Radiation Damage in the TEM

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Radiation damage can be useful (e-beam and UV lithography)

but the main interest of a microscopist
is to eliminate or **control** the damage.

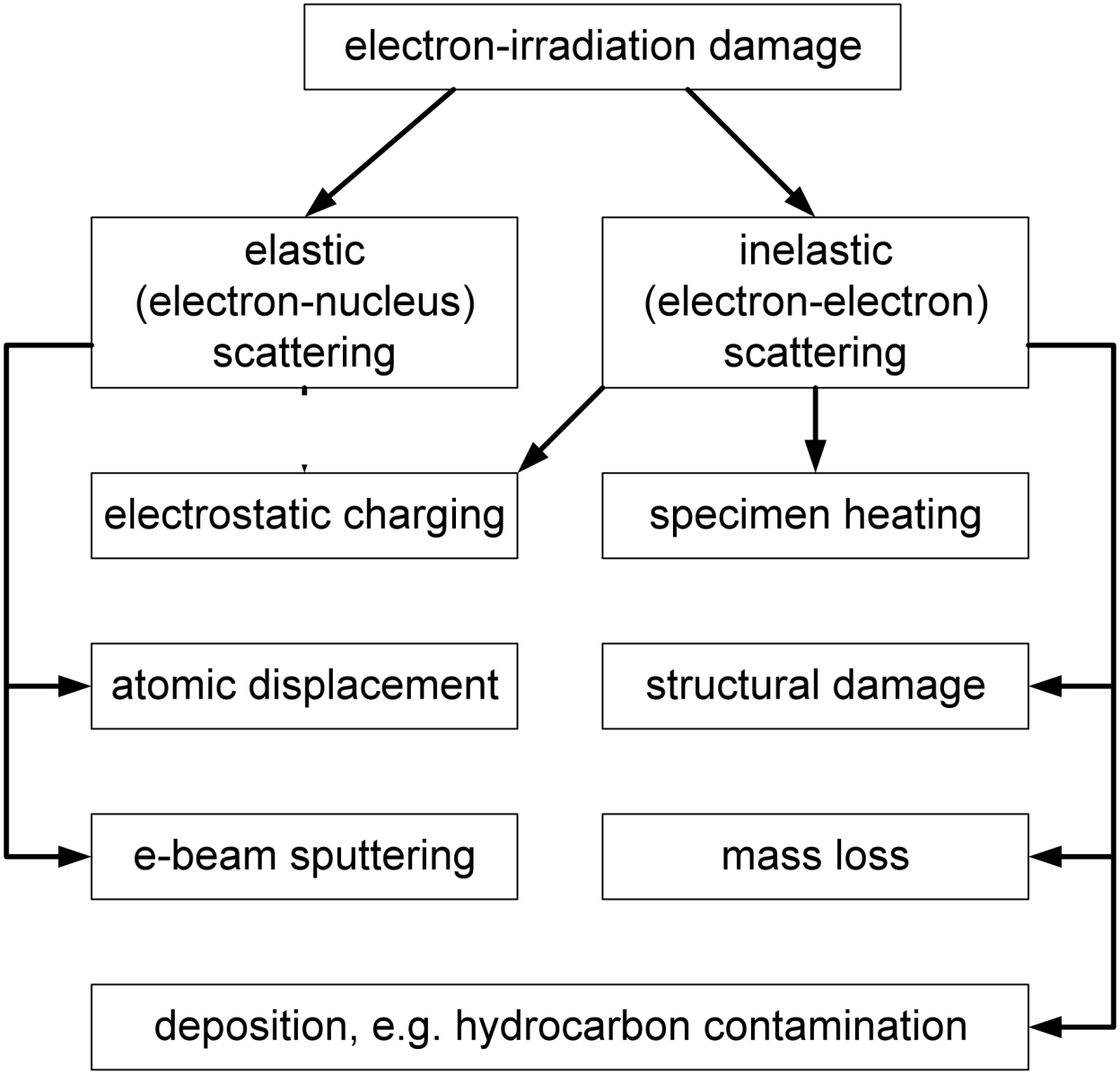
The observable kinds of damage are:

Structural damage (at the atomic level,
seen in a HREM image or electron-diffraction pattern,
or over larger length scales)

Mass loss (sample gets thinner, develops a hole etc.)

Charging effects (often seen as image distortion)

Beam-induced contamination (still with us!)



ALL effects can be important, not necessarily in same specimen

Two **mechanisms** of irradiation damage:

Knock-on displacement (due to elastic scattering)

Observable in **conductors** (metals, some semiconductors)

Disappears for $E_0 <$ threshold value

Independent of temperature (more or less)

Radiolysis or ionization damage (from inelastic scattering)

Severe in organic materials, overwhelming knock-on damage

Damage/volume ***increases*** with decreasing E_0

(**no threshold** above $E_0 = 1$ keV)

Reduced (factor 3 – 10) by cooling the specimen

Knock-on damage effects are…

Atom displacement in the bulk

Atom displacement at grain boundaries

Atom displacement *from* a surface (e-beam sputtering)

Atom displacement *along* a surface (radiation-enhanced diffusion)

Displacement of *adatoms* on top of a surface

Decreasing displacement energy E_d

leading to lower **threshold** E_0^{th} :

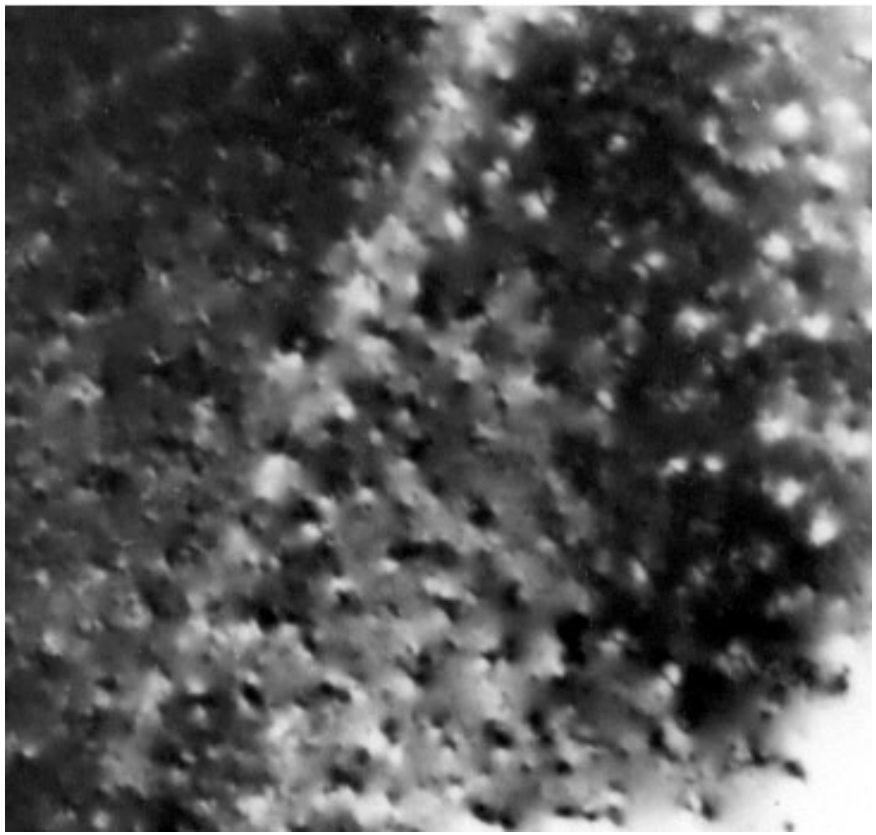
$$E_0^{th} = (511\ \text{keV})[1+AE_d/561\text{eV}]^{1/2} - 1]$$

from energy/momentum conservation, for 180° scattering

Bulk (volume) displacement → defect clusters

material	E_d(eV)	E_{th}(keV)
diamond	80	330
graphite	34	150
aluminum	17	180
copper	20	420
gold	34	1320
MgO	60	330,460

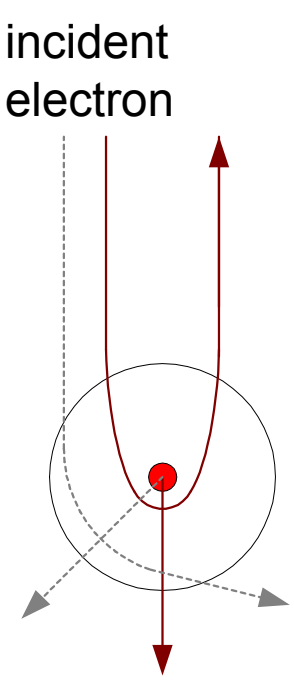
Simulation of neutron damage in nuclear fuel rods etc.



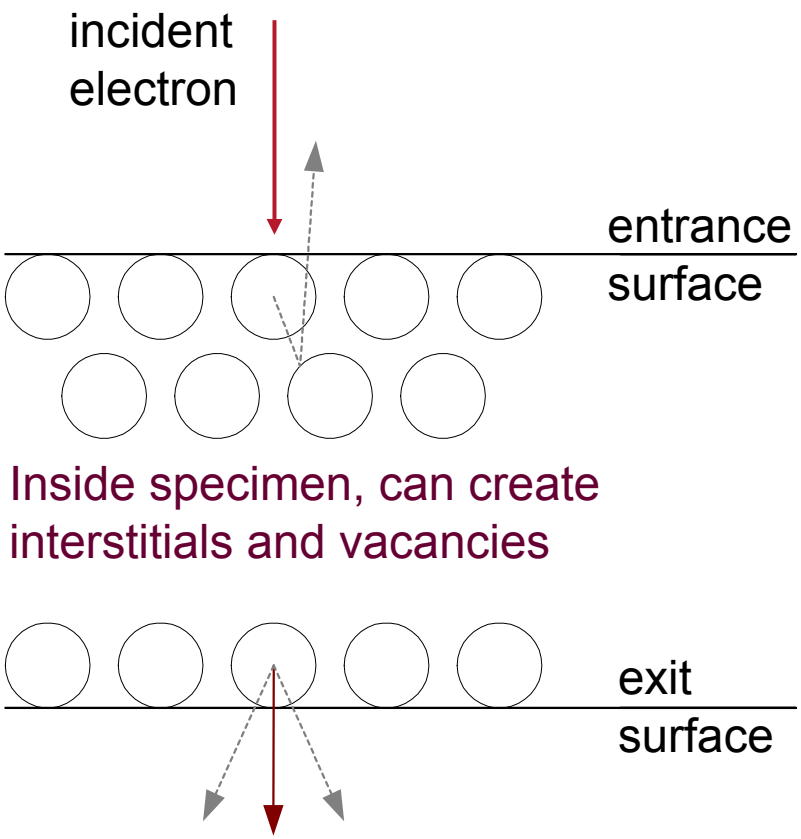
Graphite irradiated by 200keV electrons for 10 minutes at 600°C (Dose ~ 500 C/cm^2)

Egerton, Phil. Mag. 35 (1977) 1425.

Electron-induced sputtering



high-angle ‘elastic’
collisions with
a single atom

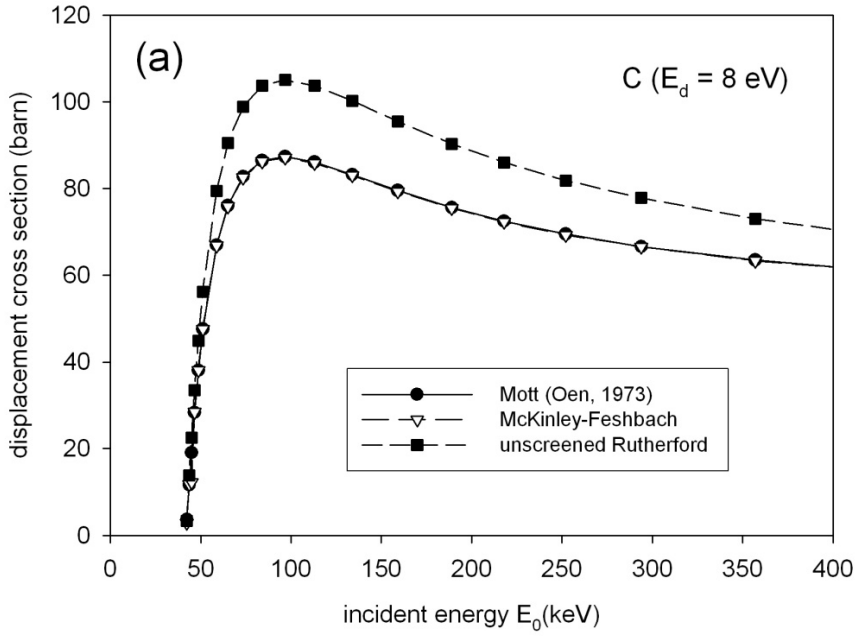


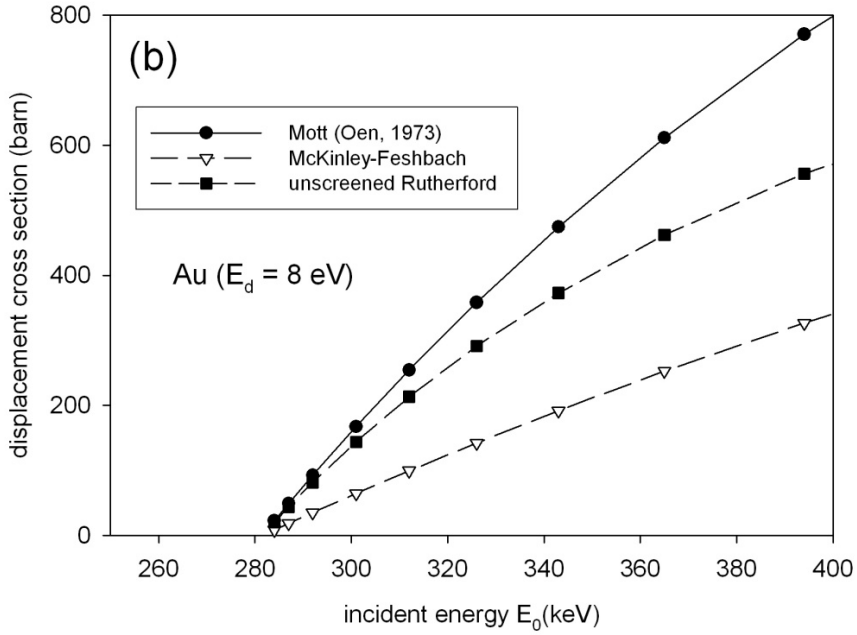
Inside specimen, can create
interstitials and vacancies

Calculated cross sections for e-sputtering

No effect below **threshold** energy.

Thinning rate
(in monolayer/s)
= σ(J/e) ~ **10**
for σ = 100 barn
and J =10^4A/cm^2
(10pA in 1nm^2)
J >10^6 A/cm^2 for
CFEG & C_s-corr.





Observed thinning rate may be less than calculated:

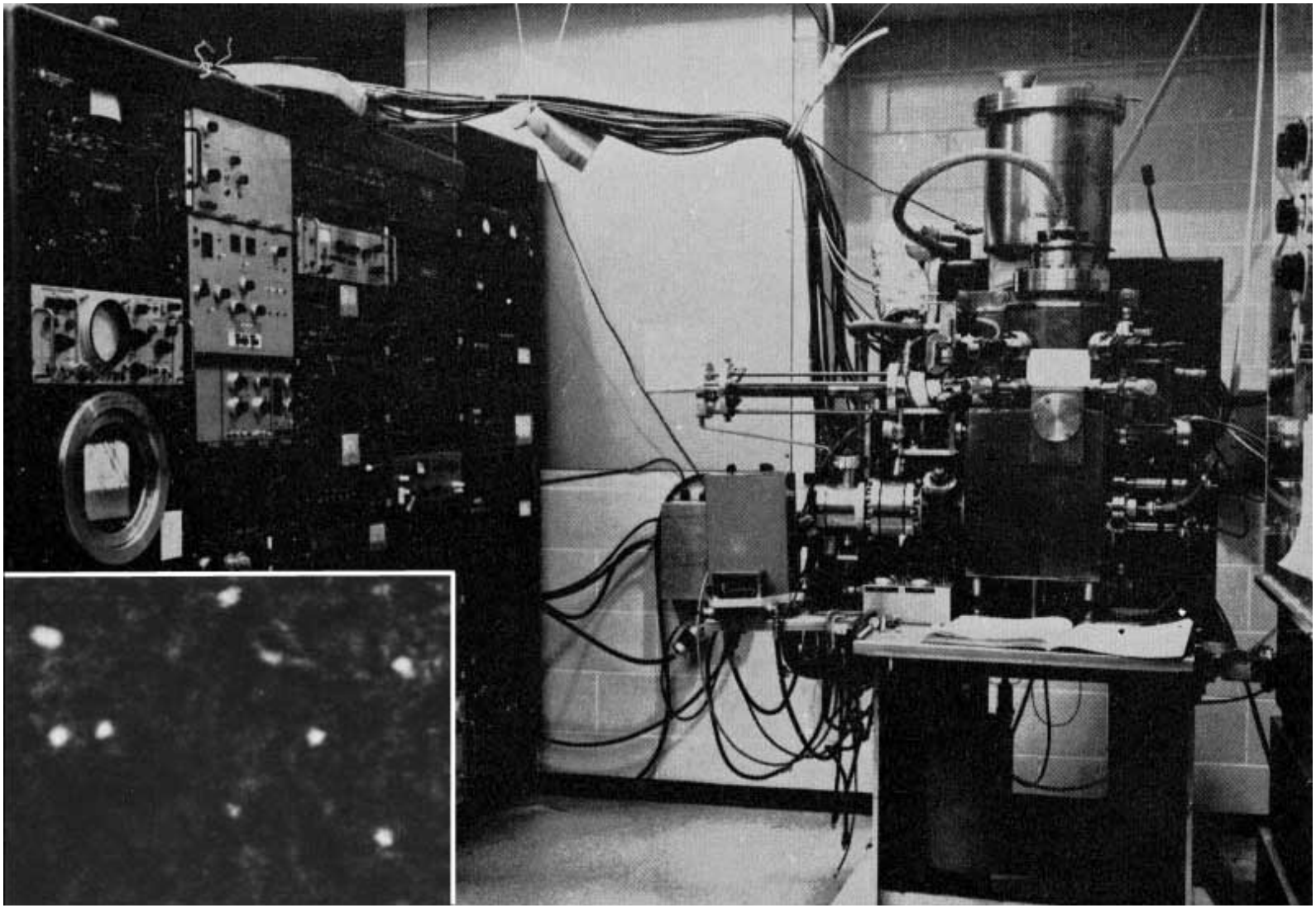
1. Surface contamination layers (protection of the surface)

2. Only part of the energy transfer used to eject atoms (reduces rate but does not change threshold)

3. Displacement energy E_d > sublimation energy E_s

   $E_d = (5/3)\ E_s$ seems a good approximation for fcc metals see Egerton *et al*. Ultramicroscopy 110(2010) 991.

CFEG-STEM (Crewe *et al*., Chicago, 1970's)



images of atoms

beam diameter ~ 0.5nm

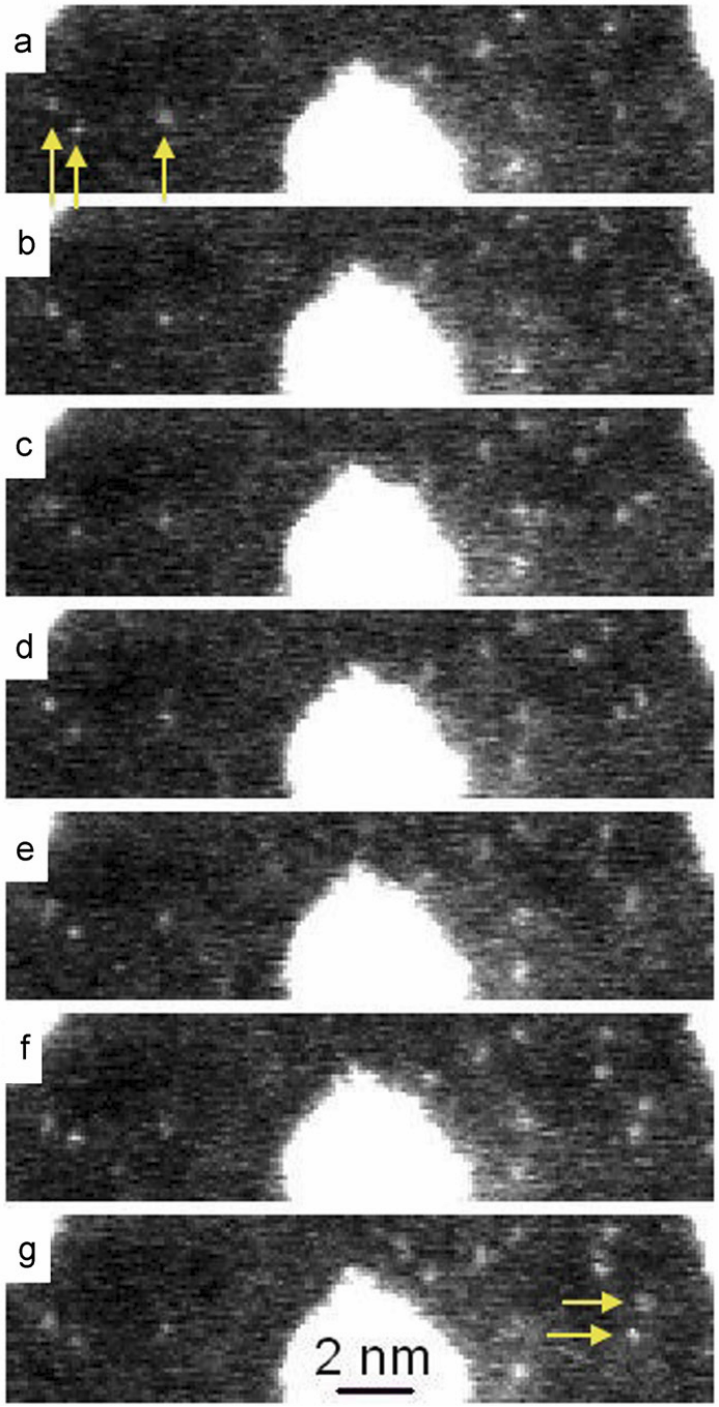
Motion of Au atoms seen in HAADF images (0.17s apart)
E_0 = 200 keV, 1.2nA STEM probe

Scanning transmission electron microscopy: Albert Crewe's vision and beyond

Ondrej L. Krivanek, Matthew F. Chisholm, Matthew F. Murfitt, Niklas Dellby
Ultramicroscopy (2012)

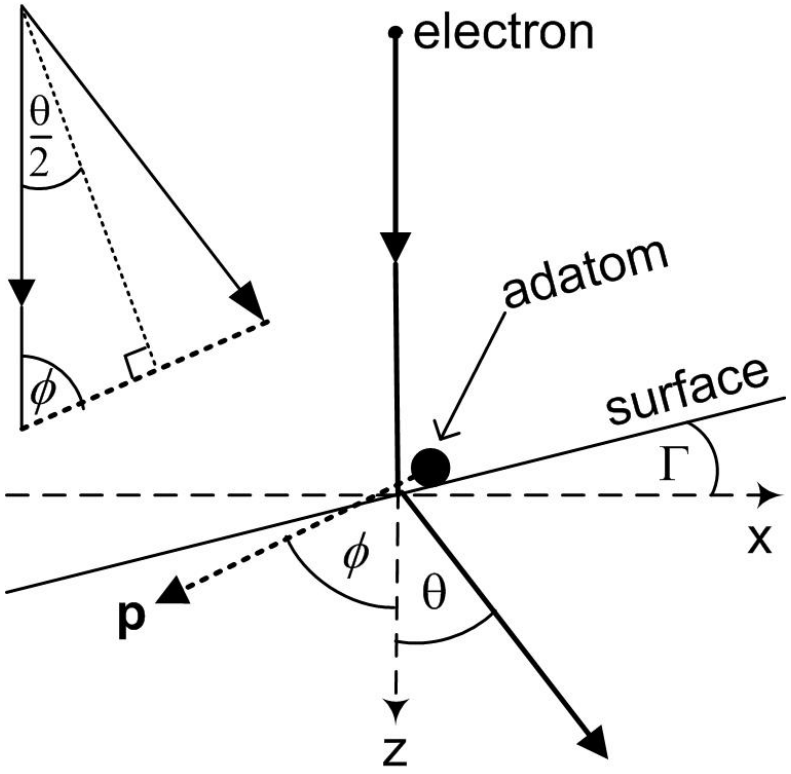
Vertical atoms mark stationary atoms, horizontal arrows mark mobile atoms.

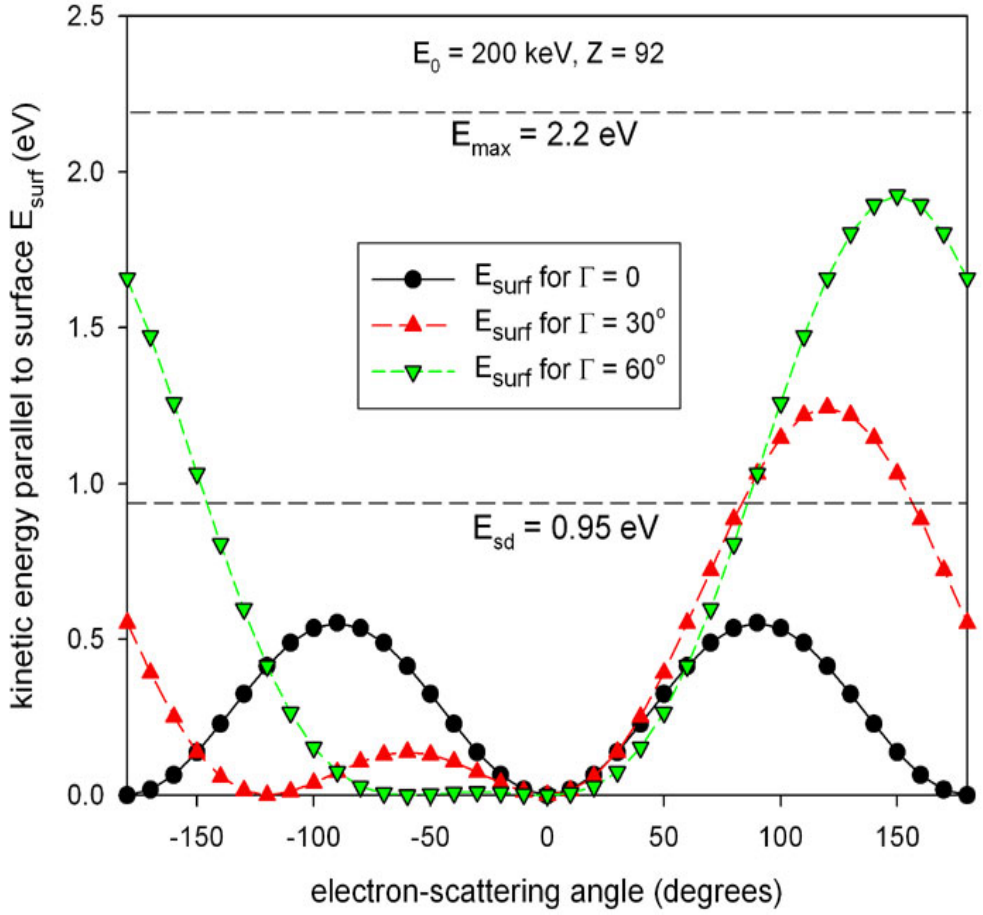
Support = amorphous carbon.



Energy transfer to **surface** atoms or adatoms on a substrate

$E_{surf} = E_{max} \sin^2(\theta/2) \cos^2(\theta/2 - \Gamma)$





Normal: symmetric for ± angles and KE is maximum for θ = ± 90°

Oblique: higher energy transfer possible → lower threshold

For E_0 = 200 keV (top)

and E_0 = 60 keV (bottom),

atom displacement rate
as a function of surface-diffusion energy E_{sd}(eV)

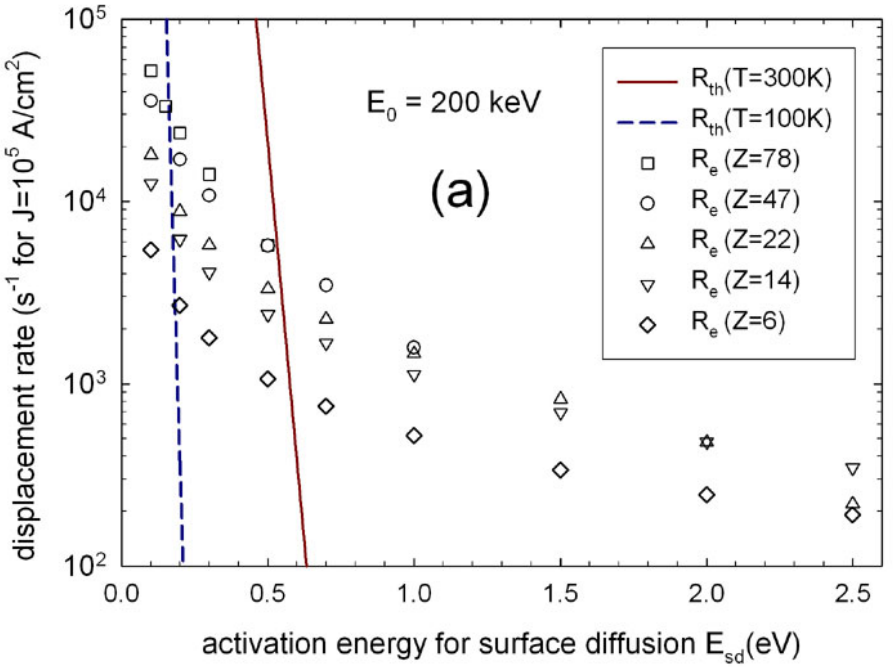
for Pt,Ag,Ti,Si & C atoms (hollow data points)

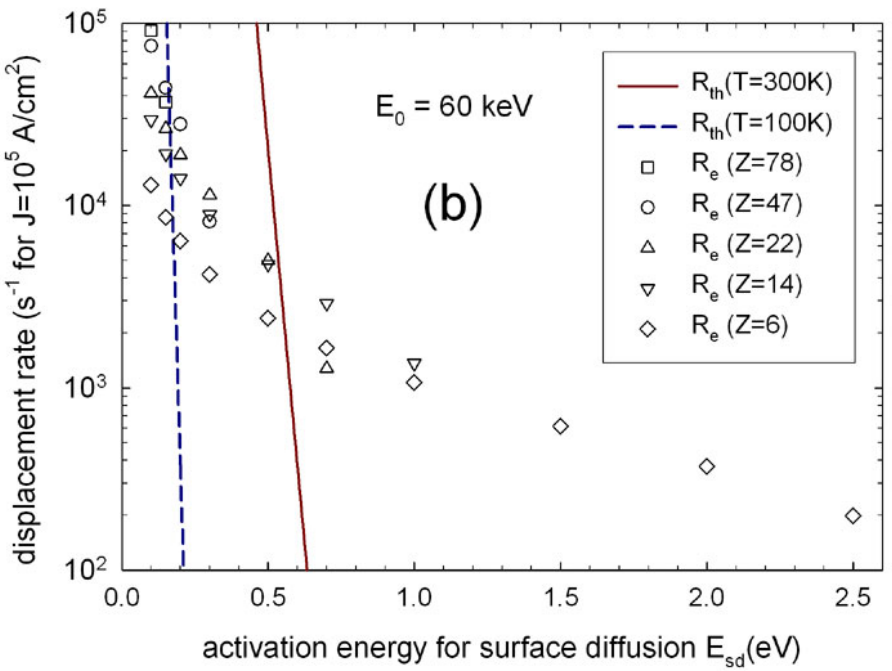
compared to thermal rate at 300 K (brown line) and 100 K (blue line).

Thermal predominates for

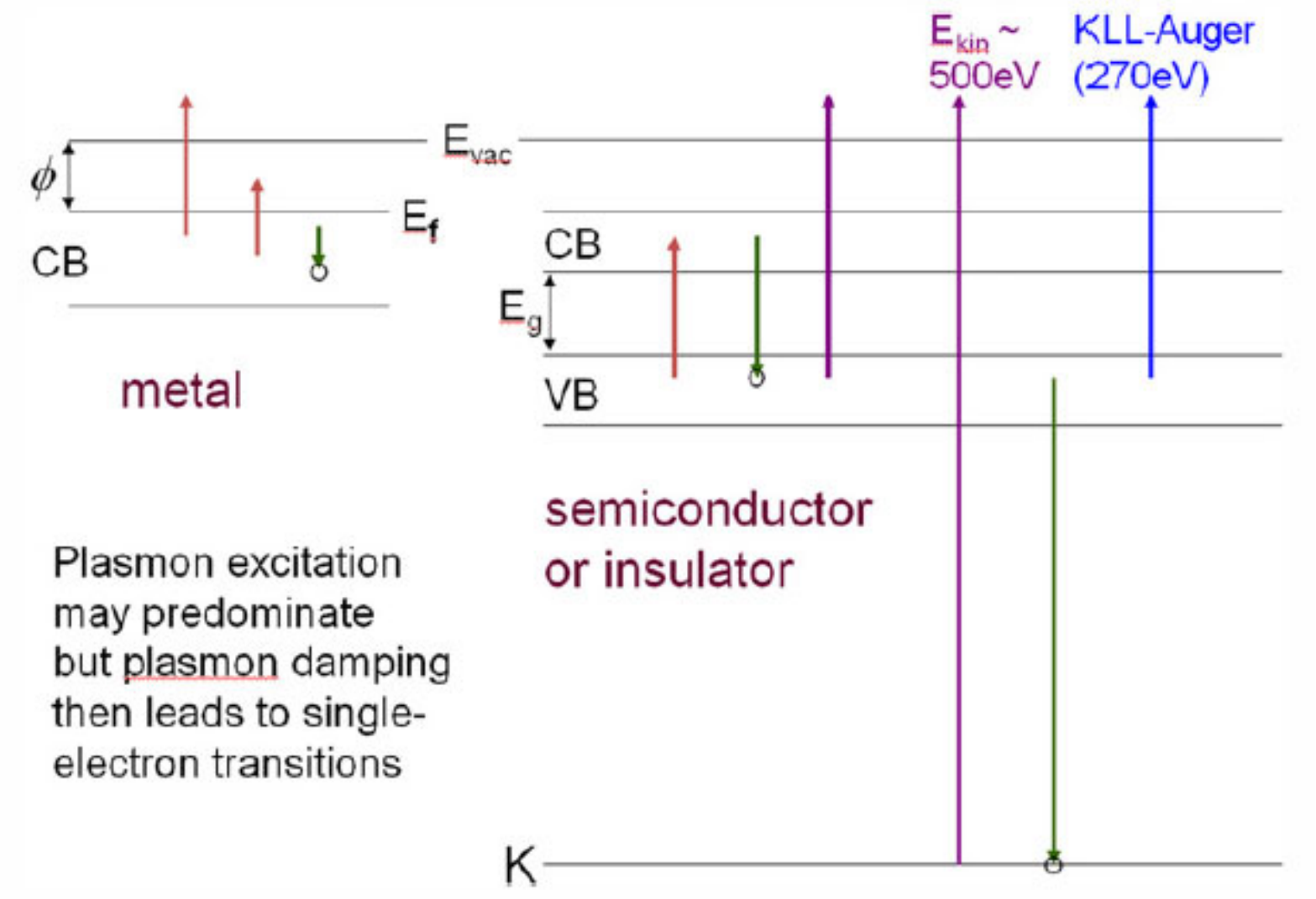
E_{sd} < 0.5 eV (T=300 K) or
E_{sd} < 0.2 eV (T=100 K)

for typical J and E_0(keV)



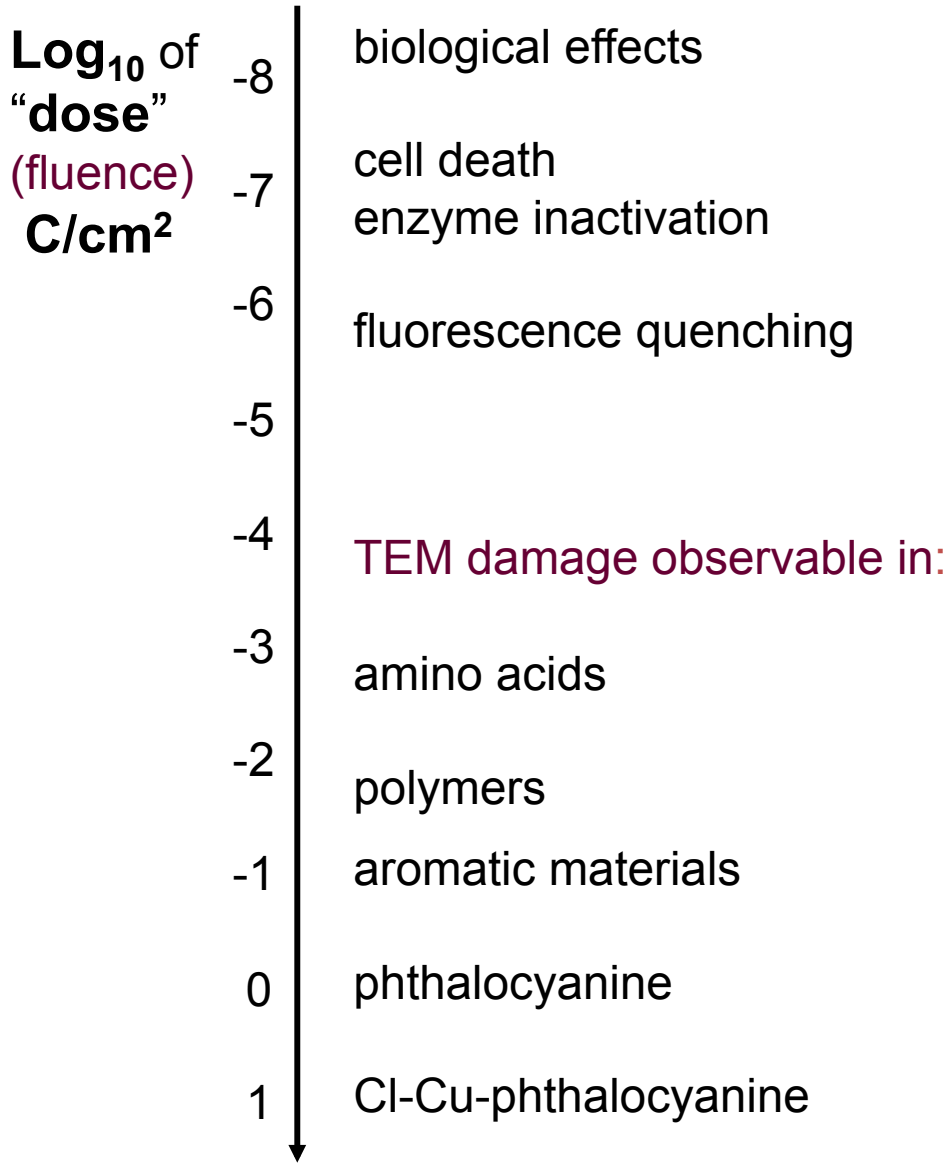


Radiolysis (ionization damage)



Range of radiolysis

From Reimer and Kohl (2008), p.468

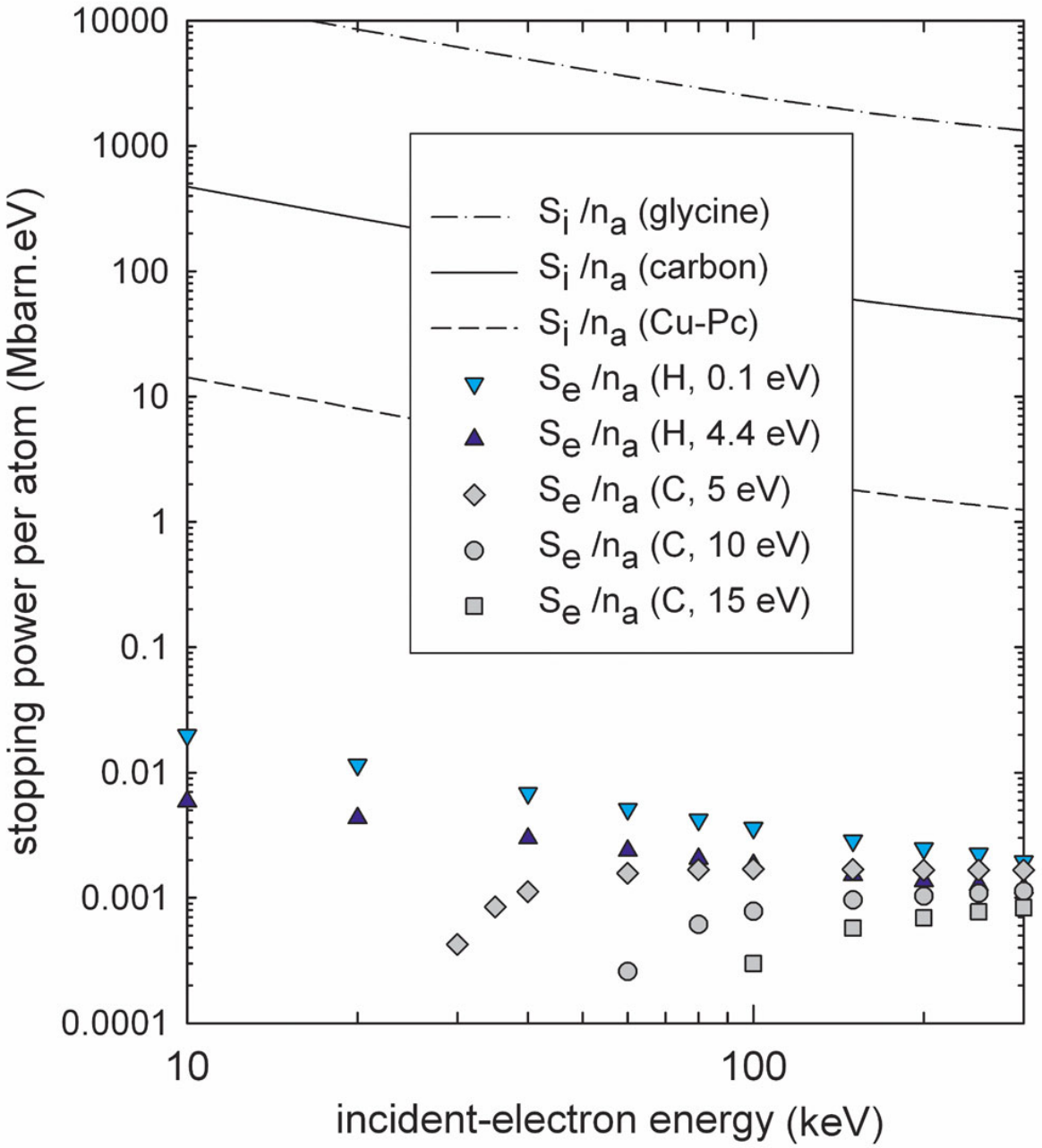


In organics, radiolysis is *much* more efficient than knock-on displacement

Stopping power

of organic materials due to electronic excitation (inelastic scattering) and causing radiolysis (ionization damage)

Stopping power due to knock-on displacement of C and H atoms



see Microscopy Research & Technique (2012)

Energy deposited per inelastic event

damage source	⟨E⟩	P	P. ⟨E⟩
8keV x-ray			
photo-ionization	5eV	1	5
photoelectrons/SE	8000	1	8000
Auger electron	280	0.02	5
400eV x-ray			
photo-ionization	5eV	1	5
photoelectron/SE	4000	0.5	200
Auger electron	280	0.5	140
100keV electron			
primary ionization	5eV	1	5
slow secondaries	25	0.92	23
fast secondaries	150	0.07	11
KLL Auger electron	980	0.013	13

←Damage

X-ray damage due mainly to photoelectrons

Electron damage is mainly due to **secondary electrons**

Measurement of radiation damage

Diffraction pattern (outside spots or rings fade first)
Low-loss or core-loss fine structure
These measure structural change (local atomic motion)

Mass loss (central diffracted beam, hole drilling etc.)
Loss of selected elements (from EELS, EDXS)
These may involve longer-range atomic motion (diffusion)

Critical or characteristic dose (D_c) is the dose at which some feature (diffraction spot, energy-loss peak) decreases in intensity by a factor of e = 2.718
or becomes invisible.

Radiation units

X-ray community and radiation chemists measure radiation dose as deposited energy per unit mass, in units of Gray (= J/kg) or MegaGray (MGy)

Electron microscopists use "dose" = fluence = (beam current density)(time) = Coulomb/cm^2 or particles/area : e/nm^2 or e/Angstrom^2

$$\text{Grays} = \text{C/cm}^2 \;\; X \;\; [E_{av}(\text{eV}) / \text{IMFP(nm)}] \; [10^4 / \rho(\text{g/cm}^3)]$$

For 100keV electrons and typical organic material, IMFP ~ 100 nm, E_{av} ~ 35 eV per inelastic collision and ρ ~ 1.4 g/cm^3, giving 1 C/cm^2 = 2500 MGy
or 1 electron/Angstrom^2 = 4 MGy

Critical or characteristic dose D_c:

Amino acid (l-valine): 0.002 C/cm^2 = 5 MGy
Chlorinated Cu-phalocyanine: 30 C/cm^2 = 75,000 MGy

Control of Radiation Damage

Minimize the dose (low-dose techniques)

Maximize the signal (phase plate, TEM mode etc.)

Cool the specimen (liquid nitrogen or helium)

Encapsulate the specimen (coating, nanotubes)

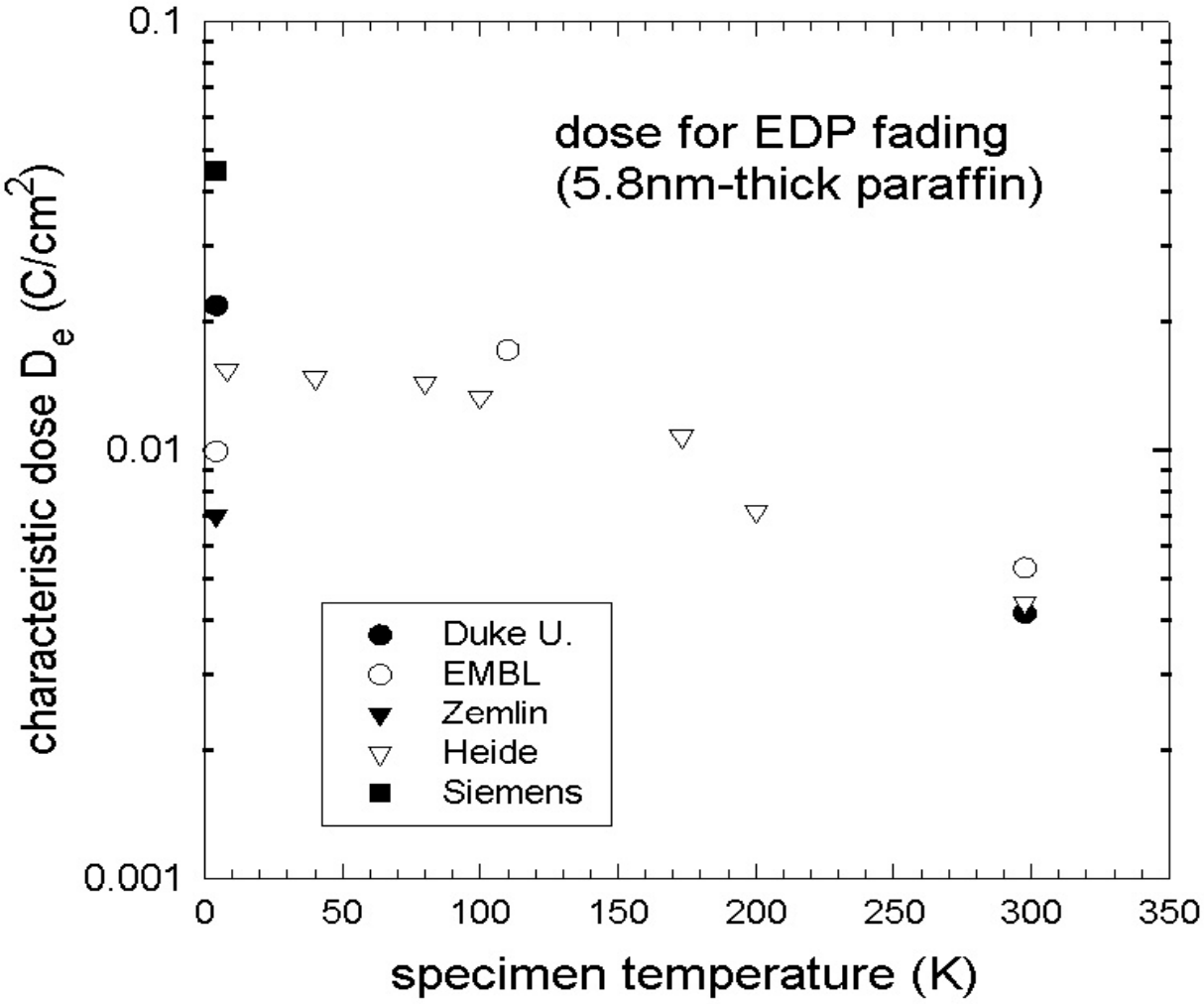
Adjust incident intensity (if dose-rate effect)

Reduce the incident energy (if there's a threshold)

Reduce the beam diameter (mechanical effects)

Use aloof mode or 'leapfrog' scan (vibEELS)

Cooling to 100 K reduces ***structural damage*** by factor ~ 3

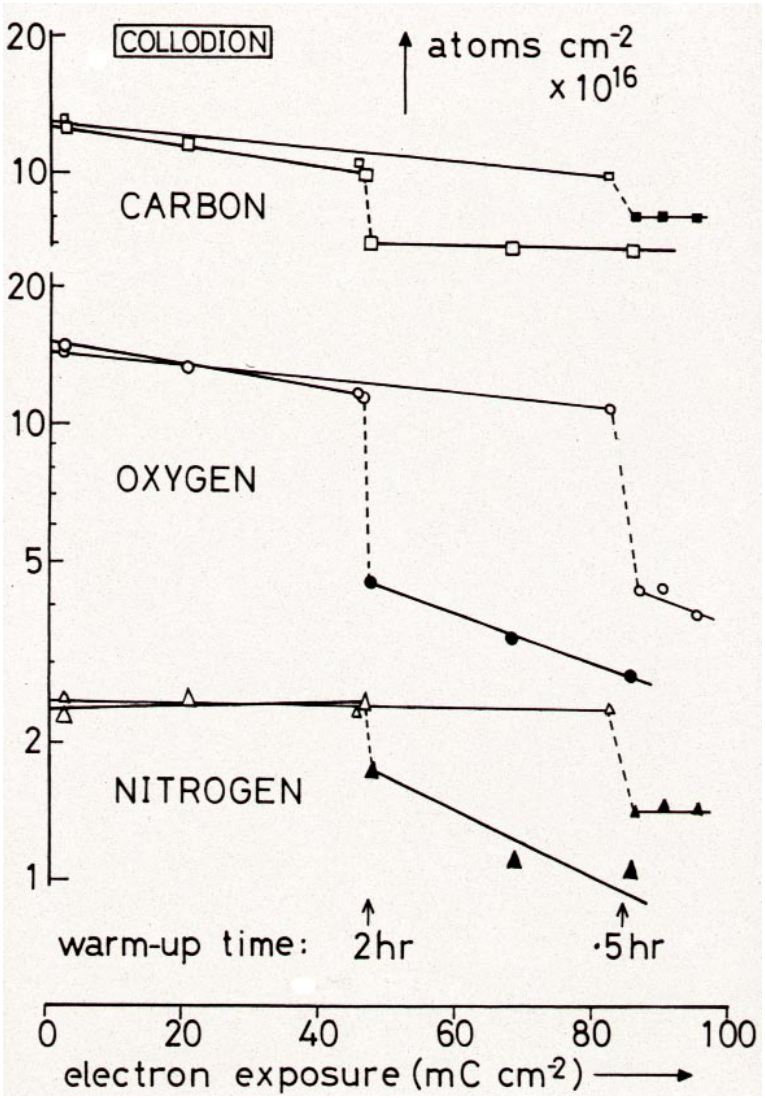


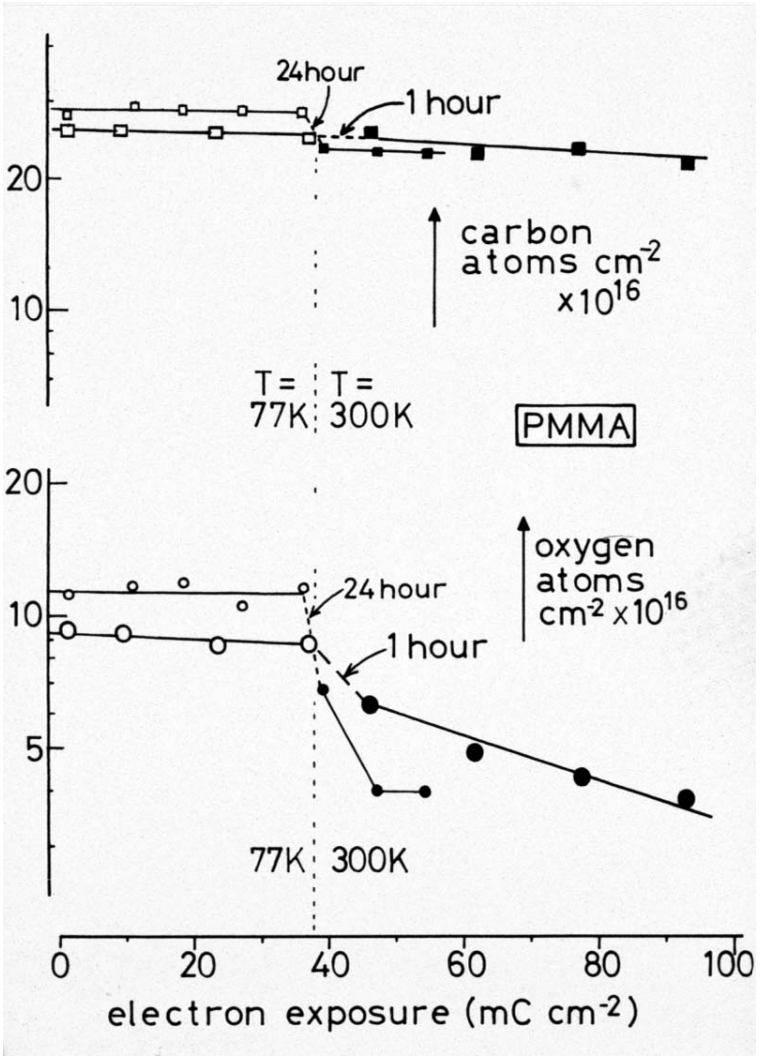
International Experimental Study Group, 1986.
J. Microscopy **141**, 385-391.

EELS **mass-loss** measurements at 300 K and 100 K

specimen	element removed	(100K/300K) D_c ratio
nitrocellulose	N	120
nitrocellulose	O	90
nitrocellulose	C	5
poly(viny formal)	O	30
poly(methy methacrylate)	O	8
poly(methy methacrylate	C	1.6
polycarbonate	O	> 10
carrageenan	O	20
carrageenan	C	12
chlorinated CuPhalocyanine	Cl	3

Mass loss **does occur** when the specimen warms to room temperature (dashed lines below)





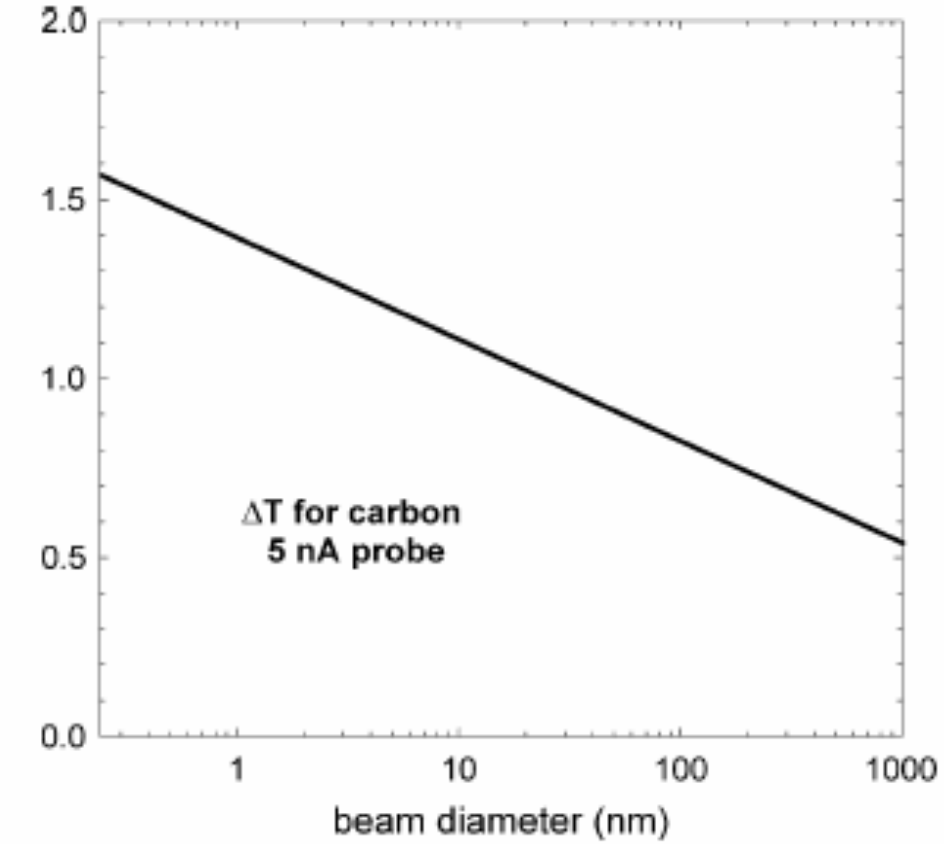
Cooling the specimen also offsets heating effect of the beam *but* temperature rise is small for a small probe (small current)

power input =
$I(\text{Amp})E_m(\text{eV})[1-\exp(t/\lambda_i)]$

$= 4\pi\kappa t(\Delta T)[0.58+2\ln(2R_0/d)]^{-1}$

$+ \pi d^2\varepsilon\sigma(T^4-T_0^4)/2$ ← radiation

1. Radiation term usually negligible
2. ΔT is then independent of specimen thickness
3. ΔT small unless I > 100 nA, for most beam diameters



With radial conduction,
ΔT increases only slowly with decrease in beam diameter d

Carbon or metal coating

reduces the characteristic dose for mass loss
or loss of crystallinity by a factor between 1.5 and 6

Method	Analysed material	t_a (nm)	Coating material	t_c (nm)	Protection factor	Ref.
Diffraction	Coronene	50	Al	7	3	Salih & Cosslett (1974)
			Au	7	5	
EELS:						
O loss	Collodion	15	C	15	1.7	Egerton (1980)
Diffraction	Perylene	7	C		3.0	Fryer & Holland (1984)
(complete	Pc	10	C		2.7	
extinction	$Cl_{16}CuPc$	10	C		6.1	
of spots)	$Br_{16}CuPc$	11	C		6.0	
EELS	$Cl_{16}CuPc$	5	C	5	~ 4	Egerton et al. (1987)
(halogen	LiF	8	C	5	1.5	
loss)	CaF_2	11	C	12	5.7	

Graphene coating

The pristine atomic structure of MoS_2 monolayer protected from electron radiation damage by graphene.

Gerardo Algara-Siller, Simon Kurasch, Mona Sedighi,
Ossi Lehtinen and Ute Kaiser, Ulm University, Germany

Sample	ΔN	N	ϕ (e/nm^2)	σ (barn)
MoS_2	116	3176	8.2×10^7	4.5(4)
G/MoS_2	43	2894	9.7×10^7	1.5(2)
MoS_2/G	177	5294	7.0×10^8	0.48(4)
$G/MoS_2/G$	5	3090	2.14×10^9	0.008(3)

Atoms lost dose sensitivity

Mechanisms for coating effect:

1. Conductive coating prevents charging

2. Conductive coating supplies electrons → fast recombination

3. Damage is nucleated at a surface or interface

4. Coating acts as a diffusion barrier for “volatile species”

Carbon nanotubes and C_{60} peapods have been used to encapsulate small molecules or atomic clusters, giving protection due to the ***cage effect*** (steric hindrance).

Damage less at low current density ?

Advantage: less beam heating (small for small probes)

→ less chance of **thermal** decomposition and characteristic dose not reduced by heating

Disadvantage: longer recording time, specimen drift

But does characteristic dose depend on *dose rate*?

Organics are very beam-sensitive, so dose rate is *usually* low and there is negligible dose-rate effect .

Inorganics: evidence of a current-density **threshold** for hole drilling in **oxides** – example of a **dose-rate effect**.

Time dependence of radiation damage

Primary process:

absorption (x-rays) or inelastic scattering (electrons) < 1 fs

→ core- or valence-electron excitation (single-electron or plasmon)

→ bond breakage (may not be permanent, damage not 100% efficient)

→ creation of photelectrons or secondary electrons, Auger electrons

Secondary processes:

additional damage created by secondary electrons (~80% in PMMA)
or photoelectrons (predominant damage process for hard x-rays)

motion of atomic nuclei, leading to structural damage > 50 fs
(thermal motion may contribute → temperature dependence of damage)

Tertiary processes include: ns, ms, s, days...

Loss of crystalline structure

Diffusion from or into the irradiated area (composition change)

Escape of material from the specimen (mass loss)

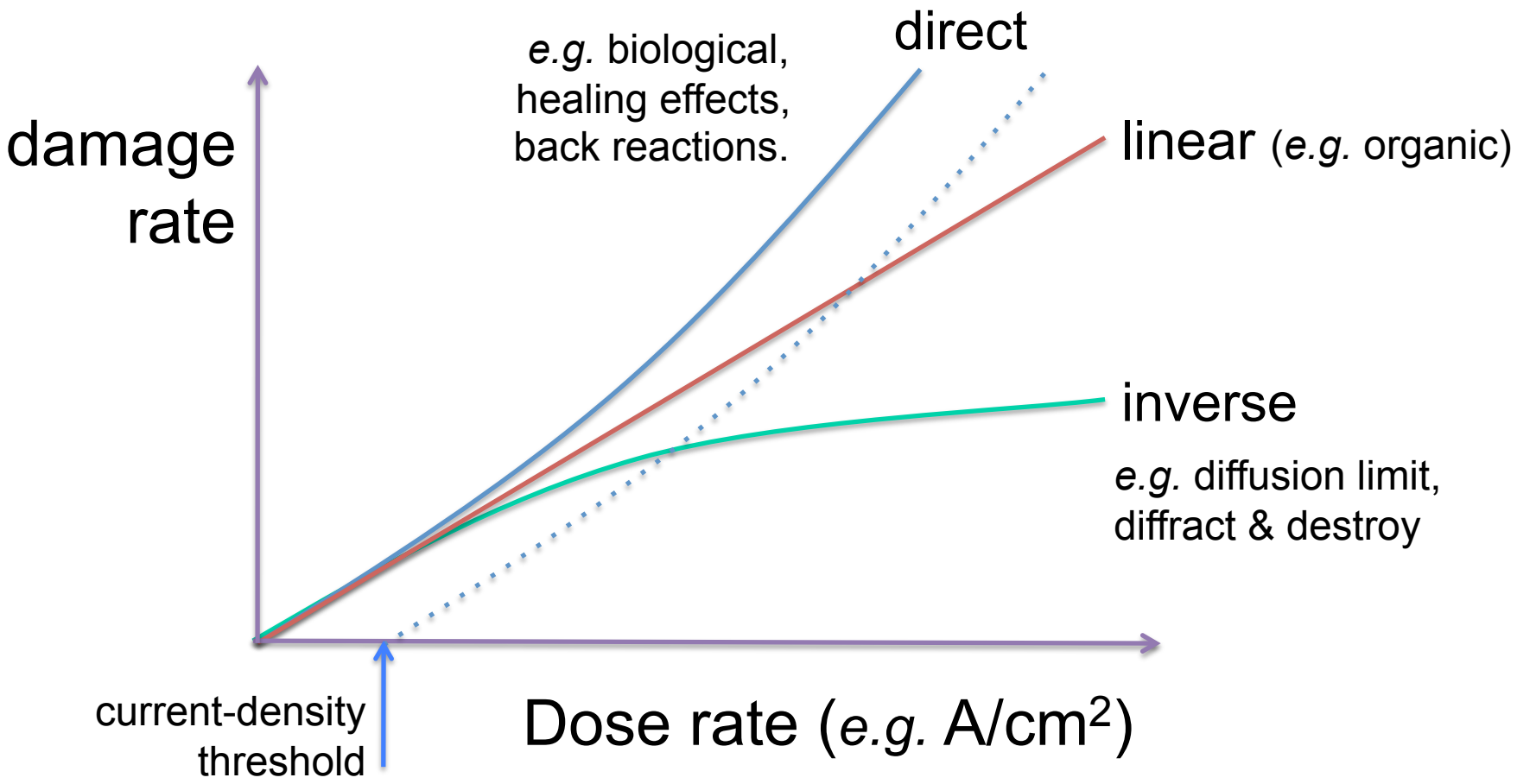
Dielectric breakdown due to charge buildup

Disruption of biological processes (e.g. cell death)

Slower processes involve a time delay

→ dose-rate dependence of damage

damage rate = dose rate x sensitivity



Examples of (direct and inverse) dose-rate effects

Sub-ps x-ray pulses allow diffract & destroy (Chapman et al., 2011) inverse
Difficult with electrons: www.ascimaging.com/content/1/1/5

Diffusion limits mass loss or precipitatio: expect an inverse effect
Diffusion allows recovery (Jiang & Spence, 2012) direct, with threshold

Damage causes mechanical motion (Downing, 1987) direct
Beam heating in polymer (Beamson; Egerton & Rauf, 1999) direct

Electrostatic charging causes dielectric breakdown or Coulomb explosion
→hole formation in oxides (Humphreys *et al*.) direct, threshold

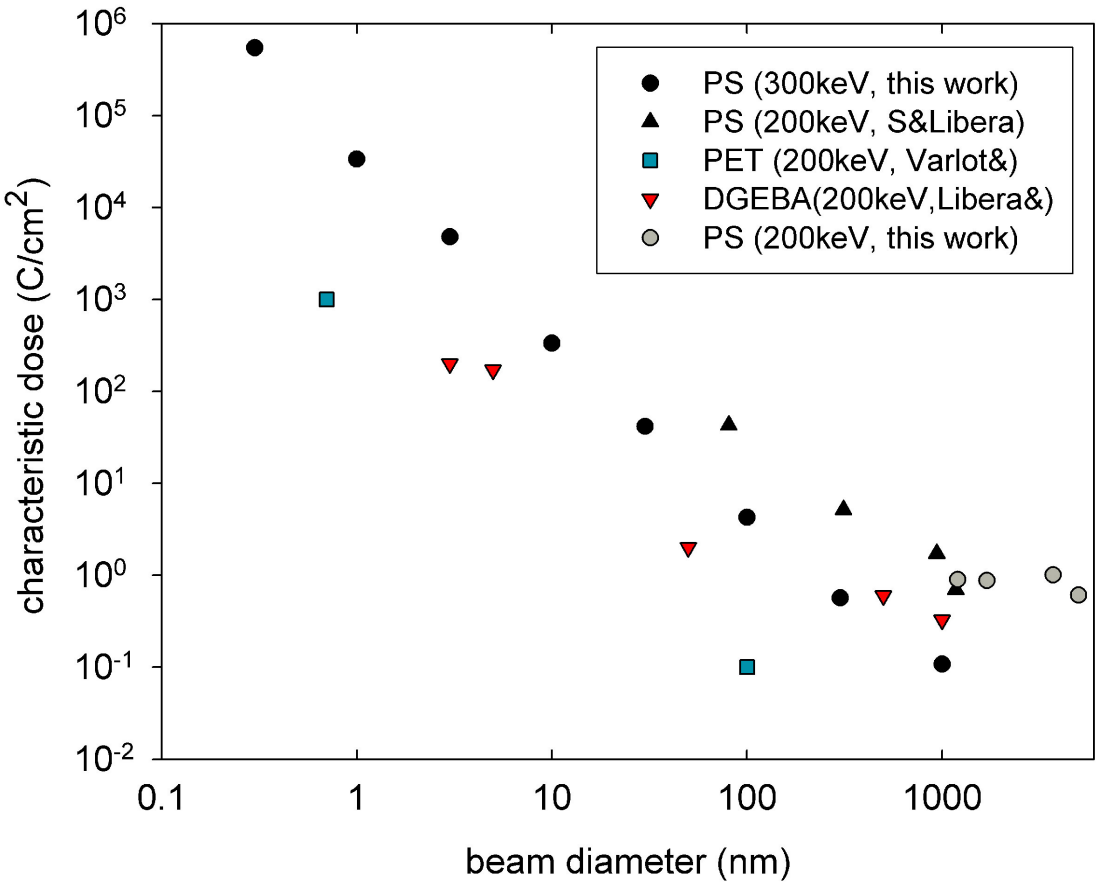
Implications:

STEM, STXM give *high dose rate* during *short dwell time*.
Scanning is **beneficial** if the dose-rate effect is inverse.
Fixed-beam microscopy would give more damage for the same information.

Diffusion effects continue after irradiation: better to scan once only
[wet chromosomes, Williams et al. J. Microsc. 170 (1993) 155]

Less damage for small-diameter electron-beam ?

1. Overall warping of specimen affects image blurr, spectroscopy.
2. Some damage may be collateral (outside the probe),
   reviewed by Egerton, Lazar & Libera, *Micron* **43** (2012) 2-7.



Less damage at low incident-electron energy ?

Lower KE *sounds* less damaging, but means **more** inelastic scattering: energy deposition is higher (~$1/v^2$)

However, inelastic signal increases in same proportion (~$1/v^2$)
Elastic signal also increases, approximately as much (~$1/v^2$).

Conclusion: information/damage ratio is independent of E_0.

But this argument is too simplistic…

1. Signal ~ t/v^2, larger E_0 allows larger thickness, higher signal.
2. What really matters is SNR *for given amount of damage*.

For BF-TEM imaging, this SNR $\propto$ v for small thickness.

For PC-TEM, ADF-STEM, EELS: SNR is independent of incident-electron speed v , but factor #1 still applies.

Reminder: **knock-on damage** always has a threshold incident energy, so a sufficiently low kV can be beneficial.

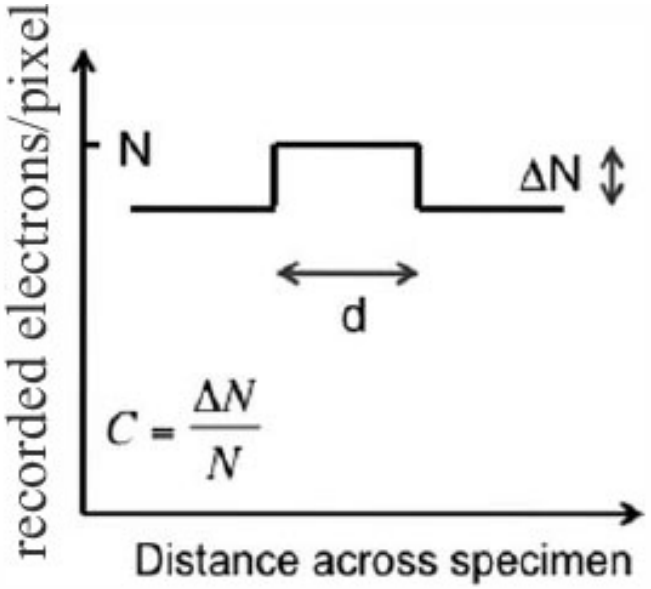
Dose-limited ***resolution*** (in image, spectrum):

signal ΔN = (SNR)(noise) = (SNR)(DQE . F. N)$^{1/2}$ leads to

resolution d = (SNR) **C**$^{-1}$(DQE. F.D/e)$^{-1/2}$

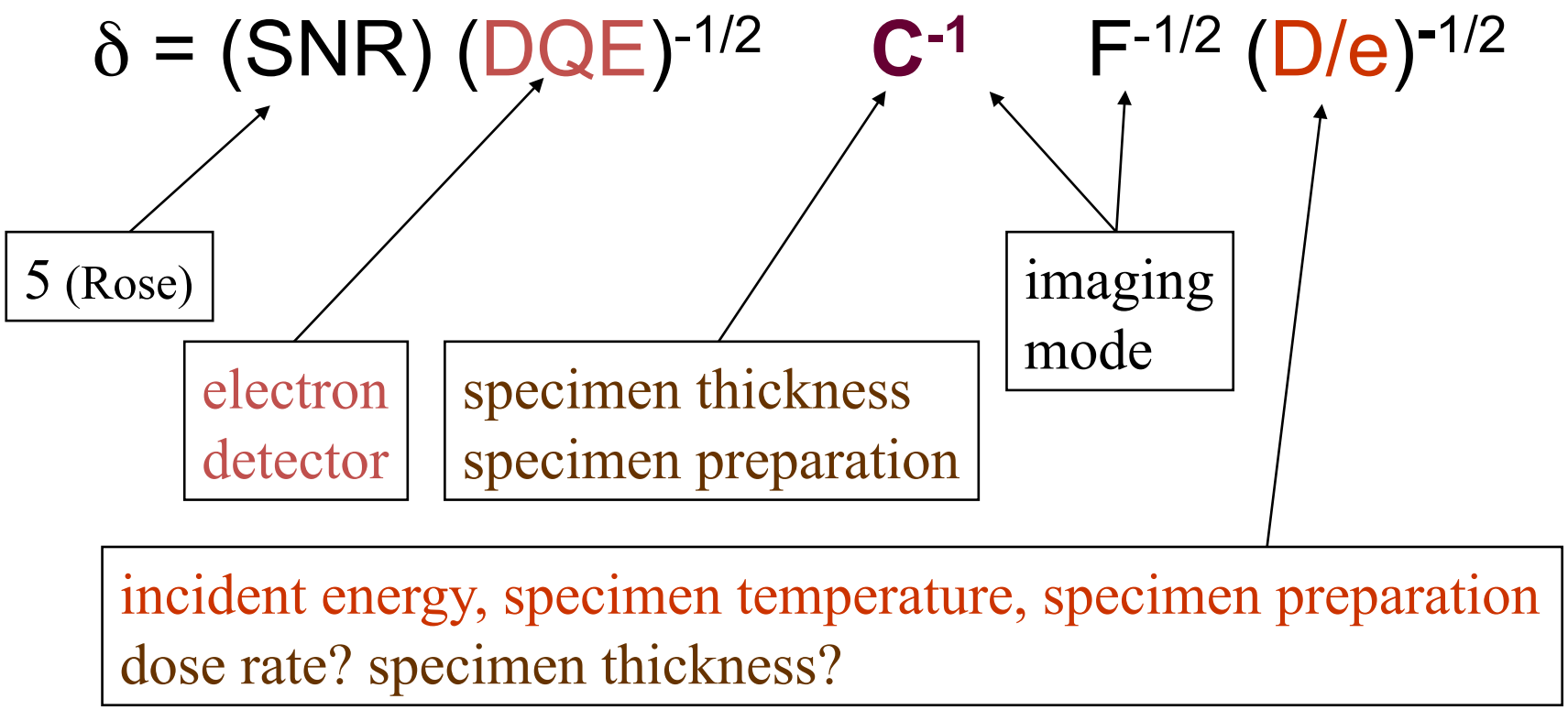
not the only factor affecting resolution

C = contrast between resolution elements
D/e = dose in electrons/area (if D in Coulomb)
DQE = performance of recording system
F = specimen/detector attenuation (e.g. objective aperture)

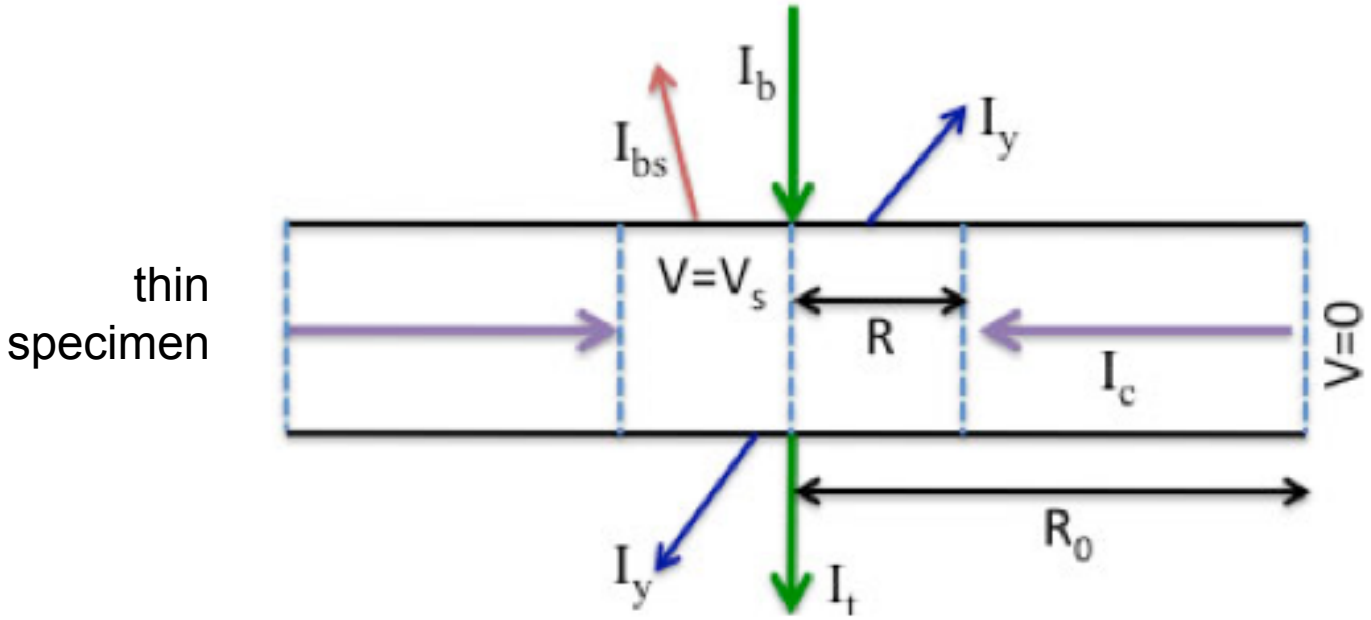


SNR = 5 (Rose),
DQE = 0.2 @Nyquist frequency
C = 0.1 (10% contrast)
F = 0.8 (thin specimen)
D = 0.01 C/cm^2 (organic)
gives **d ~ 5 nm**
>> instrumental resolution

Variables affecting dose-limited **resolution:**



Damage due to **electrostatic charging**



$I_b + I_c = I_t + 2I_y + I_{bs}$ ← current balance

$I_y = Y(V_s)\, I_b$ ← SE + Auger yield

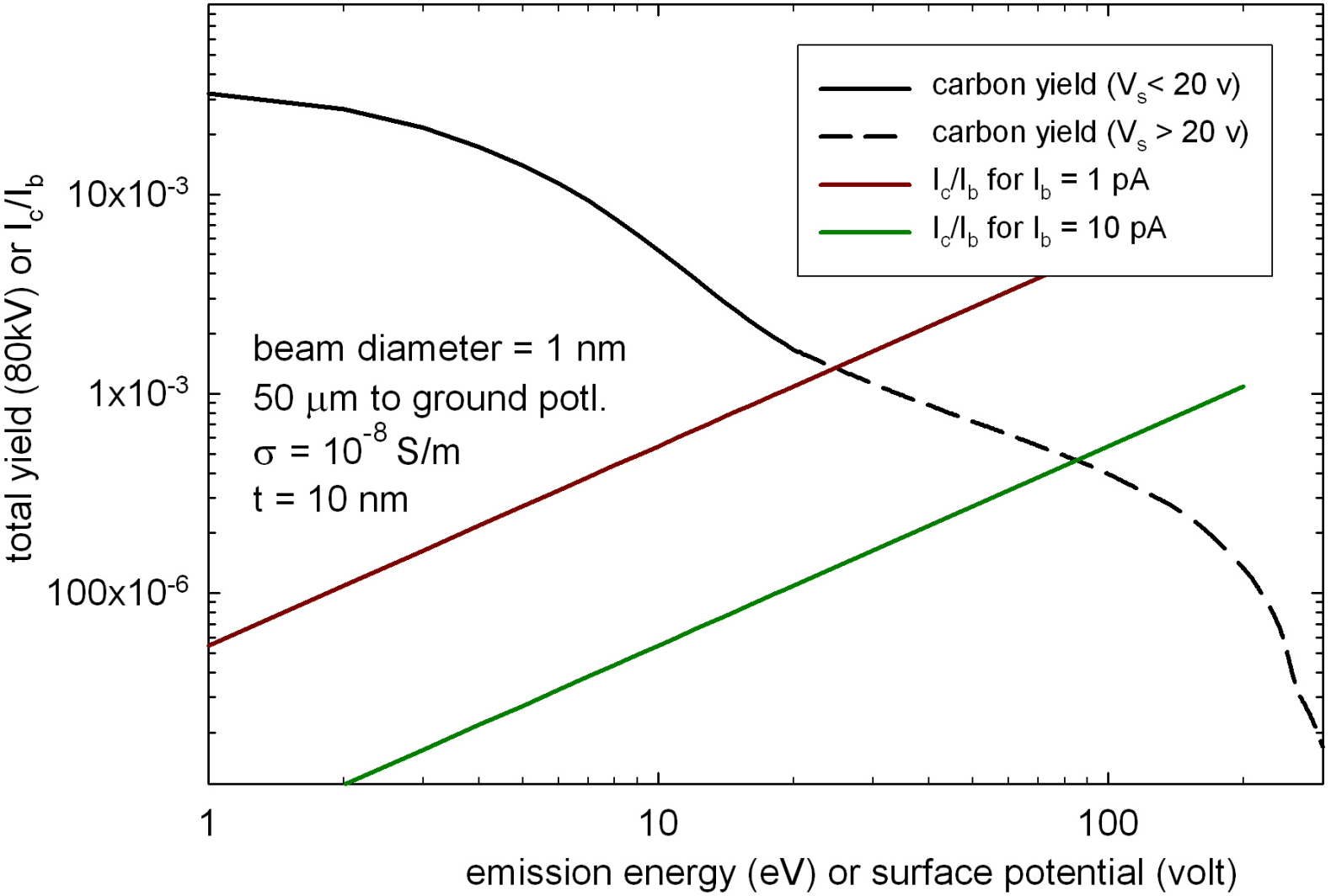
$I_c = (2\pi rt)\sigma(dV/dr)$ ← Ohm's law

$(2prt)\varepsilon(dV/dr) = Q$ ← Gauss theorem

leads to $Q = I_c\varepsilon/\sigma$ ← total charge Q

$V_s = \{Q/(2\pi\varepsilon t)\} \ln(R_0/R) = (R^2r/2e) \ln(R_0/R)$ ← surface potential

Possible steady state (intersection of yield curve and Ohm's law)



Possible damage consequences:

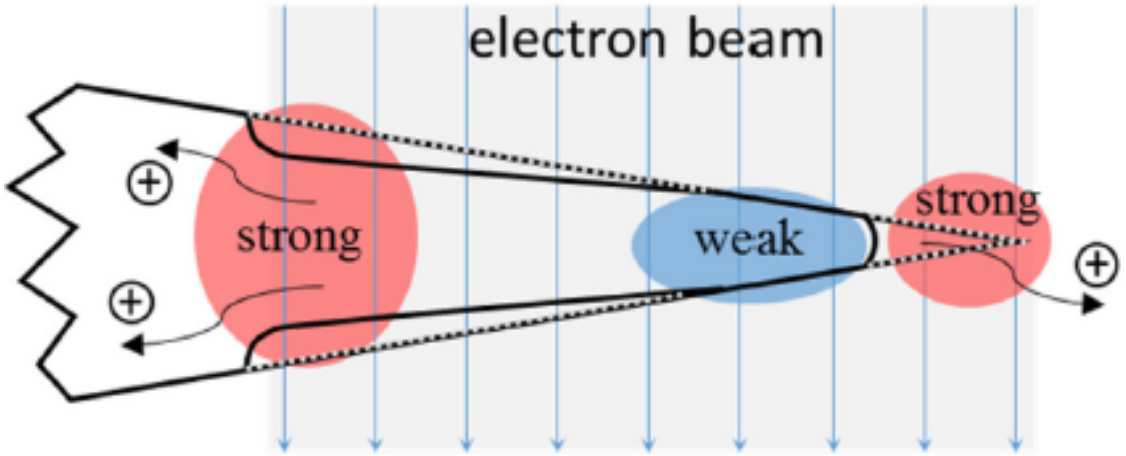
Charge buildup Q → image distortion, repulsion effects

or → ion emission, hole drilling (Humphreys *et al*., Cazaux)

Internal electrostatic field → dielectric breakdown

or → drift of ions, concentration gradient, ionic diffusion

(may reverse after beam is removed)



N. Jiang,
Micron
83 (2016) 79-92

Summary: minimizing damage effects

	cool sample?	coat sample?	other
knock-on	little effect	YES	reduce kV (threshold?)
radiolysis	YES	YES	maximize signal, etc.
charging	NO !	YES	reduce beam current

Varying beam current, kV and temperature may help to **distinguish** the mechanism.

Estimating the electron dose that produces change can also be useful for distinguishing **RAD**iolysis and **K**nock-**O**n **S**puttering →

Material	D_c (C/m²)	Mechanism
Amino acids	20–50	RAD
Hydrocarbons	50–200	RAD
Nucleic acids	10^2–10^4	RAD
Aromatic organics	10^3–10^4	RAD
NaCl	10^2	RAD
Zeolite	10^3–10^4	RAD
Amorphous C	4×10^7	KOS
Cr_2N	10^9	KOS
Graphene	10^{10}	KOS