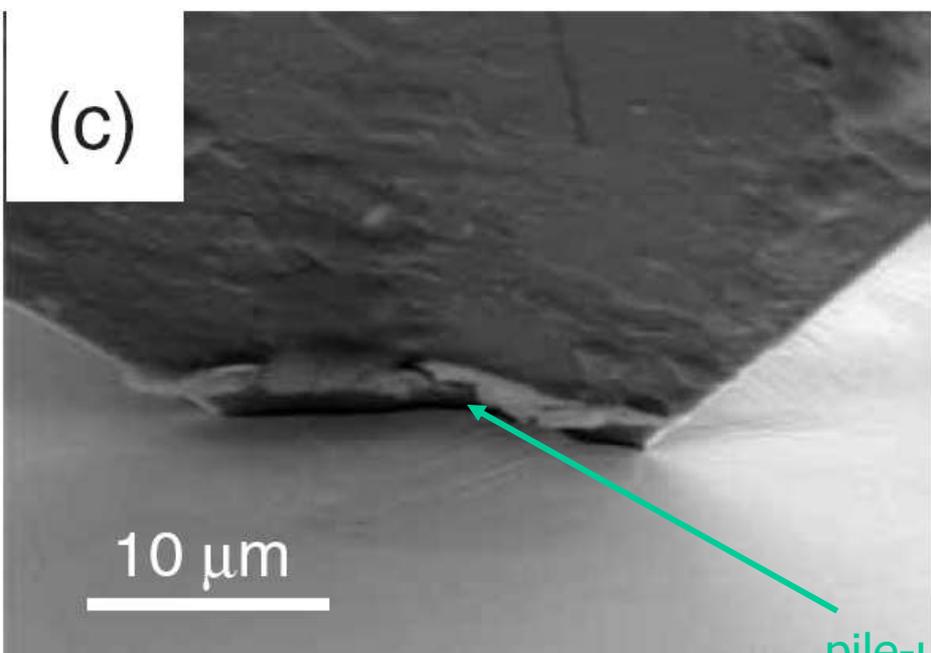


Kontaktdruck bei erstem Pop-In sehr ähnlich theoretischer Festigkeit !

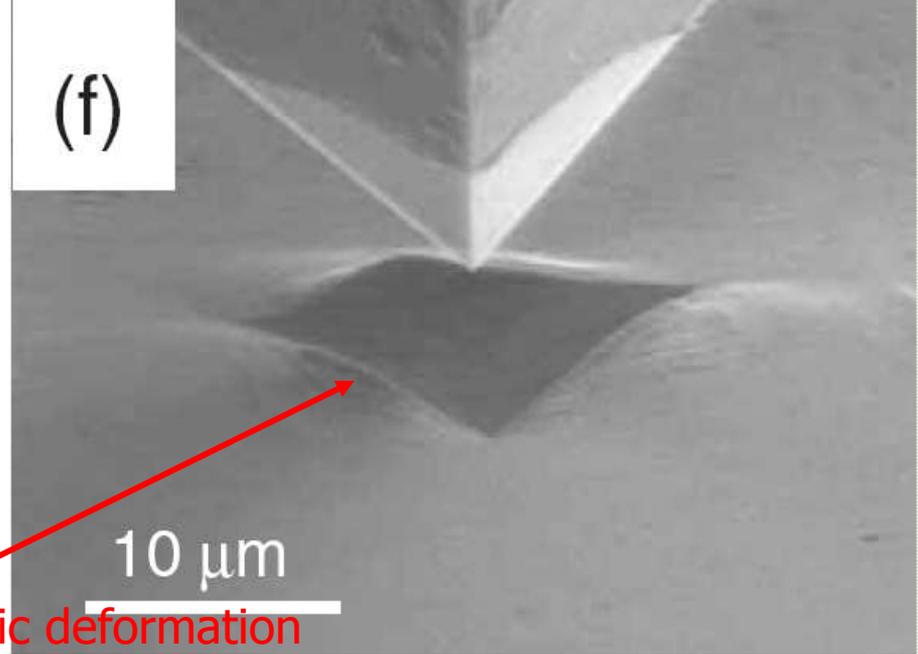
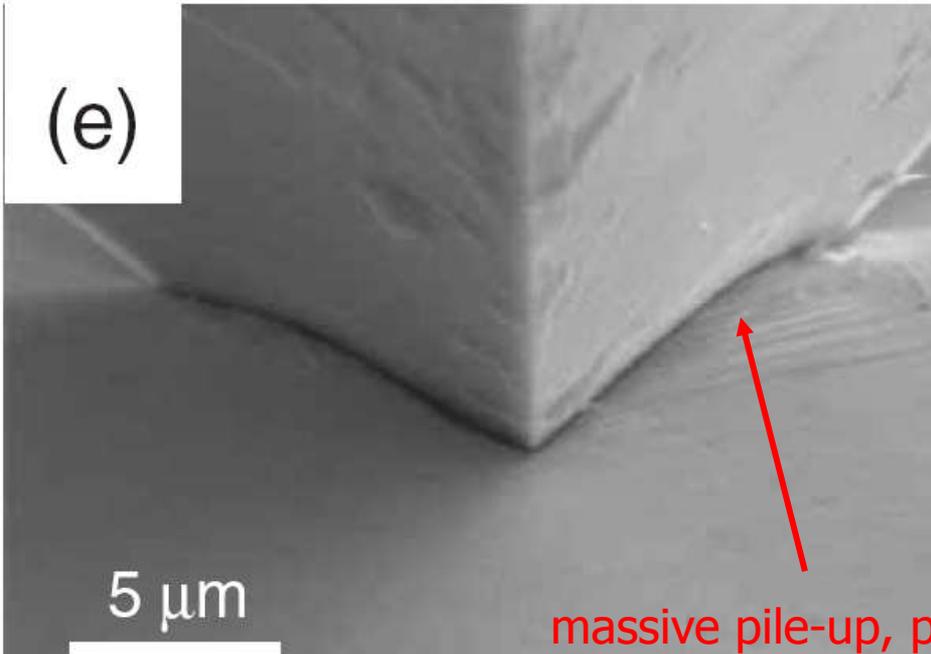


SEM indentation in sapphire, 981 mN

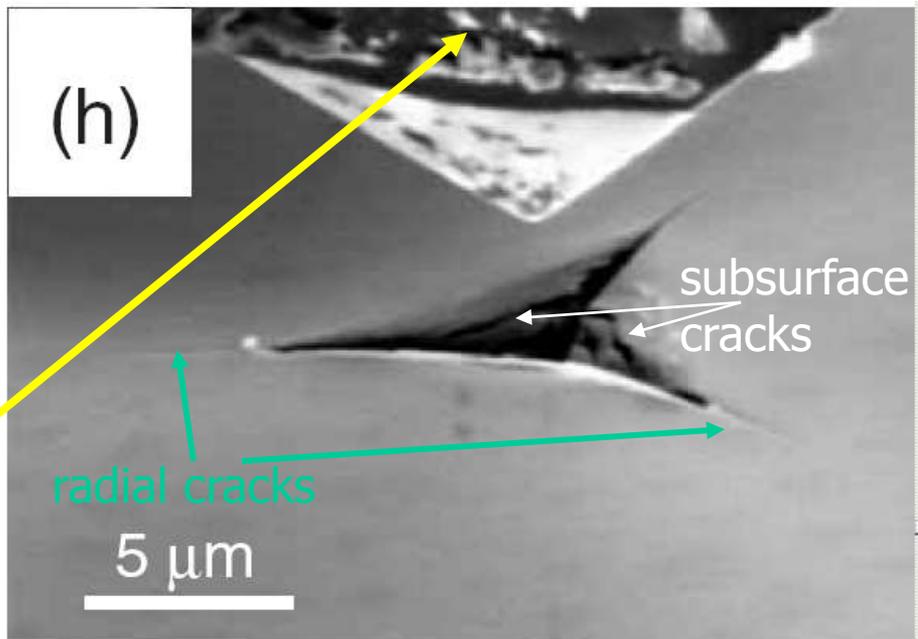
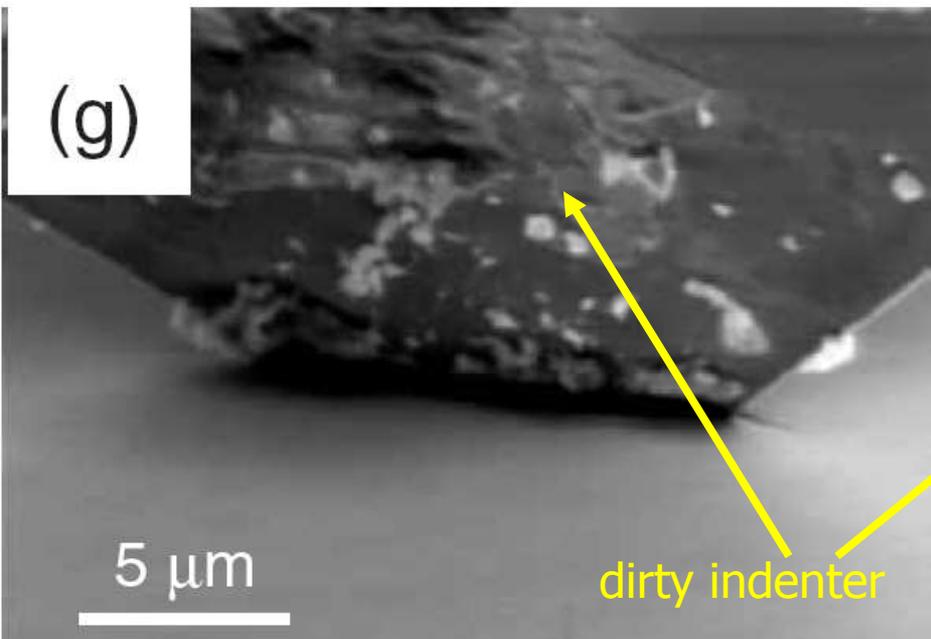
fracture



SEM indentation in Ni, 343 mN



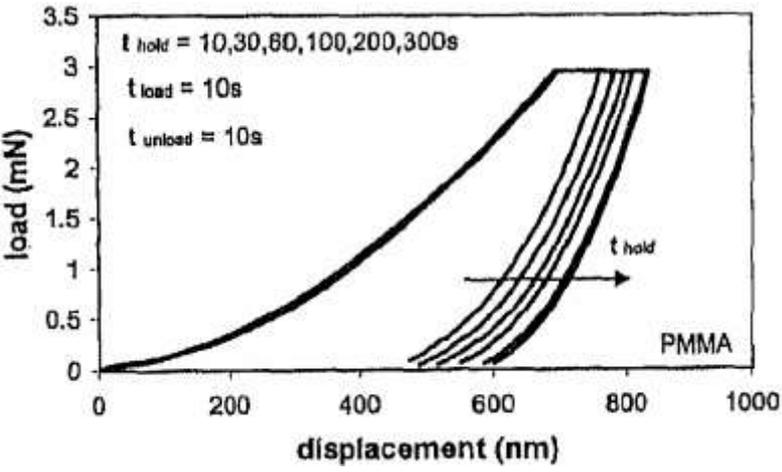
SEM indentation in W, 981 mN



SEM indentation in glassy carbon, 343 mN

# Nanoindentation in organic materials, special problems

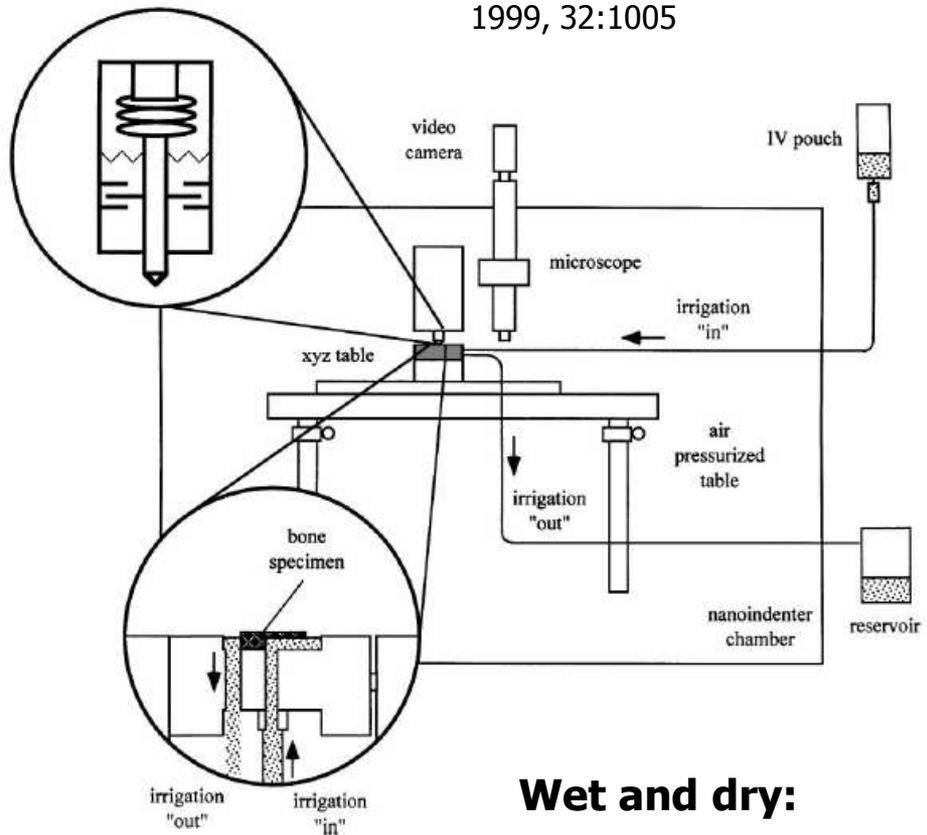
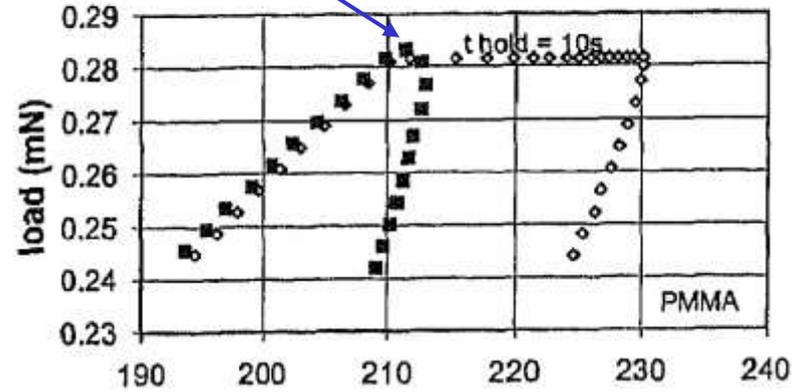
Zysset et al, J Biomech  
1999, 32:1005



## Viscoelasticity and – plasticity

Influence of hold time  
Falsification of elastic modulus by creep

### THE "NOSE" PROBLEM



## Wet and dry:

Early experiments to keep samples wet.

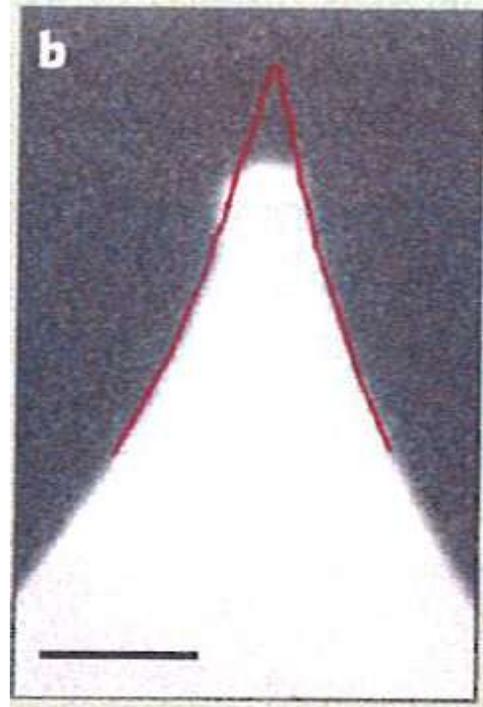
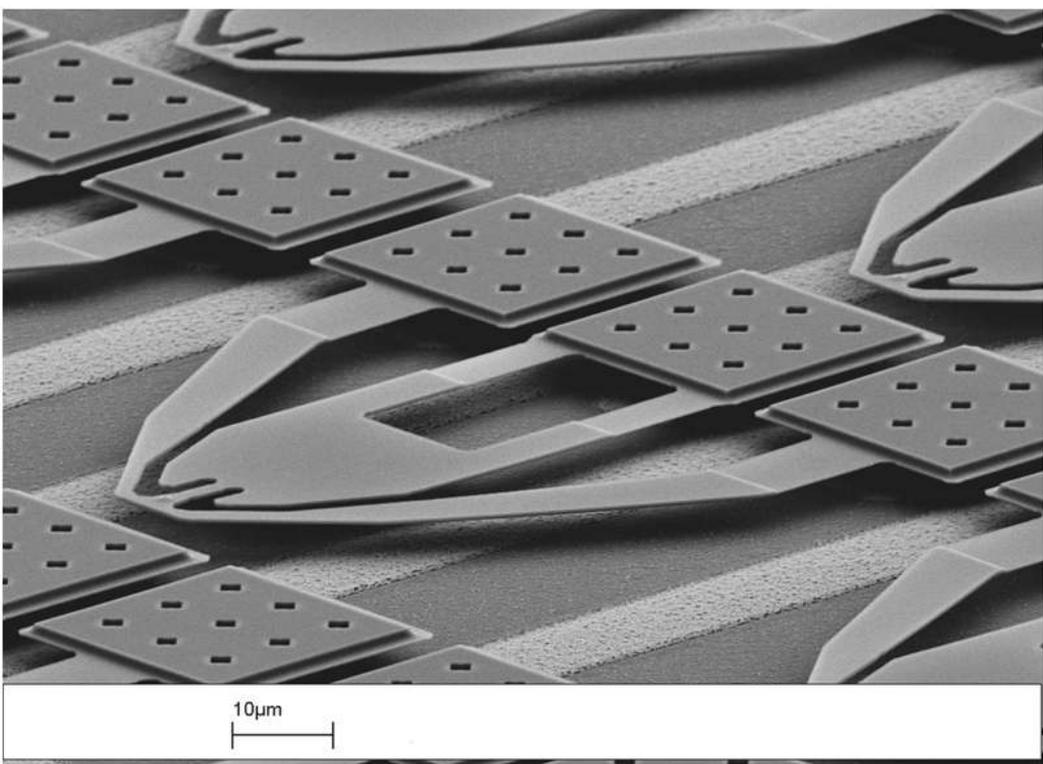
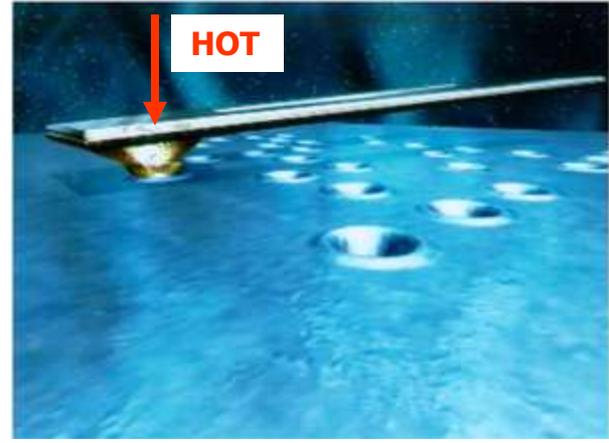
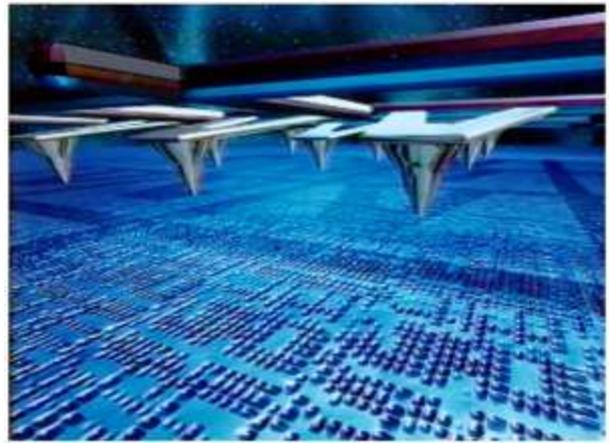
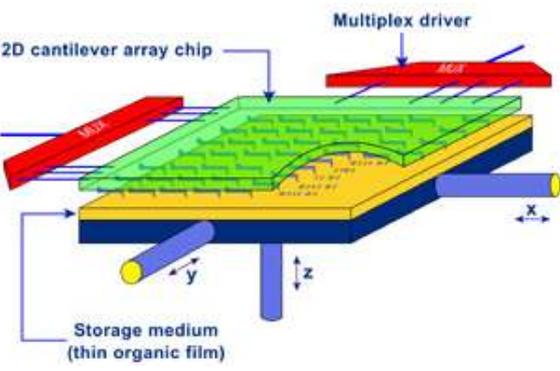
# Übersicht über einige Untersuchungsmethoden, Wiederholung

Info über	Methode	+	-
Chemie	AES	elementspezifisch	i.a. nicht für Spurenelemente
	SIMS, SNMS	gut für Spurenelemente, Atomcluster -> Nachbarn	allgemein schwer zu quantifizieren, leicht destruktiv
	ESCA - UPS - XPS	Information über chemische Bindungen	ohne Synchrotron eingeschränkt (UV - X-Ray)
	FIM - Atomsonde	Chemie+Topologie mit atomarer Ortsauflösung	total destruktiv Spitzenpräparation
Topo- logie	LEED, HAS	auch fehlerhafte Strukturen „grosse“ Flächen (mm <sup>2</sup> )	Streuverfahren, nicht ein- deutig
	STM, AFM	atomare Ortsauflösung	„kleine“ Flächen (μm <sup>2</sup> ), eingeschränkte chem. Analyse Höhenangabe problematisch
	XPD	indirektes Verfahren	Höhenangabe

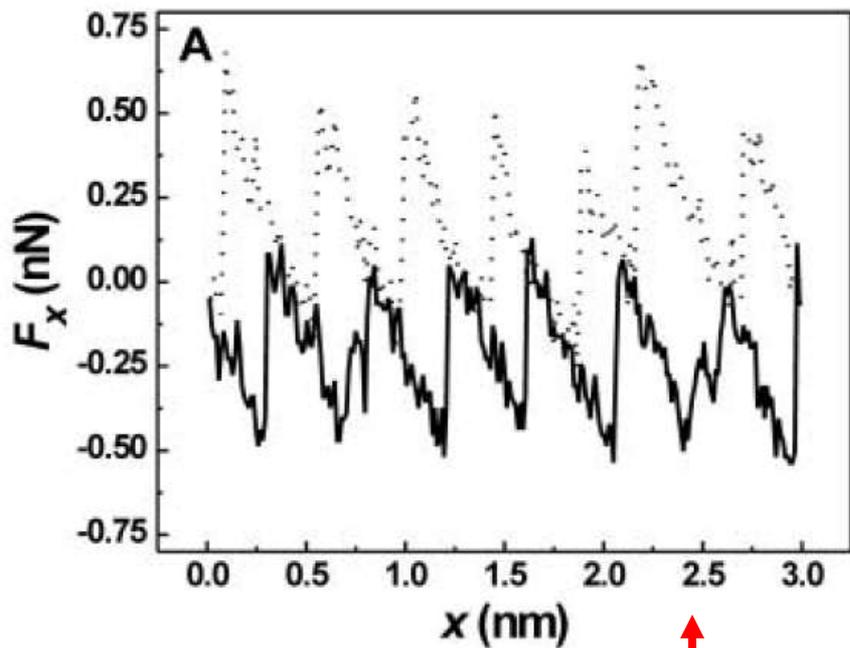
# Projekt „Millipede“ .. IBM

## "MILLIPEDE"

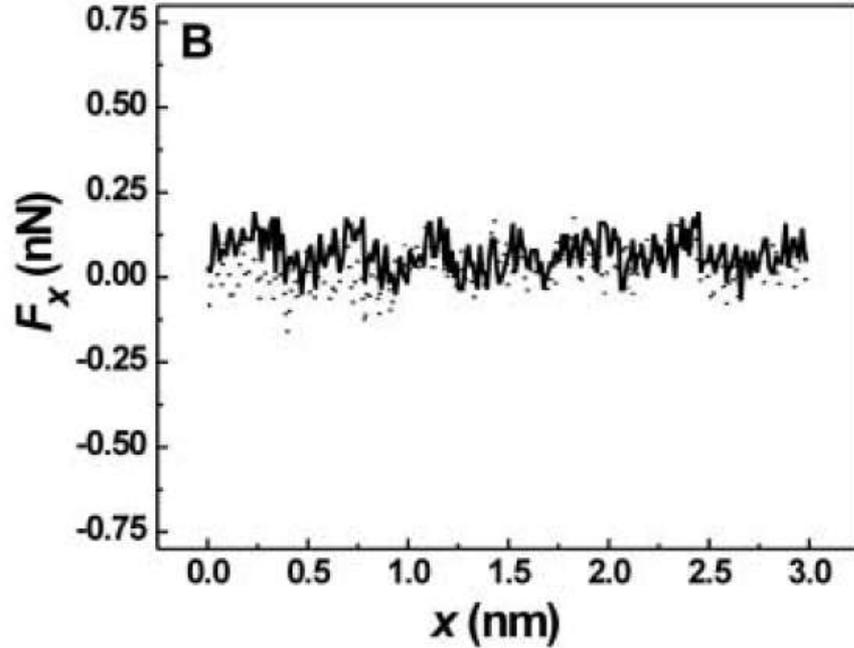
Highly parallel, very dense AFM data storage system



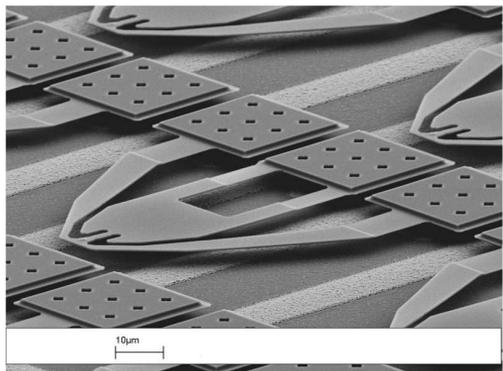
Tip wear



Lateral force AFM tip/NaCl  
stick-slip



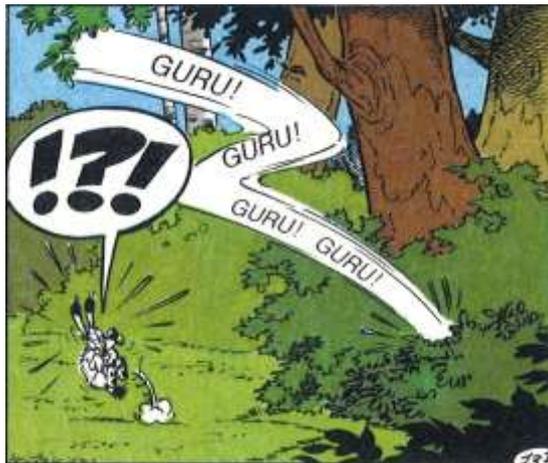
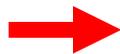
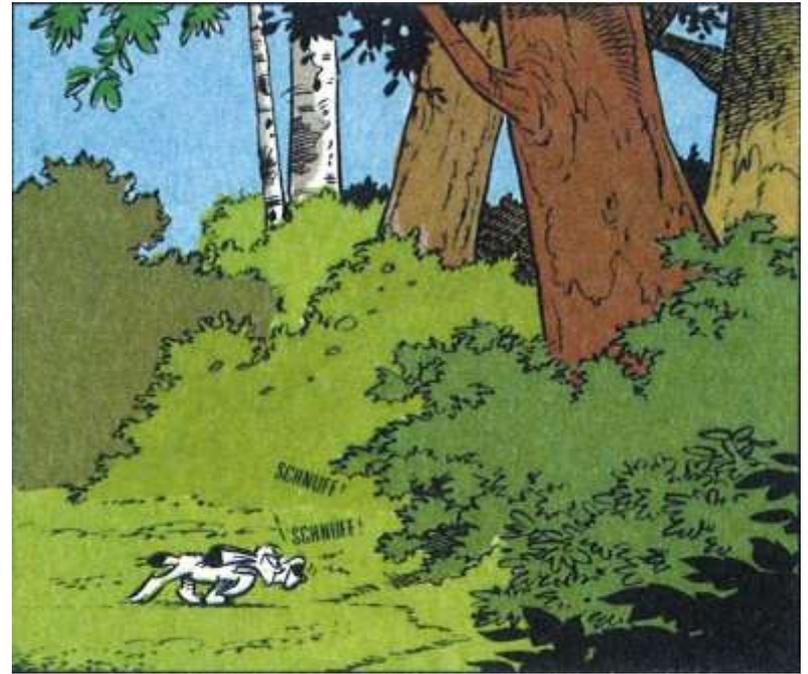
Lateral force AFM tip/NaCl  
Oscillating cantilever, NO stick-slip !



**NO TIP WEAR**  
Gnecco, Nature 461 (2009), 178



# Spurenanalyse



## Was sind „Spuren“ ?

Stahlwerk: traditionell Gew%, alles unter 0,1% = „unvermeidbare Verunreinigungen“

Life Sciences: besser ppm (parts per million), also 1 Atom (Molekül) **X** in  $10^6$  Atomen (Molekülen) **Oft auch missbraucht: „Gew.ppm“**

Seit etwa 1970 zugänglich: ppb (parts per billion) also 1 Atom (Molekül) **X** in  $10^9$  Atomen (Molekülen)

Nur mit modernen physikalischen Methoden zugänglich: ppt, (part per trillion), also 1 Atom (Molekül) **X** in  $10^{12}$  Atomen (Molekülen)

Beispiele:

Wasserhärte:  $1^\circ \text{ dH} \sim 17.8 \text{ mg Kalkbildner/Liter} = 17.8 \text{ ppmGew}$

**Unser Wasser hat meist  $10 \dots 15^\circ \text{ dH}$ , also  $178 \dots 267 \text{ mg/L}$**

Schwermetalle (As, U, ...) im Trinkwasser: WHO-Limit:  $10 \mu\text{g/L}$  ( $\sim 10 \text{ ppbGew}$ )

Grenze: im ppt-Bereich praktisch *alles* nachweisbar

## Nachweismethoden für „Spuren“

Stahlwerk: 1/10 %: analyt. Chemie, Funken- & Laserspektroskopie, GDOS

Life Sciences: ppm (parts per million): Mikrochemie, physikalische Sensoren

ppb (parts per billion): mikrochemisch schwierig (doppelt destilliertes Wasser, Platin- oder Teflongefäße...), bevorzugter Einsatz massenspektroskopischer Methoden

ppt, (part per trillion): praktisch nur mit massenspektroskopischen Methoden zugänglich

Ausnahme: Marie Curie: aus 5 Tonnen Pechblendeabfällen -> 1 dezigramm Radium, also  $5 \times 10^6$  g -> 0.1 g ... 20 ppt !!

Stoßrichtungen der Spurenanalyse:

- a) „vernünftige“ Menge Substanz, darin kleine (sehr kleine) Konzentration des Unbekannten
- b) kleine (sehr kleine) Menge Substanz, „vernünftige“ Konzentration des Unbekannten
- c) **beides !**

# Beispiele Spurenanalyse

## Life Sciences:

### Feste Phase:

Schwermetalle im Boden („Bauer Huber“) -> Schwermetallanreicherung in Pflanzen

Beispiel Wiesloch bei Sinsheim: 2000 Jahre Pb-Sn - Abbau

Flotationsrückstände: Pb -> 15 g/kg, Sb, Cd -> 600 mg/kg, As -> 30 g/kg,

Tl -> 3 g/kg

Grundwasser: As -> 63 mg/kg, Tl -> 300µg/kg

aber: Löslichkeit abhängig von Oxydationsstufe, pH-Wert etc !

Problem: Klärschlamm als Dünger

## Flüssige Phase:

Schwermetall im Wasser:

Beispiel Bangladesh: As in Tiefbrunnen -> 250 µg/kg, (WHO Limit: 10 µg/kg)

PCBs, Herbizide, Pestizide in Milch

Blei in Wein aus antiken Weinkühlern (Pewter = „Zinn“!)

Selen aus Selen-Rot Glasur in Salatessig

Ölanalyse bei Strahltriebwerken

## Gasphase:

CO aus undichten Rauchfängen (10 ppm über 1/2 h -> 50% tödlich)

## Medizin:

Selen-Therapie

Reinheit von Medikamenten

## Biologie:

Schwermetallanreicherung in Bakterienzellen – wie und wo? (-> Abbildung)

## Kunst und Archäologie:

Spurenelemente in Metallen und anderen Materialien als Herkunftshinweis

Beispiel „Römische Bronzestatue“

Beispiel Fernhandel mit Bimsstein im Mittelmeerraum

Farbige Bemalung in Kirchenräumen

Anilinfarben, Titan-weiß

$^{14}\text{C}$ -Altersbestimmung

Datierung prähistorischer Cu und Pb Abbau in Wales – Torfmoor Pb -> 500 mg/kg !

## Forensik:

Chemische Zusammensetzung von Fingerabdrücken, „DNA-Fingerprinting“

Analyse von Staub und Schmutz an Kleidung, Schuhen, Lacksplitter bei Unfällen mit Fahrerflucht ...

Haaranalyse – Geschichte von Gifteinwirkung

## Anwendung von Spurenanalyse



Wissenschaft	Thema	Forderung	Problem(e)
Life Sciences, Biologie, Medizin	Lebensmittelqualität, Wirksamkeit von Medikamenten	Spurenanalyse zusätzlich Abbildung	Moleküle hoher Massenzahl kein Vakuum
Kunst – Archäologie	Herkunft, Echtheit, Techniken der Herstellung	Spurenanalyse zusätzlich Abbildung nichtdestruktiv	Moleküle hoher Massenzahl kein Vakuum
Forensik (Aufklärung von Verbrechen)	Fingerabdrücke	Spurenanalyse (Öl, Drogen, DNA ...)	Moleküle hoher Massenzahl

## Ein kleiner Abweg: wieviel Material brauchen wir denn für eine Spurenanalyse?

**Annahme:** Wir suchen etwas wirklich Seltenes, vermutete Konzentration 1 ppt

**Annahme:** Wir können die Atome (Moleküle) dieses etwas identifizieren und zählen

**Annahme:** um eine einigermaßen verlässliche Statistik zu erhalten, wollen wir 100 Atome (Moleküle) dieses etwas zählen

**Annahme:** unser Analysenapparat hat eine Effizienz von 10%

Dann müssen in unserer Probe mindestens 1000 Atome (Moleküle) des Gesuchten enthalten sein.

Bei 1 ppt muss also die Probe  $1000 \times 10^{12}$  Atome (Moleküle) insgesamt  $10^{15}$  Atome (Moleküle) enthalten.

Für ein Metall (Cu, Fe, ..) wäre das eine 1-atomige Lage von  $1 \text{ cm}^2$  Grösse.

Anders gerechnet ist das ca.  $10^{-9}$  mol.

1 mol Fe, Cu, ... hat ca.  $10 \text{ cm}^3$ , also brauchen wir  $10^{-8} \text{ cm}^3$  oder  $10 \times 10 \times 100 \text{ } \mu\text{m}^3$

In Wasser: 1 mol hat 18 g oder  $\text{cm}^3$  also brauchen wir  $10 \times 10 \times 180 \text{ } \mu\text{m}^3$

Menschliches Haar: Durchmesser ca.  $10 \text{ } \mu\text{m}$

# Physikalische Methoden der Spurenanalyse

... ganz einfach: Atome (Moleküle) der unbekanntes Spezies **X**

a) identifizieren und b) abzählen.

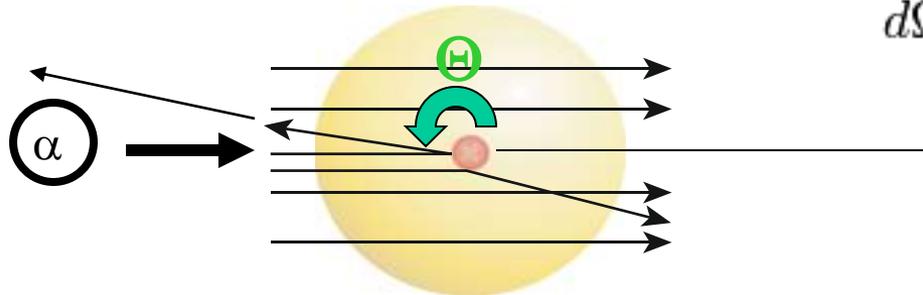
Charakteristisch für ein Atom: **Ordnungszahl Z = Kernladung**

Messmethode: Rutherford – Backscattering (Streuung leichter Ionen, z.B.  $\alpha$ -Teilchen an Atomkernen)

$$E(\text{rück}) = k \cdot E(\text{ein})$$

$$k = \left( \frac{m_1 \cos \theta_1 \pm \sqrt{m_2^2 - m_1^2 (\sin \theta_1)^2}}{m_1 + m_2} \right)^2$$

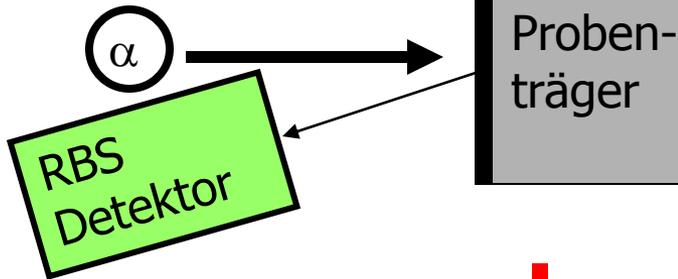
$$\frac{d\omega}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4E_0} \right)^2 \frac{1}{(\sin \theta/2)^4}$$



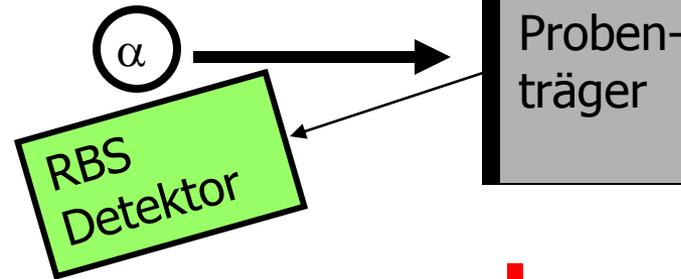
aber ...

2 Versuche:

a) Graphit



b) Masut



Versuchsergebnis:

100 % Kohlenstoff

?

100 % Kohlenstoff

**Keine ideale Messmethode, versagt zur Gänze bei Molekülen!**

## 2. Anlauf: was haben Atome und Moleküle noch?

das Atom- bzw. Molekulargewicht !

nicht ganz so charakteristisch, Probleme mit:

Isotopen (gleiche Kernladung  $Z$ , verschiedene Neutronenzahl)

Isobaren (verschiedene Kernladung  $Z$ , gleiche Masse)

Isomeren (Molekülen gleicher Summenformel, verschiedener Struktur)

Abhilfe:

1) In der Natur treten Isotope mit einer praktisch konstanten Häufigkeitsverteilung auf -> „Fingerprint“

2) Moleküle unbekannter Struktur: Zertrümmern und Teile identifizieren

## Beispiele:

1) Ein Atom mit  $A = 3$  *könnte* sein:

Tritium ( ${}^3_1\text{H}$ ) oder Helium ( ${}^3_2\text{He}$ ). Beide sind sehr selten.

Also ***muss*** im Fall Tritium daneben ein riesiges (viele Größenordnungen!) Signal von Wasserstoff ( ${}^1_1\text{H}$ ), im Fall Helium ein riesiges Signal von Helium ( ${}^4_2\text{He}$ ) auftreten. **Übrigens sind  ${}^3_1\text{H}$  und  ${}^3_2\text{He}$  nicht ganz exakt gleich schwer (Unterschied: ca 0.027%) – das kann ein gutes Massenspektrometer unterscheiden!**

2) Es gibt natürlich eine astronomische Anzahl von Molekülen mit z.B. 1067 Dalton Masse. Aber (fast) jedes Molekül hat „Sollbruchstellen“, an denen man es leicht zerbrechen kann. Vergleich mit bekannten Molekülen !



neues Problem: Ionen treten mit Vorliebe mit verschiedenen Ladungen auf: positiv oder negativ, einfach, zweifach, ... -fach geladen.

Erinnerung:

Quadrupol – MS: benötigt wohldefinierte Eingangsrichtung (parallel zu Achse) und Energie der Ionen, gibt nur Ausbeute für ein bestimmtes  $m/z$ , arbeitet kontinuierlich  
-> Spektrum durch Durchstimmen

Time-of-Flight (ToF) – MS: benötigt wohldefinierten Startzeitpunkt und Energie der Ionen, gibt Spektrum von  $m/z$ , arbeitet diskontinuierlich (Impuls)

Mögliche Ionenauslöser: Laserpulse, Primär-Ionenpulse (gepulstes SIMS)

Alternative: Sekundär-Ionen-Gate

Problem bei nichtleitenden Proben: Statische Aufladung

Lösung: Elektronen „Flood Gun“

# Das Sortieren von Atomen „One by One“

Walter Kutschera

Physik in unserer Zeit / 31. Jahrg. 2000 / Nr. 5

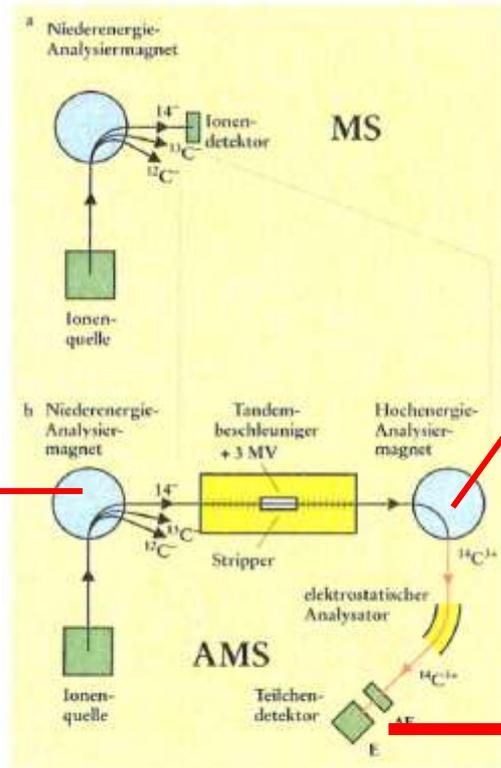
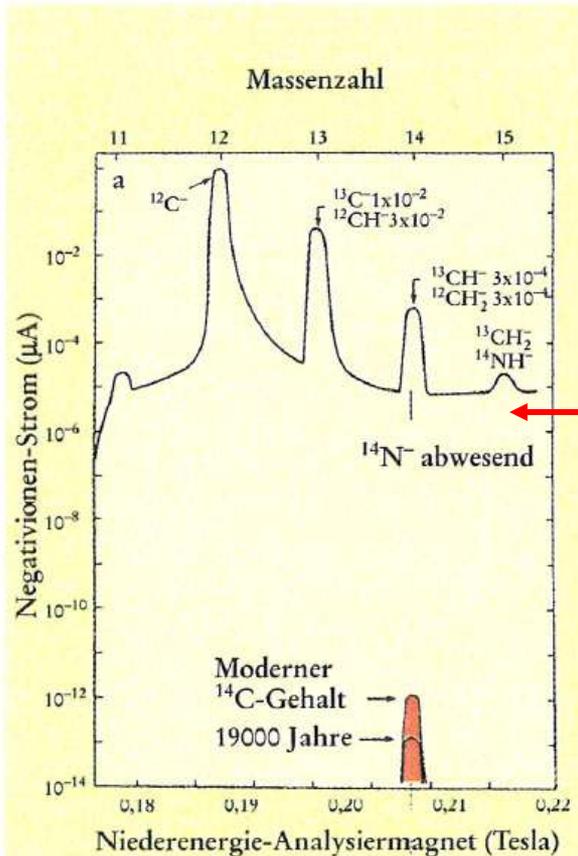
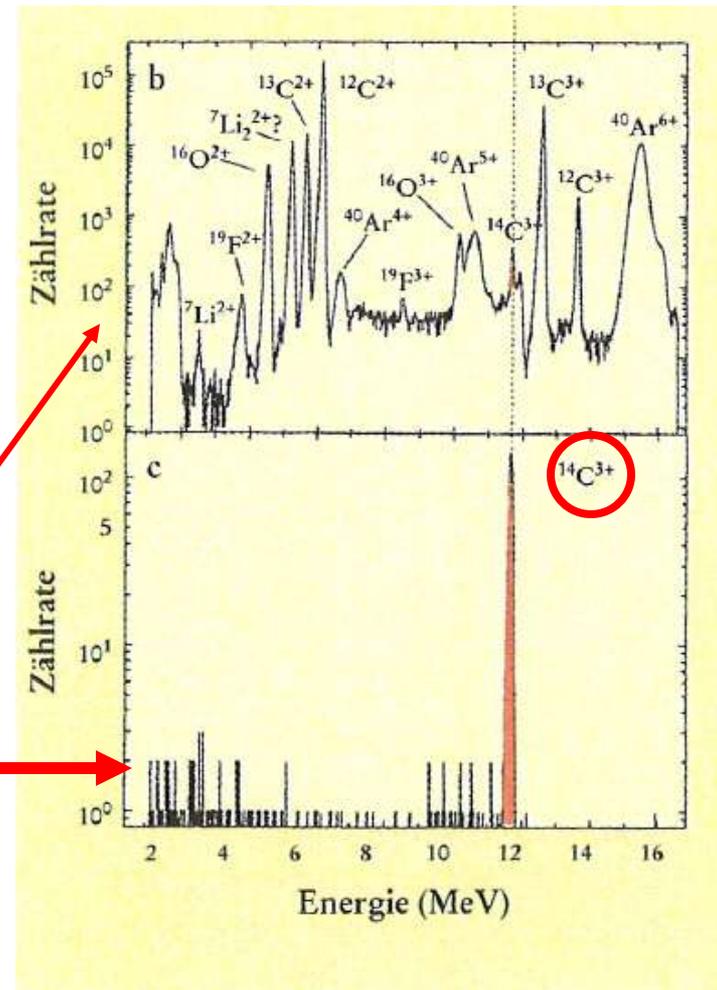
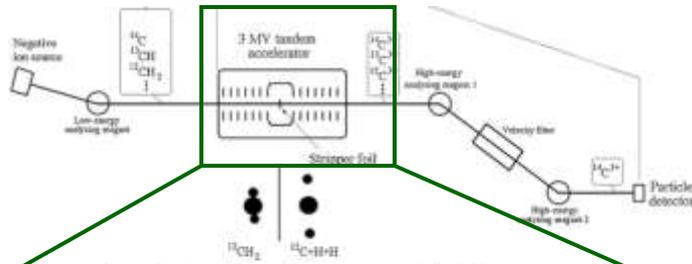


Abb. 1. Schematische Darstellung des Übergangs von konventioneller Massenspektrometrie (MS) (a) zur Beschleunigermassenspektrometrie (AMS) am Beispiel des  $^{14}\text{C}$ -Nachweises (b).

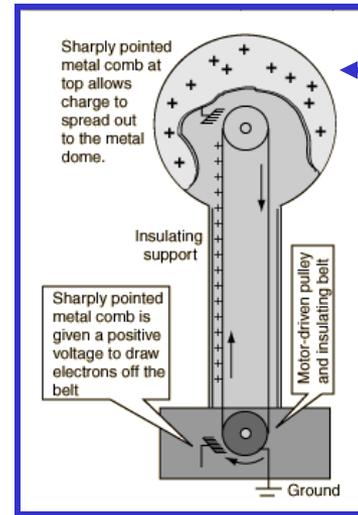
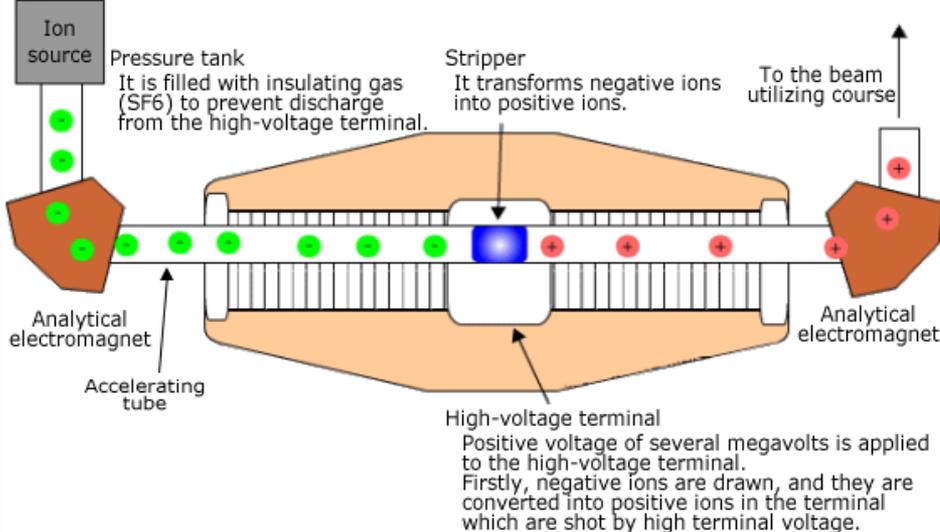


# das „Herzstück“: der Tandem-Accelerator



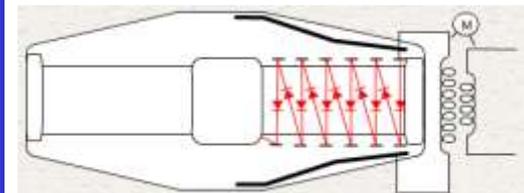
Accelerator Mass Spectrometry (AMS)

Equipment to produce negative ions  
It outputs negative ions at energy of  
around 100 to 200 keV.



Hochspannungserzeugung:

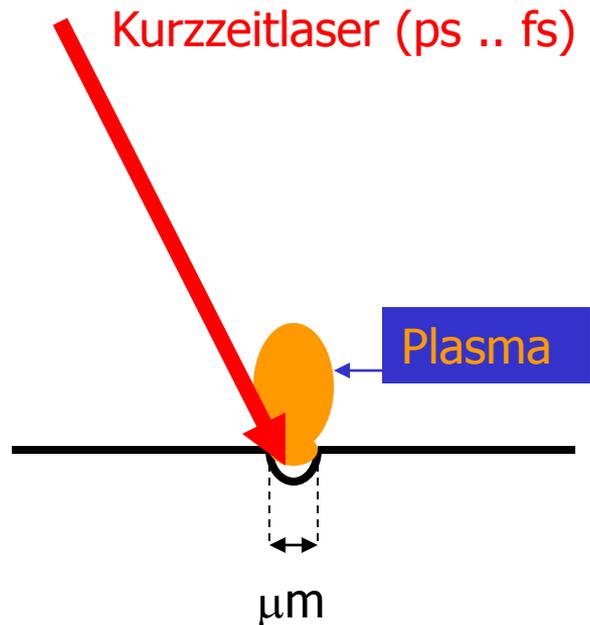
- 1) Van de Graaff - Generator
- 2) Kaskade (Cockcroft-Walton - Generator)



Alternative zu SIMS an fester Oberfläche:

2a) Laserstrahlung -> Laser Desorption Ionization

Laser ablation plasma



Fokussierter Kurzzeitlaser (ps .. fs) verdampft kleines Volumen -> bei extremer Temperatur: Plasma

Vorteil:

auch ausser Vakuum

gepulster Betrieb

Abrastern einer Oberfläche leicht

keine Aufladung nichtleitender Proben

Nachteil:

leicht destruktiv

Ausbeute für schwere (Molekül-) Ionen extrem gering

# Erzeugung von Ionen

## 2b) flüssige Phase: ESI = Electro-Spray-Ionization

### Eigenschaften:

braucht kein Vakuum

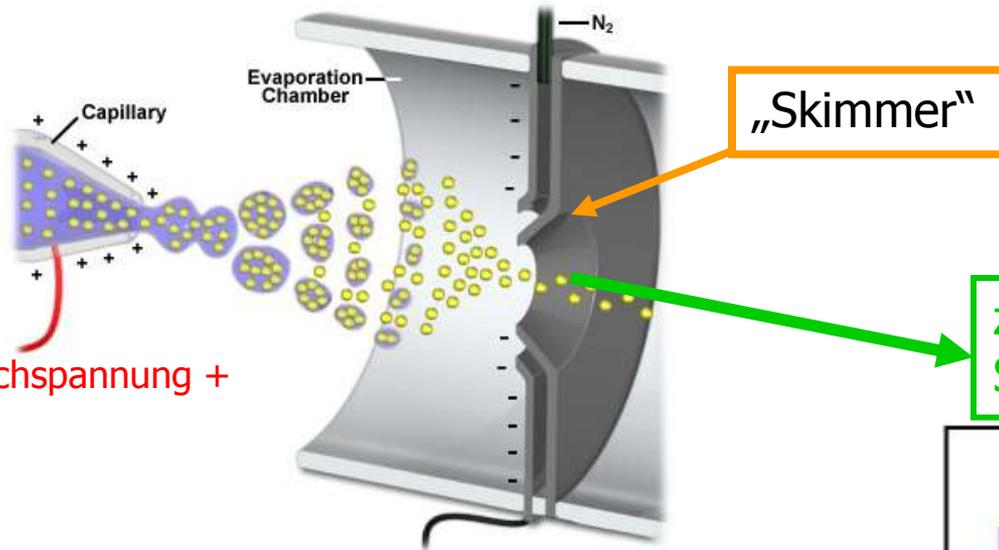
Ionen müssen durch Saugspannung abgezogen werden

kontinuierliche Arbeitsweise

keinerlei Probenpräparation

funktioniert mit verschiedenen Lösungsmitteln

zerstört Moleküle i.a. nicht

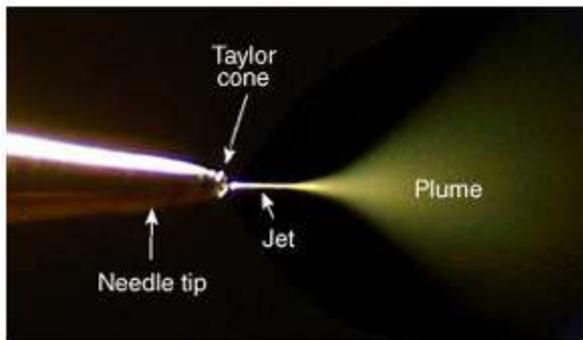


„Skimmer“

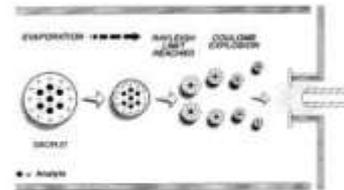
zum Spektrometer

Hochspannung +

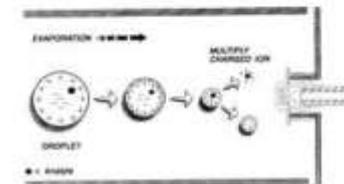
Hochspannung -



### Ionization Mechanisms



- Coulomb Fission :
  - Assumes that the increased charge density, due to solvent evaporation, causes large droplets to divide into smaller droplets eventually leading to single ions.

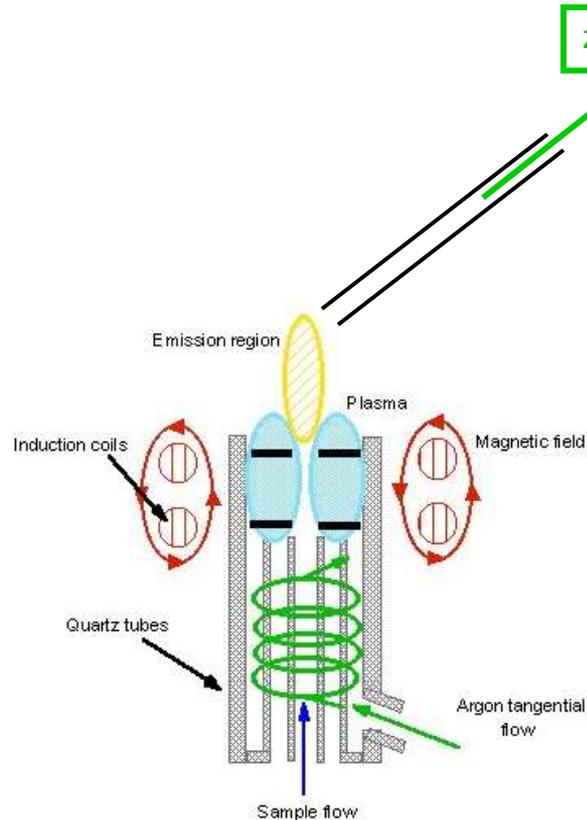


- Ion Evaporation:
  - Assumes the increased charge density that results from solvent evaporation causes Coulombic repulsion to overcome the liquid's surface tension, resulting in a release of ions from droplet surfaces

## Erzeugung von Ionen

2c) Gasphase: ICP = Inductively Coupled Plasma: elektrodenlose Gasentladung in Probengas, evtl. mit Trägergas (Ar)

zum Spektrometer



Eigenschaften:

braucht kein oder nur schlechtes Vakuum

geeignet für alles, was sich in einen Gasstrom bringen lässt

**ABER:** Vorsicht beim Eindampfen – mögliche Selektivität!

Ionen müssen durch Saugspannung abgezogen werden

kontinuierliche Arbeitsweise

keinerlei Probenpräparation, wenn Probe gasförmig

Plasma sehr heiss (10 000 K) -> alle Moleküle zerschlagen!

Kann auch als Quelle für AES (Atomic Emission Spectroscopy = Analyse der emittierten Spektren) dienen.

## A) In Vakuum

Nachweis schwerer Ionen  $m/z \gg 100$  : Sputtern mit schweren Primärionen

Xe, SF<sub>6</sub>, C<sub>60</sub> ...  
131,146,720 m/z

Applied Surface Science (2006)

Stretching the limits of static SIMS with C<sub>60</sub><sup>+</sup>

A. Delcorte \*, C. Poleunis, P. Bertrand

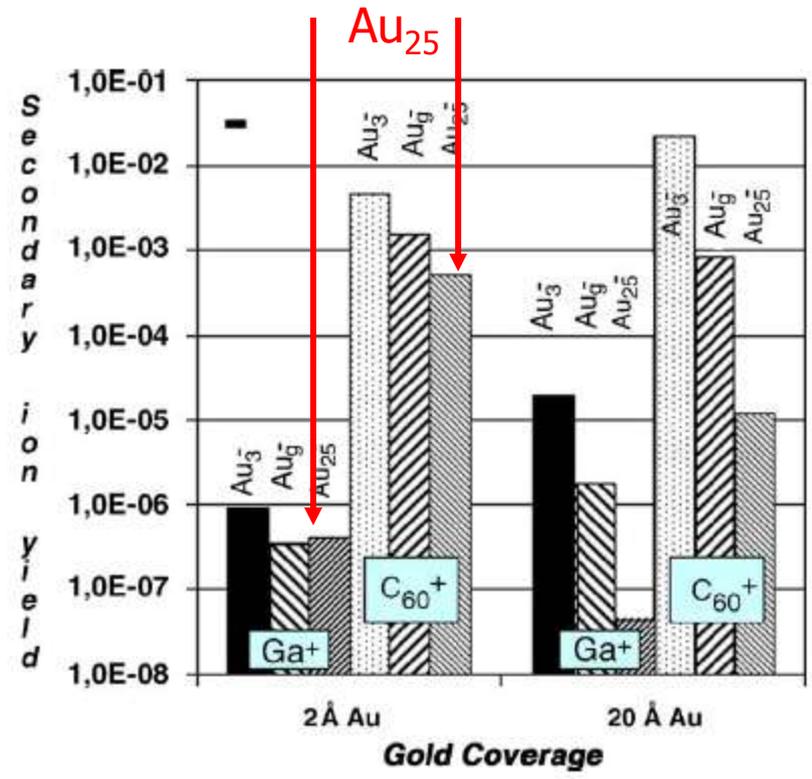


Fig. 1. Secondary ion yields of negative gold clusters (Au<sub>3</sub><sup>-</sup>, Au<sub>9</sub><sup>-</sup> and Au<sub>25</sub><sup>-</sup>) sputtered from two gold-metallized Irganox 1010 films (2 and 20 nmol Au/cm<sup>2</sup>).

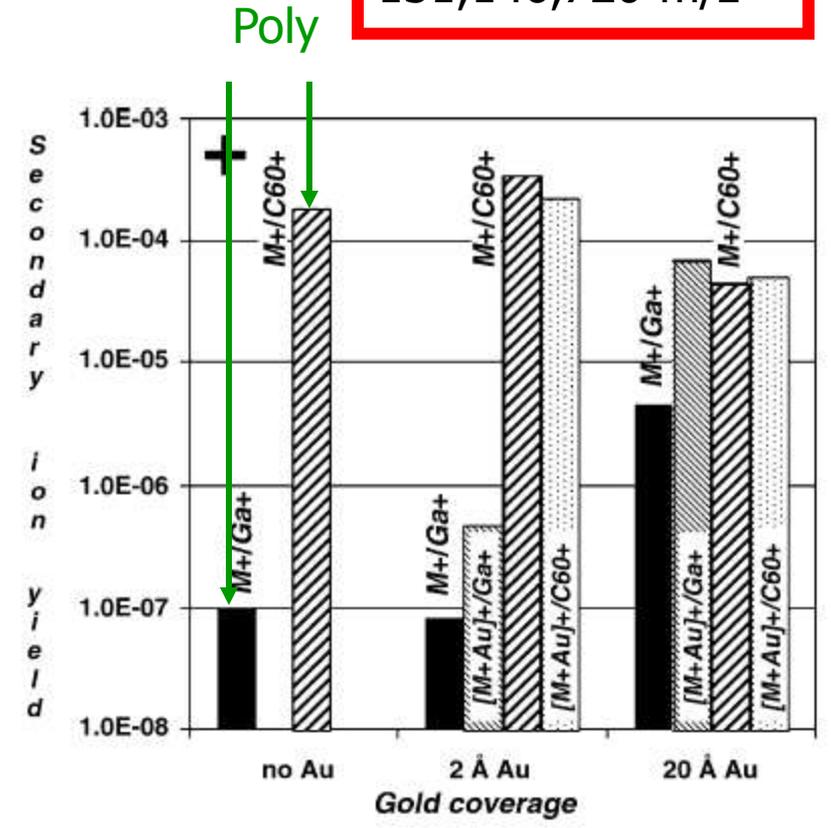


Fig. 3. Secondary ion yields of positive molecular ions, M<sup>+</sup> and quasimolecular ions (M + Au)<sup>+</sup>, sputtered from a pristine and two gold-metallized Irganox 1010 films (2 and 20 nmol Au/cm<sup>2</sup>).

# Anwendung von Massenspektroskopie in anderen Wissenschaftsgebieten

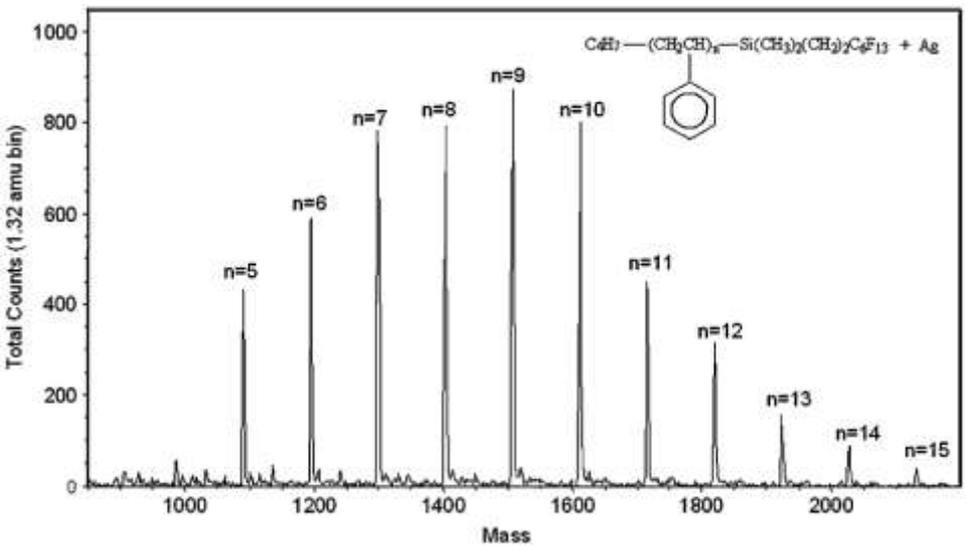
## A) In Vakuum

Analyse schwerer Ionen  $m/z \gg 100$

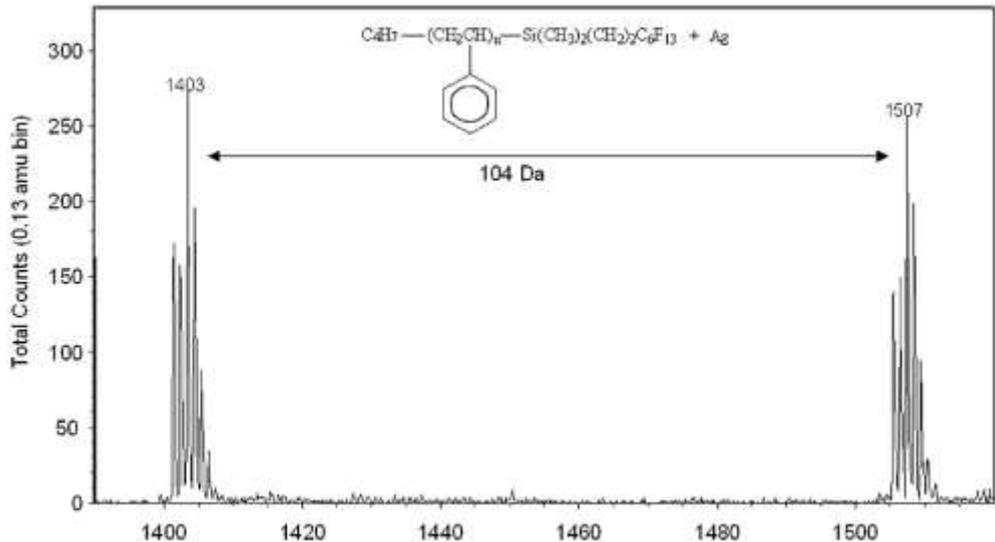
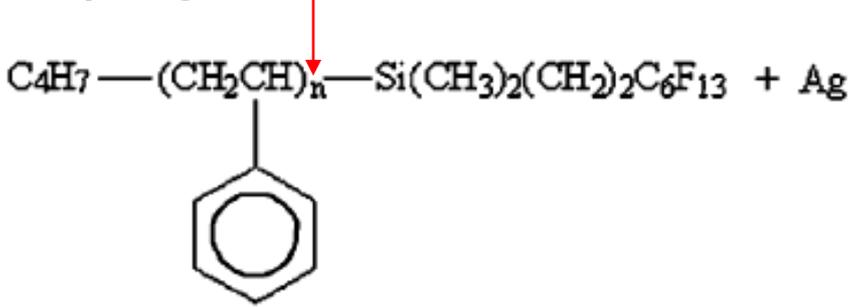
Time-of-flight secondary ion mass spectrometry: techniques and applications for the characterization of biomaterial surfaces

Biomaterials 24 (2003) 3635-3653  
Review

Anna M. Belu<sup>1</sup>, Daniel J. Graham, David G. Castner\*



a) Oligomere

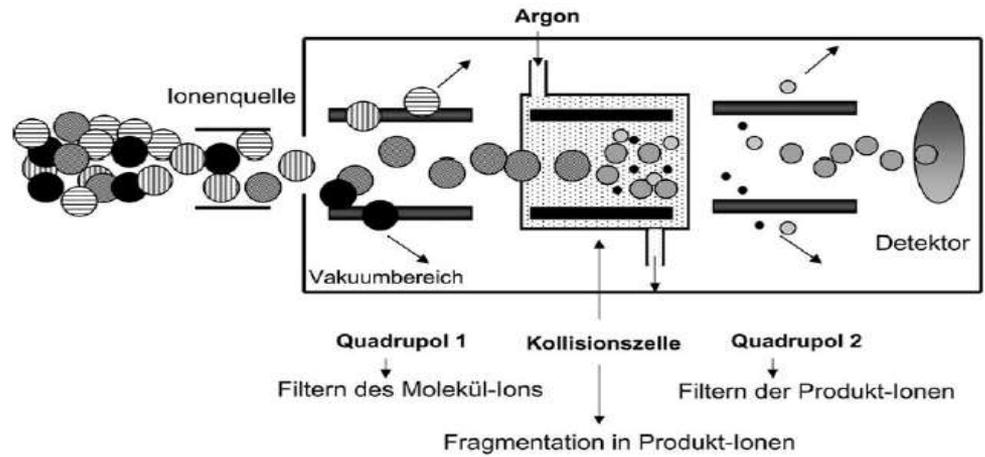


# Anwendung von Massenspektroskopie in anderen Wissenschaftsgebieten

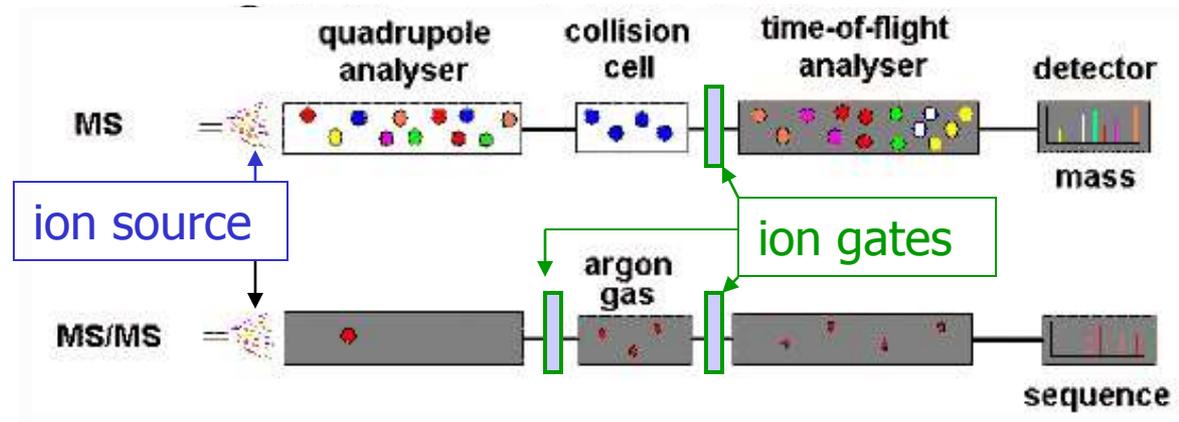
## A) In Vakuum

Analyse schwerer Ionen  $m/z \gg 100$  : „Tandem“ – Massenspektroskopie

d.h. Zerschlagen schwerer Molekülonen und Analyse der (charakteristischen) Bruchstücke



Fragmentierung durch Stöße mit Gas, Wand, Elektronenbeschuss (Ionenfalle) ...



Q - ToF

ToF - ToF

*Q-ToF mass spectrometer operating in MS (upper) and MS/MS mode (lower) modes.*

## A) In Vakuum

Analyse schwerer Ionen  $m/z \gg 100$  : „Tandem“ – Massenspektroskopie

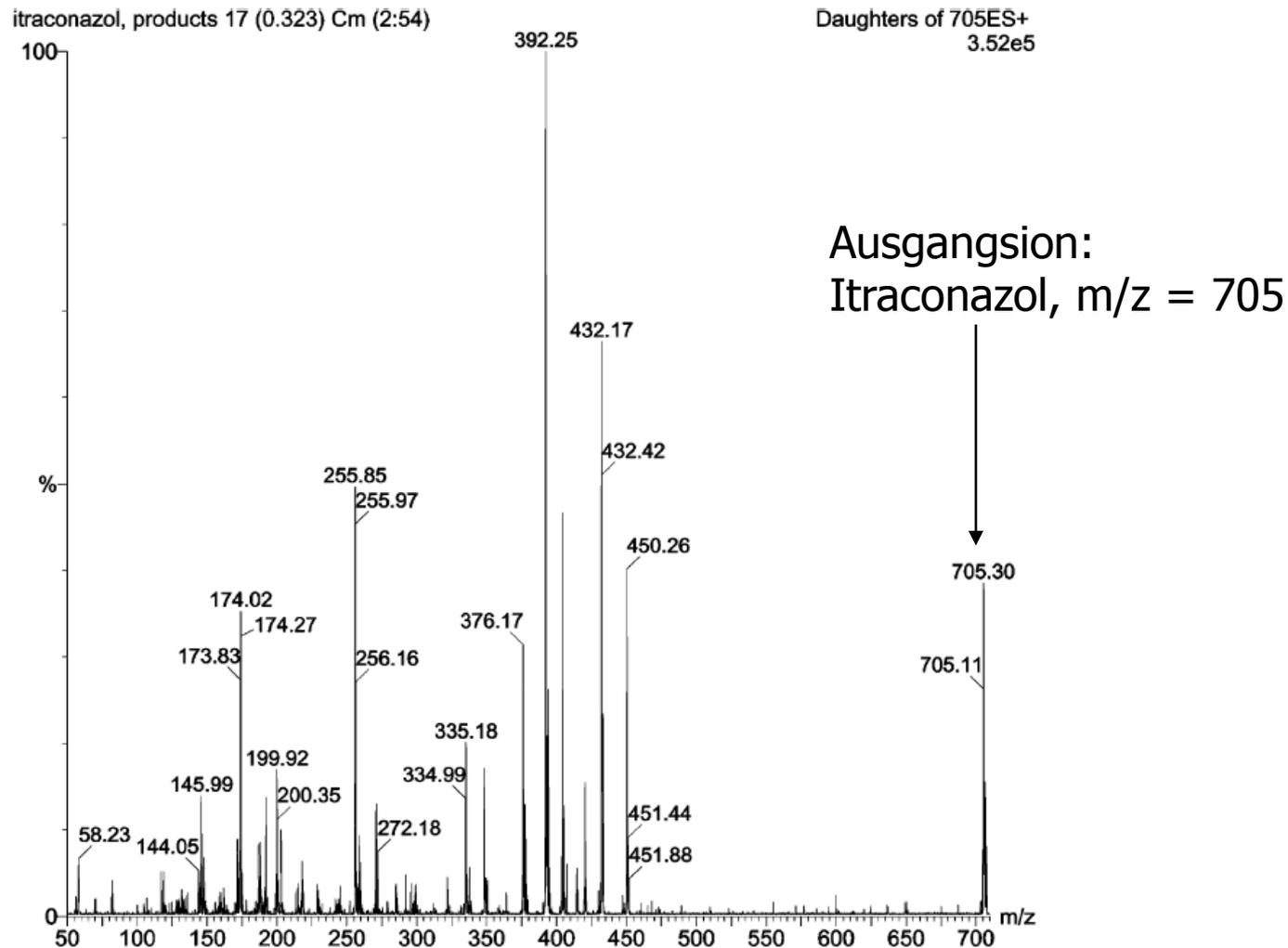
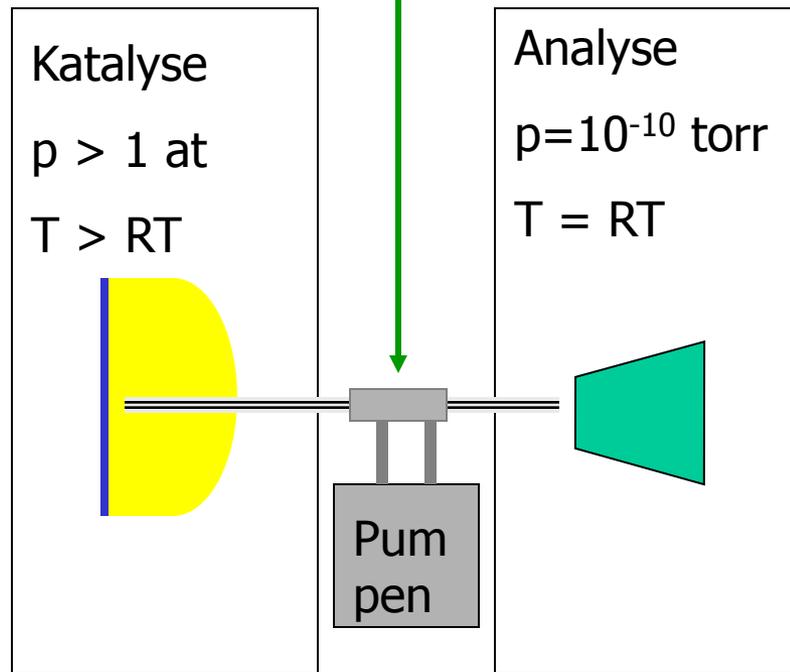


Abbildung 4 Kollisions-induziertes Desintegrationspektrum des Antimykotikums Itraconazol. X-Achse:  $m/z$  für Masse-zu-Ladungs-  
Ratio, Y-Achse: relative Signalintensität. Das Fragmentation mit 392  $m/z$  wird zur Quantifizierung genutzt (siehe Abbildung 5).

## B) Ausserhalb Vakuum

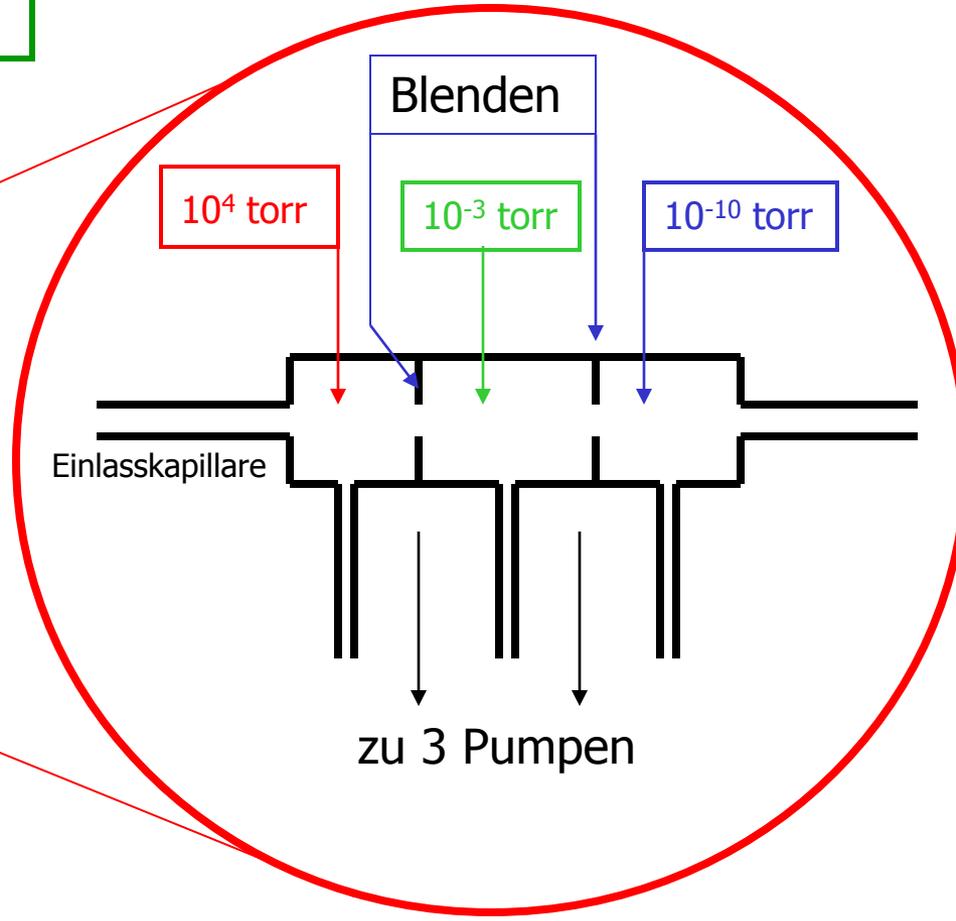
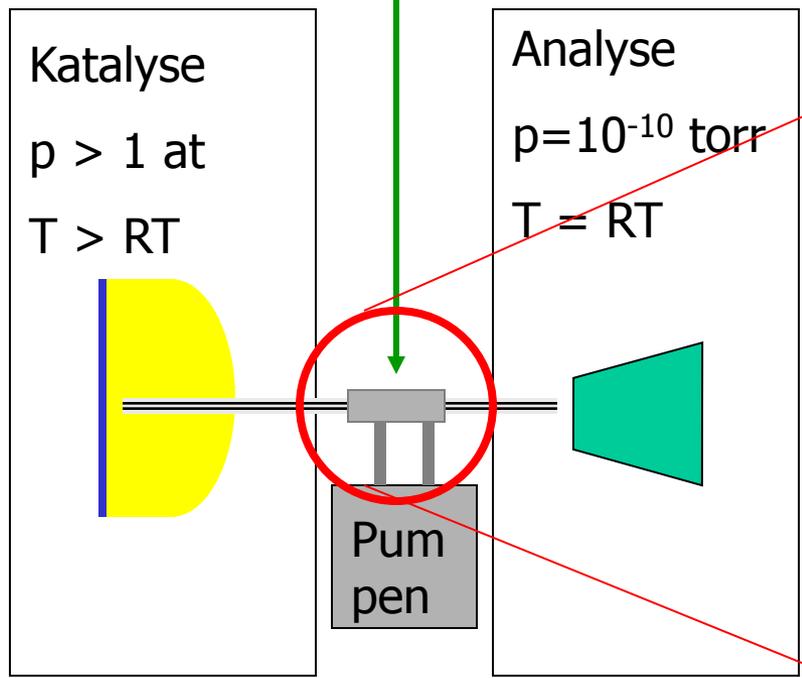
### Differentiell gepumpte Transferleitung

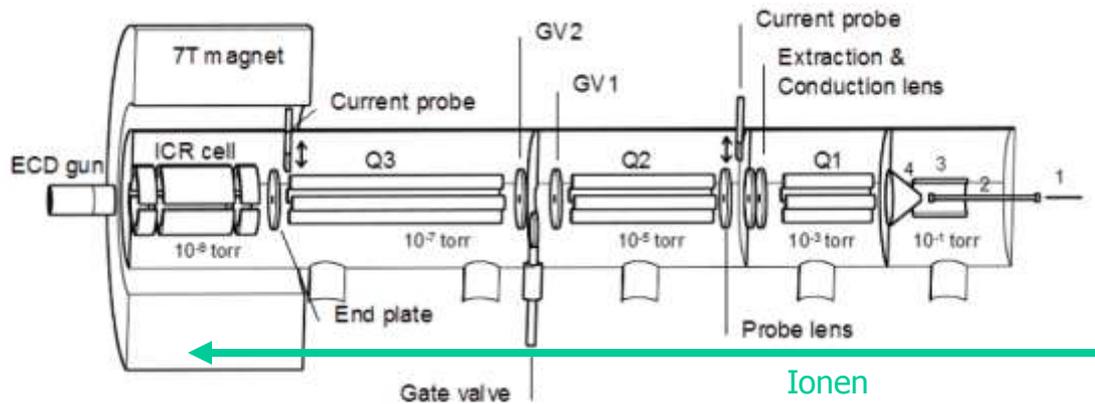


Extraktionskapillare auf einigen kV negativ  $\rightarrow$  Ionen in Richtung Kapillare geführt und auf definierte Energie gebracht.

B) Ausserhalb Vakuum

Differentiell gepumpte Transferleitung

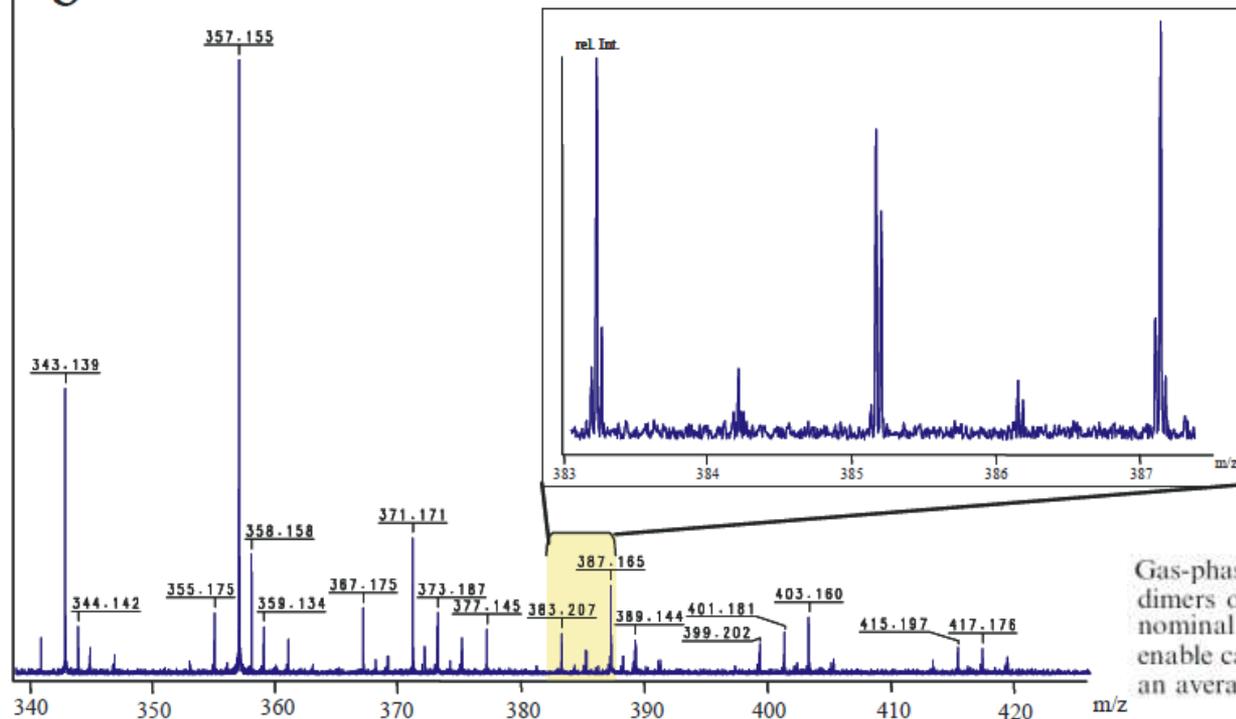




7T external electrospray FT-ICR setup at FOM-AMOLF. Indicated are three quadrupole ion guides, an open ended capacitively coupled ICR cell, the location of an electron gun for ECD several current probes to determine the ion optical transmission efficiency and the differential pumping stages with corresponding operating pressures. To bridge the gate valve between Q2 and Q3 an electrostatic Einzel lens is used consisting of GV1, GV2 and the gate valve housing as the electrodes.

rel. Int.

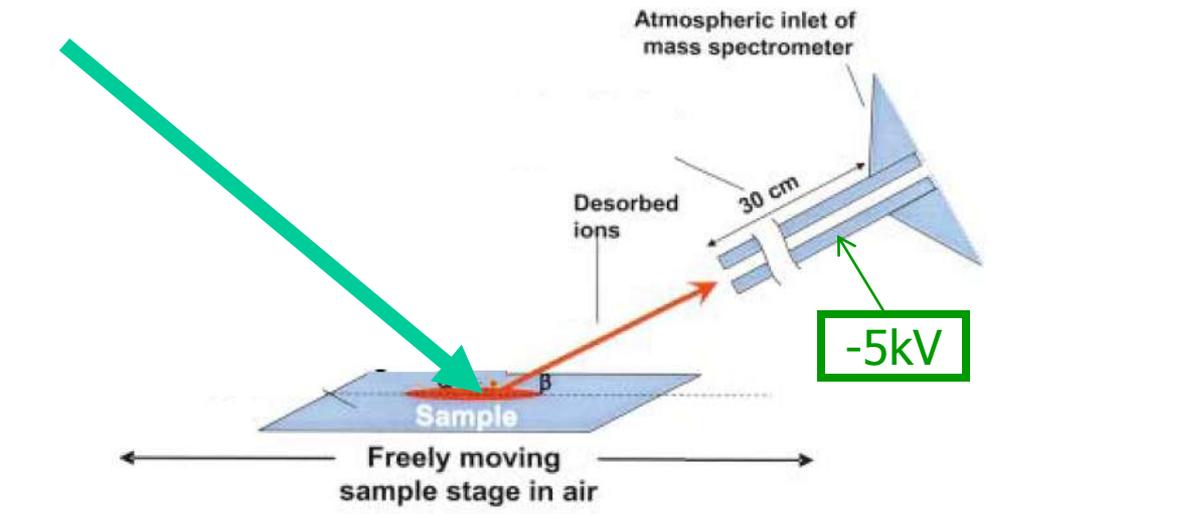
b



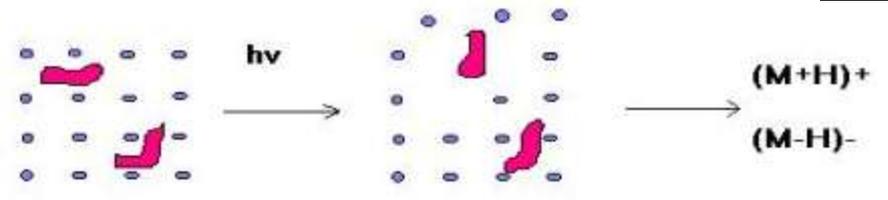
Gas-phase products from reaction of  $\alpha$ -pinene with ozone dimers of the carboxylic acids, the *insert* shows that at one nominal mass more than one signal appear. Accurate mass data enable calculation of the elemental composition of the signals with an average error of less than 2 ppm

# Anwendung von Massenspektroskopie in anderen Wissenschaftsgebieten

## B) Ausserhalb Vakuum

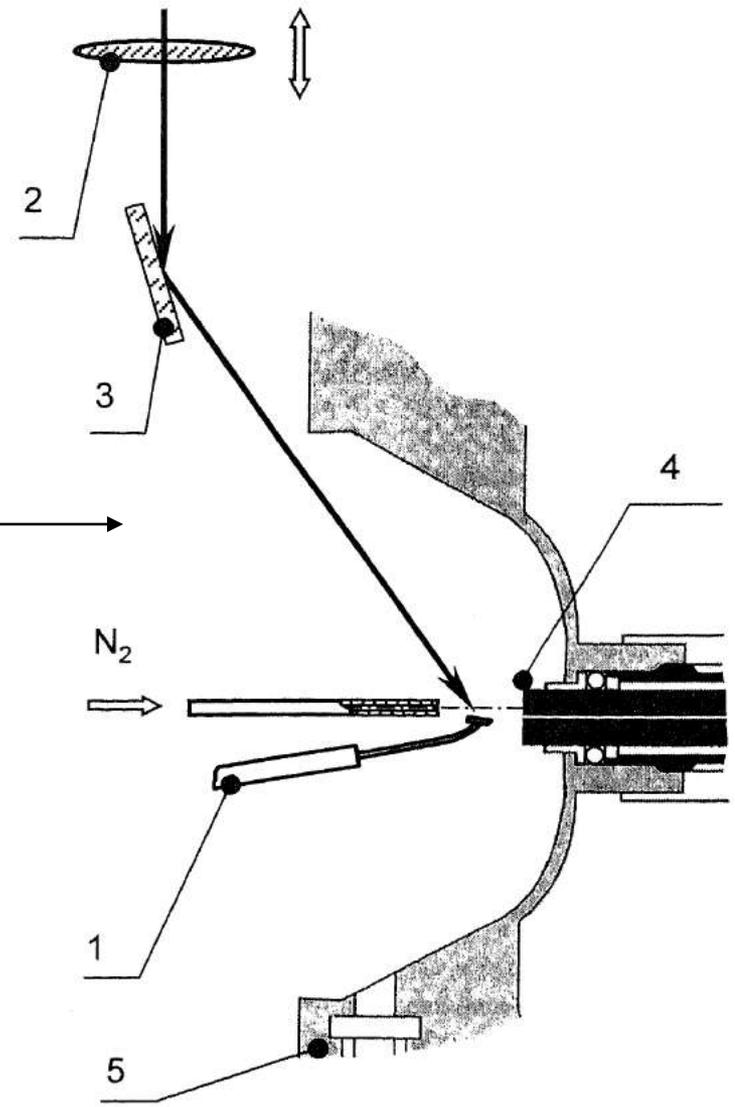


MALDI-TOF MS



- = matrix
- = analyte

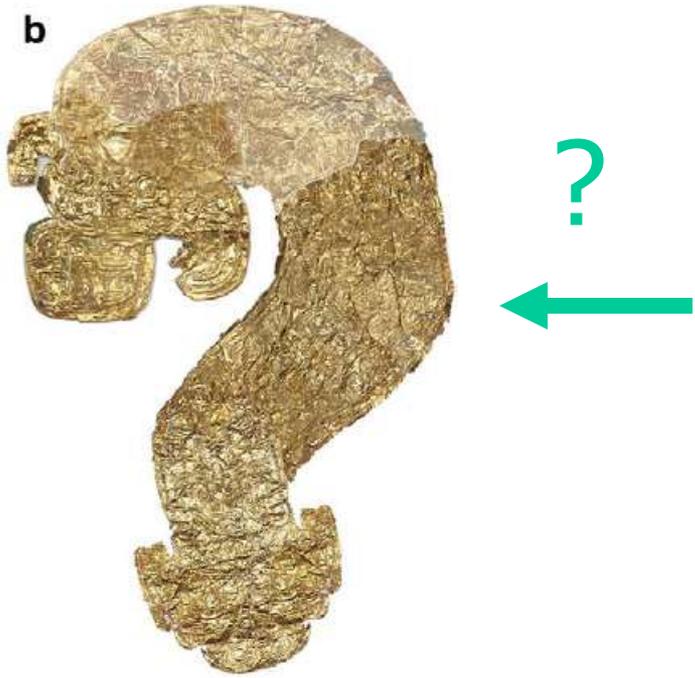
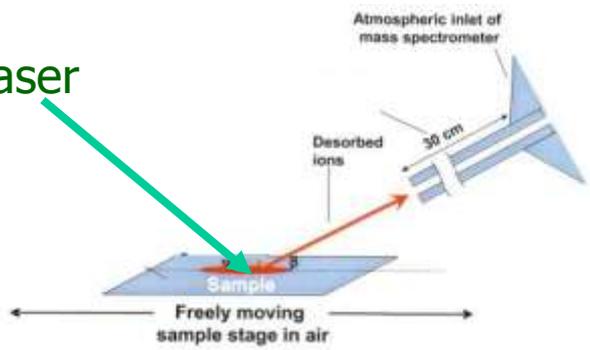
Matrix assisted laser desorption ionisation (MALDI)



# Anwendung von Massenspektroskopie in anderen Wissenschaftsgebiete

## B) Ausserhalb Vakuum

Laser



Trace element fingerprinting of ancient Chinese gold with femtosecond laser ablation-inductively coupled mass spectrometry

Lynn B. Brostoff<sup>a,\*</sup>, Jhanis J. González<sup>b</sup>, Paul Jett<sup>c</sup>, Richard E. Russo<sup>b</sup>

<sup>a</sup>Library of Congress, Preservation Research and Testing Division, 101 Independence Avenue SE, Washington, DC 20540, USA

<sup>b</sup>Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

<sup>c</sup>The Jeter Gallery of Art/Arthur M. Sandler Museum, Smithsonian Institution, Washington, DC 20561, USA

## B) Ausserhalb Vakuum

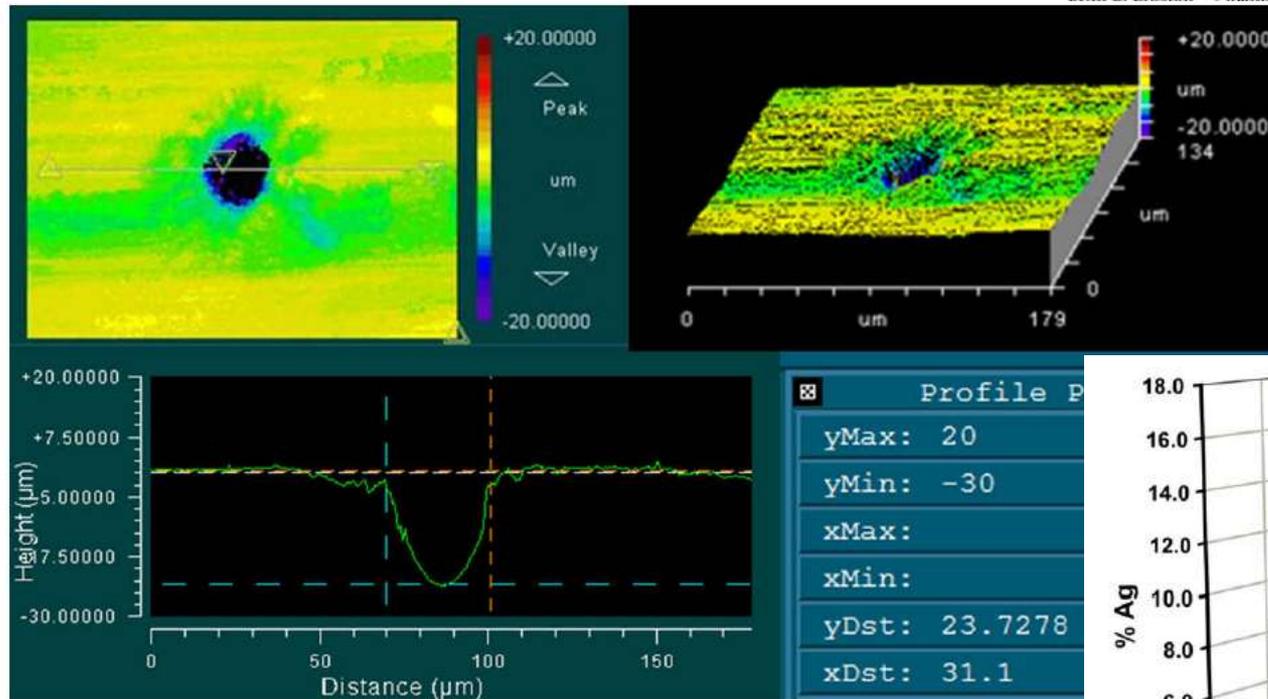


Fig. 4. White light interferometer microscope data and images and crater profile produced by femtosecond (~30 μm spot size) laser.

### Trace element fingerprinting of ancient Chinese gold with femtosecond laser ablation-inductively coupled mass spectrometry

Lynn B. Brostoff<sup>a,\*</sup>, Ibanis I. González<sup>b</sup>, Paul Jett<sup>c</sup>, Richard E. Russo<sup>b</sup>  
<sup>a</sup>Ing. Division, 301 Independence Avenue SE, Washington, DC 20540, USA  
<sup>b</sup>10001 University Ave, Berkeley, CA 94720, USA  
<sup>c</sup>Smithsonian Institution, Washington, DC 20561, USA

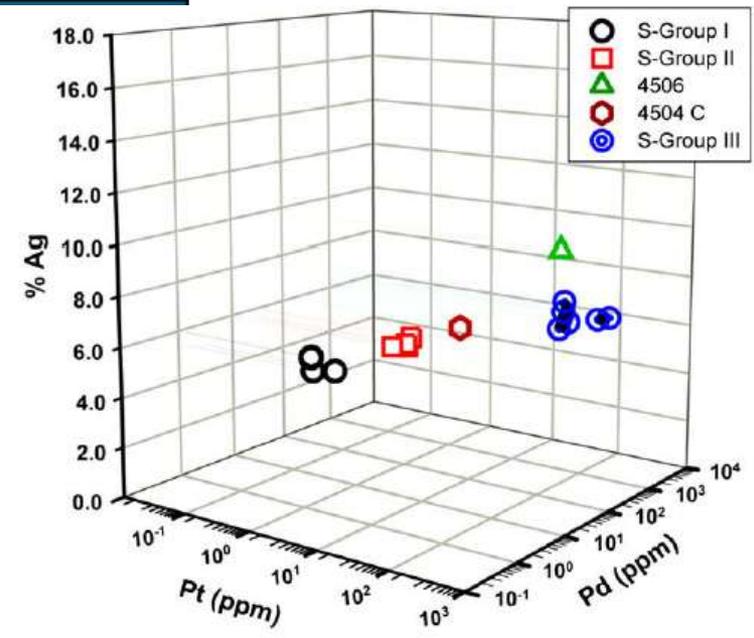


Fig. 5. Plot of Ag-Pd-Pt concentrations in Freer gold objects, as determined by femtosecond-laser ablation. Singer gold fragments: S-Group I (open circle), S-Group II (square), and S-Group III (filled circle); other gold object (upward triangle).

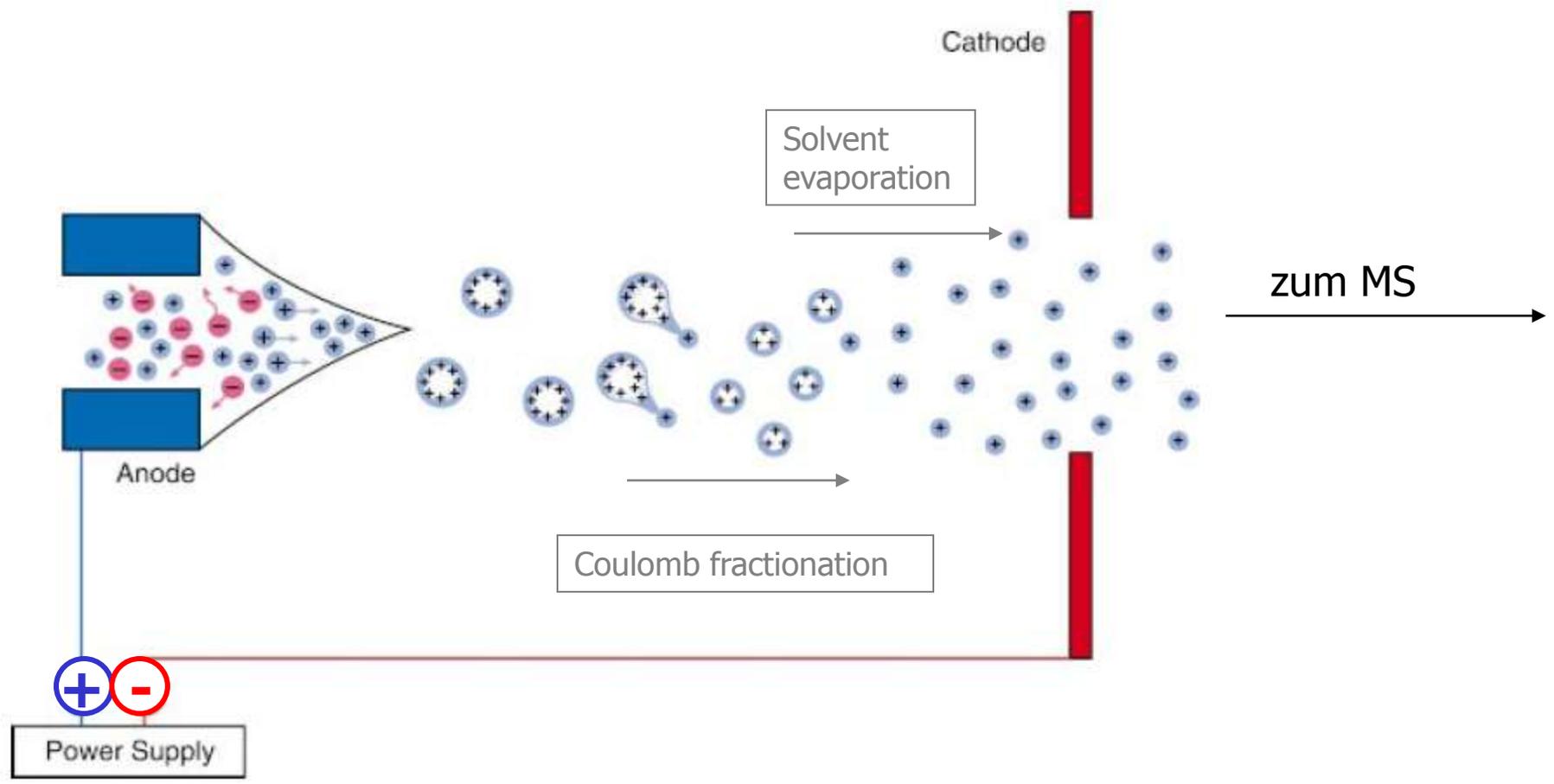
Spurenelemente Ag, Pt und Pd zur Identifikation

# Anwendung von Massenspektroskopie in anderen Wissenschaftsgebieten

## B) Ausserhalb Vakuum

Laser ablation hat geringe Ausbeute bei hohen  $m/z$ , ->

### Elektro-Spray - MS



# Anwendung von Massenspektroskopie in anderen Wissenschaftsgebieten

## B) Ausserhalb Vakuum

### Stepwise evolution of protein native structure with electrospray into the gas phase, $10^{-12}$ to $10^2$ s

Kathrin Breuker<sup>a</sup> and Fred W. McLafferty<sup>b,1</sup>  
<sup>a</sup>Institute of Organic Chemistry and Center for Molecular Biosciences Innsbruck, University of Innsbruck, Innrain 52a, Austria; and <sup>b</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301

PNAS | November 25, 2008 | vol. 105 | no. 47 | 18145–18152

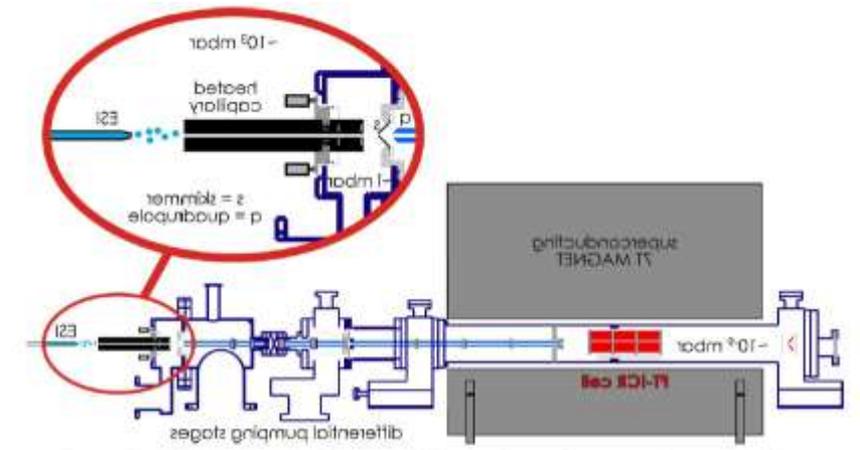


Fig. 3. Electrospray of a protein solution (from right) at atmospheric pressure with  $-1$  kV acceleration of ESI droplets into a heated capillary. Exiting ions are accelerated ( $-20$  V) into a lower pressure ( $-1$  mbar) region at under variable low energy ( $< 1$  eV) collisions, pass through a skimmer into a lower pressure region for possible higher energy ( $> 1$  eV) collisions, and are conducted into and trapped inside the measurement cell ( $-10^{-6}$  mbar) of the Fourier-transform mass spectrometer.

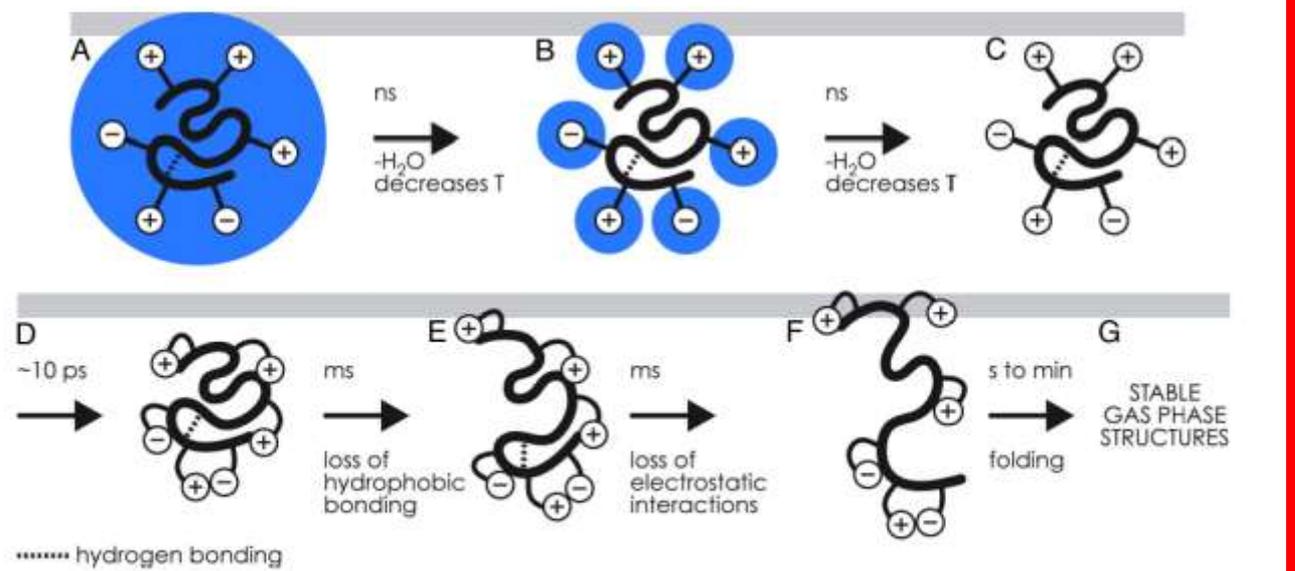


Fig. 1. Stepwise evolution after ESI of the structure of a globular protein (e.g., cytochrome c, ubiquitin). (A) Native protein covered with a monolayer of  $H_2O$ , followed by nanosecond  $H_2O$  loss and concomitant cooling. (B) Native protein with exterior ionic functionalities still hydrated undergoes ns  $H_2O$  loss and cooling. (C) The dry protein undergoes  $\sim 10$ -ps collapse of its exterior ionic functionalities. (D–G) The exterior-collapsed “near-native” protein undergoes thermal re-equilibration (D), millisecond loss of hydrophobic bonding (E), and millisecond loss of electrostatic interactions (F); the transiently unfolded ions form new noncovalent bonds in seconds, folding to more stable gaseous ion structures (G); these stabilize to energy minima conformers in minutes.

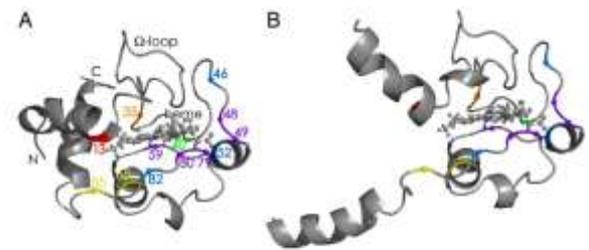


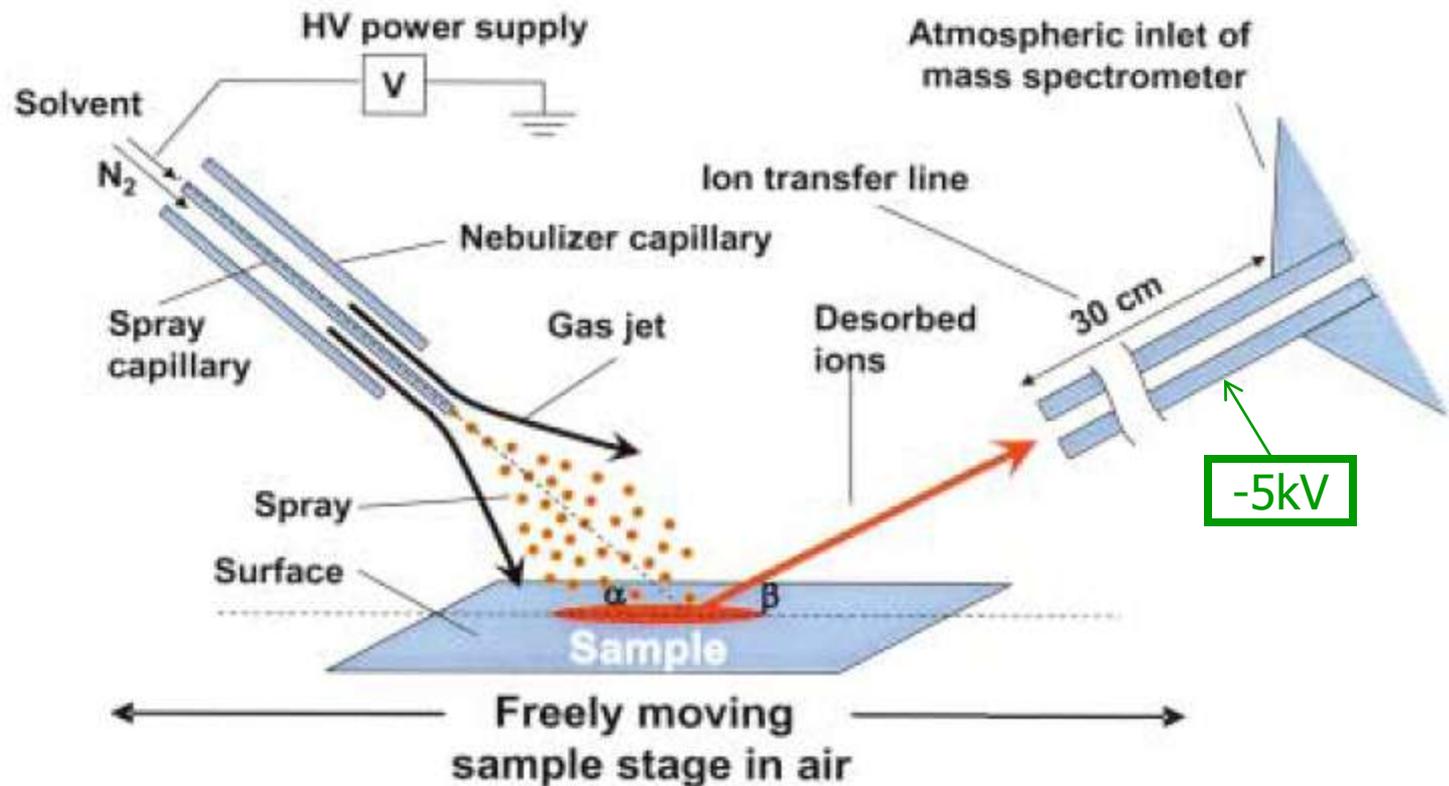
Fig. 4. Cytochrome c structures. (A) Native state, based on NMR data (31). (B) Initial gas-phase unfolding, based on NECD data (27). The order of regional stability in the gas phase, based on the reverse of the order of unfolding determined in NECD experiments, is Y48T49 = W59 = K79/M80 > F46 = N52 = F82 > T40 > L48 = I85 > L35 > K13.

B) Ausserhalb Vakuum

# Mass Spectrometry Sampling Under Ambient Conditions with Desorption Electrospray Ionization

Zoltán Takáts, *et al.*

*Science* **306**, 471 (2004);



Absolut nichtdestruktiv, Nachweis von Drogen auf der Haut möglich !

# Eine Anleihe bei der Atomsonde .. das Flugzeit-Massenspektrometer

Complex MEMS: a fully integrated TOF micro mass spectrometer

Eric Wapelhorst, Jan-Peter Hauschild\*, Jörg Müller

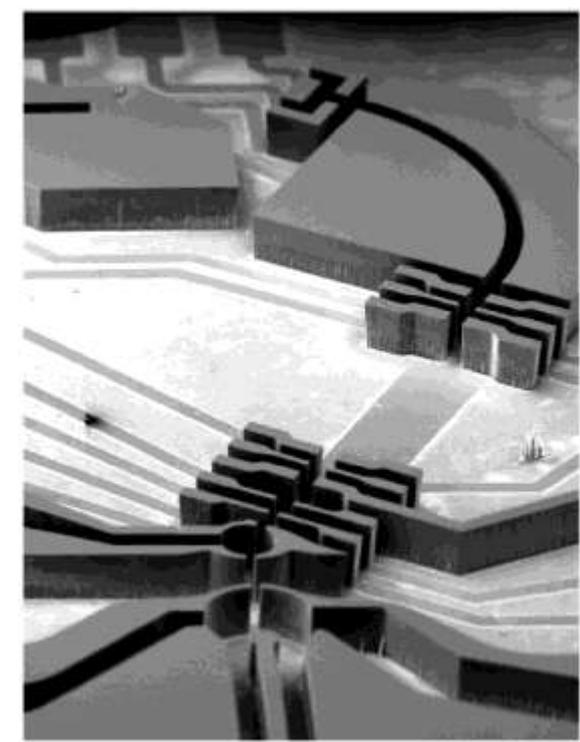
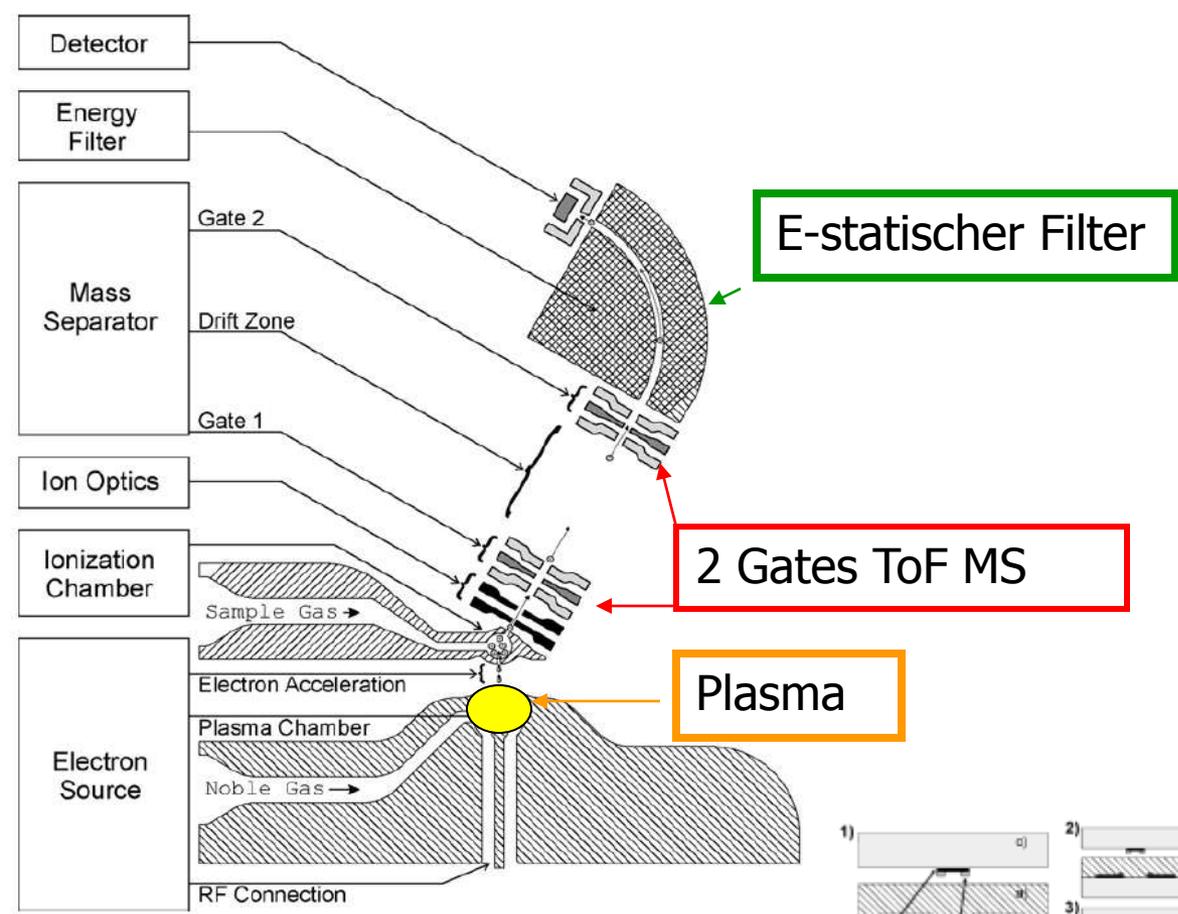


Fig. 12. SEM picture of the structures.

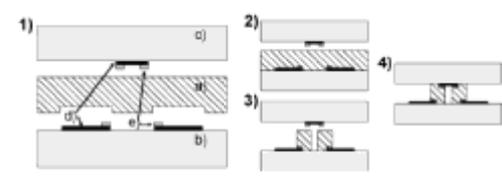


Fig. 10. Fabrication: (a) silicon, (b) bottom glass, (c) top glass, (d) nickel wires and (e) gold pads.

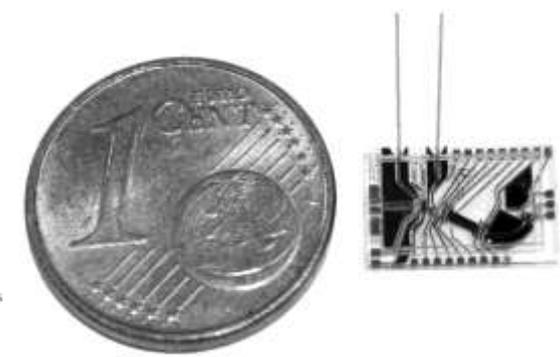


Fig. 11. Part of the MMS chip.

Spurenanalyse mit ICP – MS  
(induktiv gekoppeltes Plasma als  
Ionenquelle)

# Ambient desorption ionization mass spectrometry

Trends in Analytical Chemistry, Vol. 27, No. 4, 2008

Andre Venter, Marcela Nefliu, R. Graham Cooks

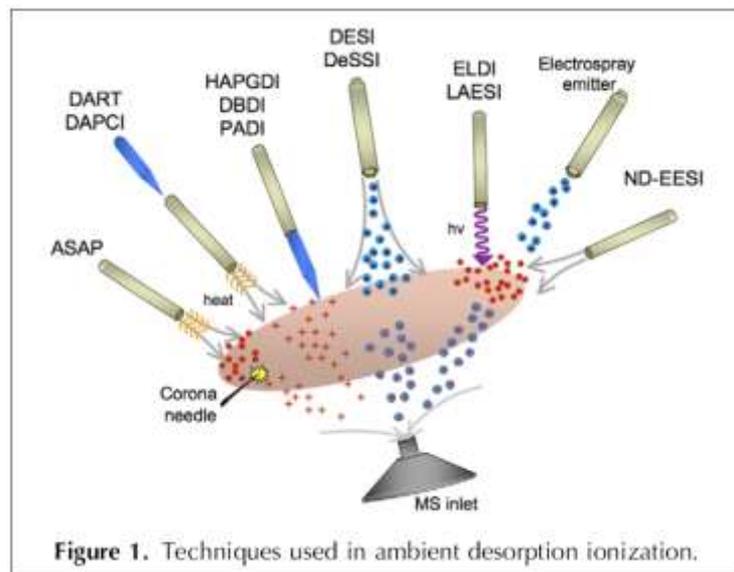


Figure 1. Techniques used in ambient desorption ionization.

Table 1. Ambient desorption ionization techniques listed in order of publication

Technique	Acronym	Date
Desorption Electrospray Ionization	DESI [1]	2004
Surface Sampling Probe	SSP [26]	2004
Direct Analysis in Real Time	DART [2]	2005
Ambient Solid Analysis Probe	ASAP [27]	2005
Electrospray Laser Desorption/Ionization	ELDI [28]	2005
Fused Droplet Electrospray Ionization	FD-ESI [29]	2005
Desorption Atmospheric Pressure Chemical Ionization	DAPCI [21]	2005
MALDI Assisted Electrospray Ionization	MALDESI [30]	2006
Extractive Electrospray Ionization	EESI [31]	2006
Desorption Sonic Spray Ionization	DeSSI [32]	2006
Plasma-Assisted Desorption/Ionization	PADI [33]	2007
Dielectric Discharge Barrier Ionization	DBDI [24]	2007
Helium Atmospheric Pressure Glow Discharge Ionization	HAPGDI [34]	2007
Neutral Desorption Extractive Electrospray Ionization	ND-EESI [35]	2007
Laser Ablation Electrospray Ionization	LAESI [36]	2007
Atmospheric Pressure Thermal Desorption Ionization	APTDI [25]	2007
Desorption Atmospheric Pressure Photo Ionization	DAPPI [37]	2007



Table 2. Demonstrated analytical figures of merit for ambient desorption ionization methods

Technique	Highest mass	LOD <sup>a</sup>	Dynamic range	Imaging capability	Lateral resolution
DESI [1,21,22]	● 66 kDa	1–10 fmol	10 <sup>3</sup>	Yes	200 μm
DART [2,38]	~1 kDa	7 fmol	~20	N/A	<3 mm
ELDI [28,39]	66 kDa	20 fmol <sup>b</sup>	N/A	N/A	N/A
SSP [40]	15 kDa	1 fmol	10 <sup>2</sup>	N/A	635 μm
DBDI [24]	<200 Da	3.5 pmol	N/A	N/A	N/A
LAESI [36]	● 66 kDa	8 fmol	10 <sup>4</sup>	Yes	300–400 μm
DAPPI [37]	<500 Da	56–670 fmol	N/A	N/A	N/A

<sup>a</sup>Amount of sample on the surface.

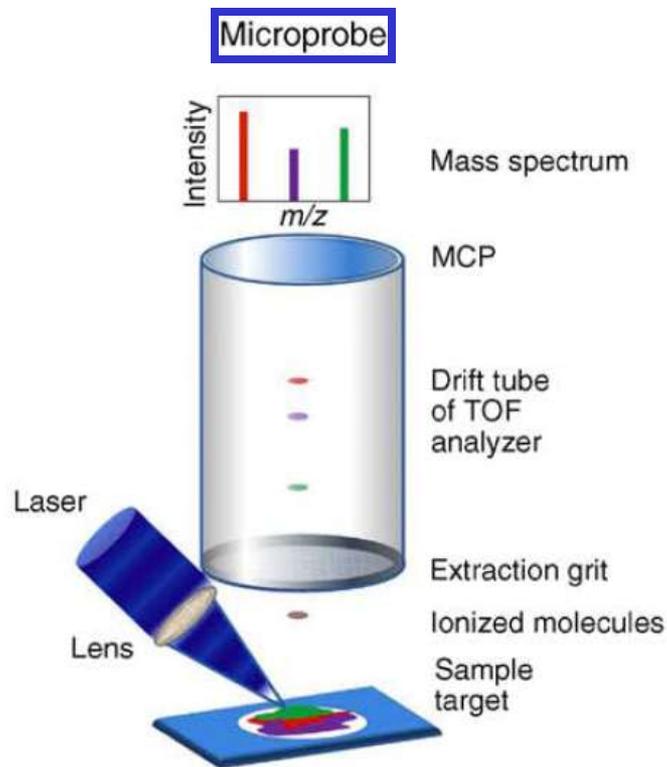
<sup>b</sup>Amount sampled by the laser beam.

# Imaging Ion microscopy

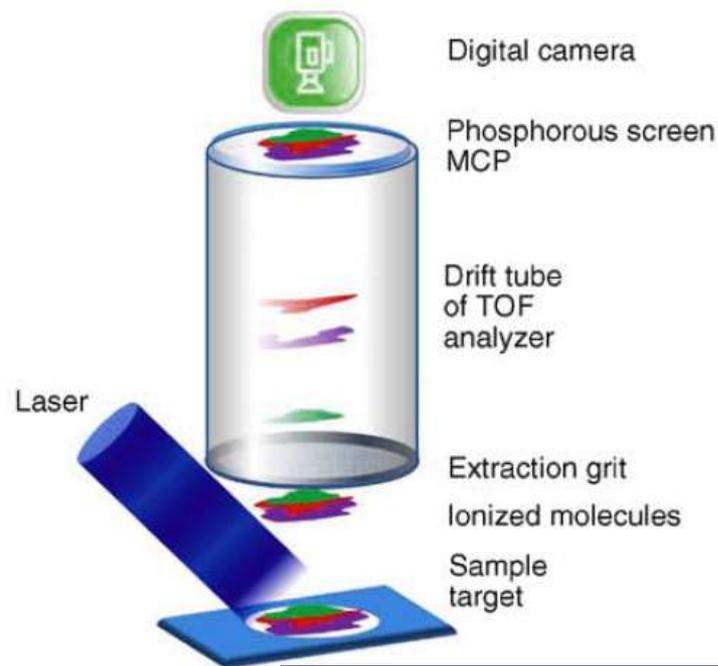
## Mass spectrometric imaging of small molecules

Aleš Svatoš

Trends in Biotechnology 28 (2010) 425–434



### Ion microscope



**MALDI - ToF**

As alternatives to organic matrices, silver [48], graphite [17,30,49,50], and colloids and nanoparticles (NP) [35,51,52] can also be used. Similar to matrix application by sublimation, the upper layer of sample is imaged without ion-interference from below the surface of the material. Owing to small particle sizes of these alternative matrices, imaging can be implemented at the cellular level. The major advantage is the low background of the resulting mass spectra and the option they offer to record mass spectra in both positive and negative ion modes.

# Imaging Ion microscopy

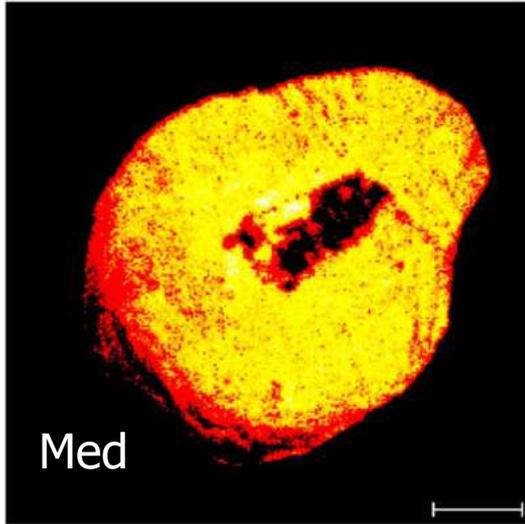
Biomaterials 24 (2003) 3635–3653

Review

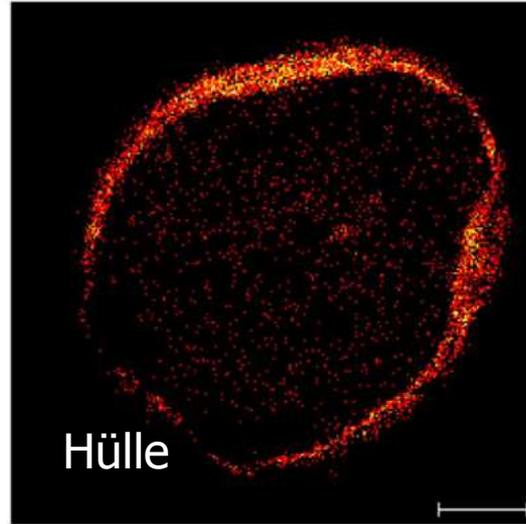
Time-of-flight secondary ion mass spectrometry: techniques and applications for the characterization of biomaterial surfaces

Anna M. Belu<sup>1</sup>, Daniel J. Graham, David G. Castner\*

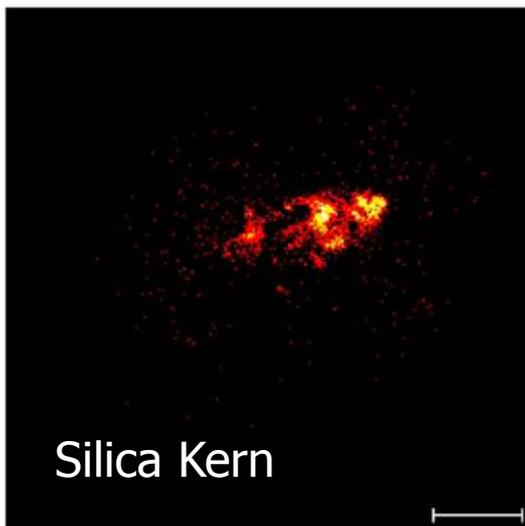
Medizin – Abbildung der Ionenverteilung



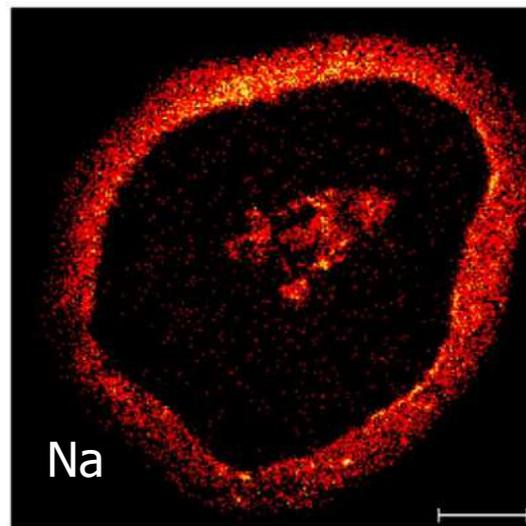
Med



Hülle



Silica Kern

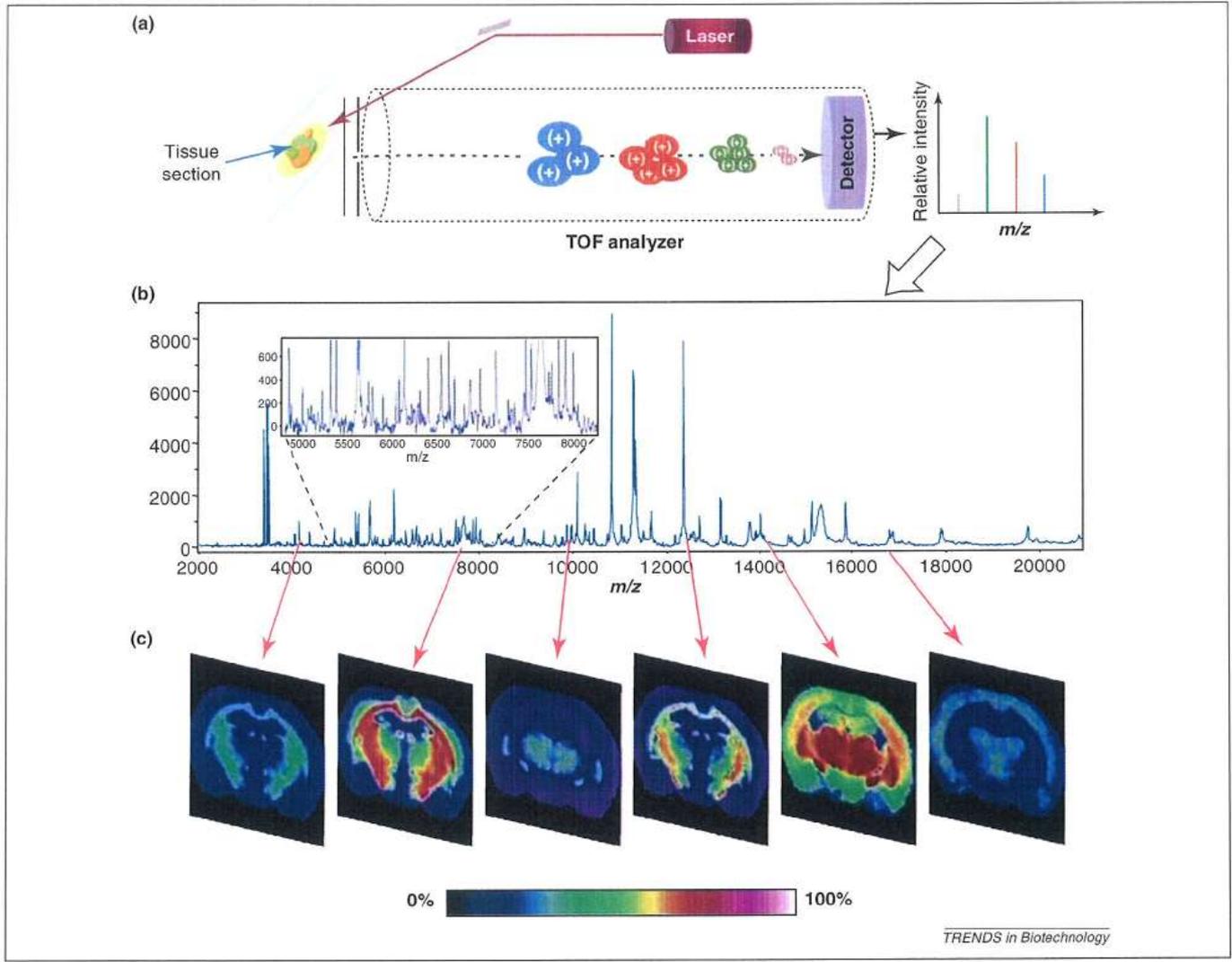


Na

Querschnitt durch Kapsel  
mit Medikament (Med =  
Metoprolol,  $m/z=268$ )

# MALDI imaging mass spectrometry of human tissue: method challenges and clinical perspectives

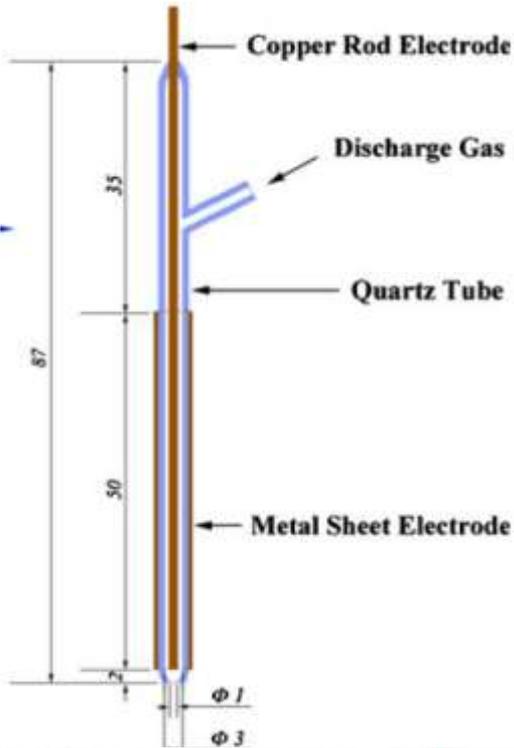
Erin H. Seeley and Richard M. Caprioli  
*Trends in Biotechnology* March 2011,



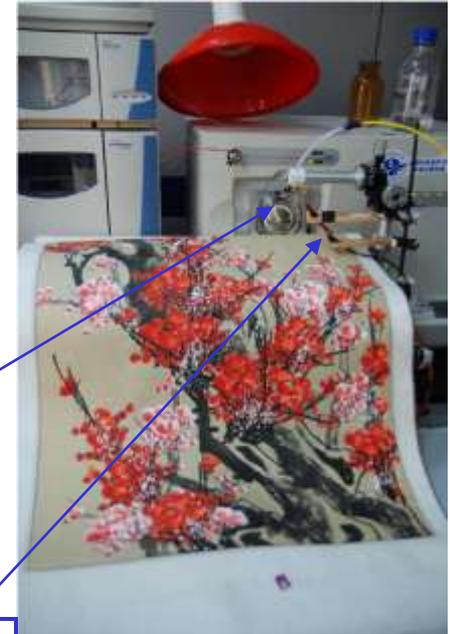
**Figure 2.** Schematic representation of the MALDI IMS process. (a) A tissue section on a conductive slide is placed in the source of the instrument and a laser is fired at the surface to desorb and ionize molecules. Analytes from each spot are separated in the TOF analyzer, their flight times converted to  $m/z$  ratio, and a spectrum recorded. (b) A representative mass spectrum collected from a tissue section. Inset shows detail and complexity of the spectrum collected. A tissue imaging experiment might result in thousands of such spectra. (c) Using an average spectrum from the entire section, ion images can be generated from each peak. Each  $m/z$  value of interest can be displayed as a function of position in the tissue section and relative intensity. Hundreds of such images can be created from a single tissue section.

# Imaging Mass Spectrometry with a Low-Temperature Plasma Probe for the Analysis of Works of Art\*\*

Yueying Liu, Xiaoxiao Ma, Ziqing Lin, Mingjia He, Guojun Han, Chengdui Yang, Zhi Xing, Sichun Zhang,\* and Xinrong Zhang

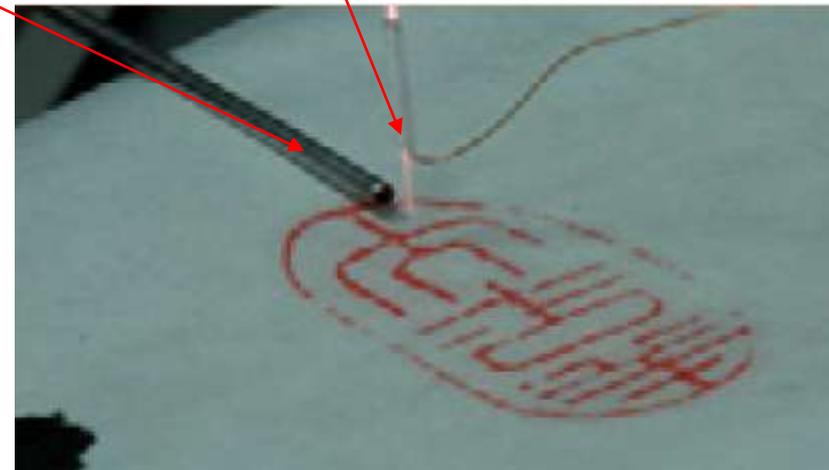
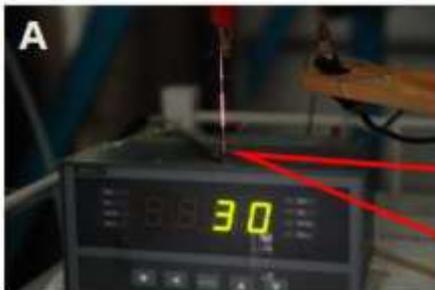


Low-temperature plasma, incident on human skin, generated in Ar at 50 W microwave power.



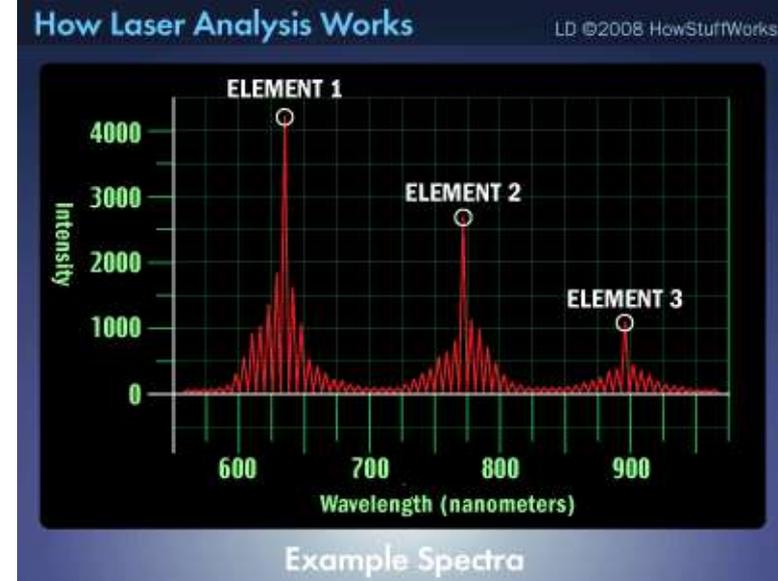
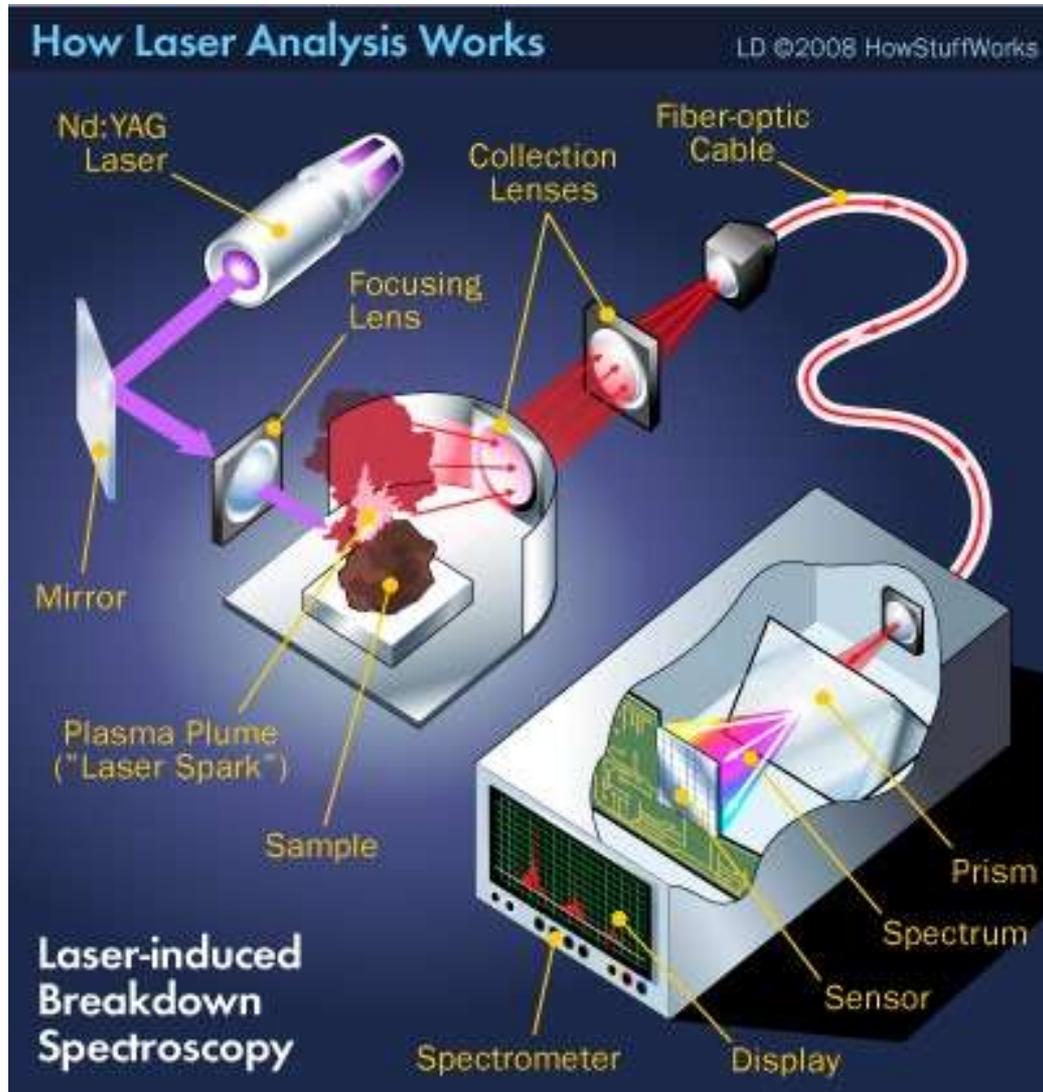
Spektrometer-Kapillare

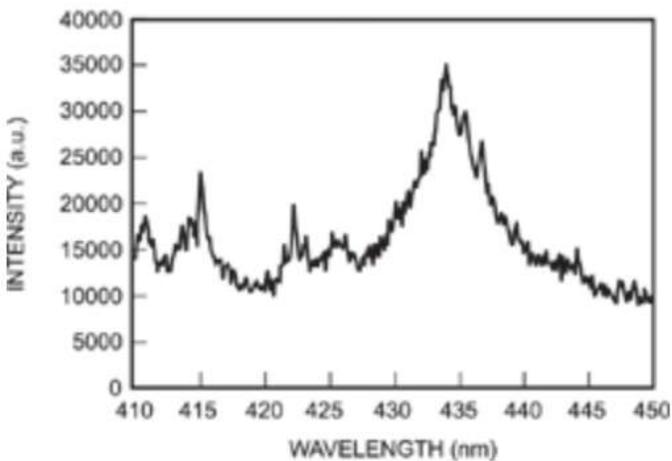
Plasma-Nadel



The temperature measurement of plasma generated by the probe.

# LIBS - Laser Induced Breakdown Spectroscopy

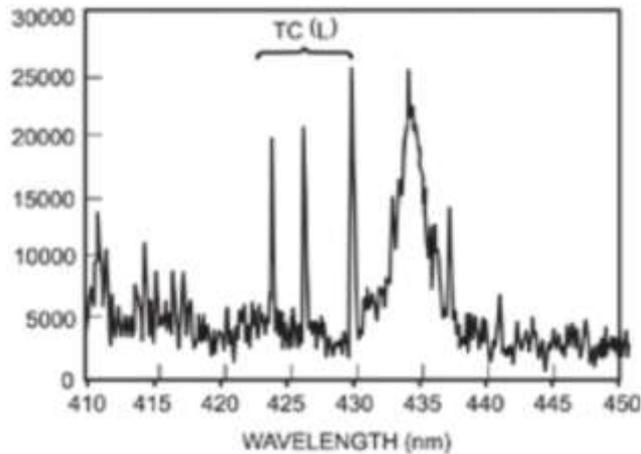




A typical spectrum seen from a solution of potassium pertechnetate dissolved in 0.1 mol l<sup>-1</sup> nitric acid

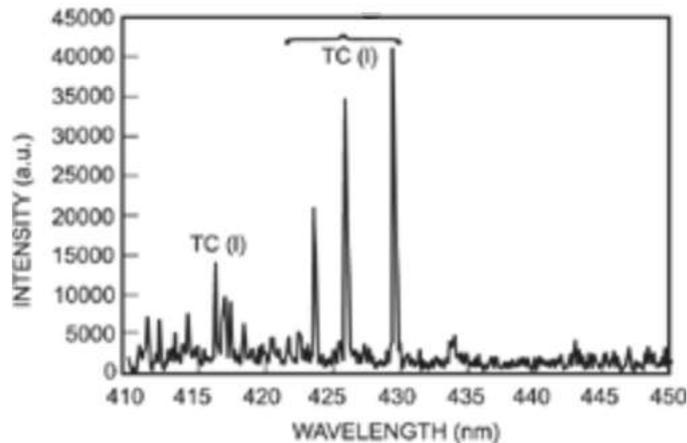
Delay 1 μs

Atomare Spektrallinien durch heisses Plasma thermisch verbreitert



Delay 5 μs

Abkühlung: Atomare Spektrallinien beginnen zu erscheinen



Delay 10 μs

Weitere Abkühlung: Atomare Spektrallinien scharf und deutlich

## Anwendung LIBS: Kontrolle bei Laser-Cleaning von Kunstobjekten



Fig. 6. Partially cleaned landscape in the fire-damaged painting. Using only a limited amount of UV light, the laser is able to reveal the bright colours the original paint layers.

Beide Bilder durch Feuer stark beschädigt. Laserabtrag der verkohlten Schichten unter Kontrolle von LIBS -> Wiederherstellung.

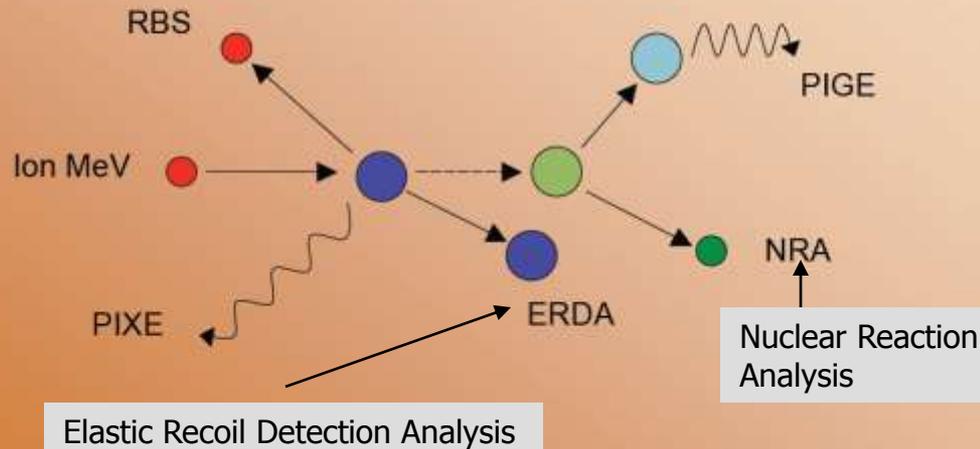


Laser Cleaning Painting  
Verheij

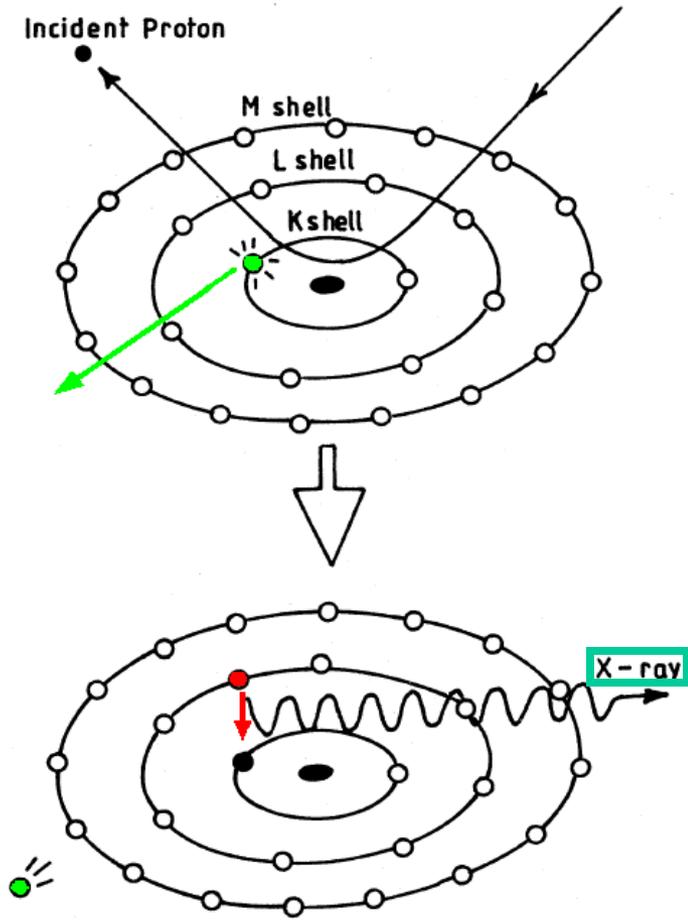
# PIXE - PIGE : particle induced X-ray - Gamma-ray Emission

## Ion Beam Analysis

MeV ion beam based techniques constitute a powerful tool for the quantitative determination of the composition and structure of matter



Possibility of mapping with a spatial resolution of  $\sim 10 \mu\text{m}$



Atom in the Sample  
The basic principle of PIXE.

Meist verwendet: Protonen, Deuterium,  $\alpha$ -Teilchen

PIXE method is mostly used for the elements heavier than Na, because the characteristic X-rays of elements with lower Z have not enough energy to penetrate into the detector sensitive volume. Besides, there is an alternative, much more probable relaxation route of inner holes which further reduces the photon yield in the light atoms. In the so called Auger decay the energy is taken away by the Auger electron. For example, the argon Ne-hole has approximately 98% probability for the nonradiative relaxation and only 2% for the X-ray emission and the things get even worse when Z is lower. Therefore the sensitivity of the PIXE method varies with Z and amounts to 1 ppm ( $\mu\text{g/g}$ ) for light elements (from Na to Cl) below 0.1 ppm for transition metals and close to 10ppm for heavier elements.

# PIXE - PIGE : particle induced X-ray - Gamma-ray Emission

Scientific laboratory, Louvre Museum

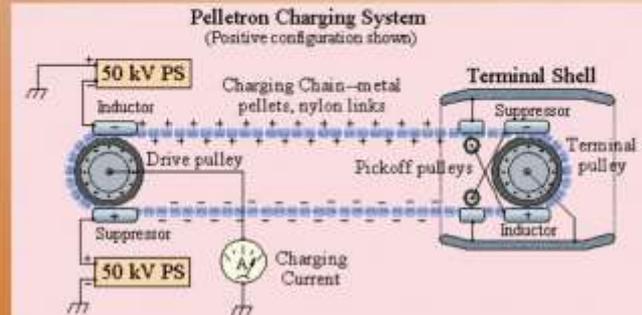
## Overview of the AGLAE facility



Nachteil: Beschleuniger

## The high voltage generator

NEC machine (pelletron) : 6SDH-2 tandem model  
2 MV terminal voltage with a turbo pumped gas stripper



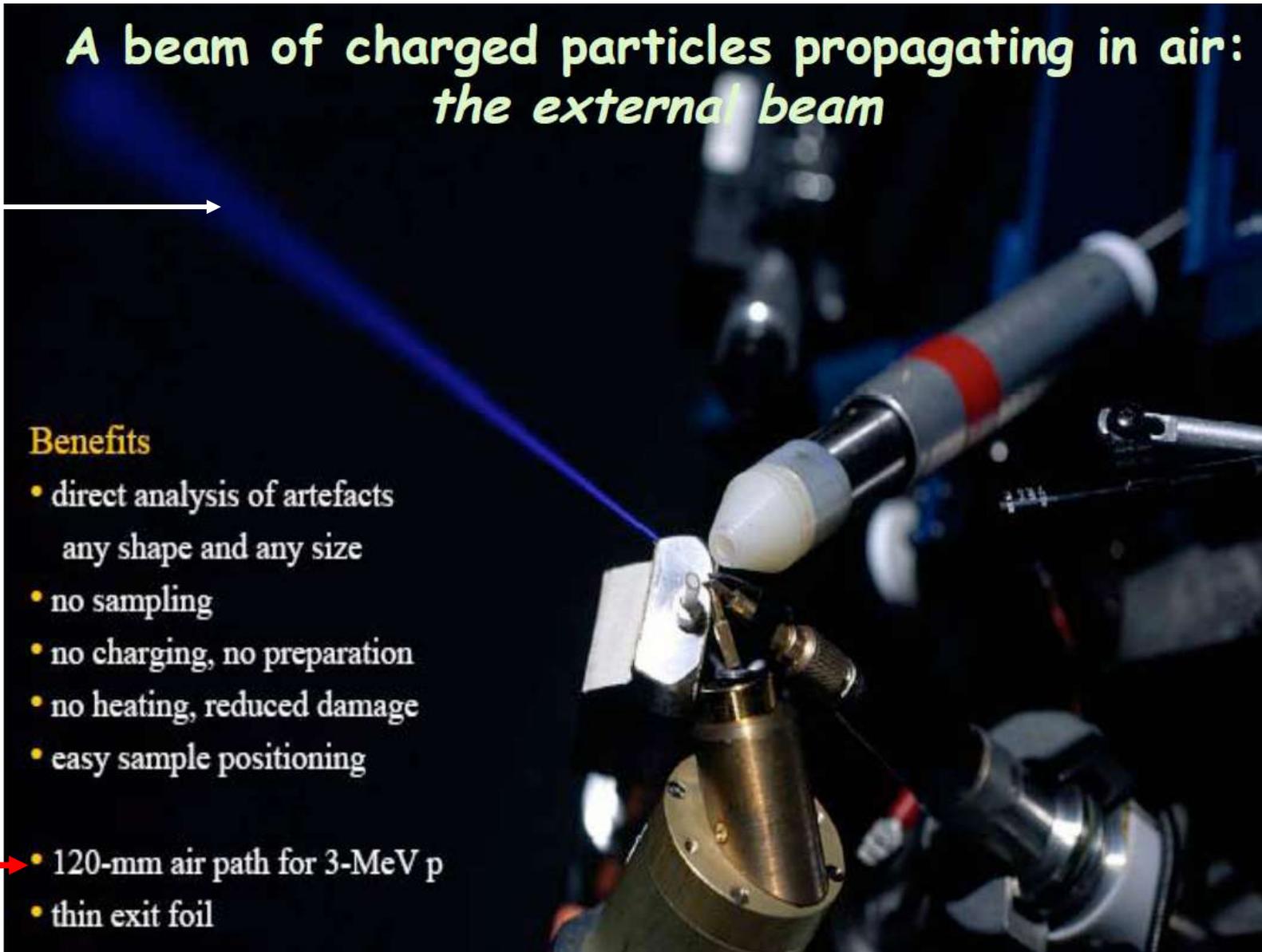
## PIXE - PIGE : particle induced X-ray - Gamma-ray Emission

### A beam of charged particles propagating in air: *the external beam*

Lumineszenz  
in Luft !

#### Benefits

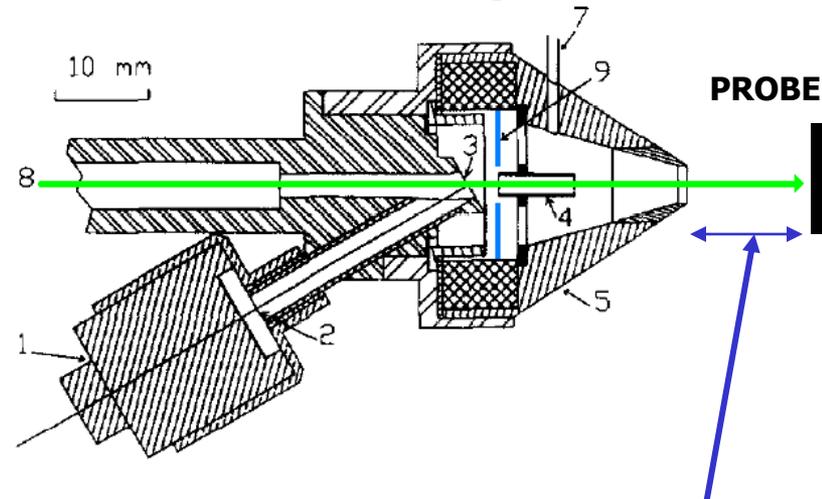
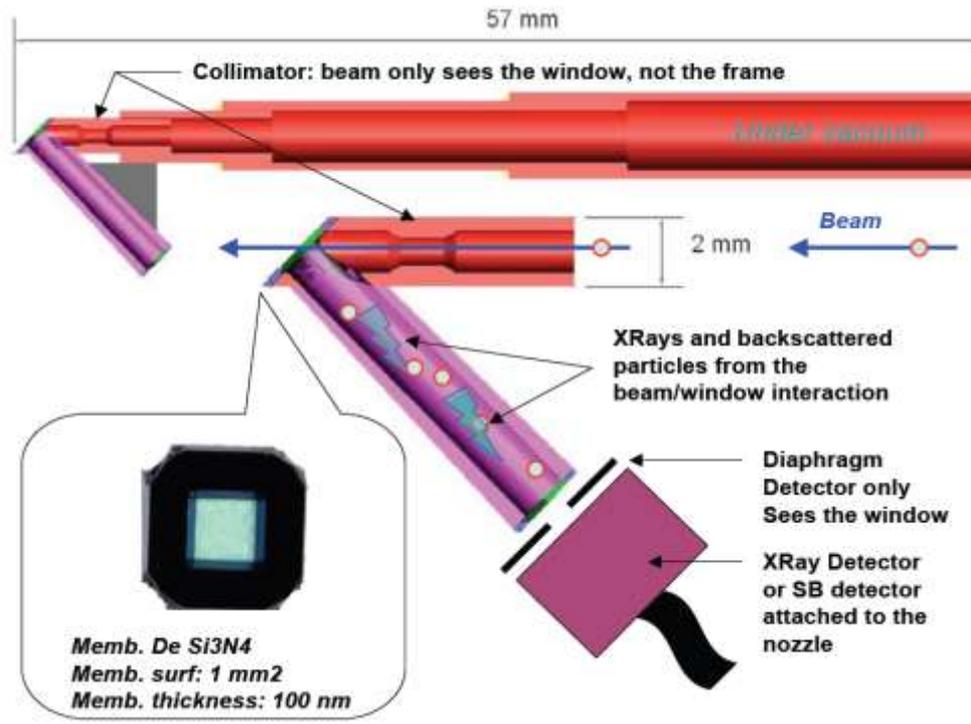
- direct analysis of artefacts  
any shape and any size
- no sampling
- no charging, no preparation
- no heating, reduced damage
- easy sample positioning
- 120-mm air path for 3-MeV p
- thin exit foil



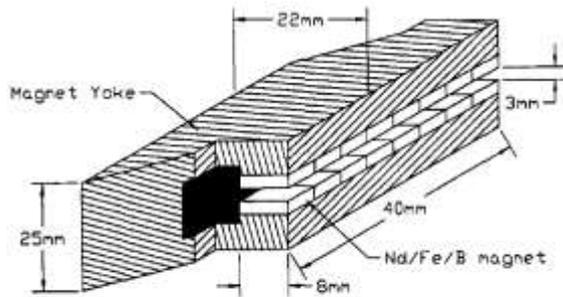
# PIXE - PIGE : particle induced X-ray - Gamma-ray Emission

Aufbau:

- ← a) Detektor unter Winkel
- b) Koaxialer Detektor



Cross section of the nozzle designed for RBS and NRA experiments: (1) RBS detector for beam monitoring; (2) 2  $\mu$ m Zr foil to insure vacuum; (3) Exit foil; (4) Brass tube to protect the detector from the incident beam; (5) Teflon insulating cone; (6) Brass head of cone; (7) Helium gas inlet; (8) Pipe under vacuum; (9) Annular surface barrier detector.

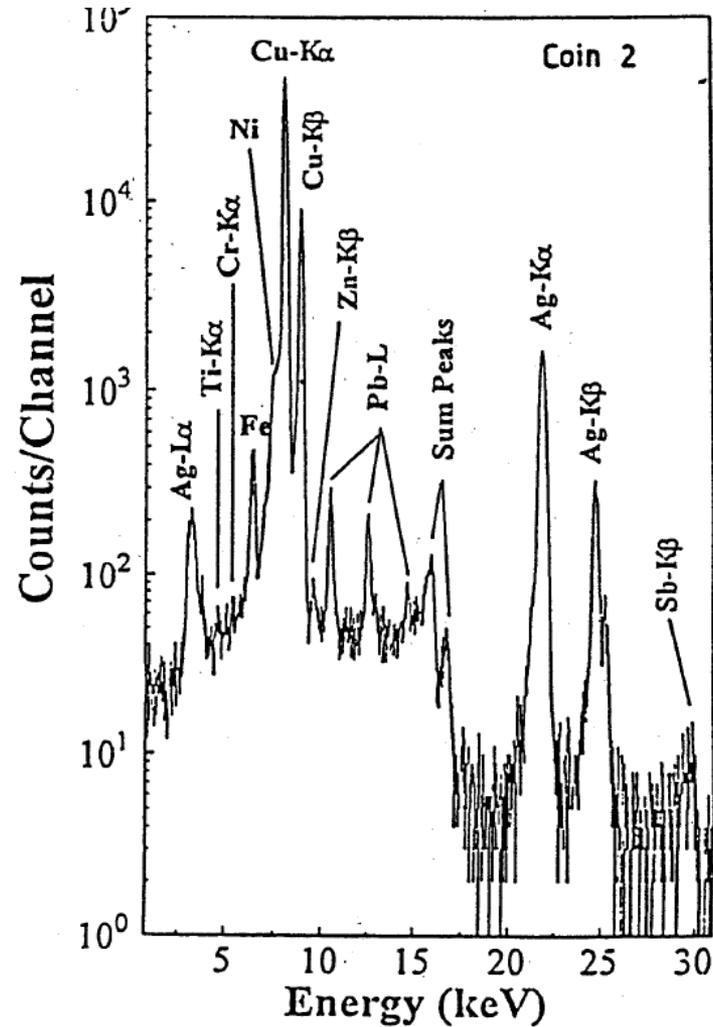
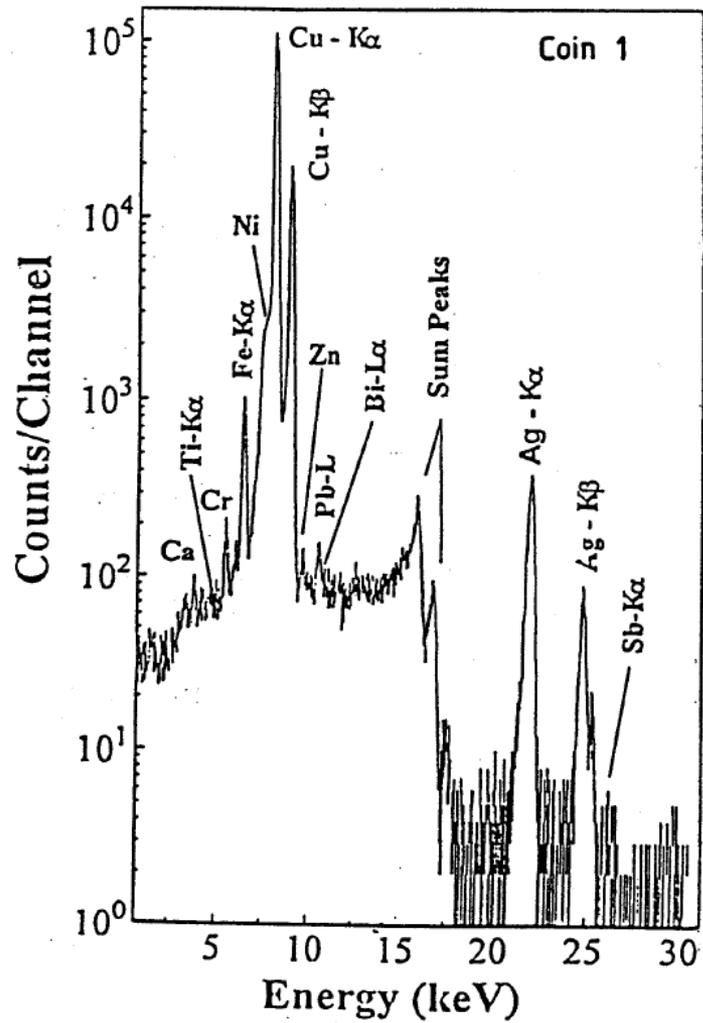


Schematic diagram of the compact magnetic deflection system. PCV with a 3 mm canal fills the gap in the magnetic field.

Um rückgestreute Teilchen vom X-ray Detektor fernzuhalten, benützt man Ablenkmagnete

**Arbeitsabstand typ. 15 mm**

# PIXE - PIGE : particle induced X-ray - Gamma-ray Emission

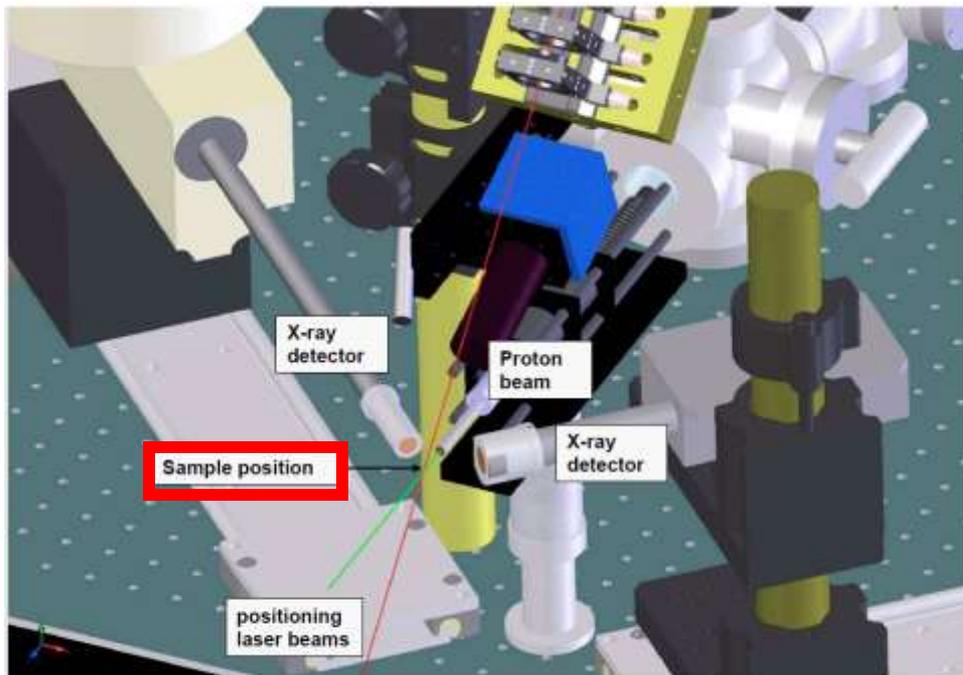


PIXE spectrum of ancient Indian coins of Hindu Sahi Dynasty (990–1015 AD).

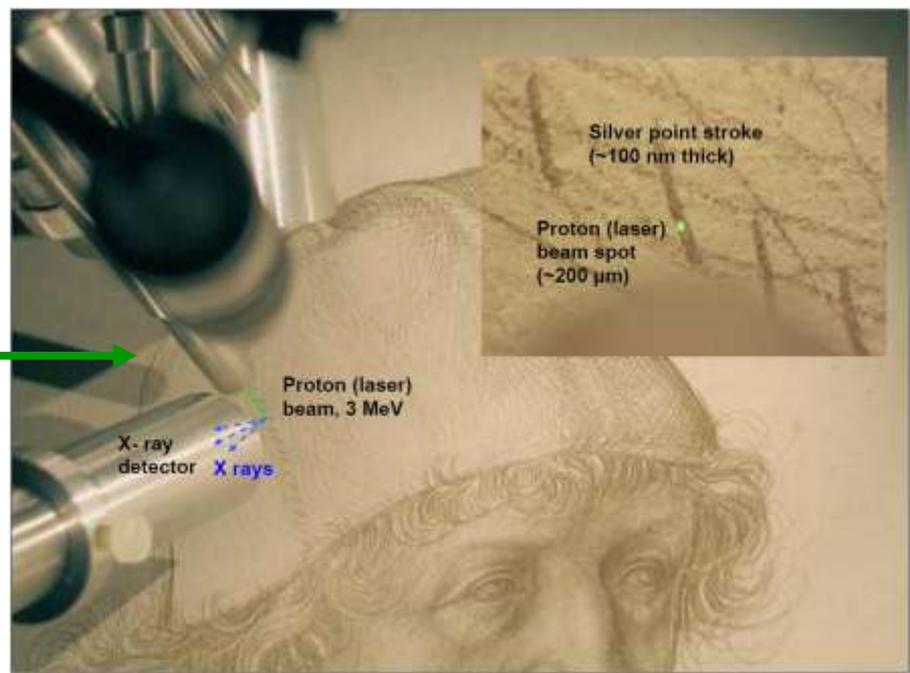
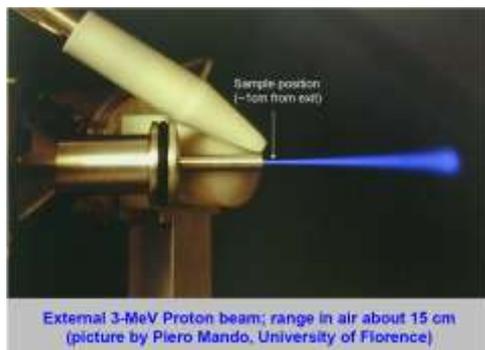
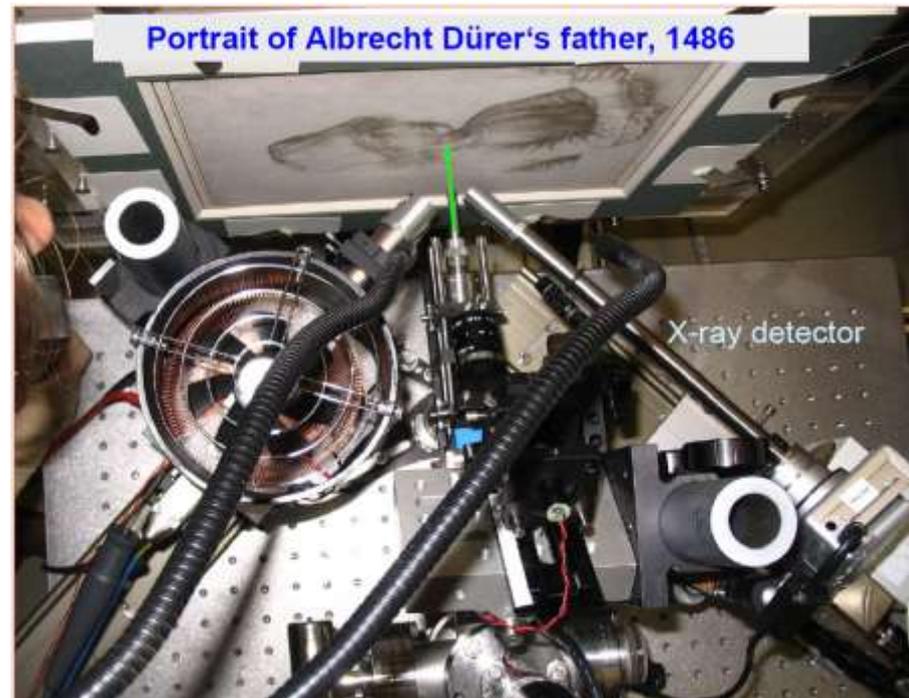
Informationstiefe:  
einige  $10 \mu m$

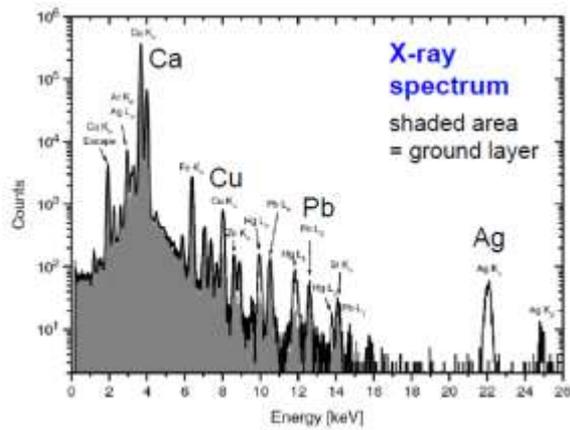
Beispiel von PIXE - Spektren

# PIXE in Wien - Objekte der Albertina



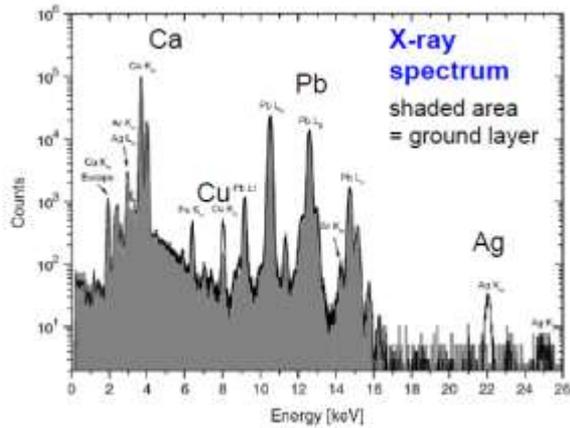
PIXE setup at the Vienna Environmental Research Accelerator (VERA)



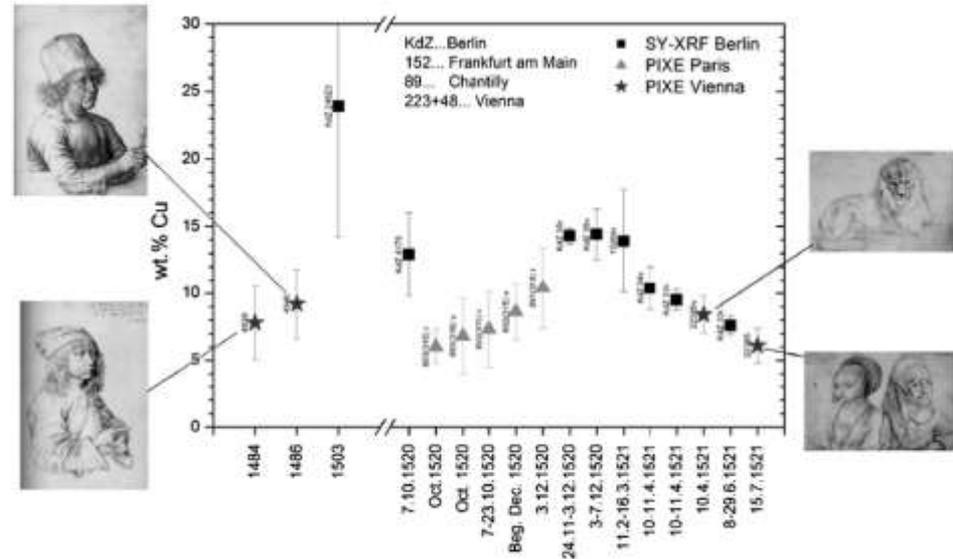


Girl in Costume of Cologne

Agnes Dürer (1521)



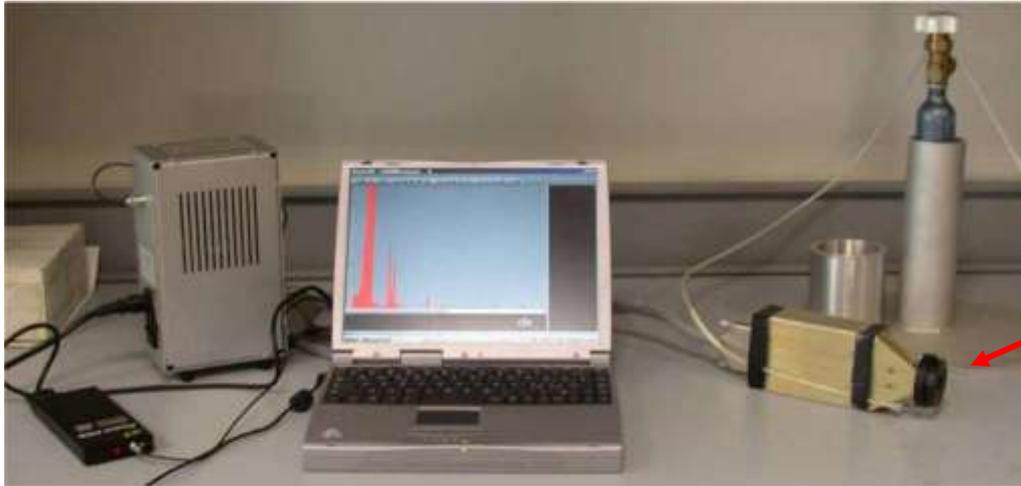
Portrait of the Artist's Father (1486)



Summary of Copper content of silverpoint drawings by Albrecht Dürer

# PIXE - PIGE : ohne Beschleuniger - transportabel

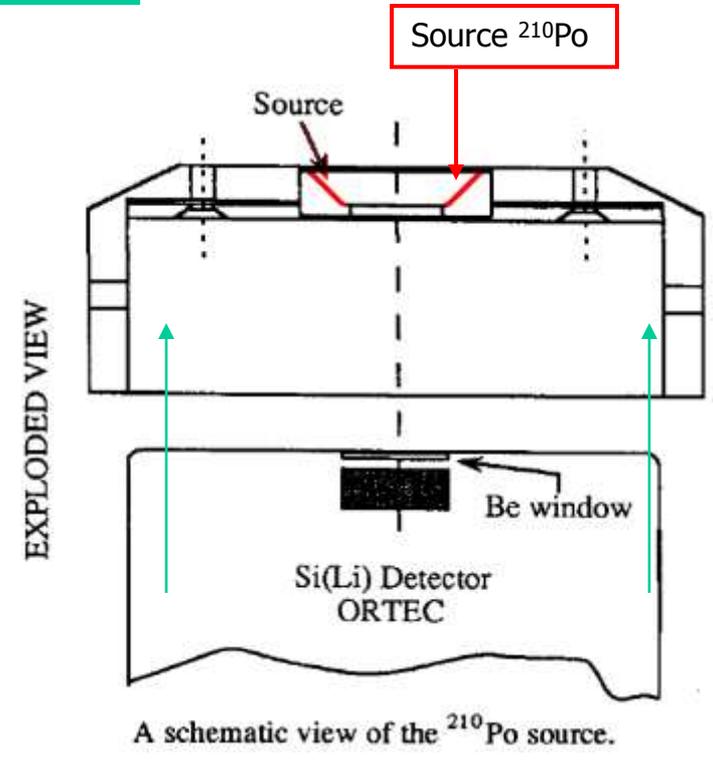
Ionenquelle: radioaktives Präparat



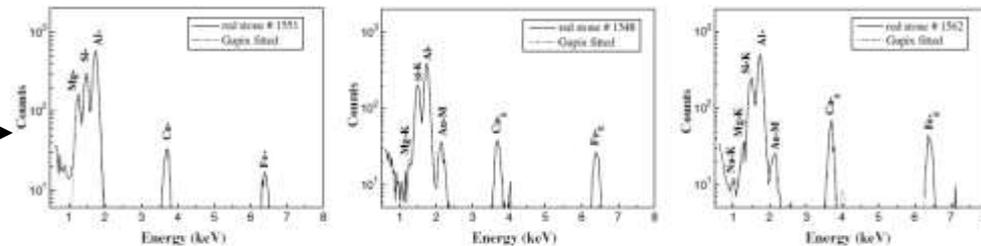
The LNS/INFN PIXE-alpha spectrometer.

Vorteil: leicht transportabel

Nachteil: längere Messzeiten,  
geringe Ortsauflösung

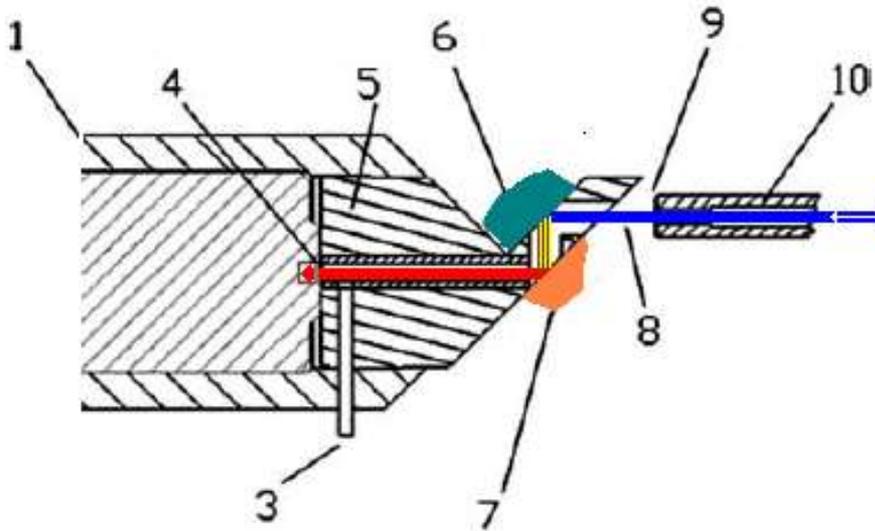


Diadem, Hellenistic, early 2nd century BC, from Thessaly. Most of the diadem parts are made of gold filigree, either with banded red stones or with inlay decoration with green and blue enamel.



PIXE-alpha X-ray spectra obtained from the three red gemstones analyzed.

## PIXE - XRF



PIXE-XRF layout for the in-air measurement of platinum in gold.

- (1) Housing of the Peltier-cooled *silicon-drift* detector
- (3) Helium inlet for cooling the intermediate As target.
- (4) Zinc absorber in front of the Si crystal.
- (6) Arsenic intermediate target.
- (7) Gold sample being analysed.
- (8) Proton beam.
- (10) Beam line.

**Proton beam**

aus Beamline trifft auf

**Intermediate Target**

erzeugt dort

**charakterist.  
Röntgenstrahlung**

diese erzeugt in

**Probe**

**Fluoreszenzstrahlung**

Das Original:

Jan Vermeer, 1632-75



Der Meisterfälscher: Han van Meegeren 1889-1947

