EE 213, Microscopic Nanocharacterization of Materials

Class website: https://ee213-winter16-01.courses.soe.ucsc.edu/
Time/place: Tu/Th 10-11:45am. Baskin 156

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EE 213. Information. W2016

Grading:

Approx. 2-3 homework sets
1 final paper about 10 pages long
1 final presentation (15 minutes)

Microscopic Nanocharacterization of Materials. 1

TENTATIVE

Introduction/Microcharacterization

Electron Beam Excitation Methods

SEM, STEM, TEM, EFEM, UFEM, etc.

Ion Beam Excitation Methods

PIXE, RBS, SIMS, HeIM

Xray Excitation Methods

Microscopy, Microprobe, PEM

Microscopic Nanocharacterization of Materials. 2

Photon Beam Excitation Methods

Wide Field, Confocal, Two photon microscopy

Superresolution Microscopy

Lensless Microscopy

Point Projection
Xrays, Atom Probe

Scanned Tip
STM, AFM, NSOM, SCM, etc.

Tomographic Methods

Comparison of Various Techniques

HOW WE VIEW THE WORLD?

SENSE	PROBE	MICROSCOPE
sight	electromagnetic radiation	light, Xray, ion, STM ,electrons
sound	acoustical radiation	acoustical, stethoscope
touch	mechanical, atomic forces	Stylus, AFM
smell	chemical	Ion conductance, Nano chemical sensor

MICROGRAPHIA:

OR SOME

Physiological Descriptions

OF

MINUTE BODIES

MADE BY

MAGNIFYING GLASSES.

WITH

OBSERVATIONS and INQUIRIES thereupon.

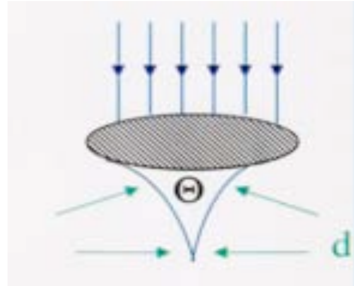
By *R. HOOKE*, Fellow of the ROYAL SOCIETY.

Non possis oculo quantum contendere Linceus,
Non tamen idcirco contemnas Lippus inungi. Horat. Ep. lib. 1.

LONDON, Printed by *Jo. Martyn*, and *Ja. Allestry*, Printers to the ROYAL SOCIETY, and are to be sold at their Shop at the *Bell* in S. *Paul's* Church-yard. M DC LX V.

Microscopy Through the Centuries

$d = \text{constant} \times \lambda / n\sin\Theta$



To get better resolution:

1) Reduce λ
electrons, Xrays, etc.

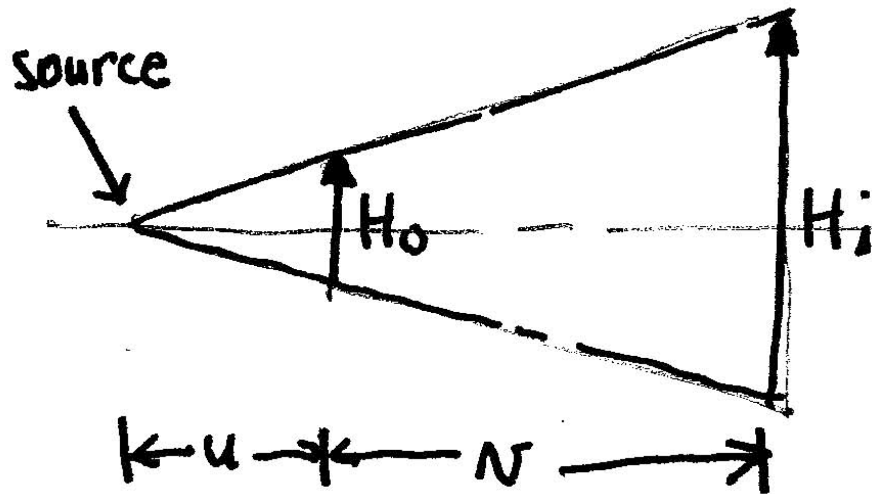
2) Increase $n\sin\Theta$
better lenses, oil

3) Decrease constant
confocal

4) Take away lenses
near field/scanned tip

5) Find the center/computation
"super resolution"

PROJECTION MICROSCOPY



$$\frac{H_i}{u+v} = \frac{H_o}{u}$$

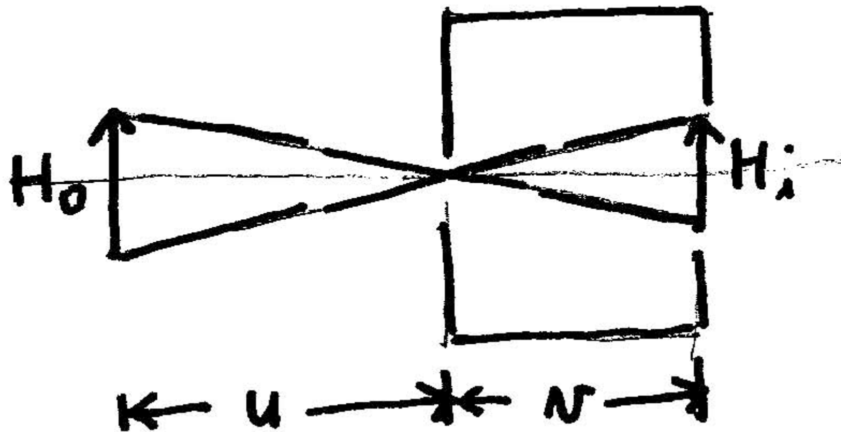
$$\frac{H_i}{H_o} = \frac{u+v}{u} = 1 + \frac{v}{u}$$

$$\frac{H_i}{H_o} \cong \frac{v}{u} \quad \text{if } v \gg u$$

↳ the "magnification"

LENSELESS IMAGING

eg/ pinhole camera



$$\frac{H_i}{v} = \frac{H_o}{u}$$

$$\boxed{H_i/H_o = \frac{v}{u}}$$

inverse of projection microscopy

Principles of the Camera Obscura

Ibn Al-Haytham, “Kitab al-Manazir” (Book of Optics, abt. 1010). Translated into Latin (1572) as “Opticae Thesaurus”

Diagram Illustrating Principles of the Camera Obscura, MS Illustration from a Résumé of Optics by Kamal al-Din al-Farisi, Istanbul, Fourteenth Century

Three centuries after Ibn al-Haytham's pioneering investigation of optics, the Persian al-Farisi extended Ibn al-Haytham's formulation of the principles underlying the phenomena of the camera obscura, familiar prototype of all photographic devices. Al-Farisi demonstrated that as apertures get smaller the images they form get sharper; he also showed that inside the device the objects' image turns top to bottom and left to right. It was in probing the fundamental nature and workings of vision and of light that Islam's scientists made what are probably their most original and important findings.

Camera Obscura
Kamal al-Din al-Farisi
14th Century

Expanded drawing from Al-Haytham

From: www.islamic-study.org/optics.htm

Seal Rocks
Sutro Baths
Merrie Way
Lands End Trail
Point Lobos Ave
Louis'
B
Camera Obscura
& Holograph
Sutro
Heights Park
48th Ave

Point Projection Microscopy: The Field Ion Microscope

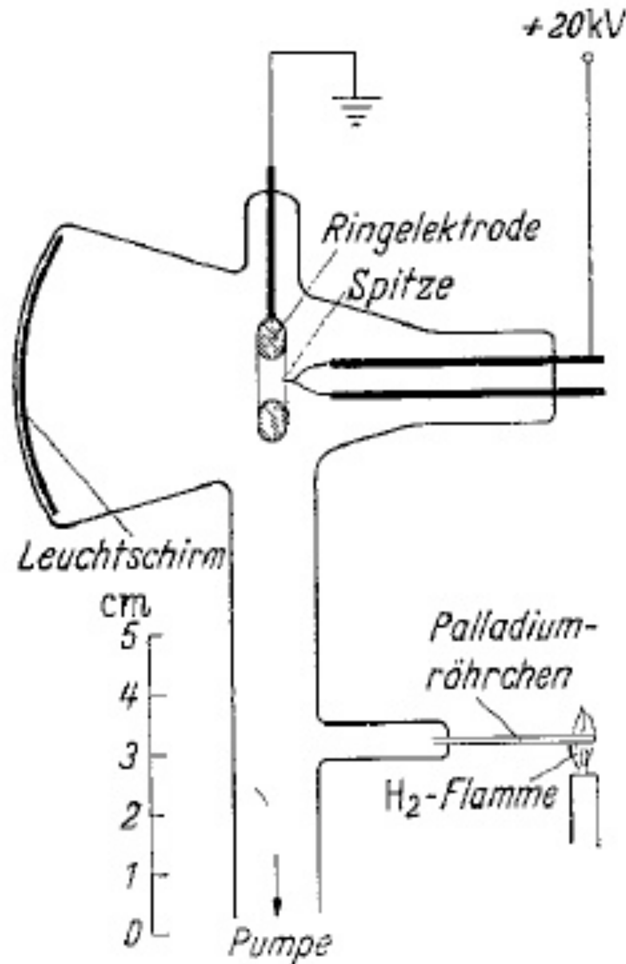


Fig. 1.
Schema des Feldionenmikroskopes.

Zeitschrift für Physik, Bd. 131, S. 136—142 (1951).

Das Feldionenmikroskop.

Von

Erwin W. Müller.

Mit 3 Figuren im Text.

(Eingegangen am 27. August 1951.)

Durch Umpolen des Feldelektronenmikroskopes kann man adsorbierte Atome als positive Ionen von der Objektspitze abreißen. Diese Felddesorption wird bis zu $3 \cdot 10^8$ V/cm verfolgt. Bei schnellem Nachschub der adsorbierten Atome ermöglicht die Feldionenemission eine mikroskopische Abbildung der Spitzenoberfläche, deren Auflösungsvermögen die Gitterkonstante erreicht.

Field Ion Micrograph: Platinum Tip

E. W. Mueller, *Science*. 149,591 (1965)

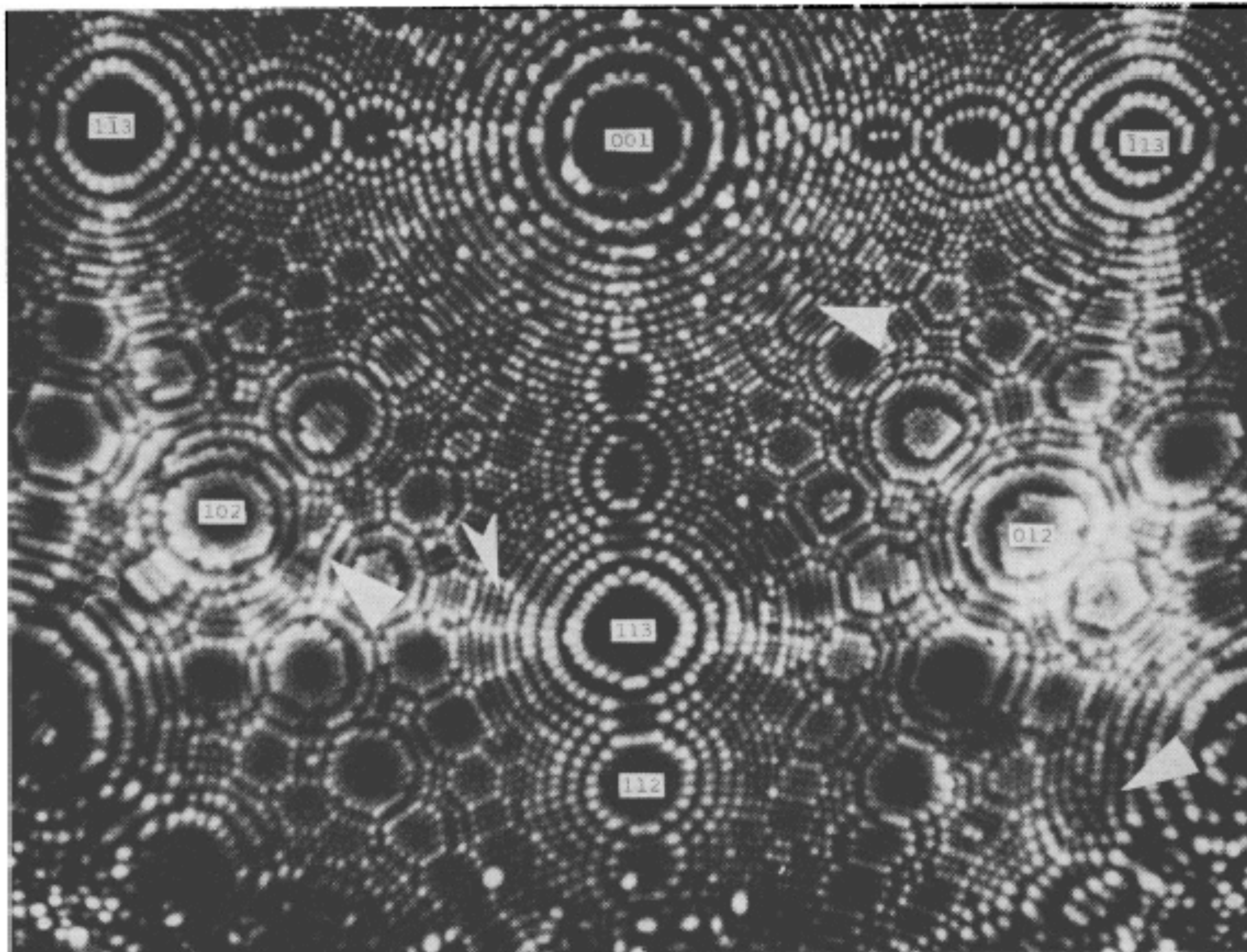
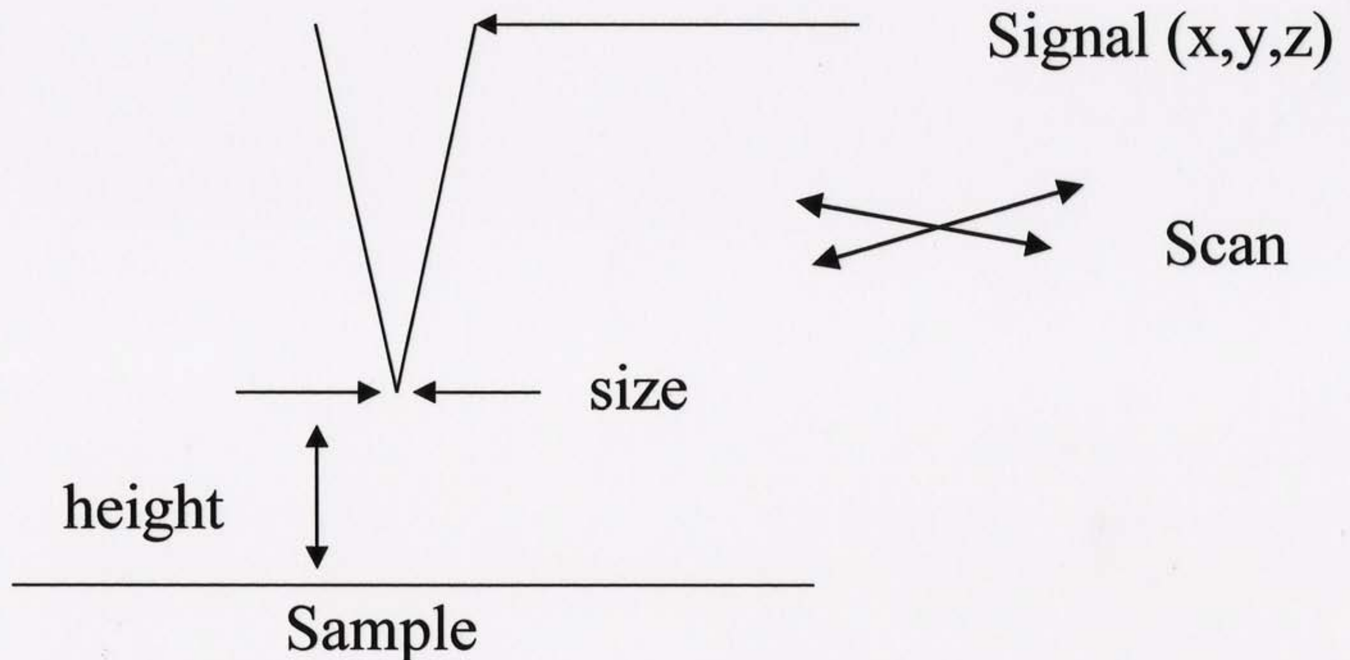


Fig. 13. Platinum crystal with a number of dislocations. The dislocation core near the (102) plane is decorated with an impurity atom, appearing as a bright spot. A vacancy is seen near the (113) plane.

Scanned Tip Microscopy

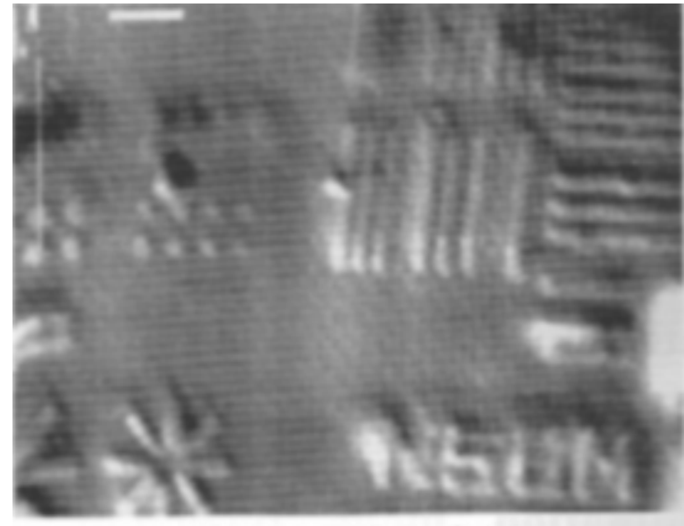


- ***Resolution is a function of size, height and mechanism used***
  - *no lenses are used*
  - *Far field optics is not involved*

Near Field Scanning Optical Microscopy (Reflection)

aluminum on silicon

400nm



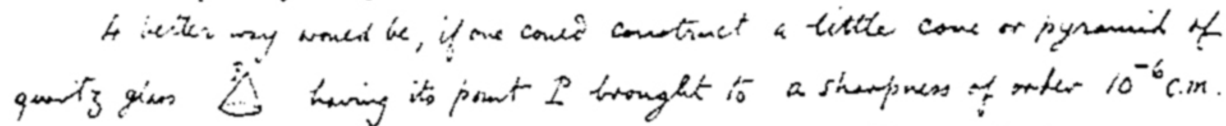
Shear force

NSOM

Cline and Isaacson, Ultramicroscopy

The Idea of Near Field Optical Imaging

There remains the possibility of a hole (Ein winziges Loch). One actually finds such holes, ready to hand, in pieces of badly silvered glass. A fragment from a cheap Thermos flask, for instance, contains countless small holes comparable in size with colloidal particles. No doubt they are due to the presence of colloidal particles on the surface of the glass, at the time of silvering. Unfortunately the silver rubs off very easily, and would be difficult to keep clean.



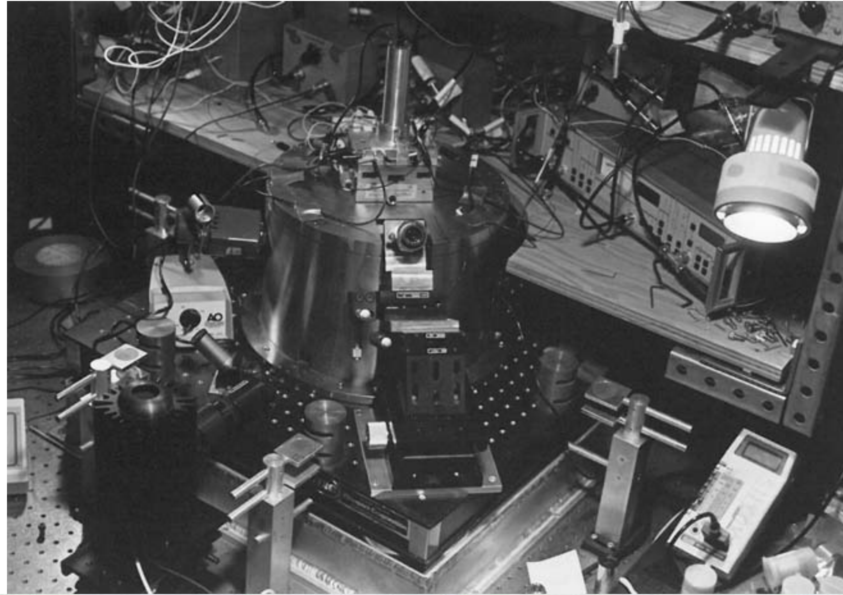
A better way would be, if one could construct a little cone or pyramid of quartz glass having its point P brought to a sharpness of order 10^{-6} cm. One could then coat the sides and point with some suitable metal (e.g. in a vacuum tube) and then remove the metal from the point, until P was just exposed.

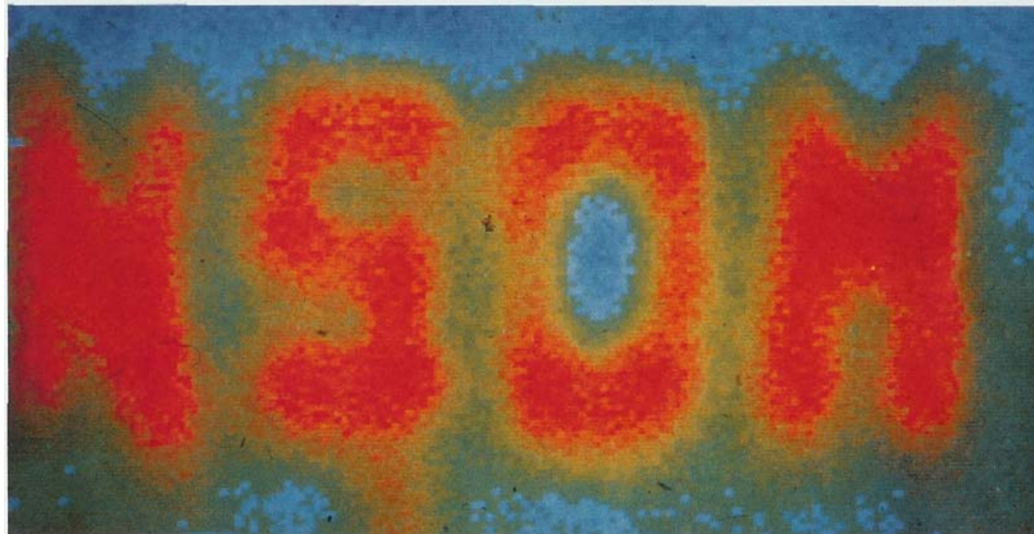
I do not think such a thing would be beyond the capacities of a clever experimenter. I know that needles can be made of quartz glass with exceedingly minute points, and there does not seem any reason why a point as sharp as 10^{-6} cm might not be secured.

FIGURE 4. Extract of letter dated 9 May 1928 from E. H. Synge to Einstein. Note the sketch of the quartz cone used as a light guide and aperture. (Courtesy of Professor J. L. Synge).

From D. McMullan, Proc. RMS. 25(2).1990.p.130

NSOM Instrument Constructed at Cornell



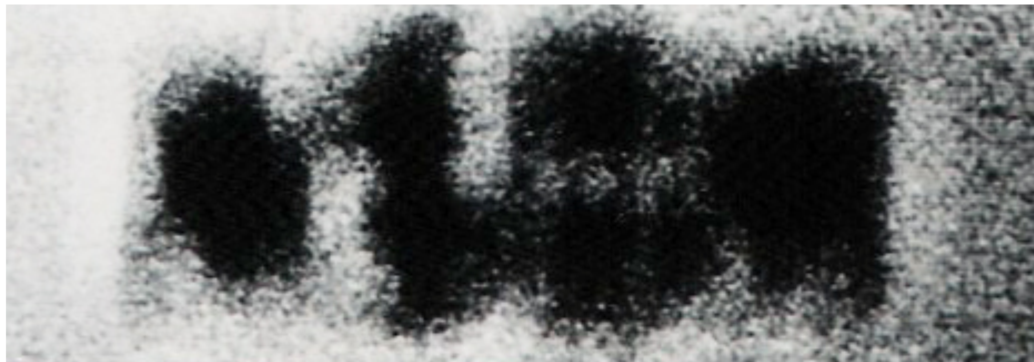


ALUMINUM LETTERS fabricated on a silicon nitride substrate imaged with a near field optical microscope. The full horizontal scale is 550 nm, the wavelength of the light being used.

M. Isaacson and E. Betzig, Cornell University

Effect of Distance on Spatial Resolution

60 nm away



600 nm away

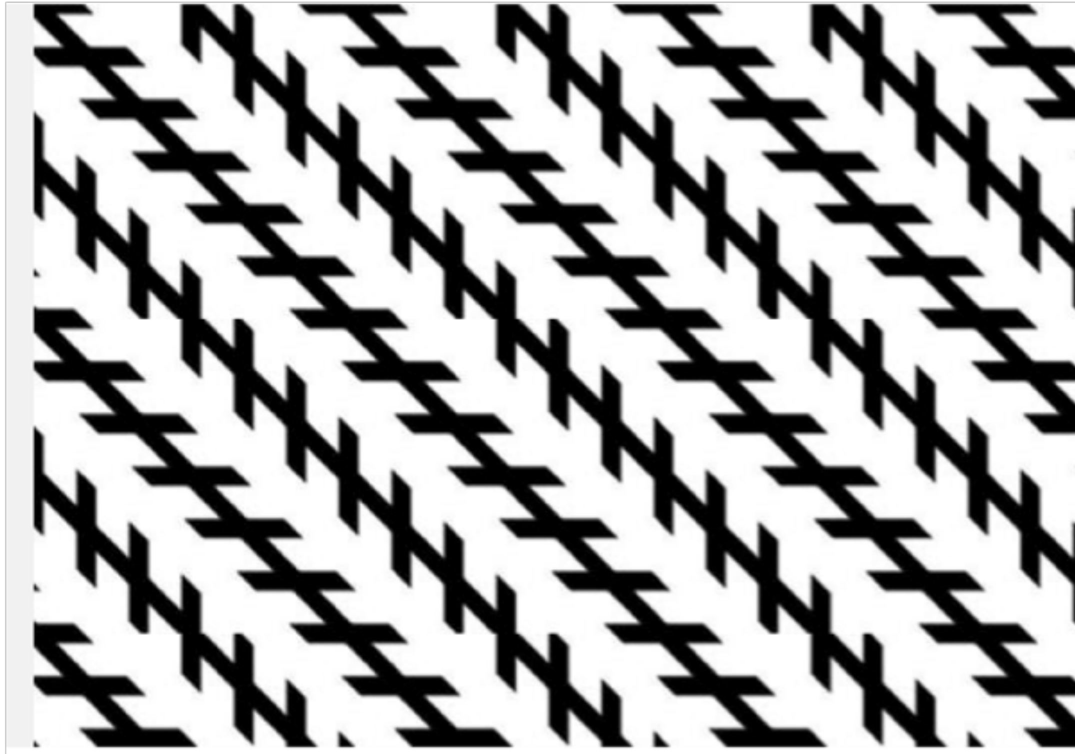
600 nm

M.Isaacson, et.al. 1990

There is nothing more deceiving than an image unless you know the rules of translation

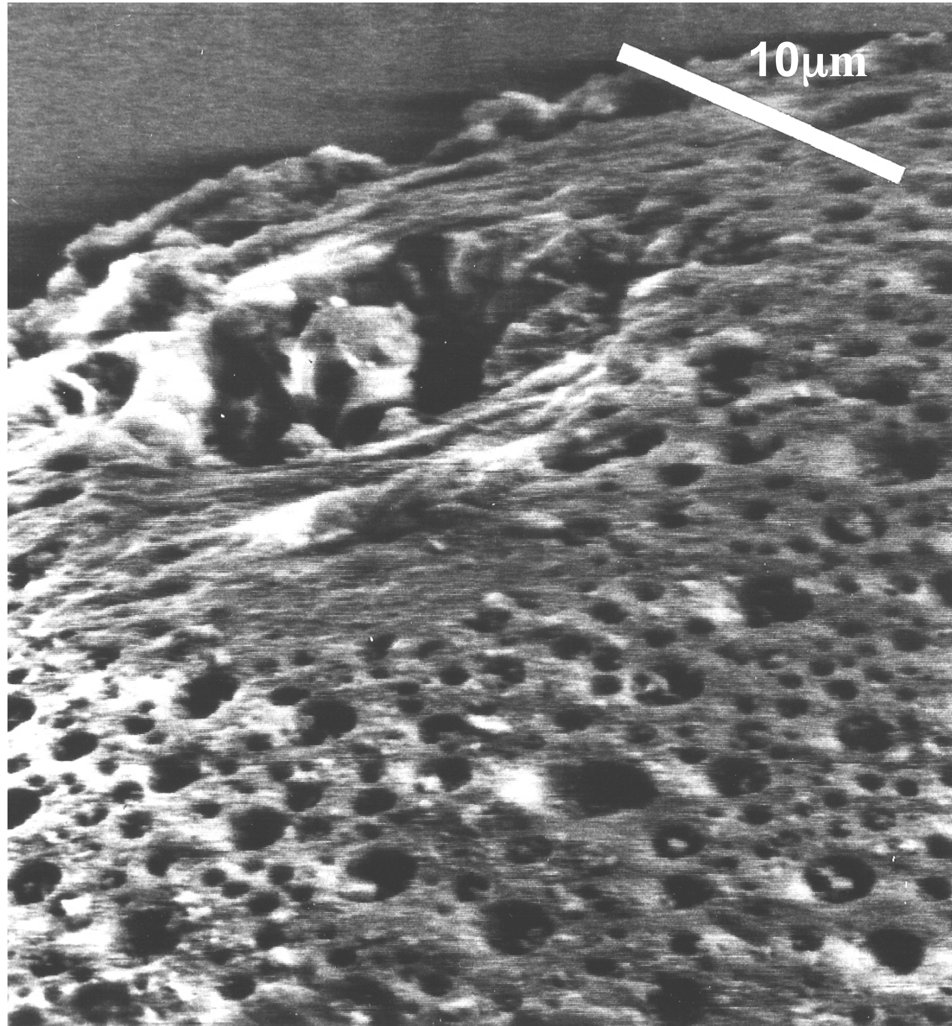
Penrose triangle

Kanizsa Triangle



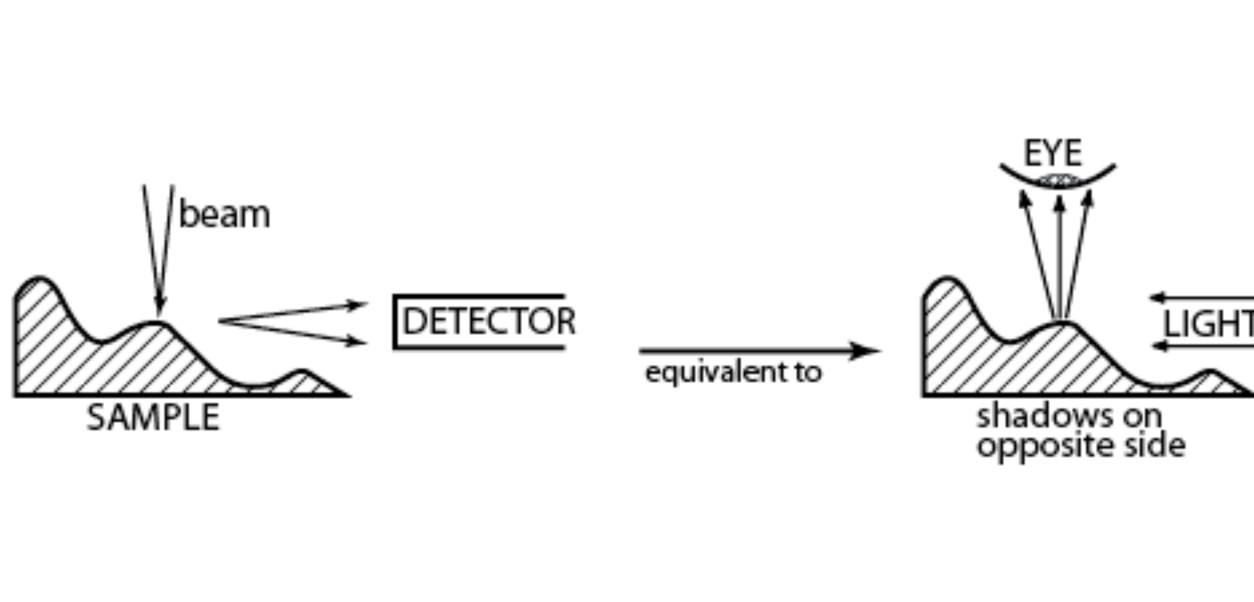
Zolner Illusion, 1860, astrophysicist

Surface of Moon Rock from Apollo 11 Mission Using Field Emission SEM, (SE image)



M. Isaacson, D. Johnson and A.V. Crewe, 1969

What does the secondary electron image in the SEM mean?"



Nanostructure characterization

wide variety of techniques:

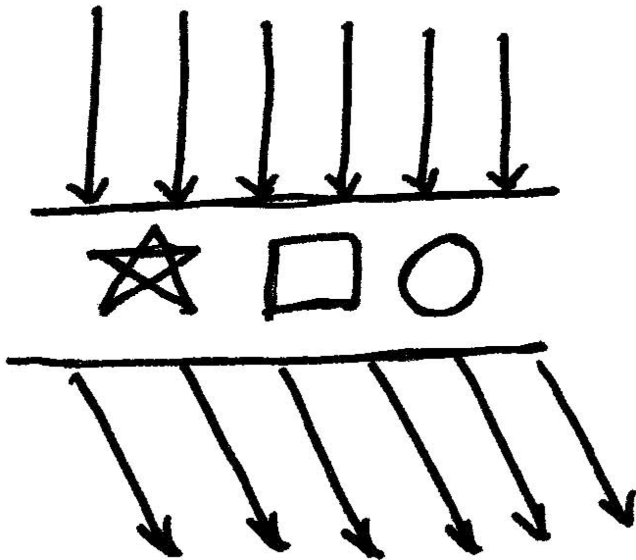
TABLE 6.2. Acronyms and Associated Terms of the Different Methods Used for Analysis

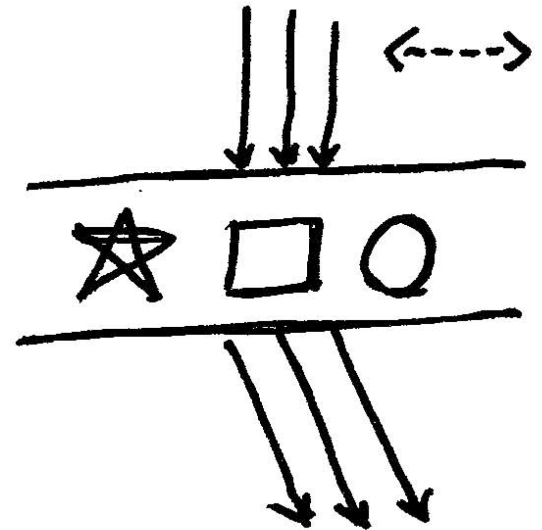
Acronym	Term
AAS	Atomic absorption spectrometry
ABSS	Atomic beam surface scattering
AEAPS	Auger electron appearance potential spectroscopy
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
APPH	Auger peak-to-peak height
APS	Appearance potential spectroscopy
ATR-IR	Attenuated total reflection-infrared spectrometry
BLE	Bombardment-induced light emission (=SCANIIR) (=IBSCA)
CMA	Cylindrical mirror analyzer
CSOM	Confocal scanning optical microscope
DAPS	Disappearance potential spectroscopy
EELS	Electron energy-loss spectrometry (=ELS)
EEM	Electron emission microscope
ELL	Ellipsometry
EMM	Electron mirror microscope
EMP(-X)	Electron probe microanalysis, used in two modes, viz., wavelength-dispersive X-ray analysis (WDX), or energy-dispersive X-ray analysis (EDX)
ESCA	Electron spectroscopy for chemical analysis (=XPS)
EXAFS	Extended X-ray absorption fine structure
FAB-MS	Fast atom bombardment-mass spectrometry
FEM	Field electron microscopy
FIM	Field ion microscopy
FWHM	Full width at half-maximum of a spectral line
GDMS	Glow discharge mass spectrometry
GDOES	Glow discharge optical emission spectrometry (=GDOS) (=GDS) (=GDL-OES)
HEIS	High-energy ion scattering (=RBS)
IBSCA	Ion bombardment surface chemical analysis
IETS	Inelastic tunneling spectroscopy
ILEED	Inelastic low-energy electron diffraction
ILS	Ionization-loss spectroscopy
IMFP	Inelastic mean free path
IMMA	Ion microprobe mass analysis
IMP	Ion microprobe
IR	Infrared absorption spectrometry
ISS	Ion scattering spectrometry (=LEIS)
LAMMA	Laser microprobe mass analysis (=LMP)
LEED	Low-energy electron diffraction
LEIS	Low-energy ion scattering (=ISS)
LERM	Low-energy reflection microscope
LMP	Laser microprobe analysis
LOES	Laser optical emission spectrometry
MFP	Mean free path
MS	Mass spectroscopy
NAA	Neutron activation analysis
NRA	Nuclear reaction analysis
NSOM	Near-field scanning optical microscope
OES	Optical emission spectrometry
PAM	Photo-acoustic microscopy (≠ AM)
PIXE	Proton-induced X-ray emission
PTFE	Polytetrafluoroethylene
RBS	Rutherford backscattering spectrometry (=HEIS)
RHEED	Reflected high-energy electron diffraction
SALI	Surface analysis by laser ionization
SAM	Scanning Auger microprobe
SCANIIR	Surface chemical analysis by neutral- and ion-induced radiation (=BLE) (=IBSCA)
SDA	Spherical deflection analyzer
SEAM	Scanning electron acoustic microscope
SEM	Scanning electron microscopy
SEXAFS	Surface-extended X-ray absorption fine structure
SIMS	Secondary-ion mass spectrometry
SLEEP	Scanning low-energy electron probe
SNMS	Sputtered neutrals mass spectrometry
SOM	Scanning optical microscope
SSMS	Spark source mass spectrometry
STEM	Scanning transmission electron microscopy
STM	Scanning tunneling microscopy
SXAPS	Soft-X-ray appearance potential spectroscopy
SXDA	Soft-X-ray emission depth analysis
TEELS	Transmission electron energy-loss spectrometry
TEM	Transmission electron microscope
TEM-ED	Transmission electron microscope–electron diffraction
TRXRFA	Total reflection X-ray fluorescence analysis
UPS	Ultraviolet photoelectron spectrometry
UV	Ultraviolet absorption spectrometry
XES	X-ray emission spectrometry
XAES	X-ray-induced Auger electron spectrometry
XPD	X-ray photoelectron diffraction
XPS	X-ray photoelectron spectrometry
XRFA	X-ray fluorescence spectrometric analysis

(after Brodie)

HOW WE VIEW THE WORLD?

SENSE	PROBE	MICROSCOPE
sight	electromagnetic radiation	light, Xray, ion, STM ,electrons
sound	acoustical radiation	acoustical, stethoscope
touch	mechanical, atomic forces	Stylus, AFM
smell	chemical	Ion conductance, Nano chemical sensor

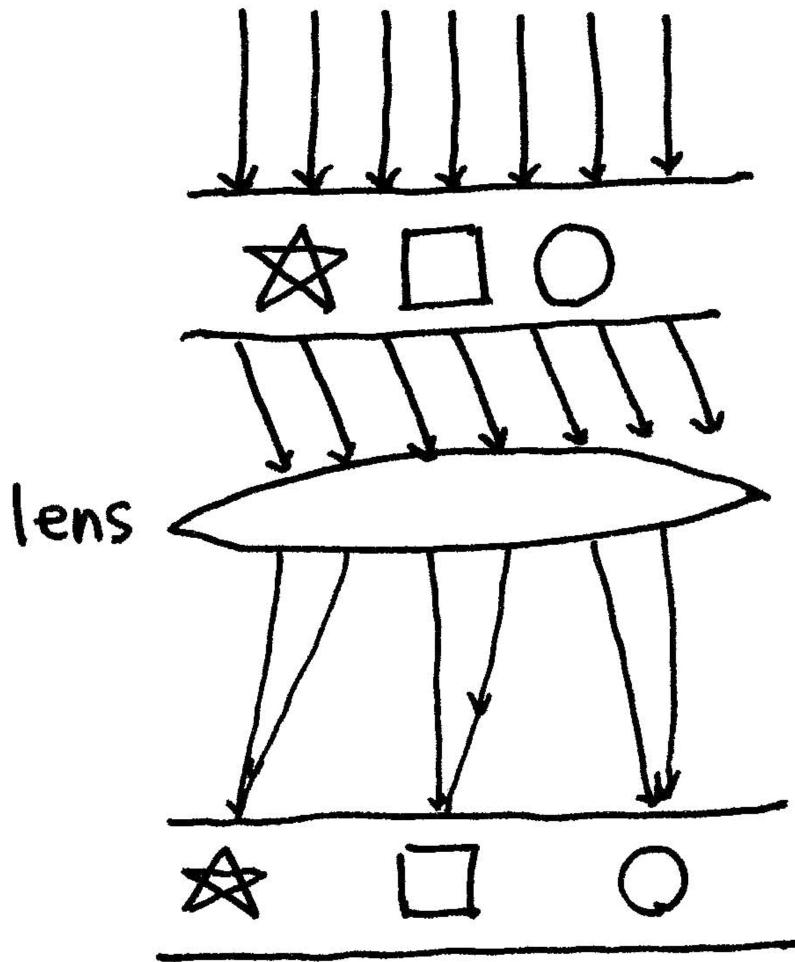


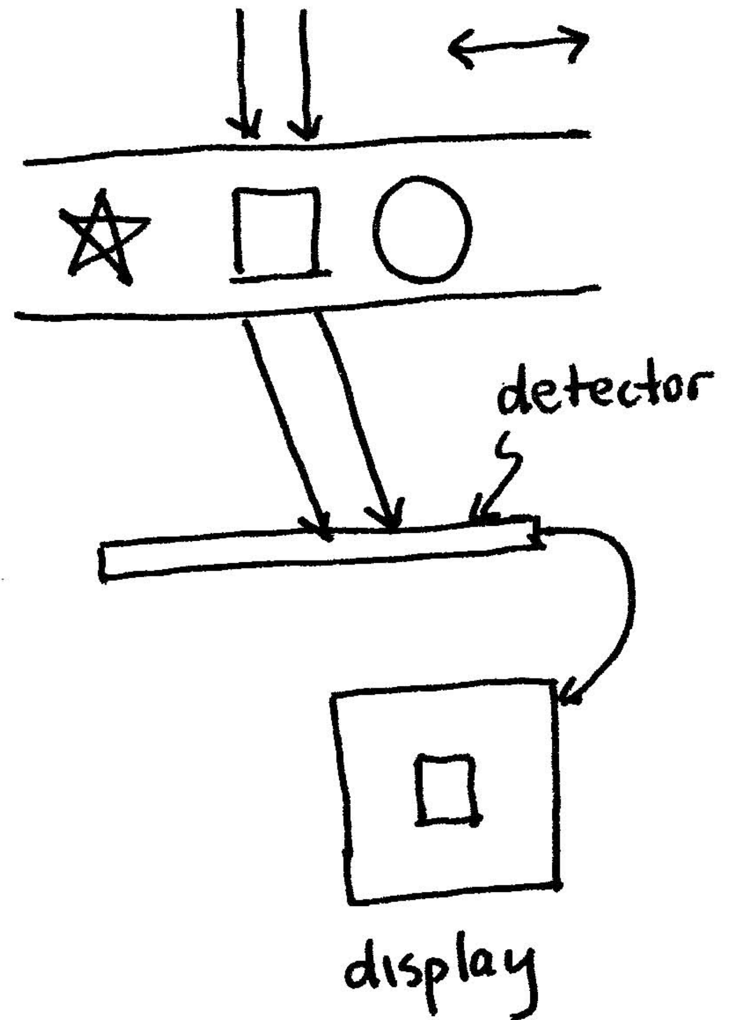


"Image"

spatially averaged

★ or □ or ○


lens
"parallel"
global imaging


detector
display
"serial"
scanning imaging

minimum detectable concentration (MDC)

ASSUME: atom density $\cong 0.08$ atoms/Å^3

cubic interrogated volume, d^3
where d = "probe" diameter

at $d = 1\mu m = 10^4 \text{Å} \Longrightarrow V = d^3 = 10^{12} \text{Å}^3$

$\therefore$ # atoms $= 8 \times 10^{10}$

$\therefore$ a concentration of 1 PPM = 8×10^4 atoms

BUT

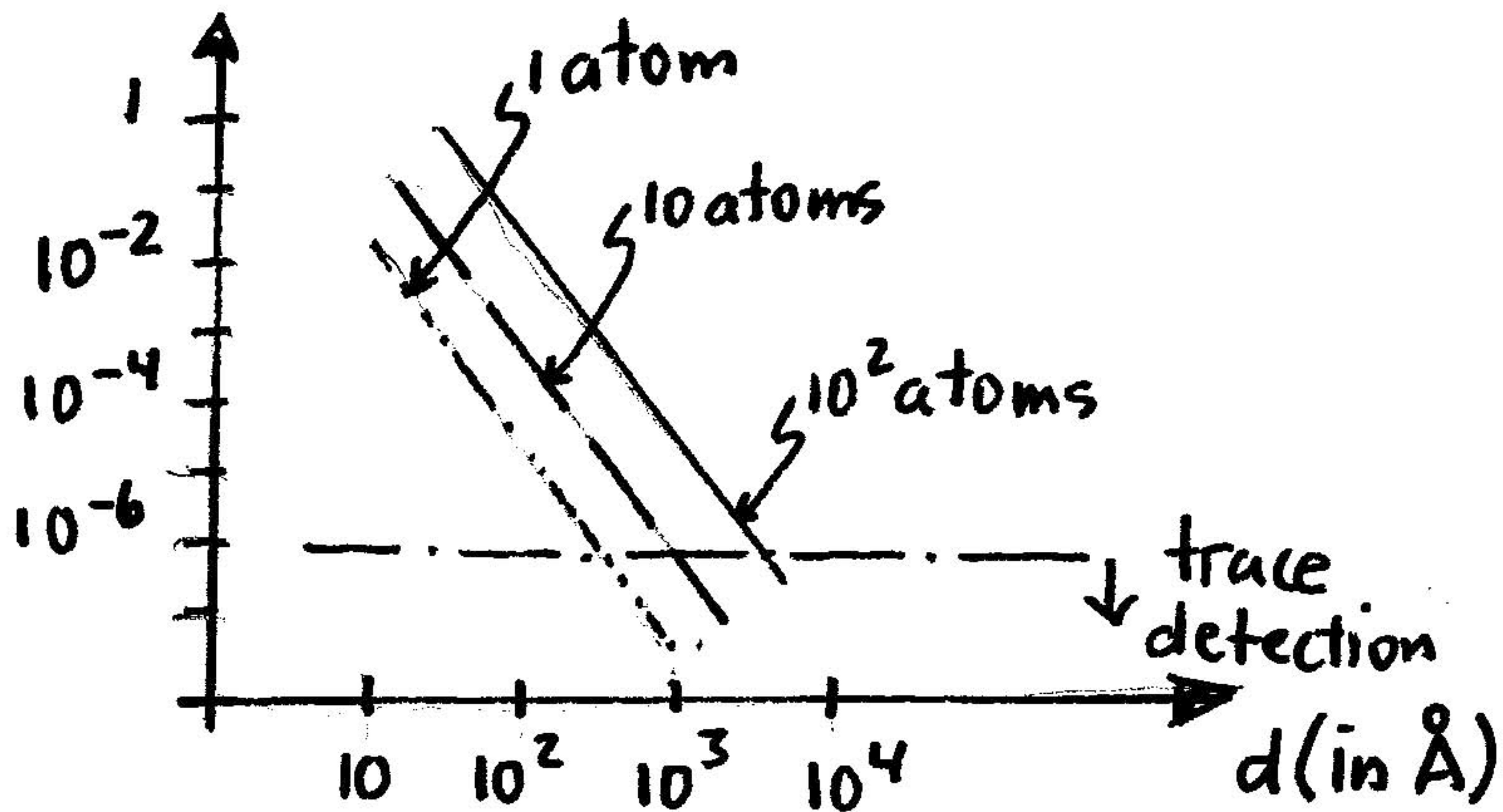
at $d = 1 nm = 10 \text{Å} \Longrightarrow V = d^3 = 10^3 \text{Å}^3$

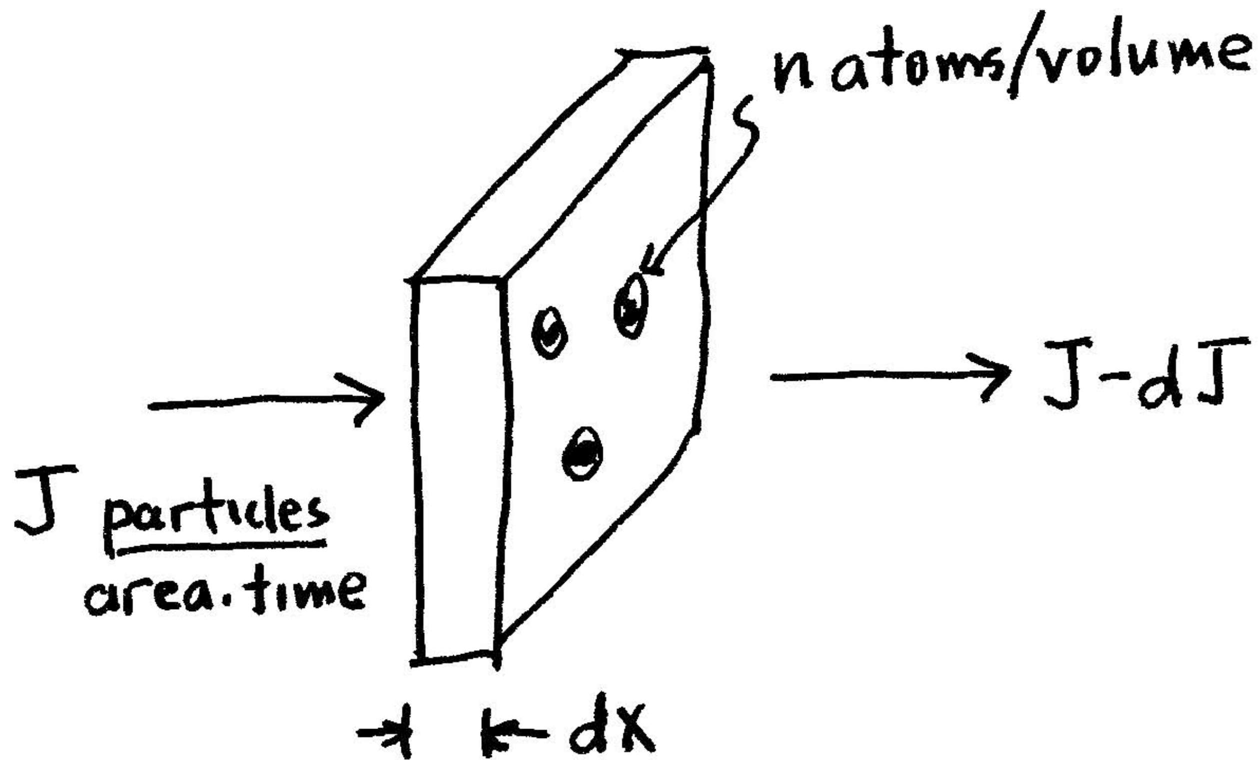
$\therefore$ # atoms = 80 !

best min. concentration detectable = 1 atom

$\approx 1/80 = .0125$

$= 1.25\%$!


Concentration
1
10^-2
10^-4
10^-6
1 atom
10 atoms
10^2 atoms
trace detection
10
10^2
10^3
10^4
d (in Å)

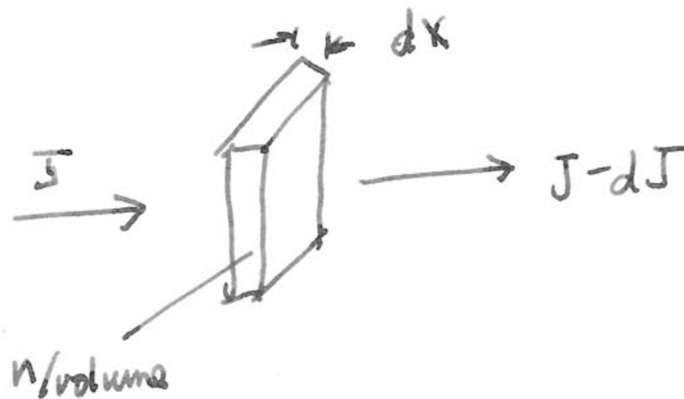


probability that interaction occurs = P

$$P = \sigma \cdot n \cdot dx$$

σ → effective interaction area/ cross-section

Interactions



$$dJ = -\sigma n\, dx \cdot J$$

σ: cross-sectional "area"

$$\therefore \frac{dJ}{J} = -\sigma n\, dx$$

$$J = J(0)\, e^{-\sigma n x}$$

$$\frac{J(x)}{J(0)} = e^{-x/\lambda}$$, where $\lambda = 1/\sigma n$

mean free path for interactions

"CROSS SECTIONS" depend upon

- interaction
- energy (velocity)
- material (Z)

examples for electrons

$E_0 = 10\,keV$

$Z = 13$

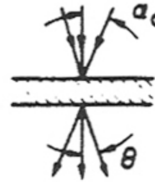
$\sigma_{INEL} \approx 10^{-1}\ \mathring{A}^2$

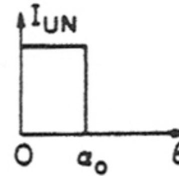
$\sigma_{EL} \approx 2.3 \times 10^{-1}\ \mathring{A}^2$

$\sigma_{K} \approx 1.8 \times 10^{-4}\ \mathring{A}^2$

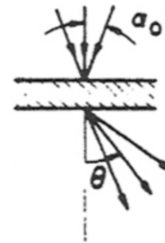
SCATTERING MECHANISMS FOR CHARACTERIZATION

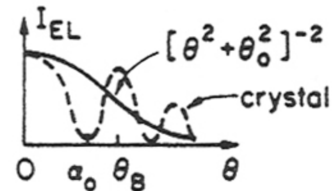
1. UNSCATTERED
   $\Delta E = 0$, $\Delta P = 0$



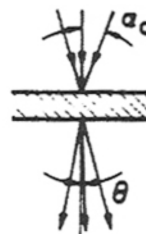


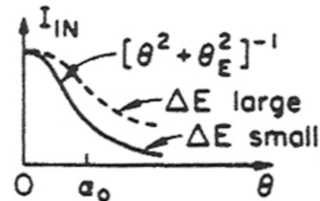
2. ELASTICALLY SCATTERED
   $\Delta E \approx 0$
   $\sigma_{EL} \sim Z^{3/2}$
   $\theta_0 \sim \lambda / 2\pi a \gtrsim \theta_B$

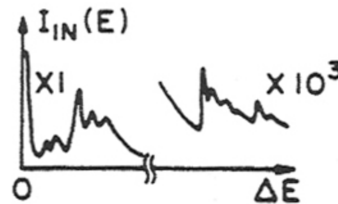




3. INELASTICALLY SCATTERED
   $\theta_E \approx \frac{\Delta E}{P_0 V_0}$
   $\sigma_{IN} \sim Z^{1/2}$
   $\frac{d\sigma_{IN}}{dE}$ material specific







EELS from nucleic acid bases

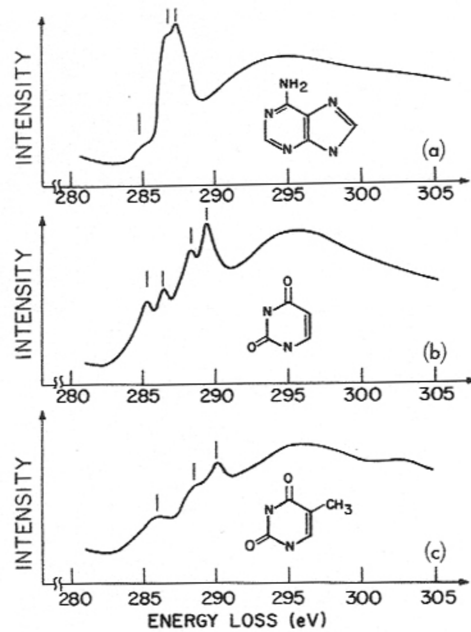


Fig. 2. Characteristic electron energy loss spectra of adenine, $C_5N_5H_5$ (a), uracil, $C_4N_2O_2H_4$ (b), and thymine, $C_5N_2O_2H_6$ (c) showing the fine structure in the region of the carbon K-shell excitation edge. The peripheral hydrogen atoms in the chemical structural formulas have been omitted for clarity.

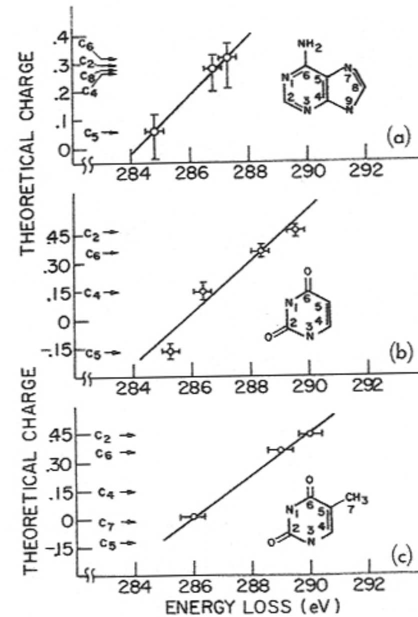
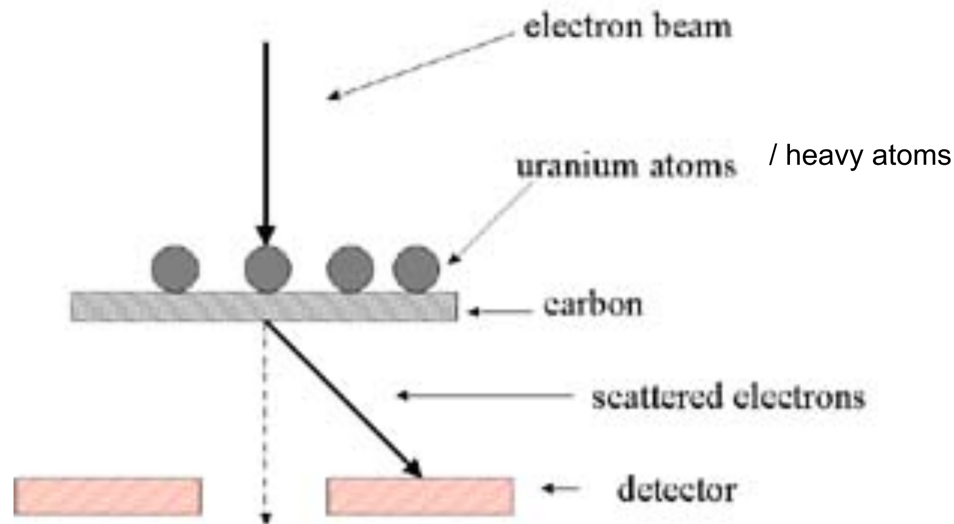


Fig. 3. Relationship between the positions of the peaks in the carbon K-shell fine structure and the theoretical atomic charge as calculated in Refs. (9) and (8). The error bars on the charge indicate the range of the theoretical values.

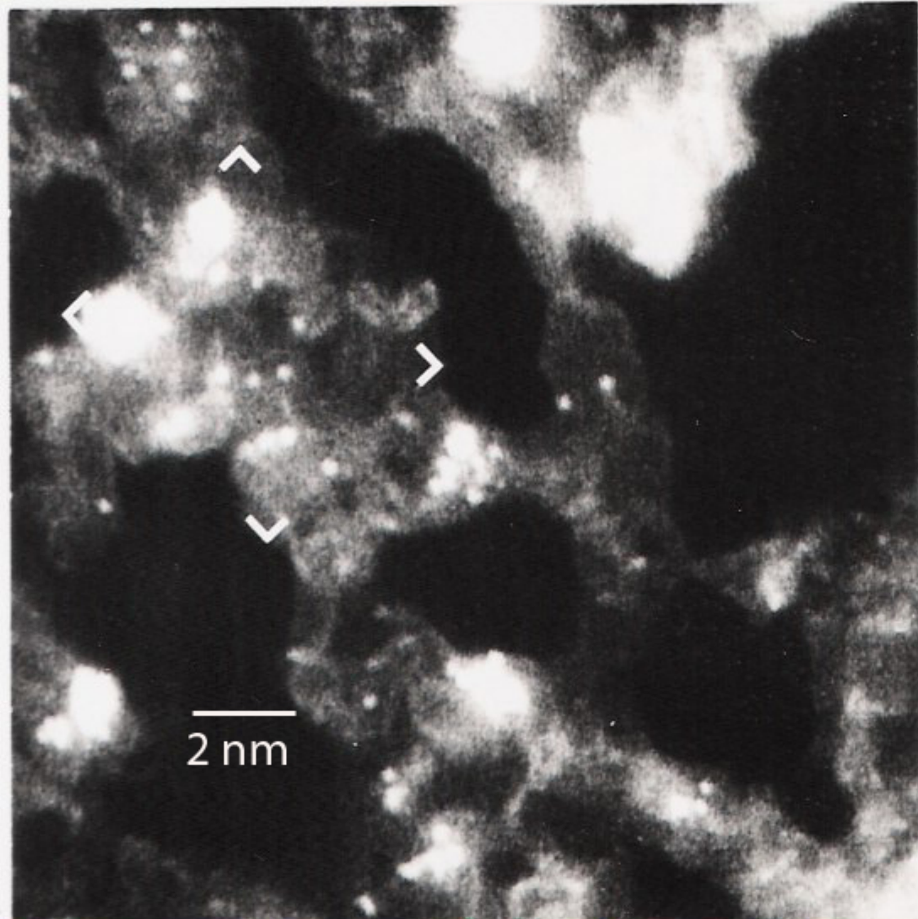
From: M. Isaacson, 1972

Nanodevices Require Atomic Characterization



Scanning Transmission Electron Microscope

Gold Atoms on 2nm thick amorphous carbon substrate



STEM Annular Dark Field Signal, 30KeV

M.Isaacson, M.Ohtsuki, M. Utlaut, D.Kopf and A.V.Crewe, 1979

Imaging single Si atom impurities in graphene

Si atoms in graphene can occupy two different sites (UltraSTEM100 images).

a

b

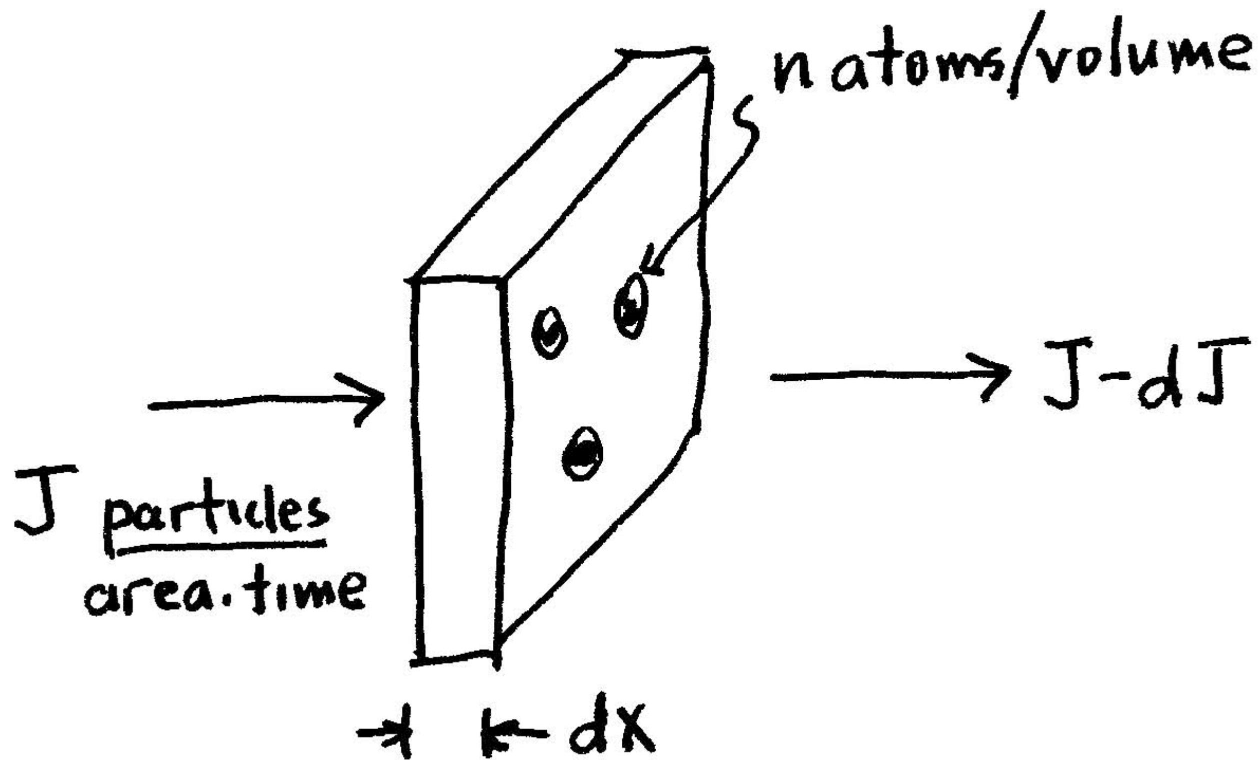
1 Å

4-fold: Si substitutes for 2 C atoms
Courtesy Wu Zhou

3-fold: Si substitutes for a single C atom
Courtesy Matt Chisholm

Can we study the bonding environment of a single atom?

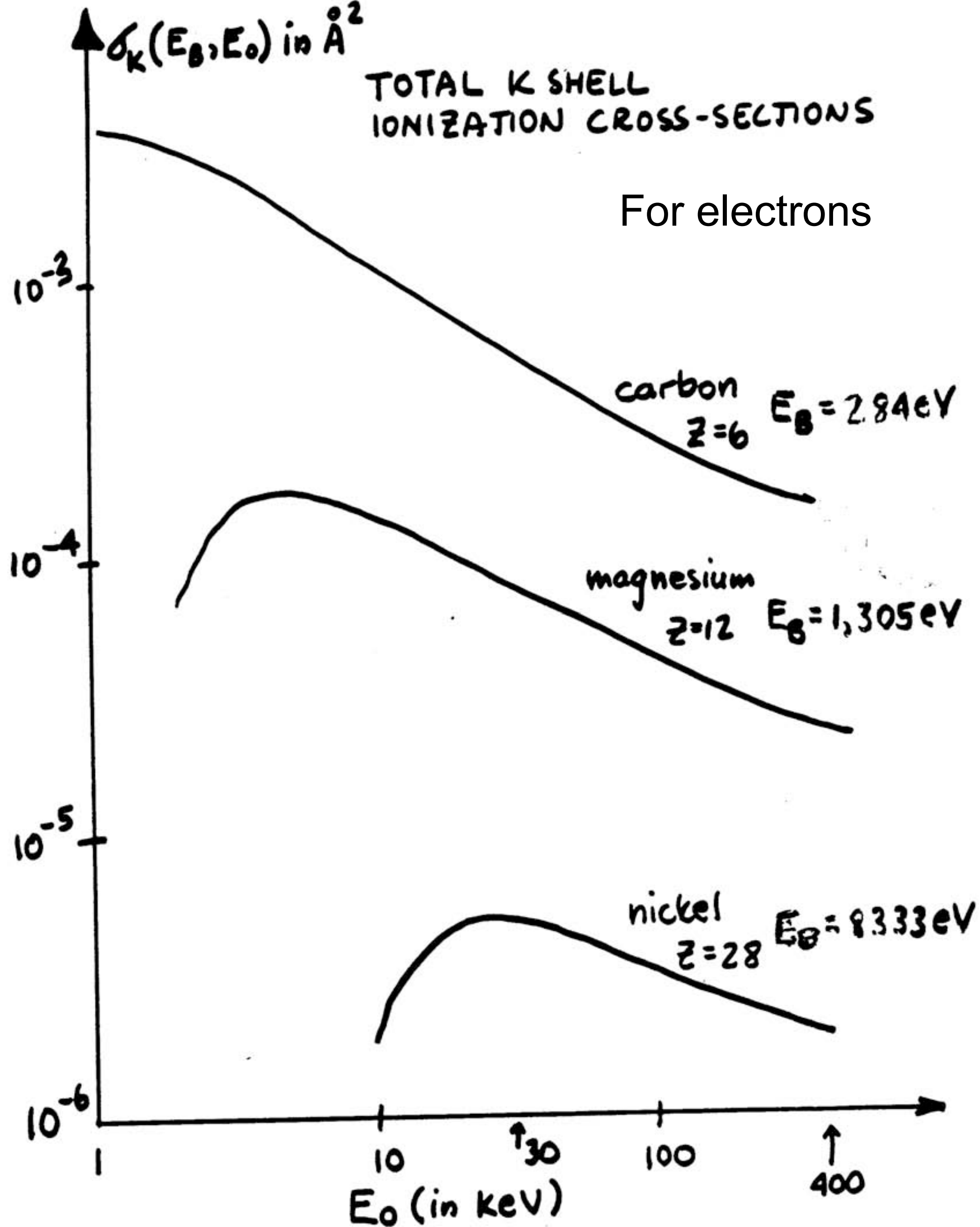
From Ondrej Krivanek

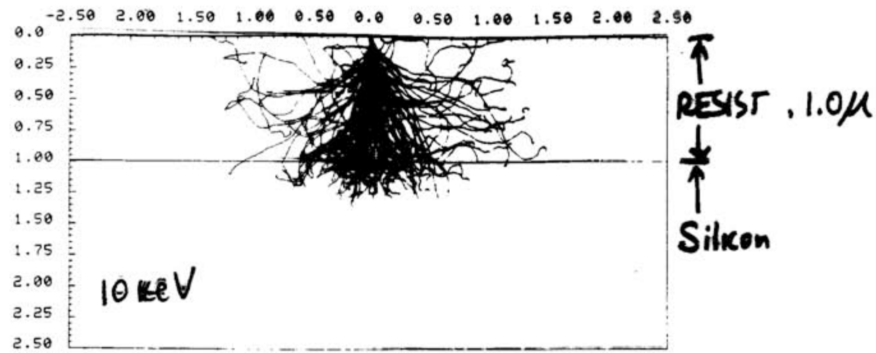


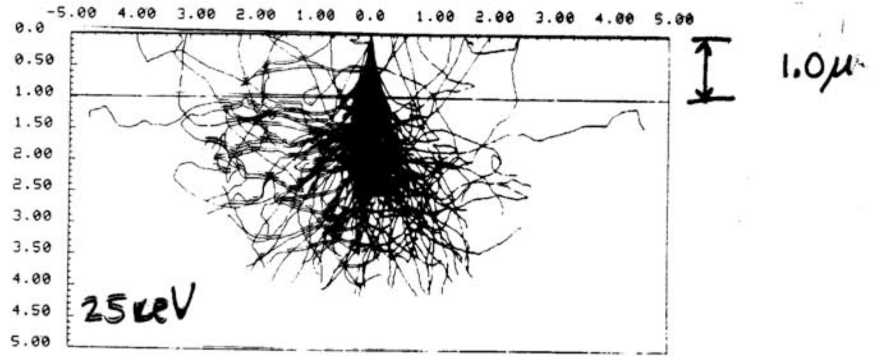
probability that interaction occurs = P

$P = \sigma \cdot n \cdot dx$

σ → effective interaction area/cross-section


$\sigma_K(E_B, E_0)$ in $\mathring{A}^2$
TOTAL K SHELL
IONIZATION CROSS-SECTIONS
For electrons
10^{-3}
10^{-4}
10^{-5}
10^{-6}
carbon
Z=6
E_B = 284eV
magnesium
Z=12
E_B = 1,305eV
nickel
Z=28
E_B = 8333eV
1
10
30
100
400
E_0 (in keV)





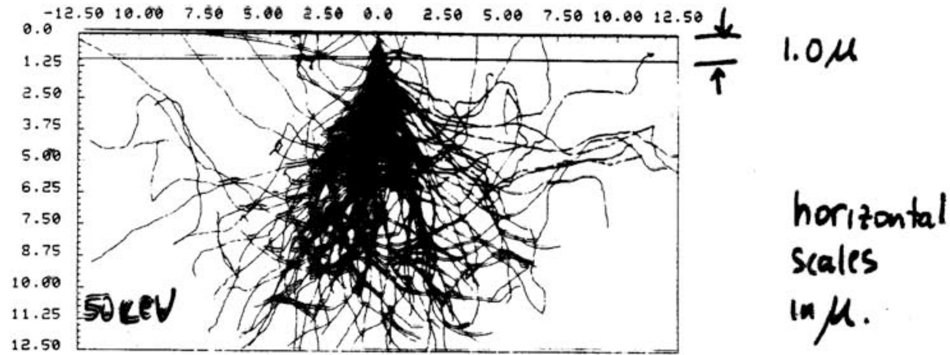
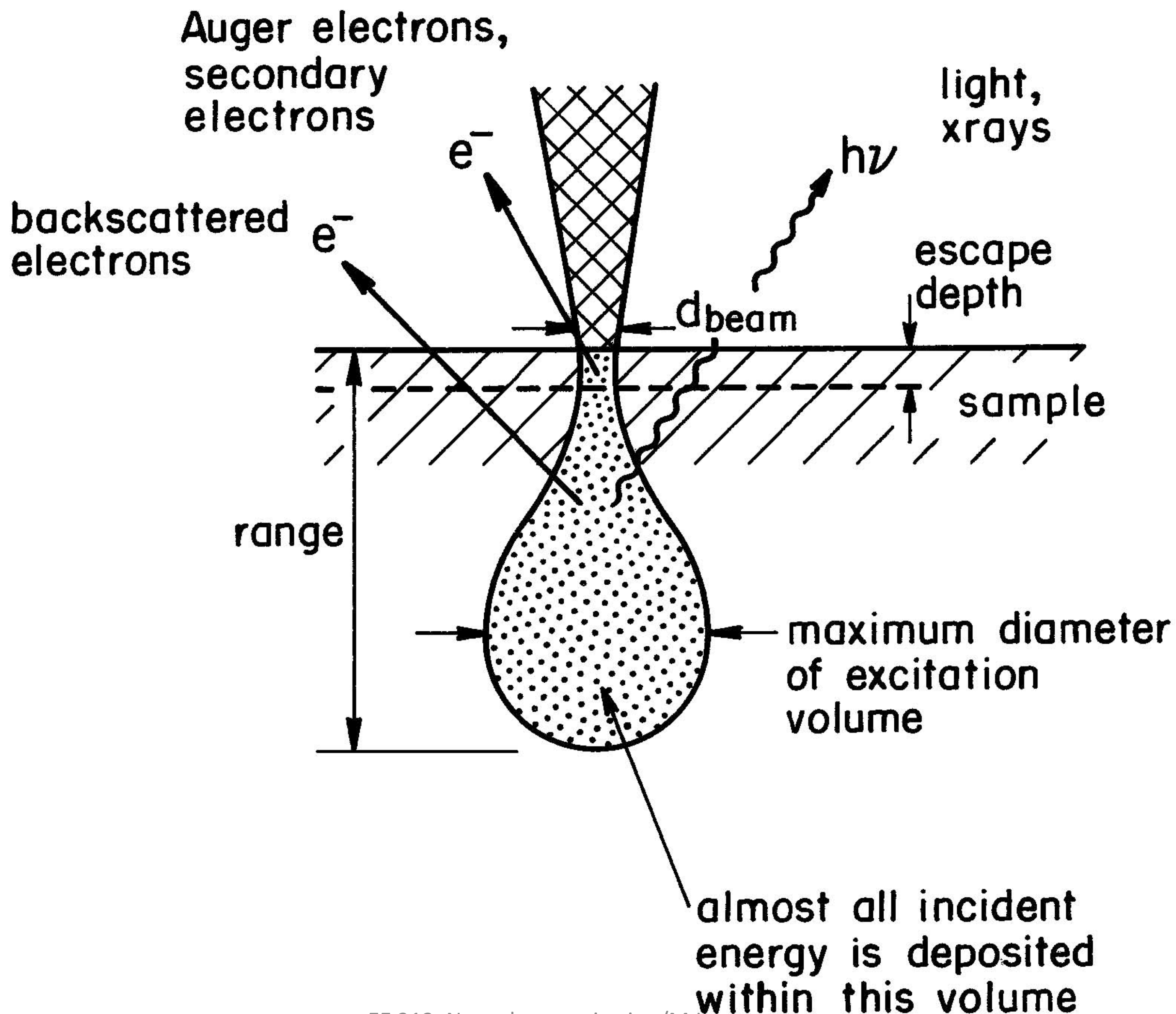
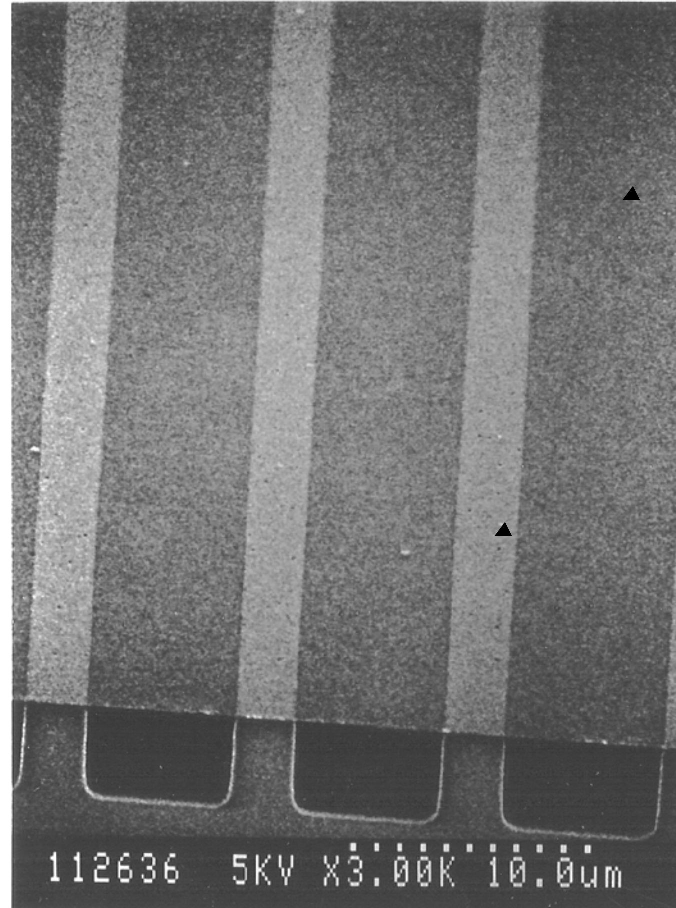


Fig. 3. Projection of 100 point source electron trajectories in a target of 1-μm-thick resist on an infinitely thick silicon substrate at (a) 10, (b) 25, and (c) 50 keV incident energy. The x and y axes are in units of micrometers.

from D. Kyser/


Auger electrons,
secondary
electrons
light,
xrays
e⁻
hν
backscattered
electrons
e⁻
escape
depth
d beam
sample
range
maximum diameter
of excitation
volume
almost all incident
energy is deposited
within this volume

100 nm Aluminum Film Self-Supported on Silicon Fingers
secondary electron image



SE only

SE + SE(BSE)

M. Isaacson and K. Lin

$$S = NJ\sigma YF$$

S = signal in counts/sec

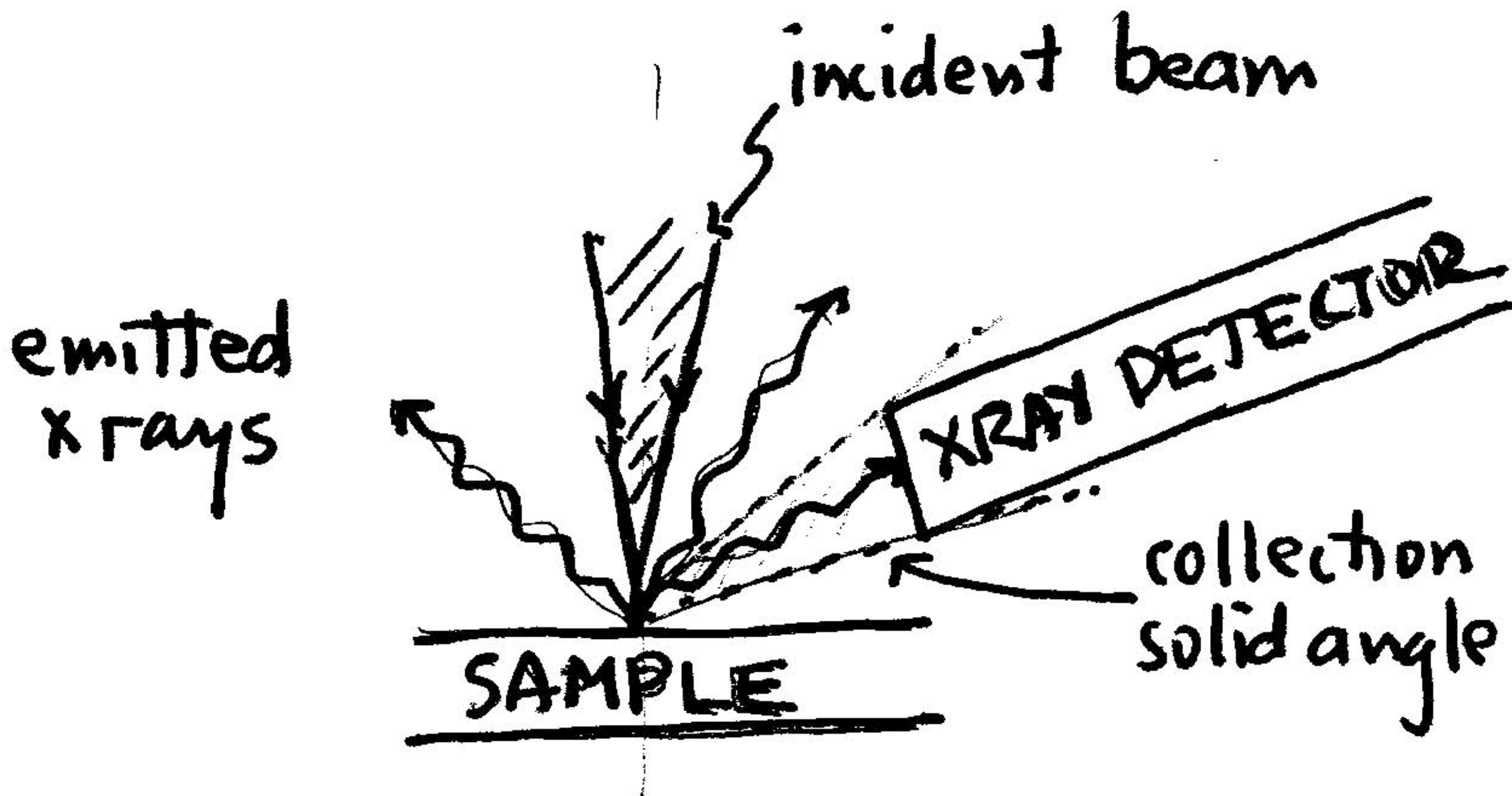
N = # atoms in volume probed

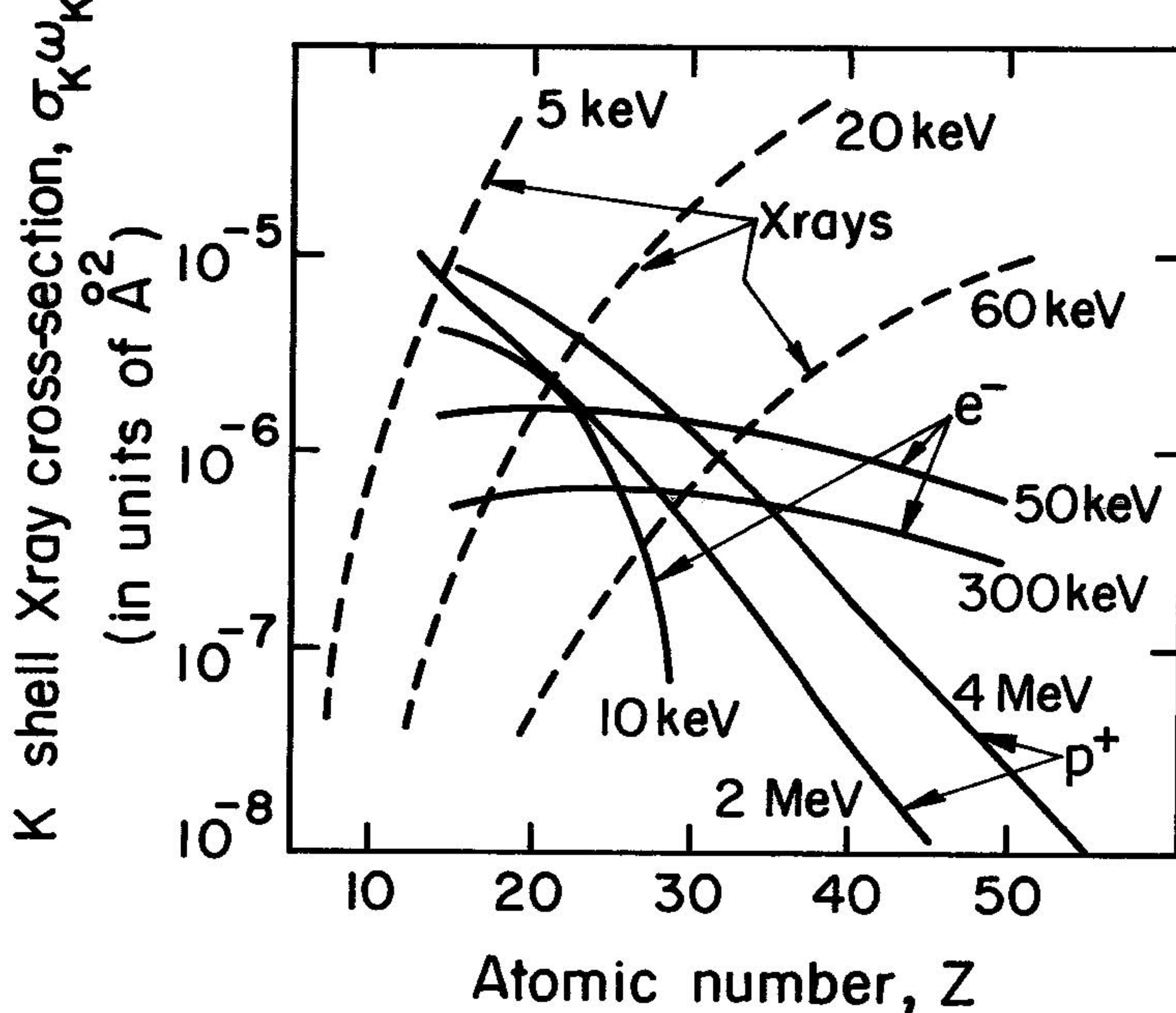
J = current density in probe (#/area/sec)

σ = cross section for interaction (area)

Y = yield of process to be detected

F = efficiency of collection


incident beam
emitted
x rays
XRAY DETECTOR
collection
solid angle
SAMPLE



K shell Xray cross-section, $\sigma_K \omega_K$
(in units of $\mathring{A}^2$)
10^{-5}
10^{-6}
10^{-7}
10^{-8}
5 keV
20 keV
Xrays
60 keV
e^-
50 keV
300 keV
10 keV
4 MeV
p^+
2 MeV
10
20
30
40
50
Atomic number, Z