- Úvod do tématiky, základní literatura.
- Interakce elektronů s pevnou látkou.
- Typy elektronových mikroskopů. TEM a SEM.
- Pracovní módy elektronových mikroskopů, konstrukce.
- Příprava vzorků pro TEM.

Základní literatura:

D. B. Williams a C. B. Carter: Transmission Electron Microscopy (4 díly, Plenum Press, NY, 1996)

J. Goldstein aj.: Scanning Electron Microscopy and X-Ray Analysis (3rd ed., Kluwer, NY, 2003)

P. B. Hirsch aj.: Electron Microscopy of Thin Crystals (Butterworths, London, 1965 nebo pozdější dotisky)

M. Karlík: Úvod do transmisní elektronové mikroskopie (vydalo nedávno nakladatelství ČVUT, Praha, 2011)

Další zdroje: www.jems-saas.ch (Pierre Stadelmann, Lausanne, CH)
www.amc.anl.gov (microscopy and microanalysis server)
…..

Historie:

první TEM: 1932 (Knoll a Ruska, Nobelova cena 1986)

1949: Heidenreich ztenčuje kovové fólie

50. léta: pozorování čarových a plošných defektů krystalové mřížky, rozvoj mikroanalytických metod, vysokovoltážní a *in situ* mikroskopie, řádkovacích módů, rozlišení ~ 0.4 nm

1956: atomové roviny (lattice fringes) v pthalokyaninech (Menter)

1957: Cowley, Moodie: základy teorie a simulace HRTEM obrazu

+

zlepšení teplotní stability, mechanické stability, kvality vakua, elektronické stability, designu čoček (CS korektory, energiové filtry), nové typy katod

+

zlepšení možnosti reprodukovatelné přípravy kvalitních tenkých fólií

↓

rozlišovací schopnost ~ 0.1 nm

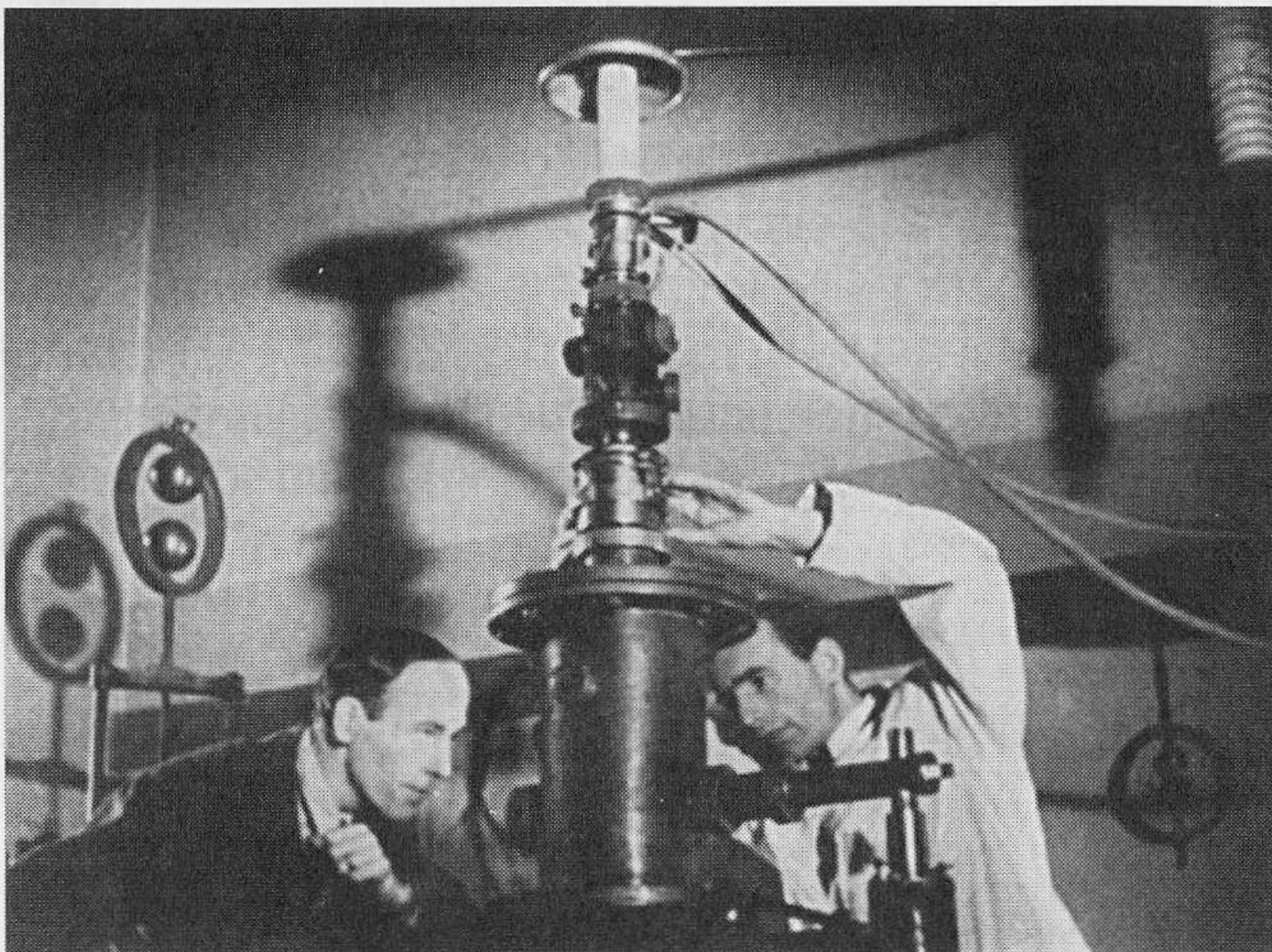


Figure 1.1. The electron microscope built by Ruska and Knoll in Berlin in the early 1930s.

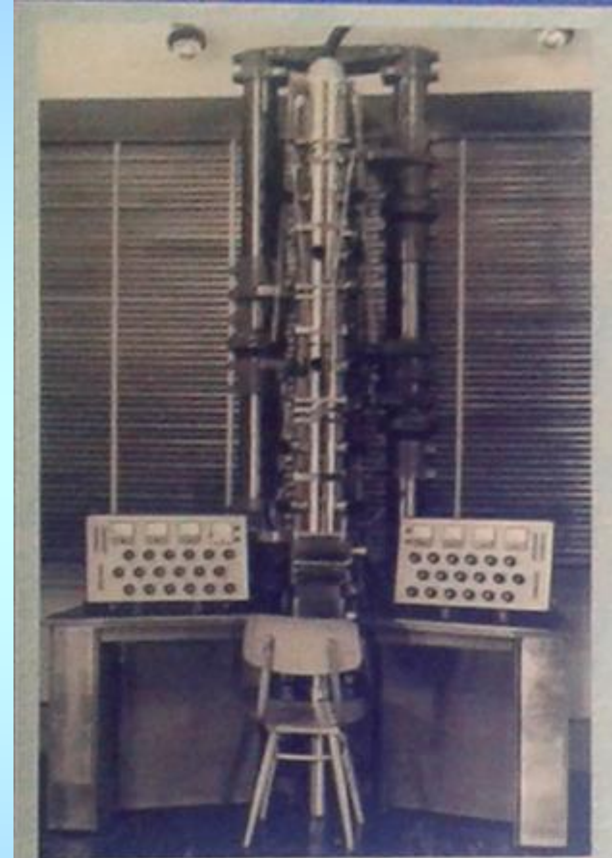
1931:
16x
2 čočky

1933:
12000x
Rozlišení lepší než světelný mikroskop

Brno, 1950

The first ("three-legged") Czechoslovak electron microscope is born in Brno

Brno, 1968



Brno: a 150 keV TEM aiming for 2 Å resolution.

Elektronové mikroskopy

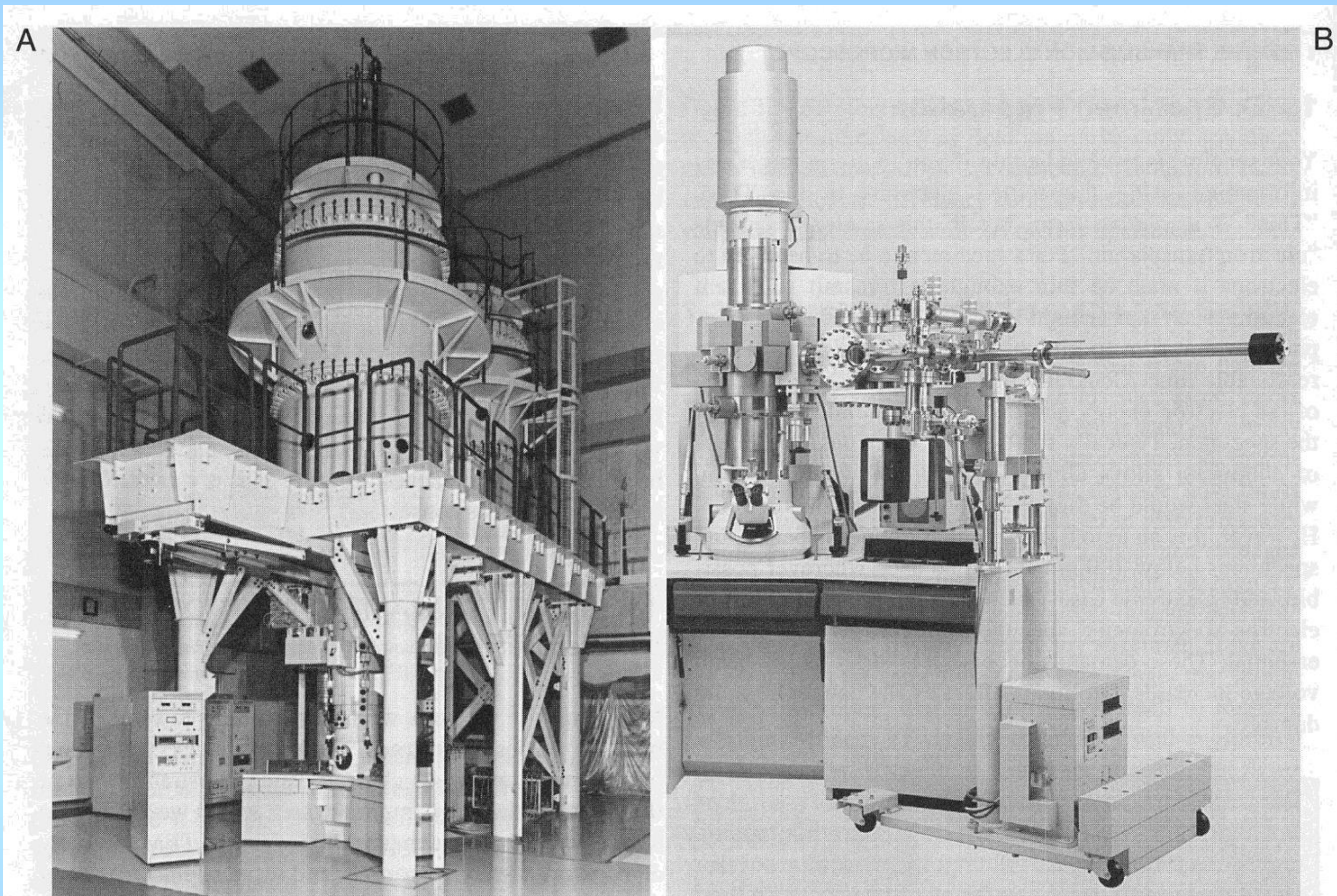


Figure 1.9. Different TEMs: (A) a JEOL 1.25-MV high voltage microscope, used for high-resolution imaging; (B) a Hitachi specialized ultrahigh vacuum TEM for high-resolution surface imaging; (C) a Philips 200-kV analytical microscope with an X-ray spectrometer attached to the stage (the liquid-N_2 dewar cools the detector); and (D) a VG dedicated 100-kV ultrahigh vacuum scanning transmission microscope. Comparison with Ruska's instrument (Figure 1.1) which is 50–60 years older is instructive.

Titan G2 60-300	Energy spread	Point resolution	Information limit	STEM resolution
Image corrector	0.7 to 0.8 eV**	80 pm	80 pm	136 pm
Probe corrector	0.7 to 0.8 eV**	200 pm	< 100 pm	80 pm
Monochromator + X-FEG	0.2 to 0.3 eV*	200 pm	80 pm	136 pm

Interakce elektronů s pevnou látkou

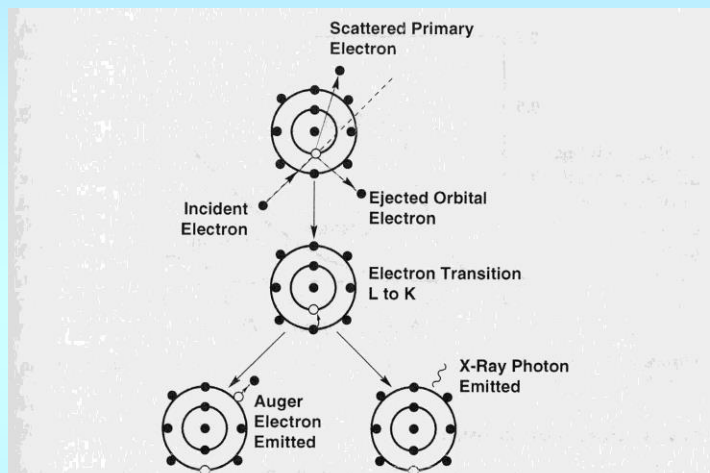


Figure 6.5. Inner shell electron ionization in an atom and subsequent de-excitation by electron transitions. The incident electron is elastically scattered. The unscattered direction of the incident electron is shown by the dotted line. The difference in energy from an electron transition is expressed either as the ejection of an energetic electron with characteristic energy (Auger process) or by the emission of a characteristic x-ray photon.

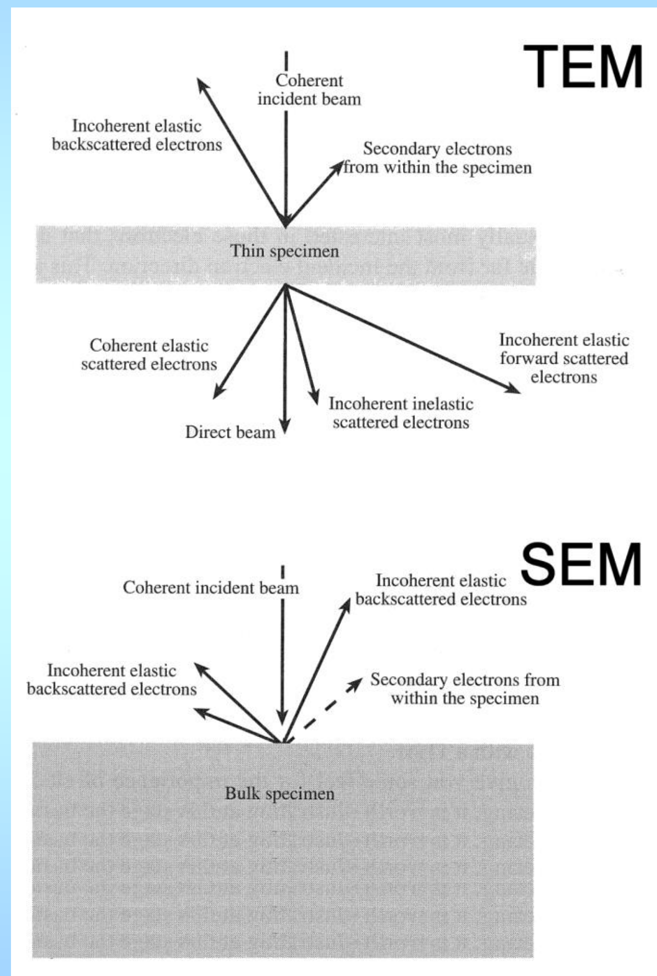


Schéma chodu elektronového svazku v TEM

A

B

Specimen

Remove aperture

Objective lens

Objective aperture (back focal plane)

Fixed

SAD aperture

Intermediate image 1

Remove aperture

Change strength

Intermediate lens

Second intermediate 'image'

Fixed strength

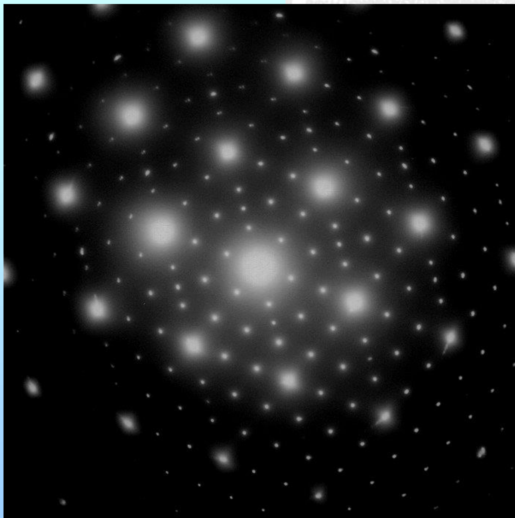
Pro

pattern

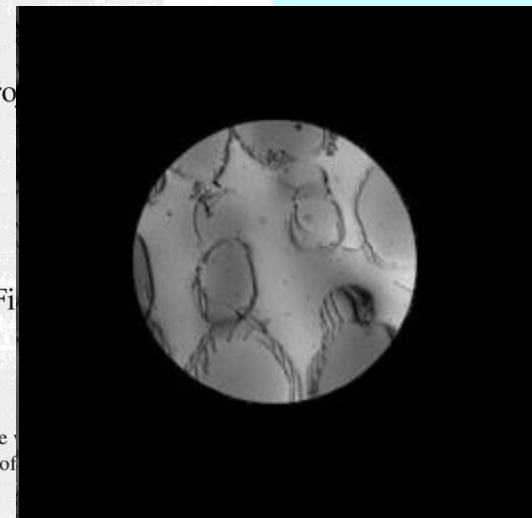
Fi

Screen

DIFRAKCE



OBRAZ

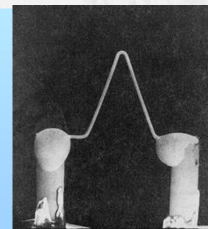
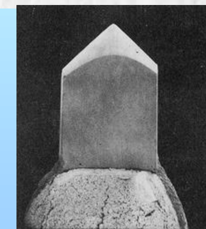
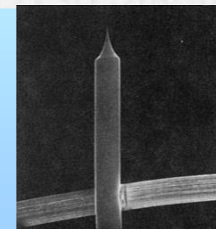


basic operations of the TEM imaging system involve (A) projecting the diffraction pattern on the v
e screen. In each case the intermediate lens selects either the back focal plane or the image plane of

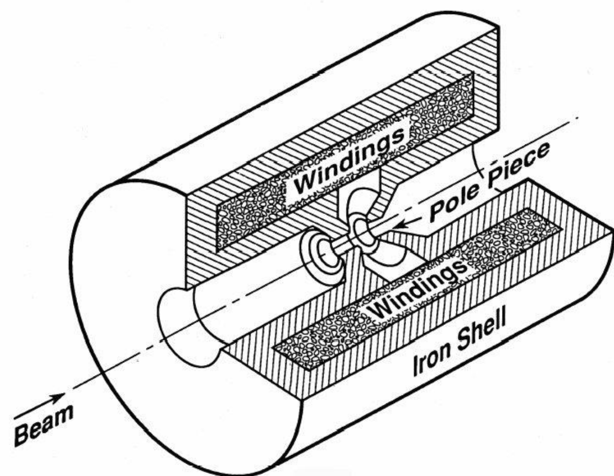
Vlastnosti elektronových zdrojů - porovnání

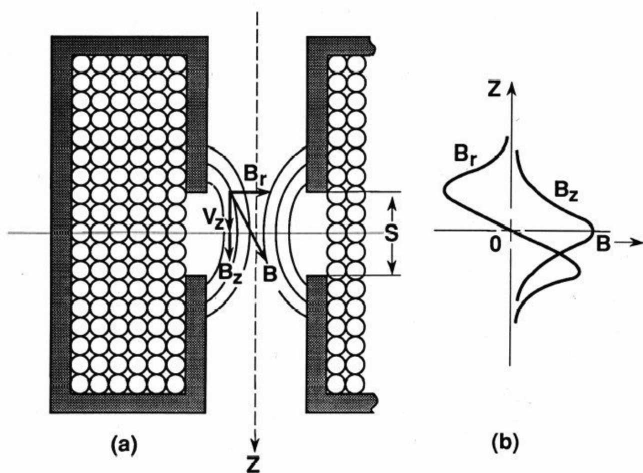
TABLE 5.1. Characteristics of the Three Principal Sources Operating at 100 kV

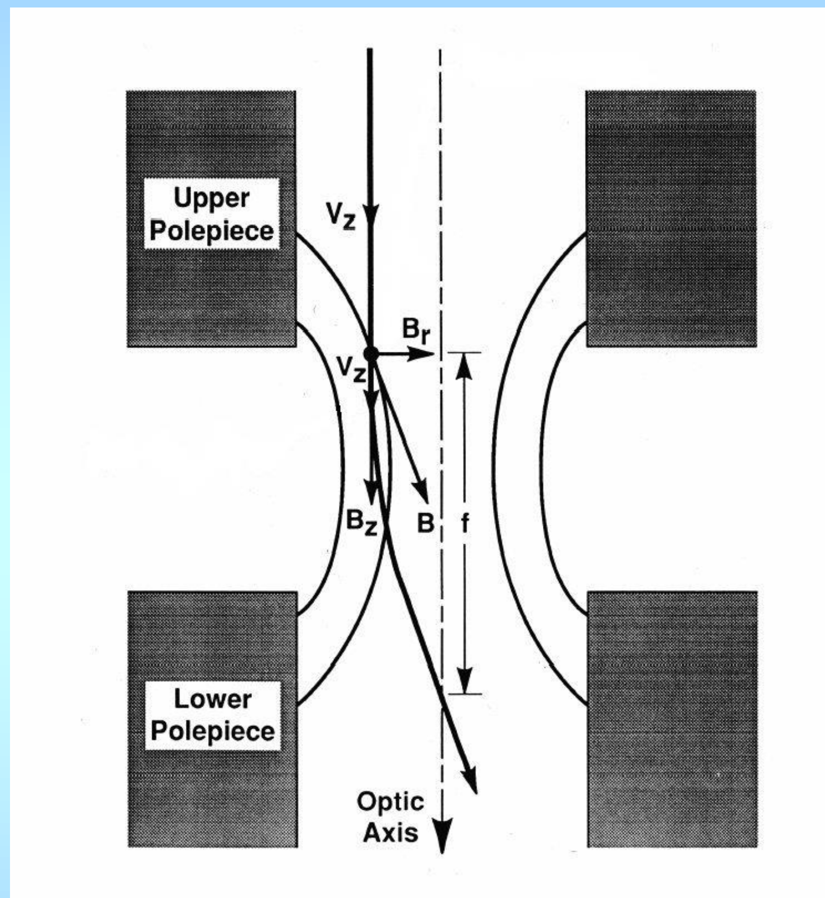
	Units	Tungsten	LaB_6	Field Emission
Work function, Φ	eV	4.5	2.4	4.5
Richardson's constant	A/m^2K^2	6×10^5	4×10^5	
Operating temperature	K	2700	1700	300
Current density	A/m^2	5×10^4	10^6	10^{10}
Crossover size	μm	50	10	<0.01
Brightness	A/m^2sr	10^9	5×10^{10}	10^{13}
Energy spread	eV	3	1.5	0.3
Emission current stability	%/hr	<1	<1	5
Vacuum	Pa	10^{-2}	10^{-4}	10^{-8}
Lifetime	hr	100	500	>1000

Elektromagnetická čočka:







$$\mathbf{F} = -e\mathbf{v} \times \mathbf{B}$$

$$F_{\theta in} = -V_z \times B_r$$

$$F_r = -V_{\theta_{in}} \times B_z$$

Vady čoček v EM: sférická vada a efekt difrakce na cloně

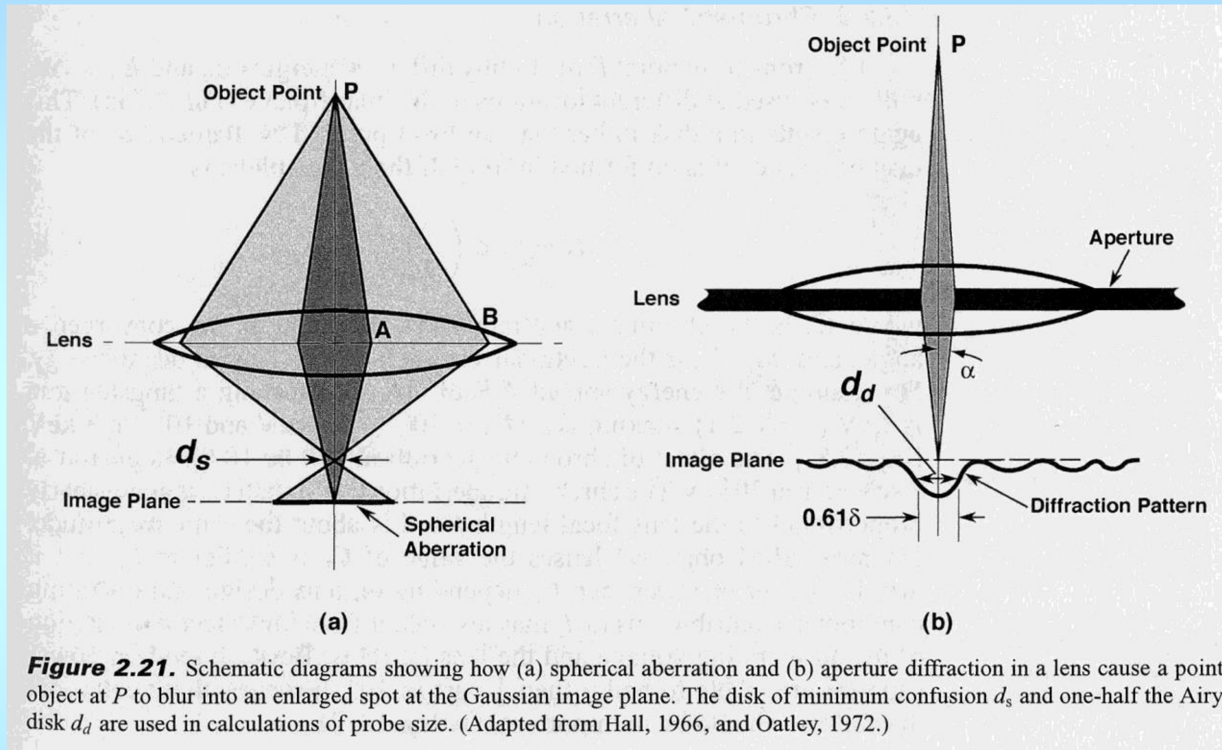


Figure 2.21. Schematic diagrams showing how (a) spherical aberration and (b) aperture diffraction in a lens cause a point object at P to blur into an enlarged spot at the Gaussian image plane. The disk of minimum confusion d_s and one-half the Airy disk d_d are used in calculations of probe size. (Adapted from Hall, 1966, and Oatley, 1972.)

$$d_s = C_s \alpha^3$$

$$C_s = 1 \div 2mm$$

$$d_d = 0.61\, \lambda / \alpha$$

Abbe, Airy

Vady čoček v EM: vliv na rozlišovací schopnost EM

$$d = \sqrt{d_d^{\,2} + d_s^{\,2}} = \sqrt{\left(0.61\lambda/\alpha\right)^2 + \left(C_s\alpha^3\right)^2}$$

$$\frac{\partial d}{\partial \alpha} = 0 \Leftrightarrow \alpha_{opt} \doteq 0.77\frac{\lambda^{1/4}}{C_s^{1/4}},\ d_{\min} \doteq 0.91\left(C_s\lambda^3\right)^{1/4} \approx 0.15nm$$

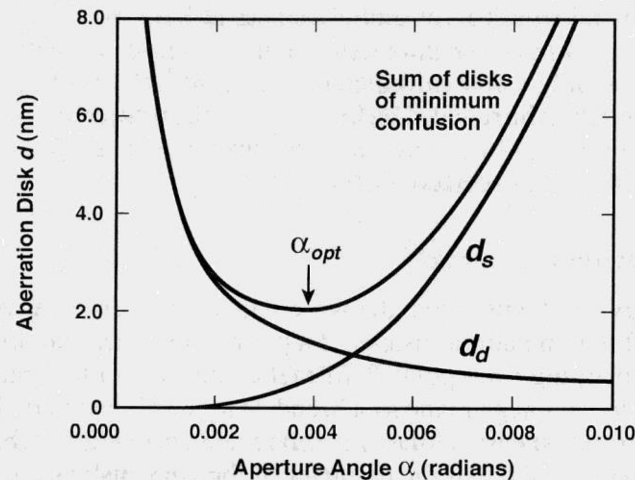
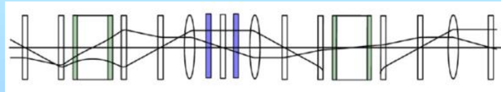


Figure 2.22. Spherical aberration disk d_s and aperture diffraction disk d_d plotted against aperture angle α. For the smallest electron probe and the best image resolution, the aperture angle is taken as α_{opt}.

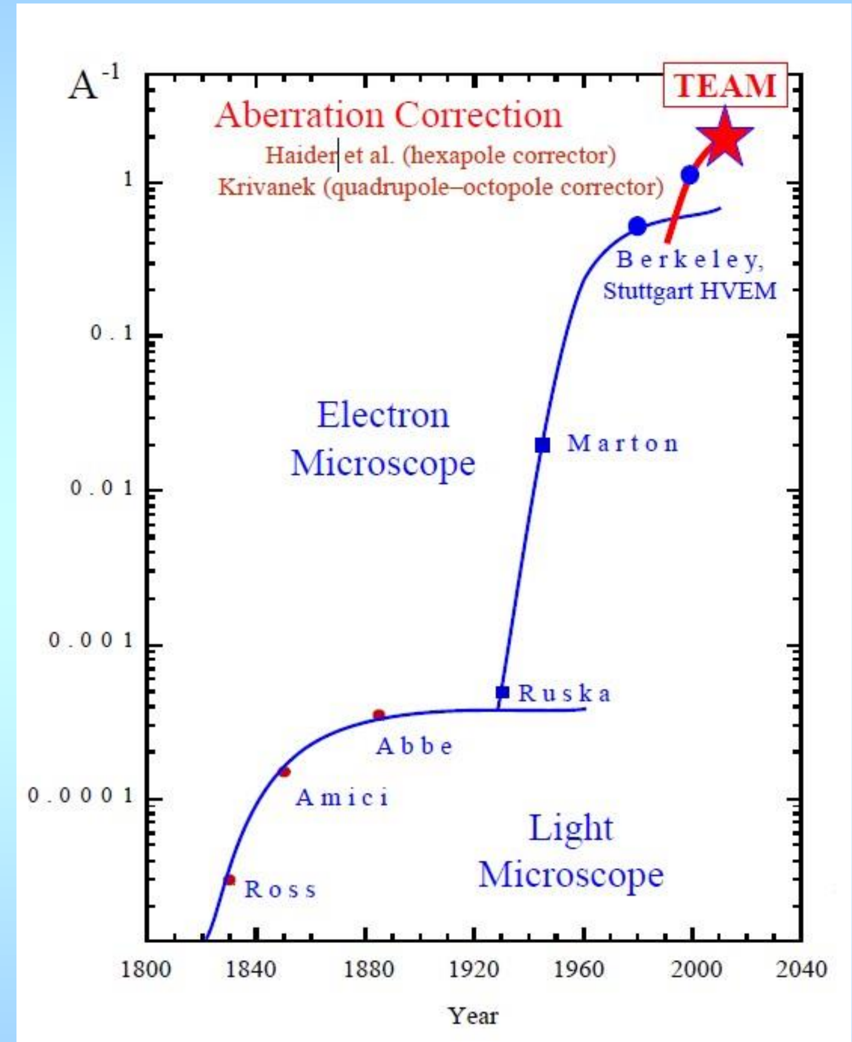
Z historie korekcí vad čoček v EM:

Otto Scherzer (1936): teorém o vadách rotačně symetrických čoček

$d \geq 100\ \lambda$
$U \leq 300\ \text{kV} \Rightarrow \lambda \geq 2\text{pm}$

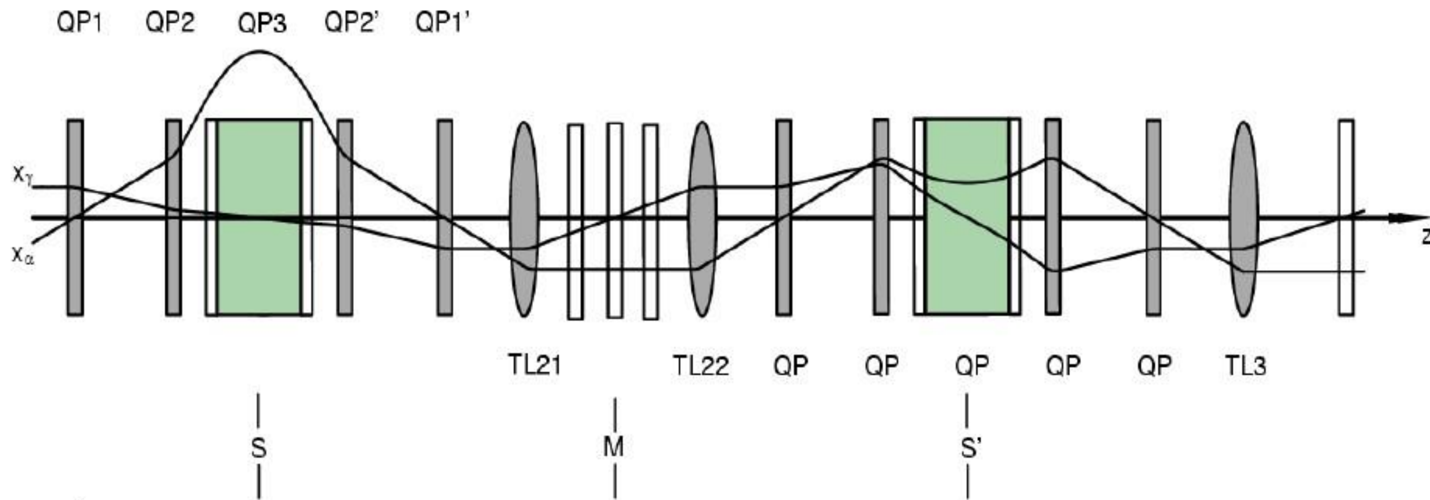
Otto Scherzer (1947): o možnosti korekce vad zařazením sad rotačně nesymetrických čoček (multipólů) 

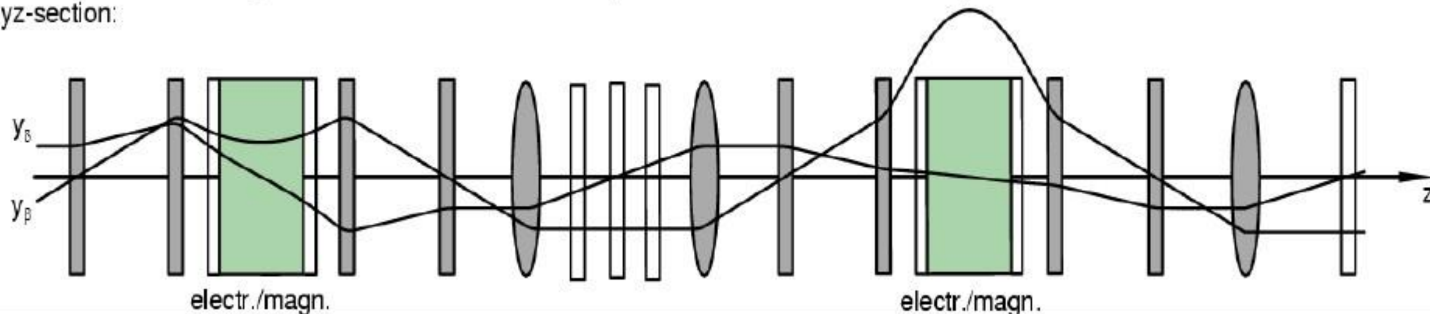
Harald H. Rose, projekt TEAM



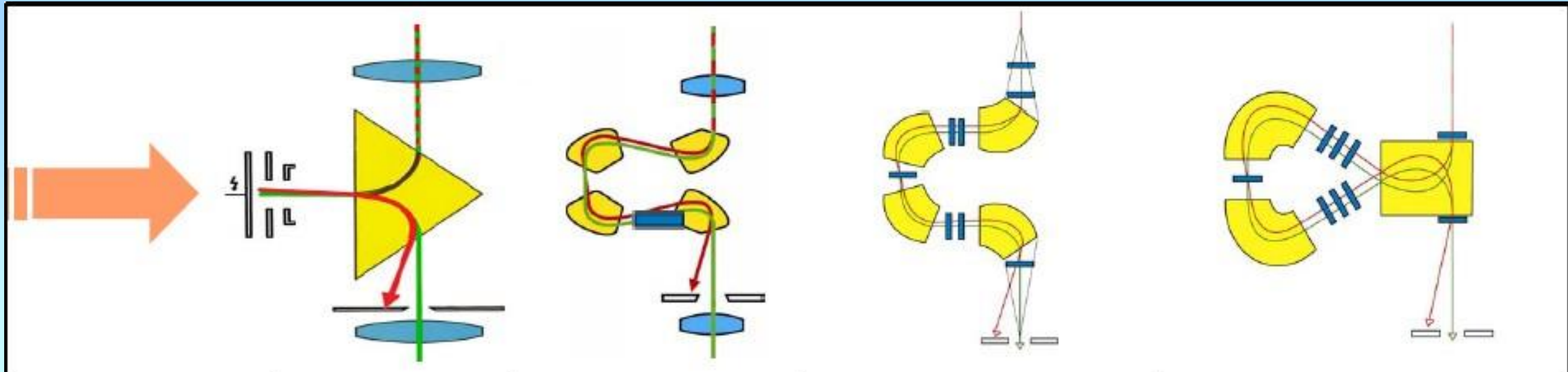
Blok korektoru:

Compound Achromator and Aplanator (Achroplanator)



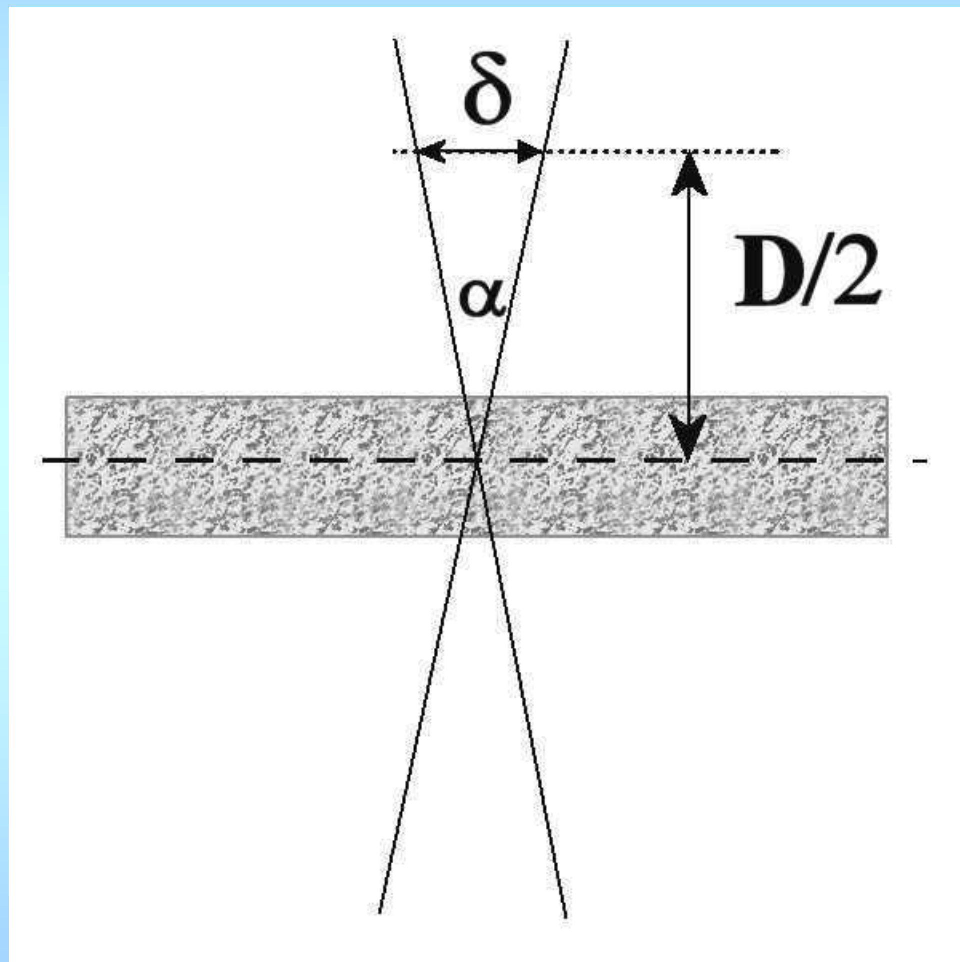


Energiové filtry:



Type and Designers	Prism – Filter Castaing-Henry	OMEGA – Filter Lanio-Krahl-Rose	Corrected OMEGA – Filter Rose-Krahl	MANDOLINE – Filter Uhlemann-Rose
First realization	Henry 1964	Krahl 1992	Krahl (FHI Berlin) 1986	Essers (Zeiss) 2005
Commercial Microscope	ZEISS EM 902	Zeiss 912 / 922	SESAMe I / II Zeiss Libra 200	Zeiss SESAMe
High Voltage	80 kV	120 kV / 200 kV	200 kV FEG	200 kV FEG
Dispersion	1,5 µm/eV (80kV)	0,75 µm/eV (200kV)	1,85 µm/eV (200kV)	6,2 µm/eV (200kV)
Correction	none	partial second-order correction	2. order corrected 3. order optimized	2. order corrected 3. order corrected
Non-Isochromaticity	23 eV	15 eV	isochromatic	isochromatic
Transmissivity @ 1eV	12×10^{-6} µm^2 (80kV)	9.3×10^{-6} µm^2 (200kV)	0.2×10^{-3} µm^2 (200kV)	11×10^{-3} µm^2 (200kV)

Hloubka pole (D) a hloubka ostrosti (D´):



$$D = \frac{2\delta}{\alpha}$$

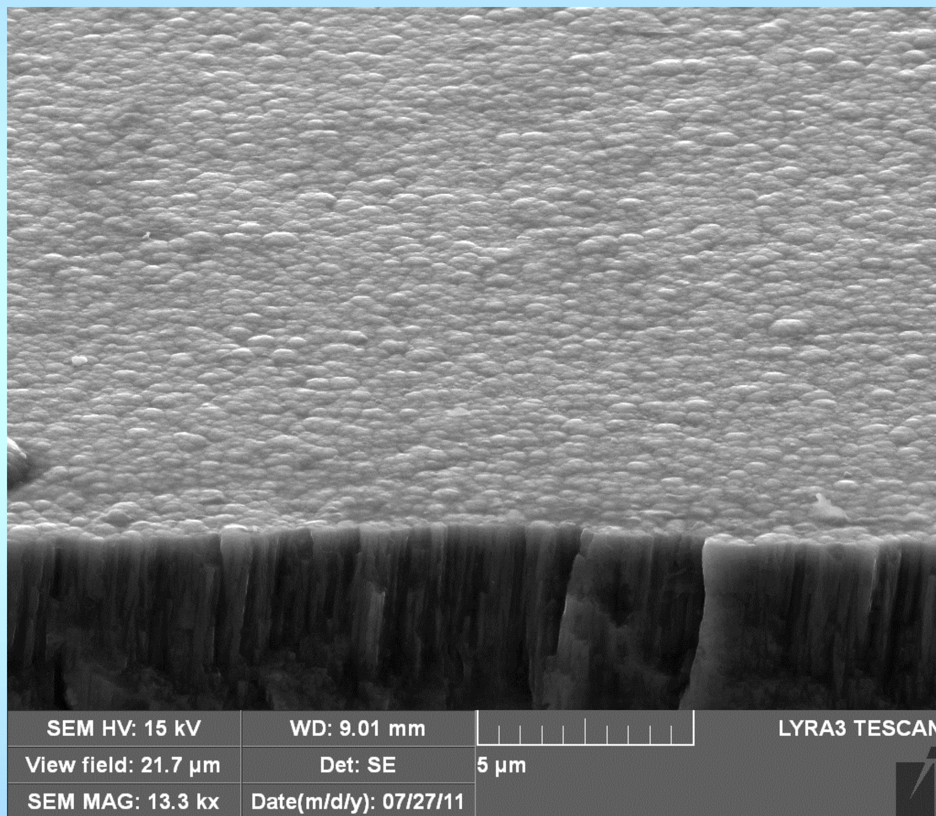
Příklad TEM:
Pro δ≈2nm, α≈6mrad je
D≈700nm>tloušťka vzorku.
Na stínítku pak

$$D' = D \cdot M^2,$$

pro M=53000 je D´≈2km!
(pro δ≈0.1nm je D´≈100m)

Hloubka pole (D) a hloubka ostrosti (D ′):

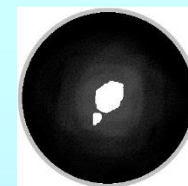
povrch vzorku skloněný 70°

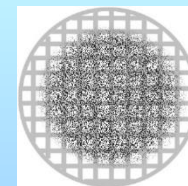


Příprava vzorků pro elektronovou mikroskopii

SEM: metalografické výbrusy, případně naleptání
základní požadavek: vodivost (+C, Au)
náročnější příprava např. pro EBSD

TEM: tenké fólie (ztenčení, důlek, finální úprava elektrolyticky nebo iontovým ztenčováním)
repliky povrchu
extrakční repliky
prášky aj. na uhlíkové blance (+Cu mřížka)
FIB





replika povrchu

extrakční replika

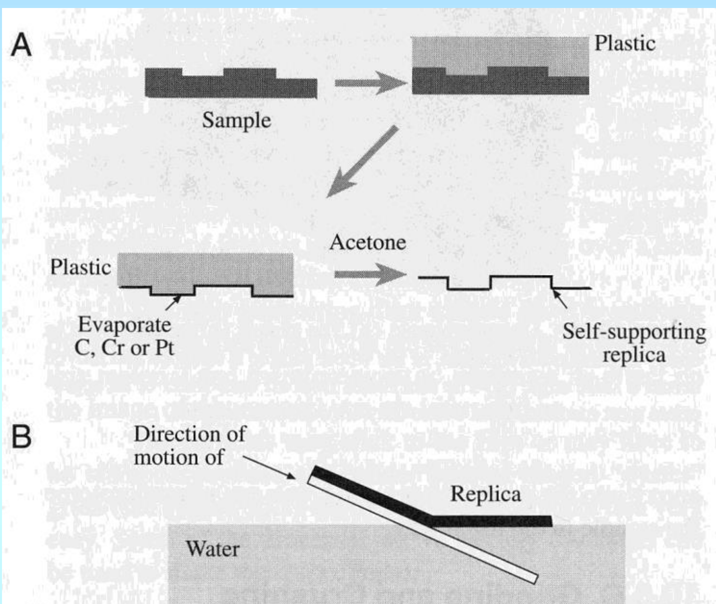


Figure 10.15. (A) Replication of a surface by the two-step method: spray acetone on the surface to be replicated before pressing a plastic (usually cellulose acetate) onto the surface which softens in contact with the acetone; the plastic is removed from the surface when it has hardened and a C, Cr, or Pt film is evaporated onto the replicated plastic surface; the plastic is then dissolved with acetone and the evaporated film retains the original topography. (B) Alternatively, the direct carbon replica of a metal surface may be floated off on distilled water after scratching the carbon and etching to free the film, which may subsequently be shadowed obliquely to enhance the topography.

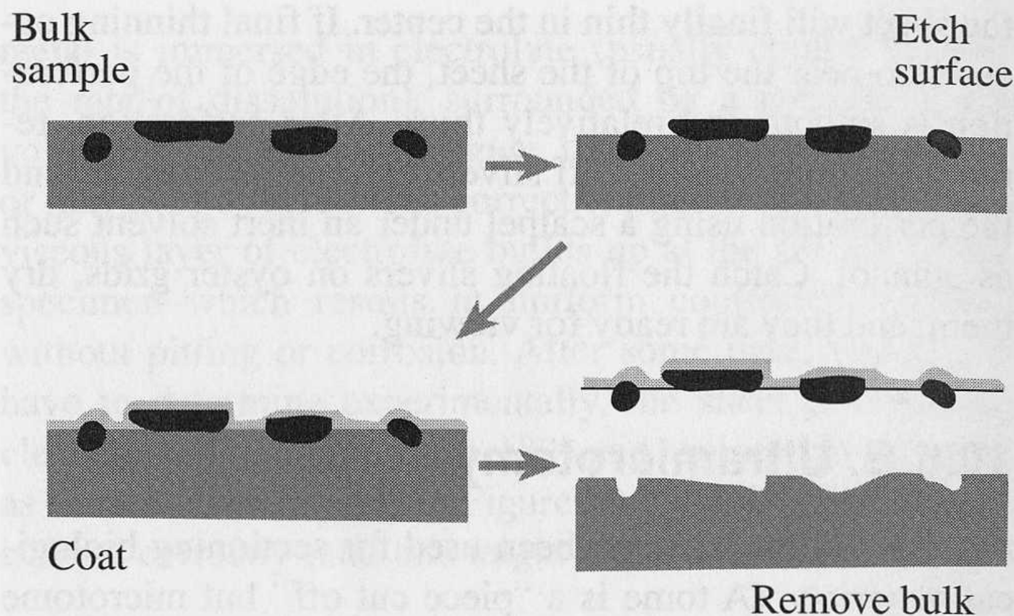
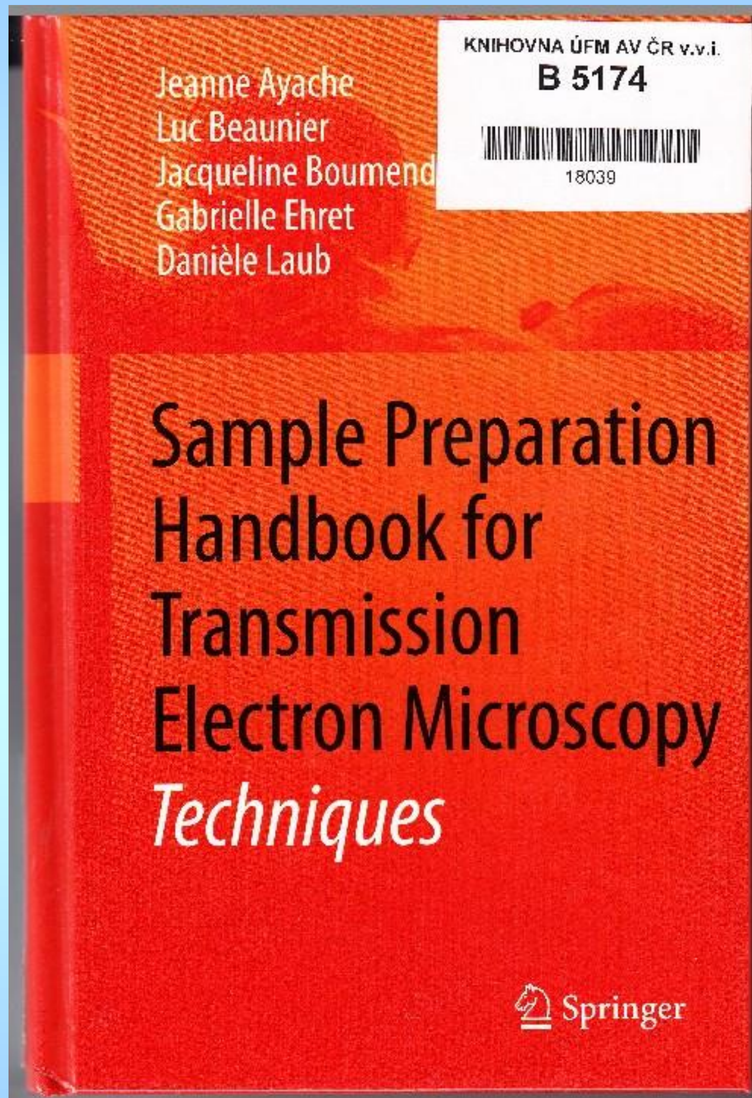


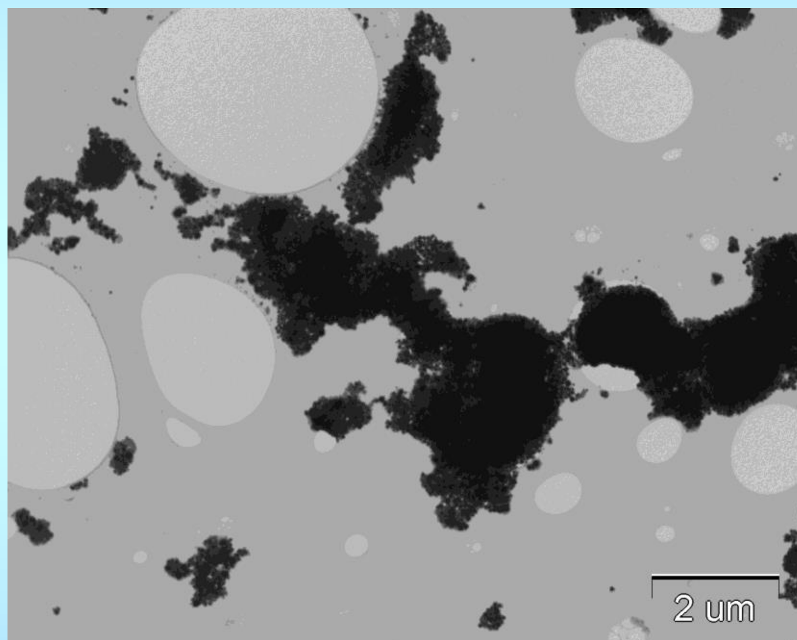
Figure 10.16. Extraction replication: particles embedded in a matrix are revealed by etching the matrix, which leaves the particles standing proud of the surface; a thin amorphous carbon film is evaporated over the particles, then the rest of the matrix is etched away leaving the particles adhering to the carbon film.

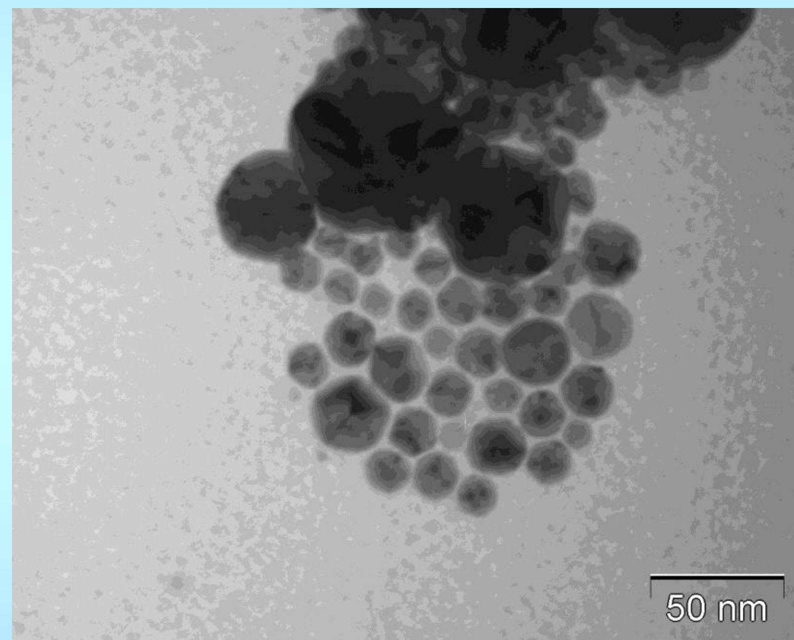


When faced with a choice,
Regardless of the path you choose,
Don't go down it halfway.
Be patient, be persistent,
Be courageous, and creative.
The reward is at the end....

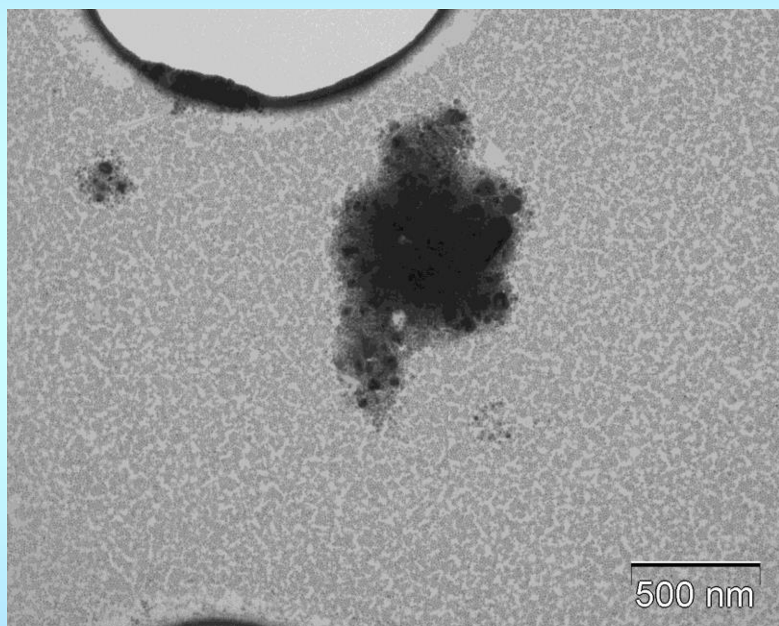
Jeanne Ayache

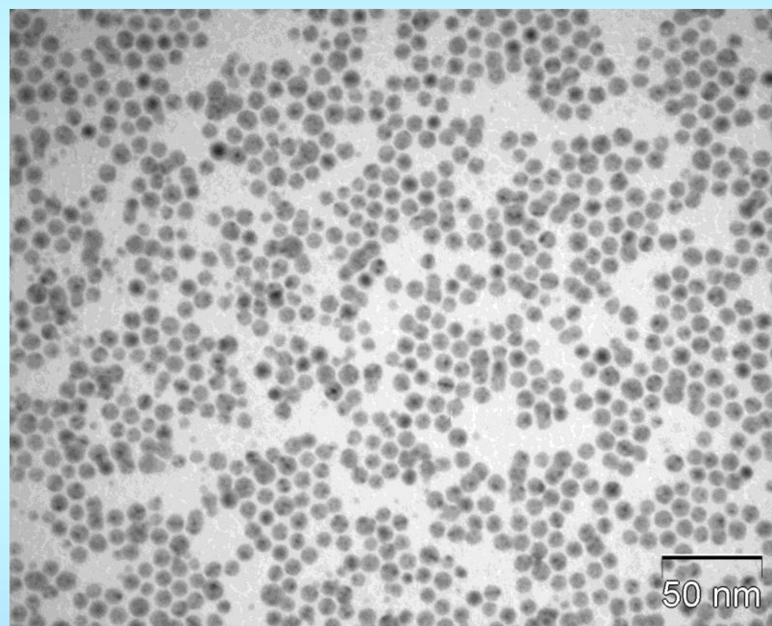
(Nano)prášky na uhlíkové blance (+Cu mřížka)



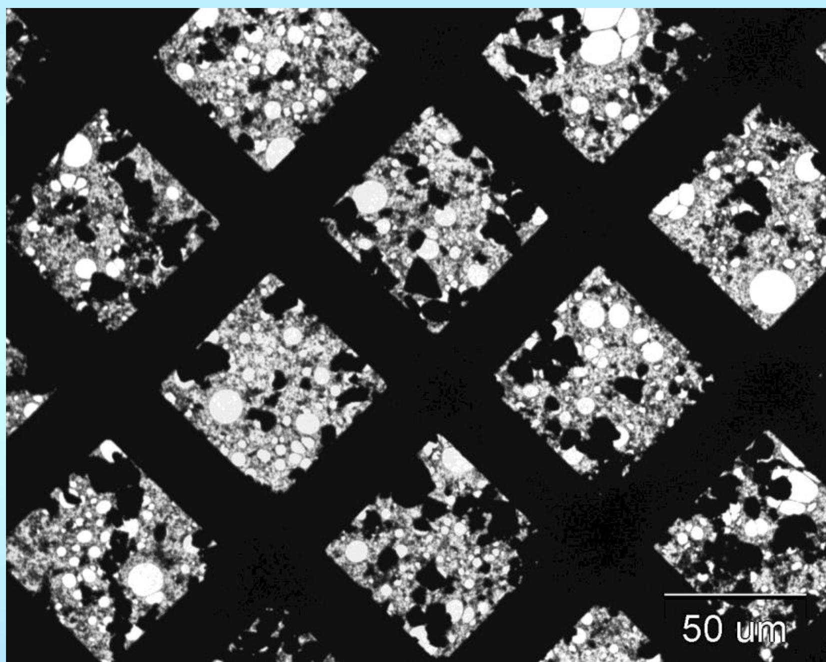


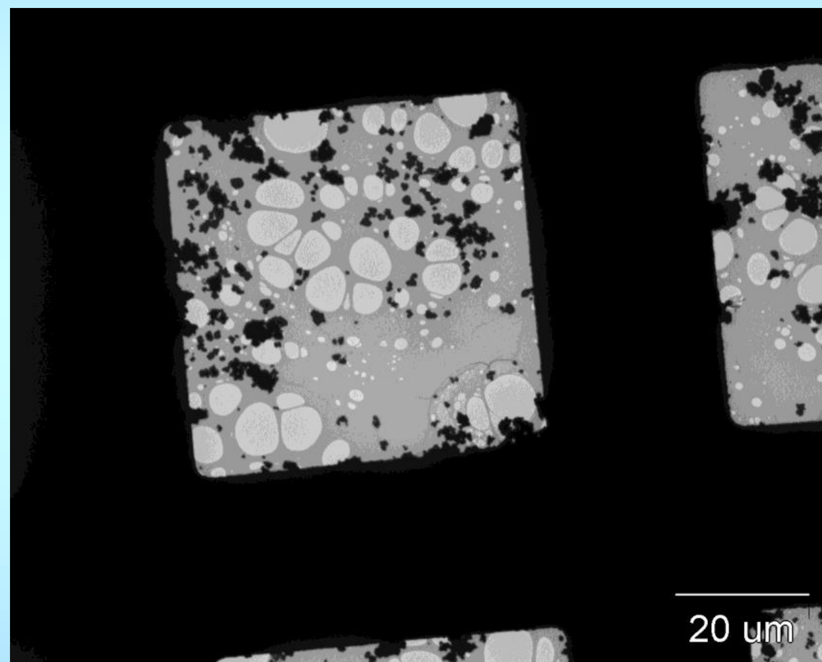
(Nano)prášky na uhlíkové blance (+Cu mřížka)





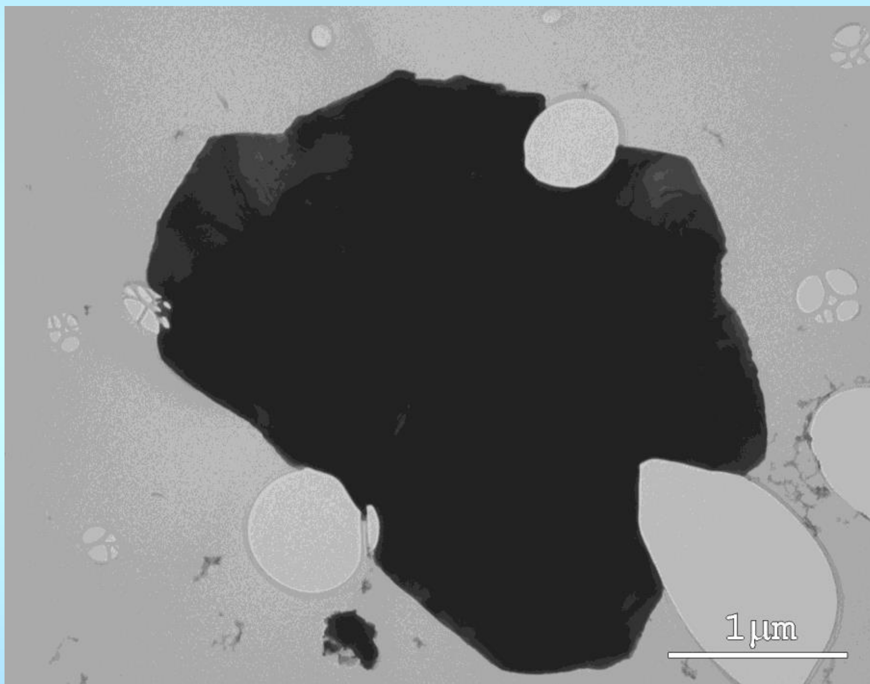
Drcený křehký vzorek na uhlíkové blance (+Cu mřížka):

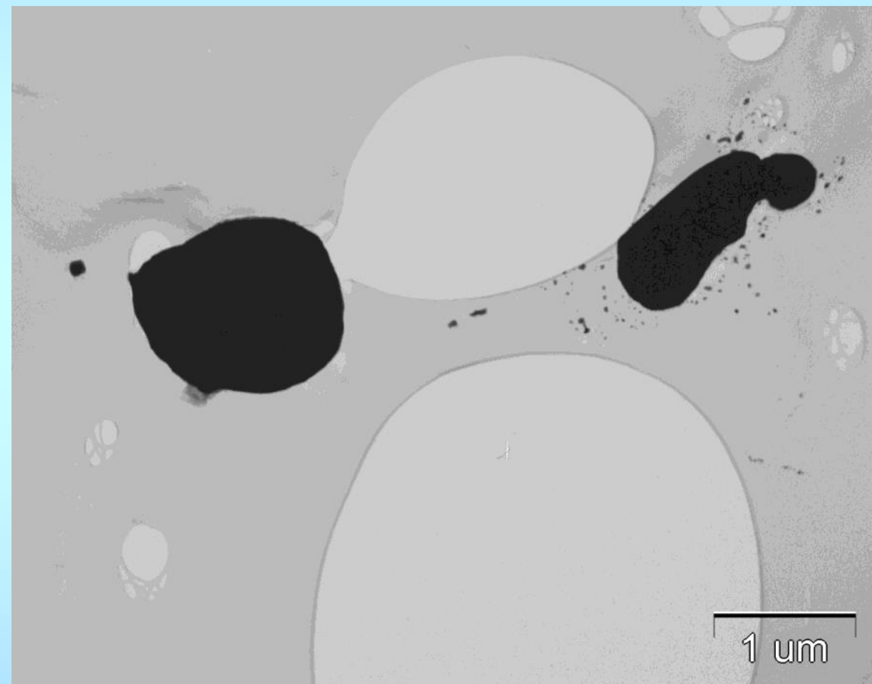




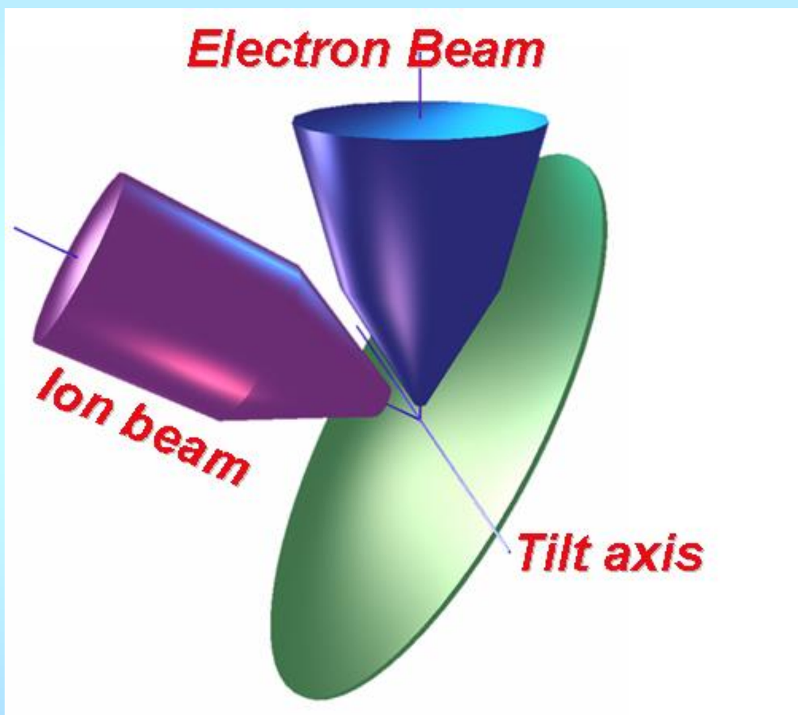
Drcený křehký vzorek na uhlíkové blance (+Cu mřížka):

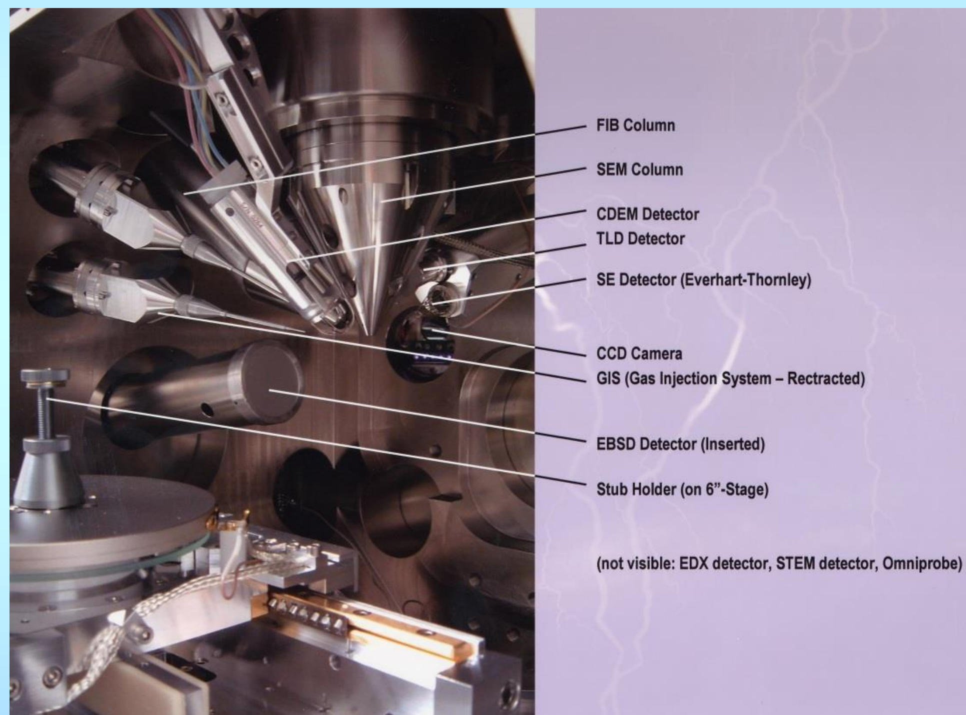
nebezpečí modifikace vzorku energetickým svazkem elektronů



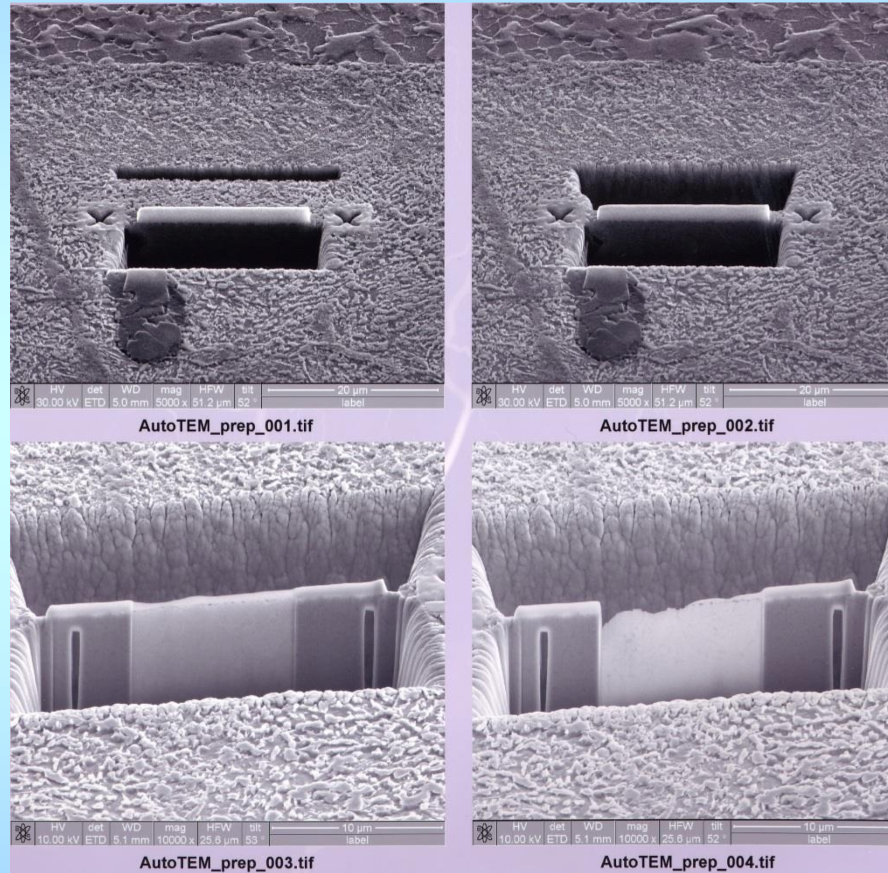


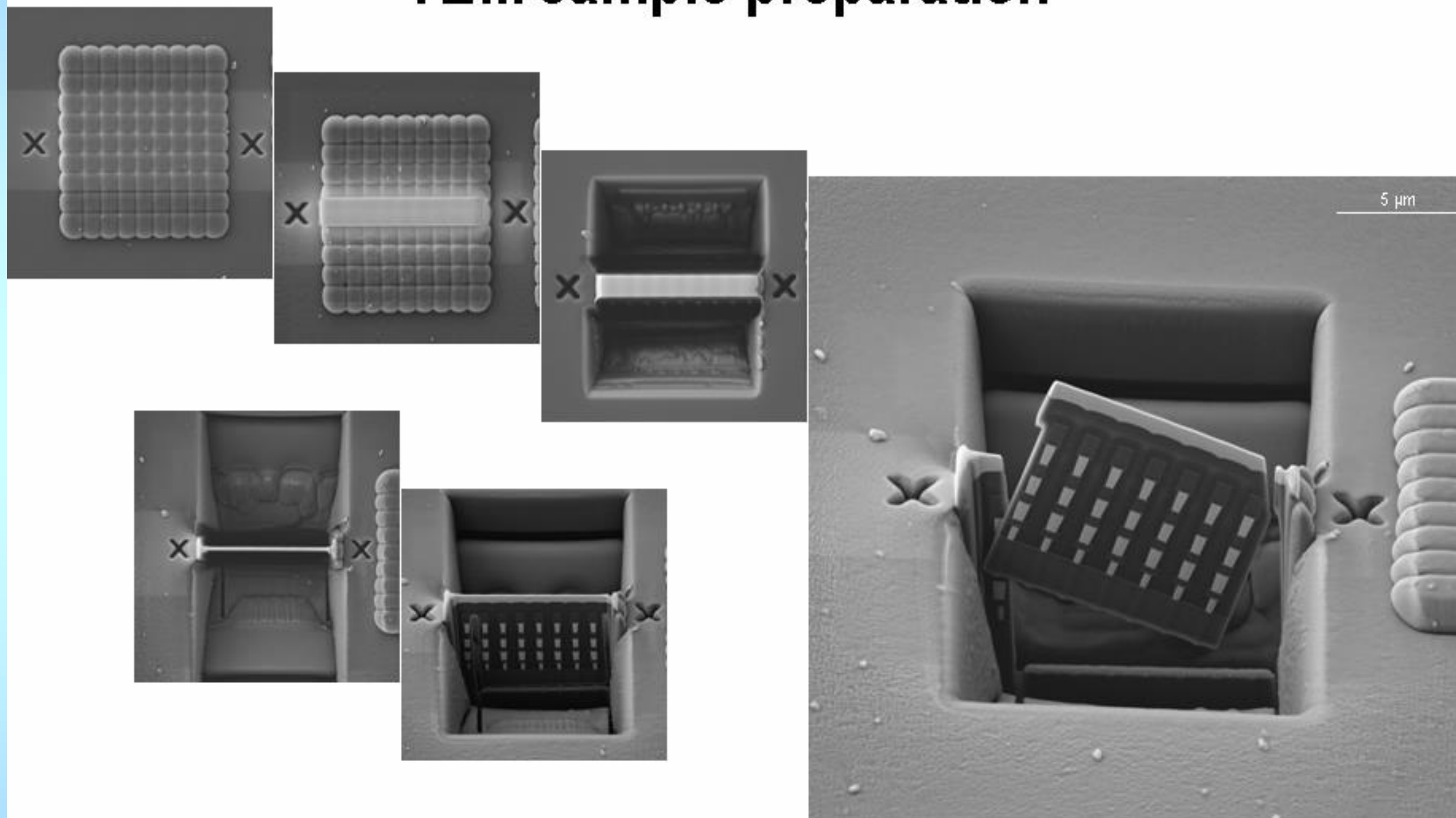
Moderní doplněk SEM: technika přípravy fólií pro TEM z míst vybraných na základě pozorování v SEM (FIB – focused ion beam)



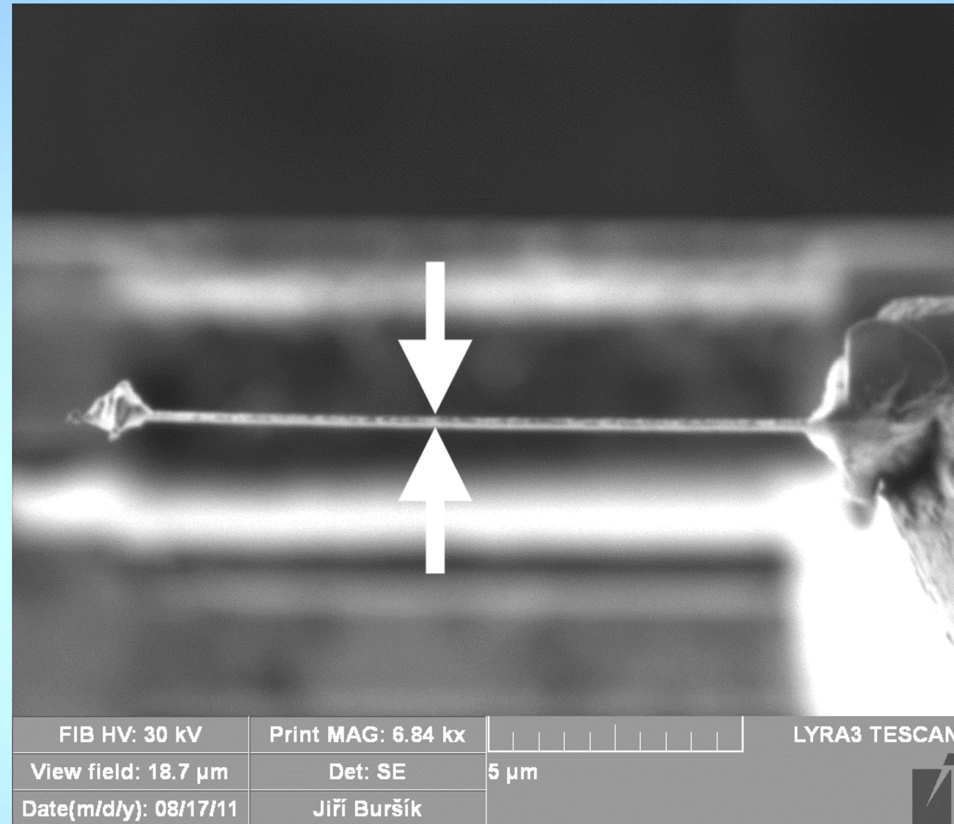


Přesný výběr oblasti vzorku pro TEM (cca 50 nm!)



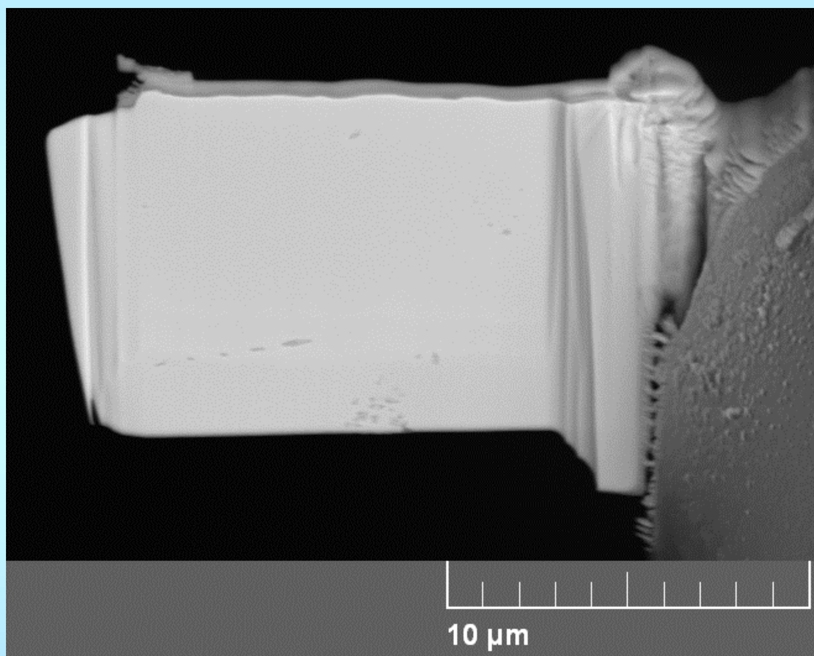

TEM sample preparation
5 µm

Příprava lamelky pro TEM pomocí FIB:

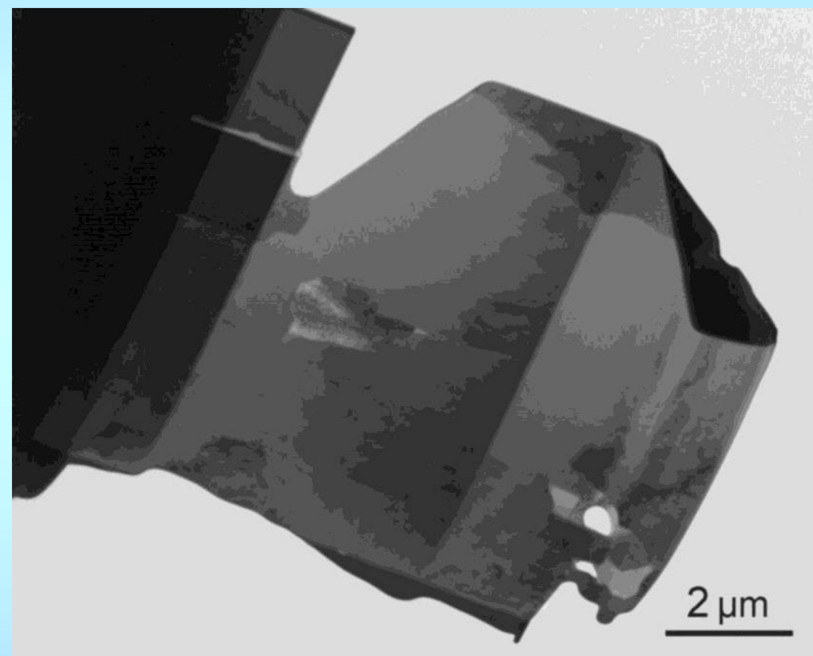


Pt ochranná vrstva 12 × 2 µm, tloušťka Pt 1÷2 µm
FIB: 30 kV, proudy 16 nA → 4 nA → 900 pA → 300 pA (diskuse artefaktů)
Dolešťování s náklonem ± 2° nebo ± 1°
Finální rozměry lamely cca 10 µm × 8 µm × 100 nm

Lamelka v SEM
před finálním ztenčením:



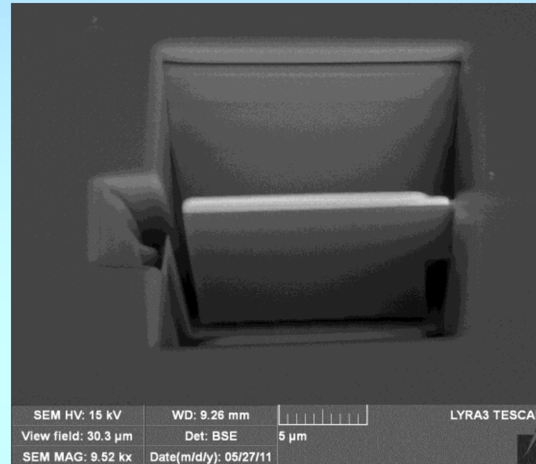
Lamelka v TEM
(přehledové zvětšení):

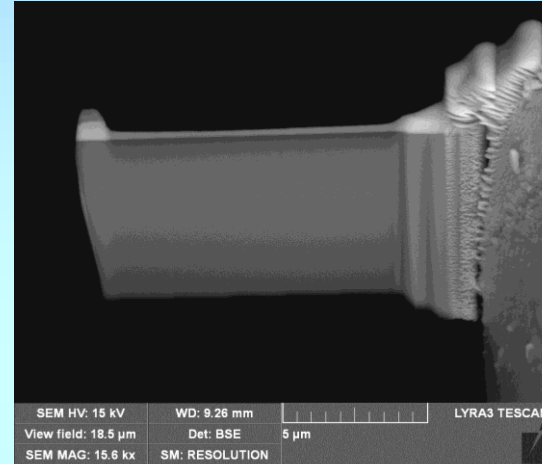


Materiál při přípravě lamelky reaguje selektivně:

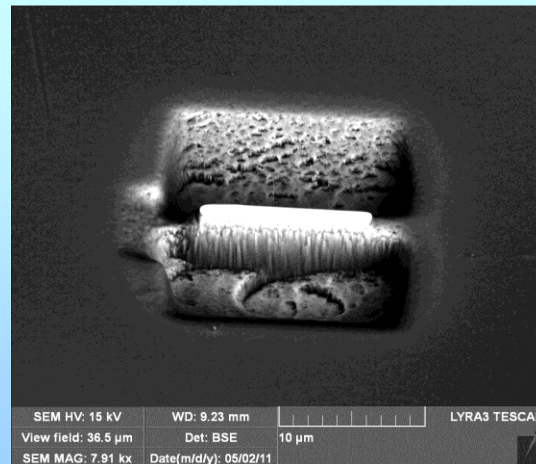
Příklad pásků Fe–Si–Nb připravených metodou melt spinning a následně žíhaných za různých podmínek

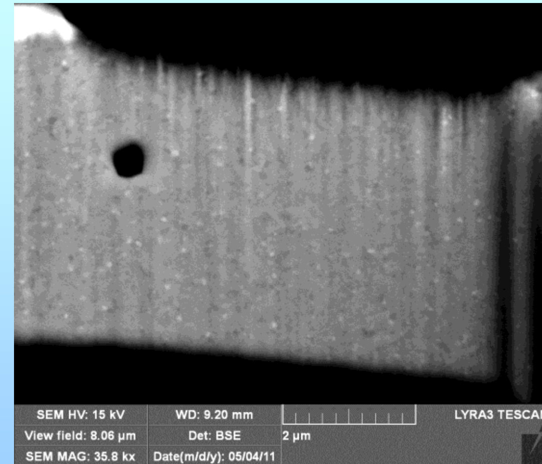
470 °C, vac.





650 °C, vac.





Další literatura: