universität wien

On 2D Materials & Their Defects
under electron irradiation

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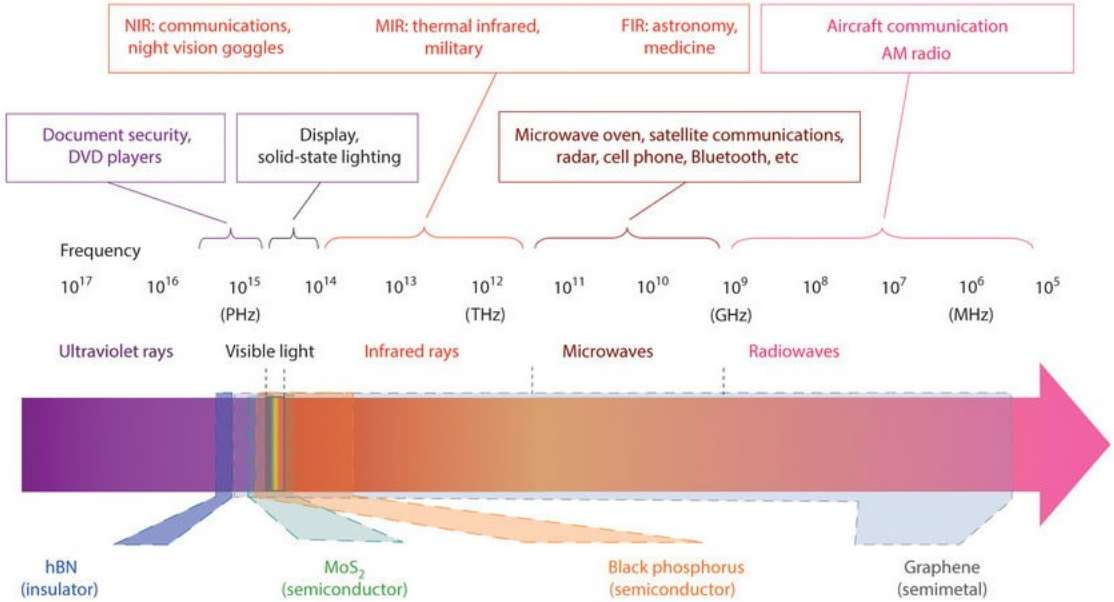
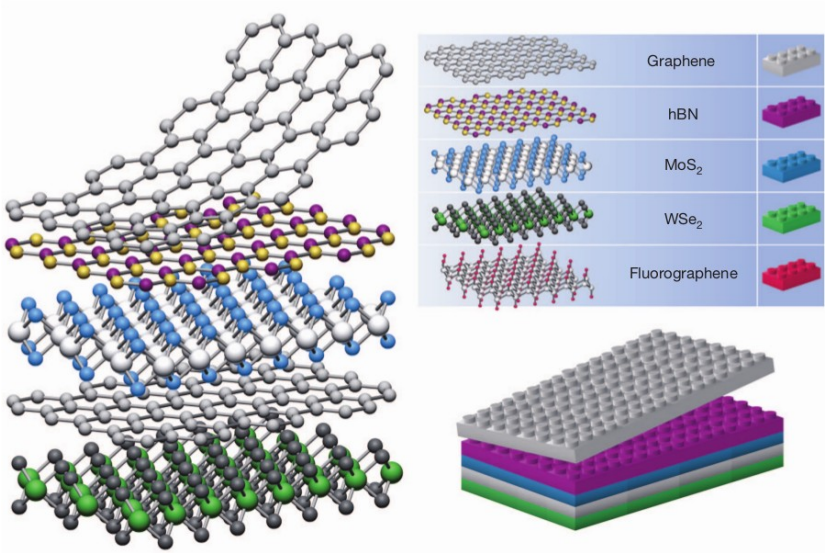
Conference on Physics of Defects in Solids: Quantum Mechanics Meets Topology
9.–13.7.2018 @ ICTP, Trieste, Italy

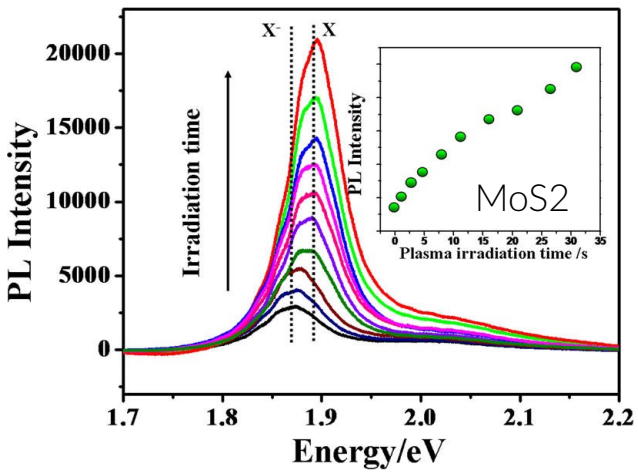
2D Materials

Xia et al., Nat. Photon. 8, 899–907 (2014)

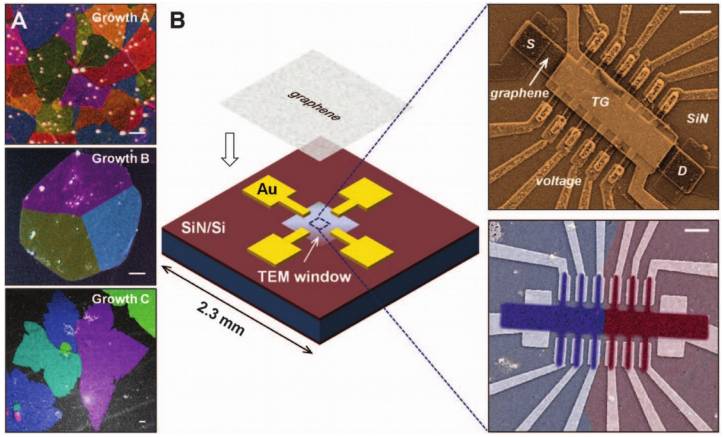


Nature 499, 419 (2013)

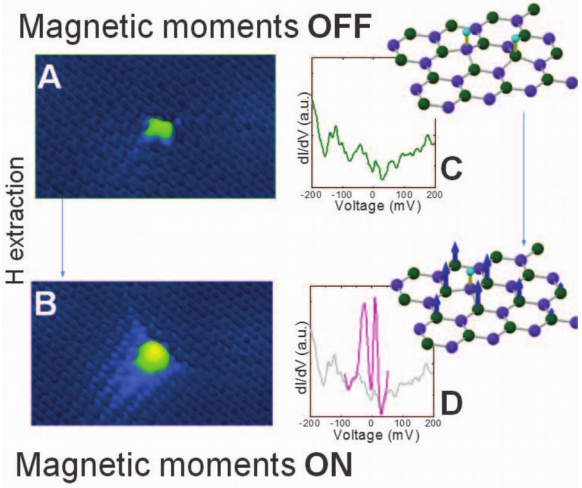




Nan et al., ACS Nano 8, 5738 (2014)

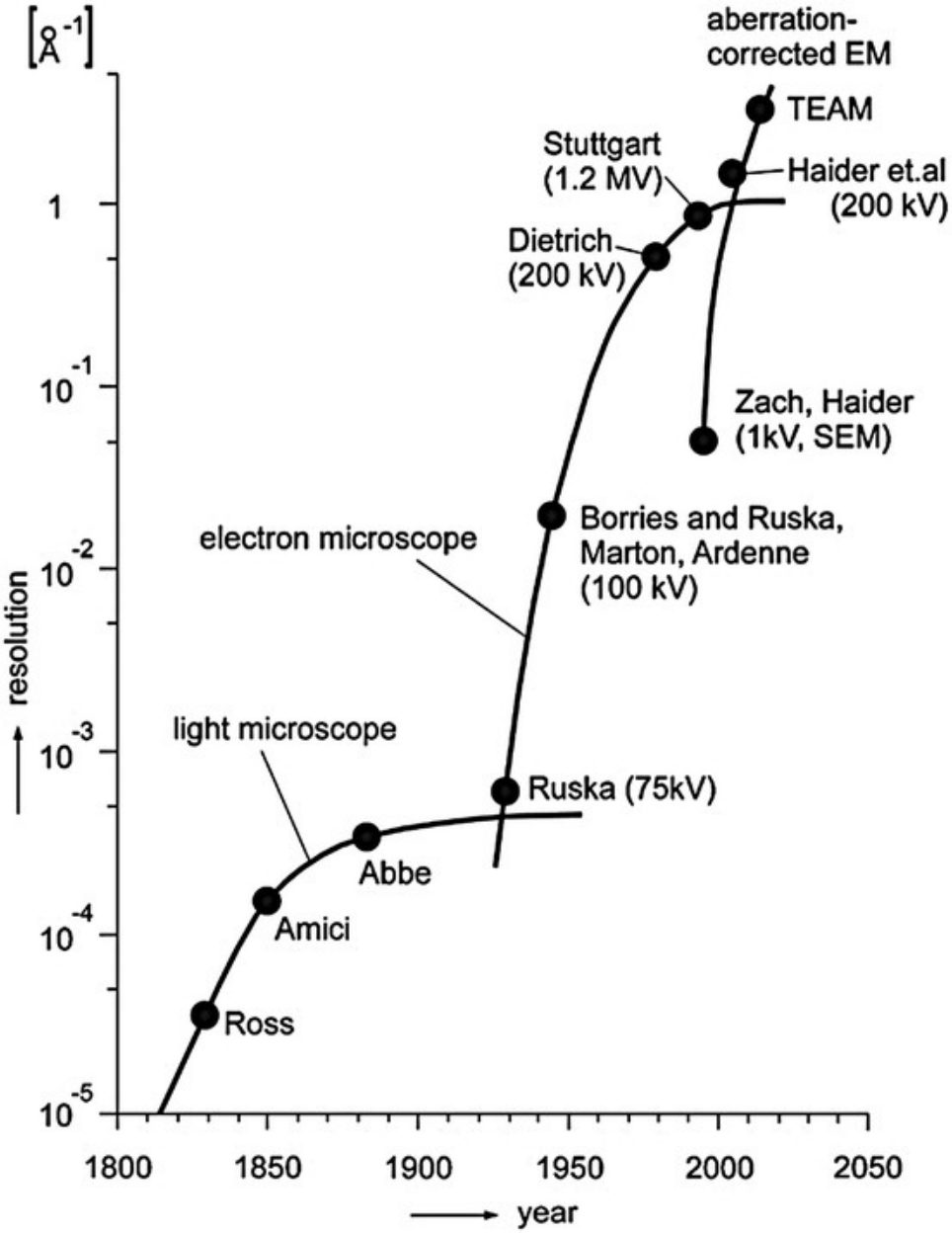


Tsen et al., Science 336, 1143 (2012)

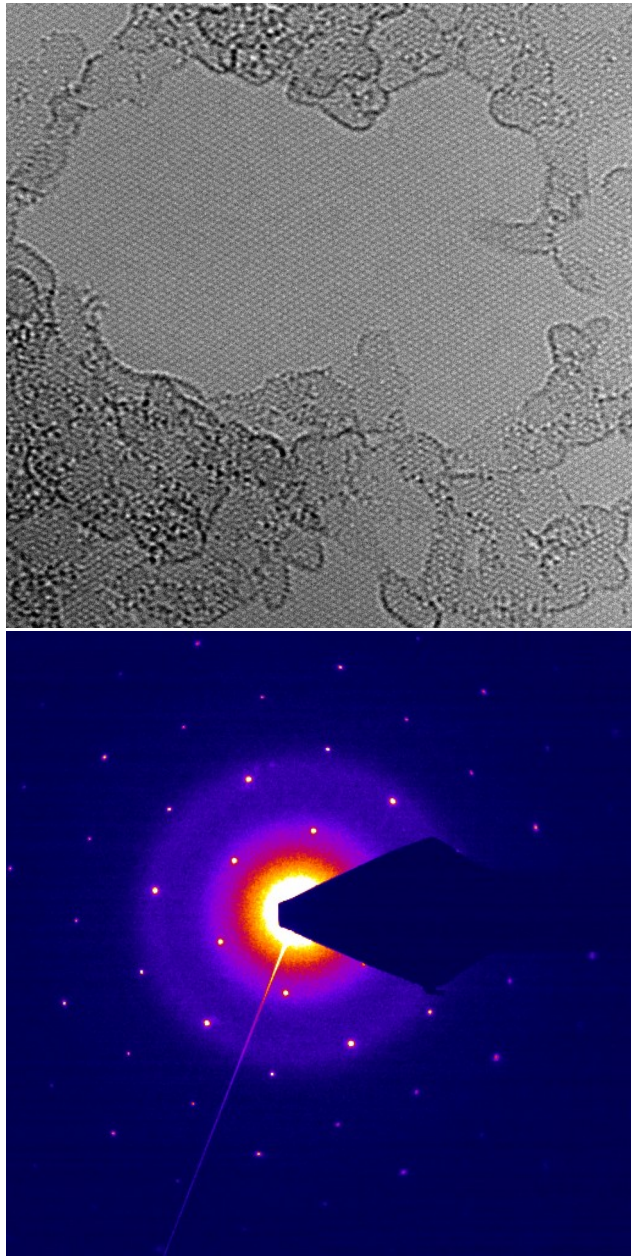


González-Herrero et al., Science 352, 437 (2016)

Transmission Electron Microscopy

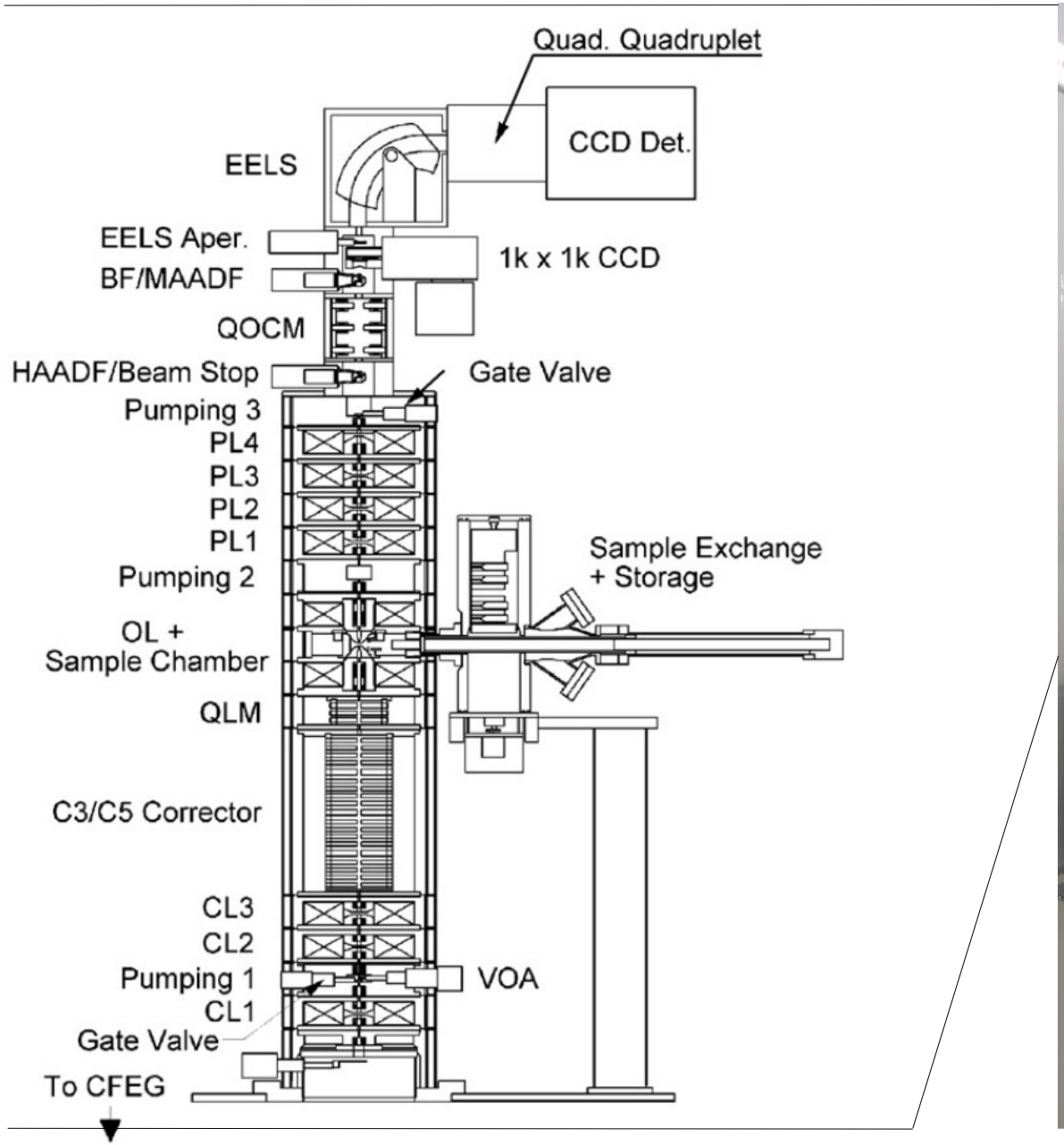


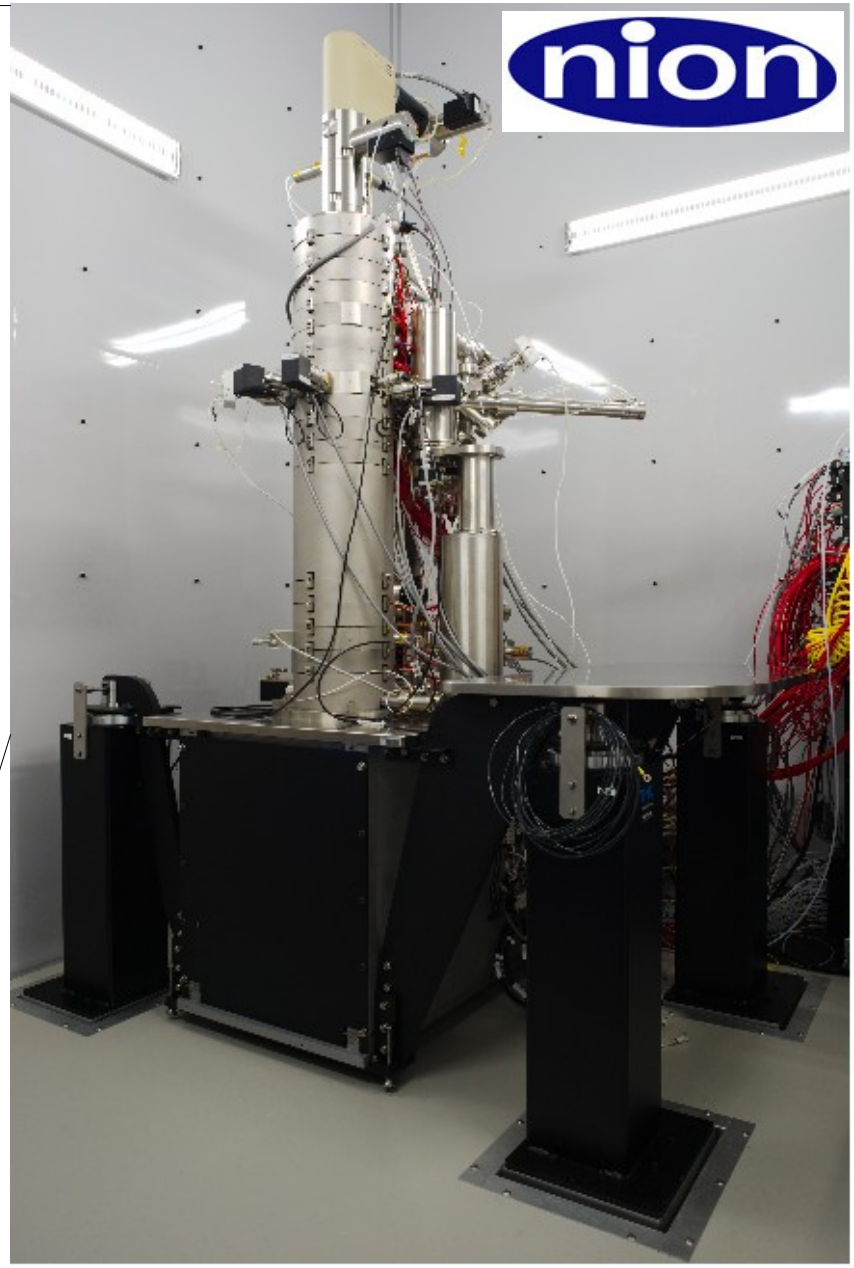
Jinschek, Chem. Commun. 50, 2696-2706 (2014)



U. Ludacka, FEI Titan 80-300 @ Vienna

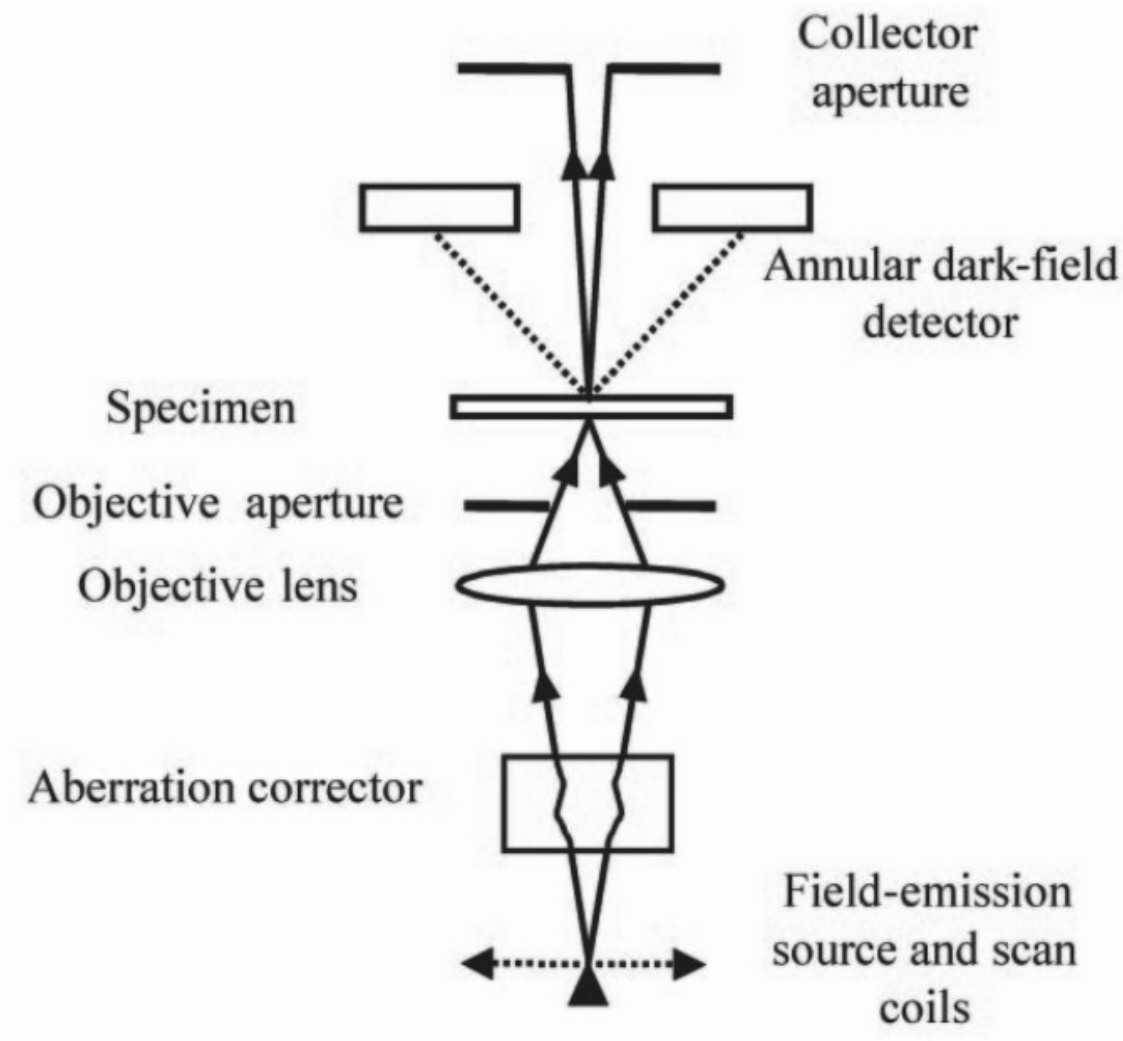
Nion UltraSTEM 100 @ Vienna





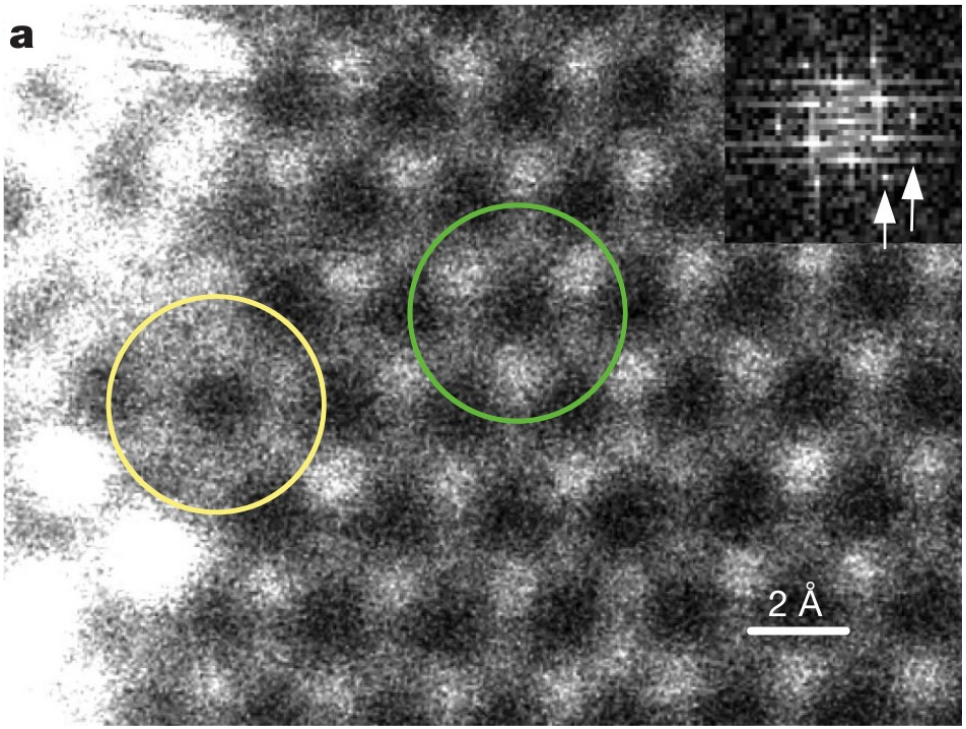
Krivanek et al., Ultramicroscopy 108, 179 (2008)

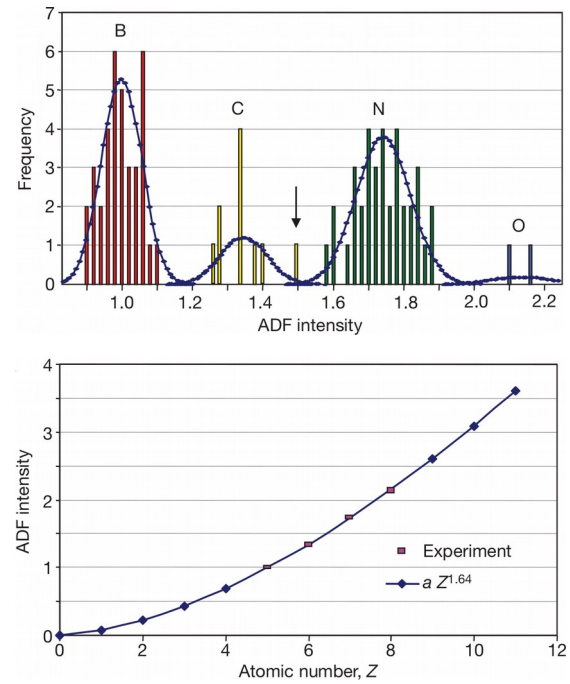
Nion UltraSTEM 100 @ Vienna

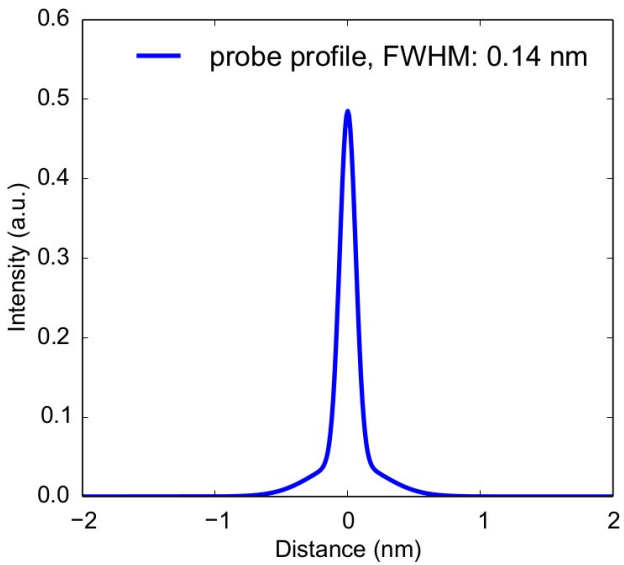


Pennycook et al., MRS Bulletin 31, 36 (2006)

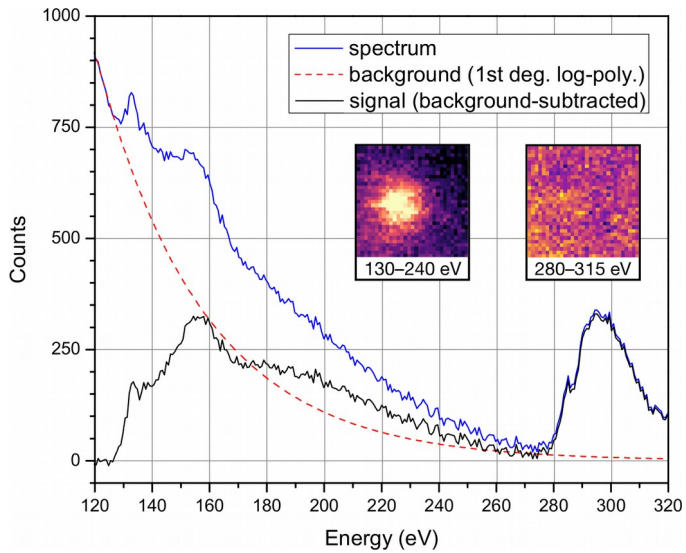
Krivanek et al., Nature 464, 571 (2010)



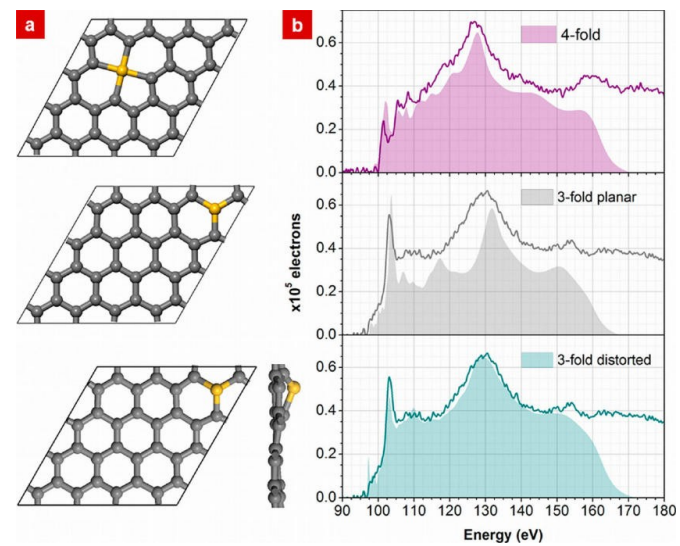




JK et al., Nat. Commun. 5, 4991 (2014)



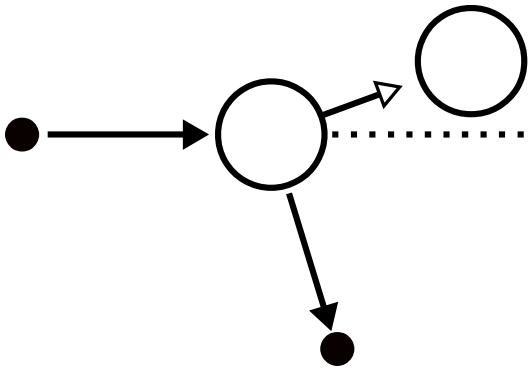
Susi, JK, et al. ,2D Mater. 4, 021013 (2017)



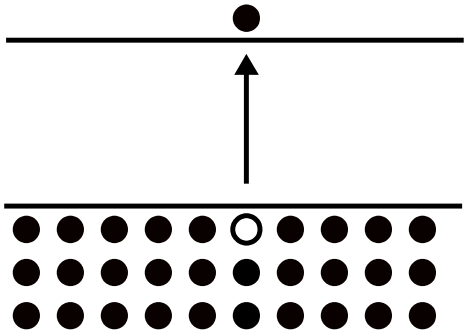
Ramasse et al, Nano Lett. 13, 4989 (2013)

Electron Beam Effects in the (S)TEM

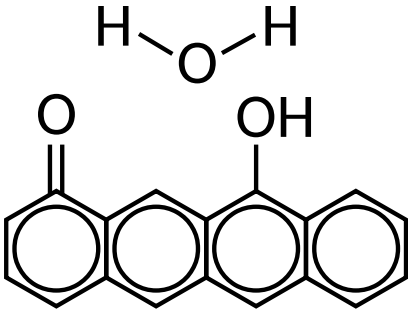
knock-on



excitations & ionization



chemical effects



Characteristic cross sections and time scales for carbon @ 100 kV

Knock-on dynamics cross section: < 1 barn time scale: 10^{-15} s	**Ionization** cross section: 10^{6} barn time scale: 10^{-15} s	**Plasmons** cross section: 10^{6} barn time scale: 10^{-13} s
Phonons (elastic collision) cross section: 10^{6} barn time scale: 10^{-12} s	**Core hole** cross section: 10^{4} barn time scale: 10^{-14} s	Beam Current: 30 pA ca. 1 e- / nm^2 / 10^{-9} s

Egerton, Ultramicroscopy 127, 100–108 (2013), Brühwiler et al., Phys. Rev. Lett. 74, 614–617 (1995), Yan et al., Nature Photon. 7, 394–399 (2013), Kang et al., Phys. Rev. B 81, 165405 (2010), Banhart, Rep. Prog. Phys. 62, 1181 (1999), Cosslett, J. Microsc. 113, 113-129 (1978)

Knock-On Process

Banhart, Rep. Prog. Phys. 62, 1181 (1999)

Conservation of energy

$$E_{\mathrm{e}}^{\mathrm{tot}} + E_{\mathrm{n}}^{\mathrm{tot}} = \tilde{E}_{\mathrm{e}}^{\ \mathrm{tot}} + \tilde{E}_{\mathrm{n}}^{\ \mathrm{tot}}$$

Conservation of momentum

$$\vec{p}_e + \vec{p}_n = \vec{\tilde{p}}_{\mathrm{e}} + \vec{\tilde{p}}_{\mathrm{n}}$$

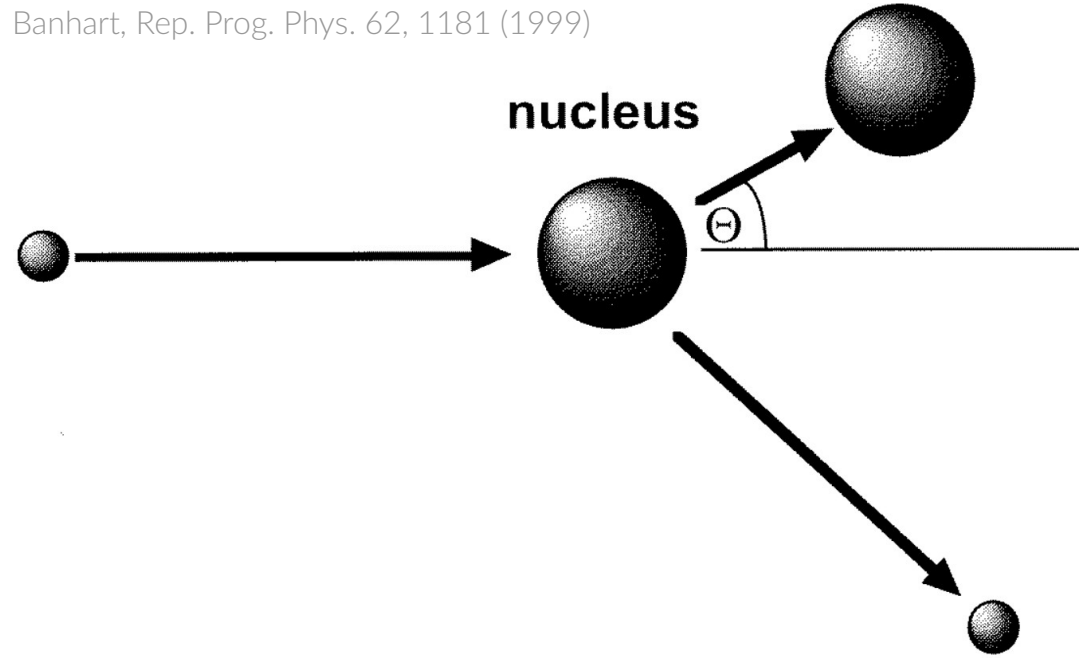


Figure 1. Geometry of scattering of a light particle (electron) by a nucleus.

Maximum energy transfer occurs for the back scattering electron and yields

$$E_{\max}(E_{\mathrm{e}}, v) = \frac{\left(2\sqrt{E_{\mathrm{e}}(E_{\mathrm{e}} + 2mc^2)} + Mvc\right)^2}{2Mc^2}$$

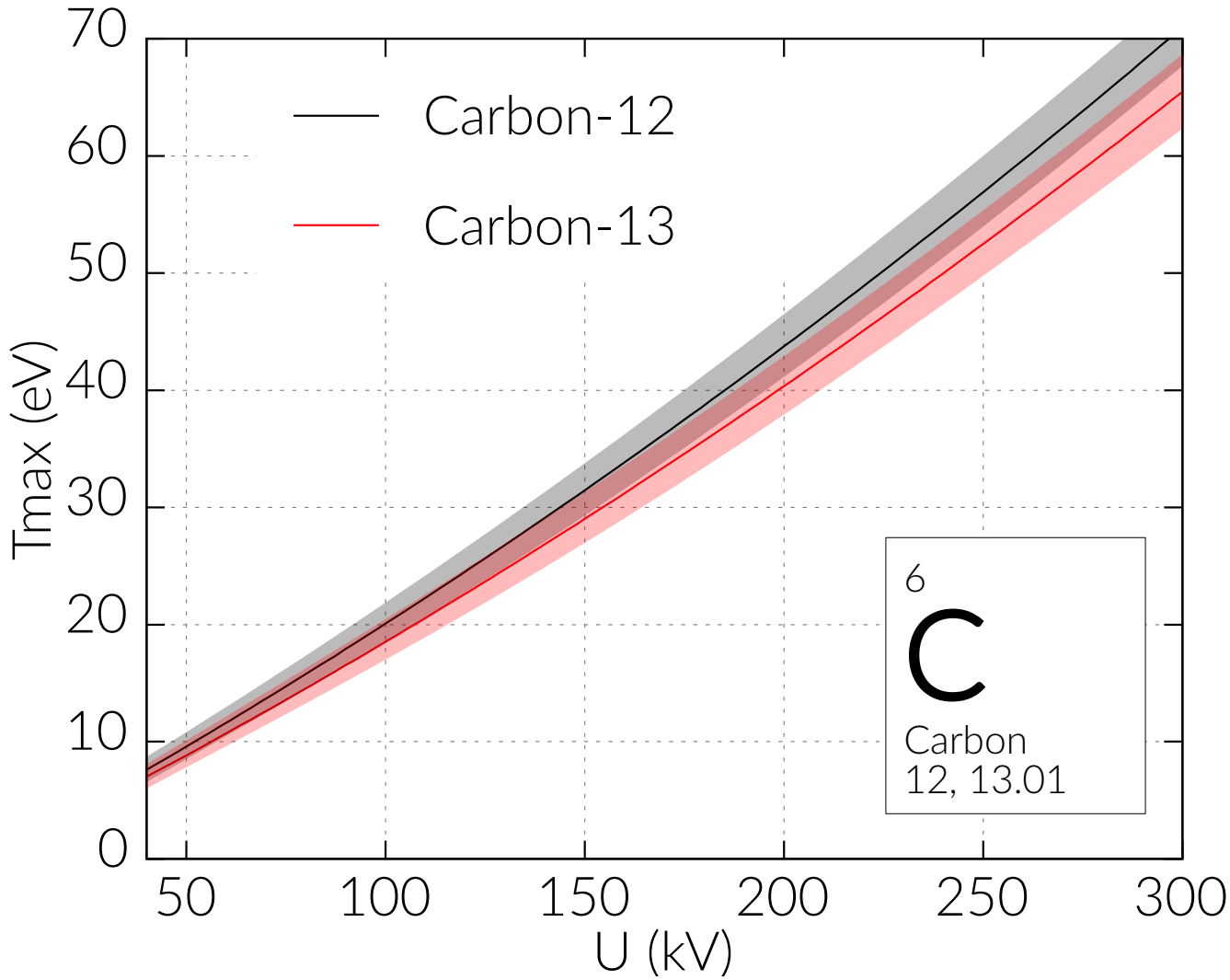
Electron energy: eU

Initial velocity of the nucleus

or $$E_{\max}(E_{\mathrm{e}}) = \frac{2E_{\mathrm{e}}(E_{\mathrm{e}} + 2m_{\mathrm{e}}c^2)}{Mc^2}$$ for $v = 0$

$$E_{\max}(E_e, v) = \frac{\left(2\sqrt{E_e(E_e + 2mc^2)} + Mvc\right)^2}{2Mc^2}$$

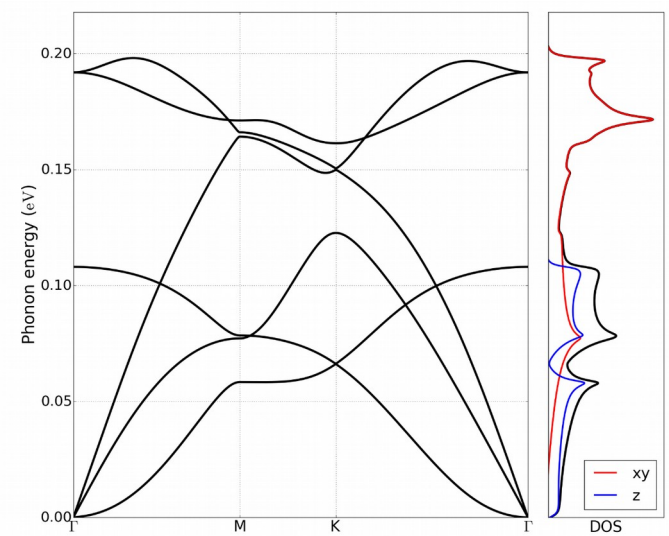
m: 0.51 MeV/c^2
M: Z x 931.49 MeV/c^2



Velocity here from kinetic theory:

$$k_B T = \frac{m\overline{v^2}}{3}$$

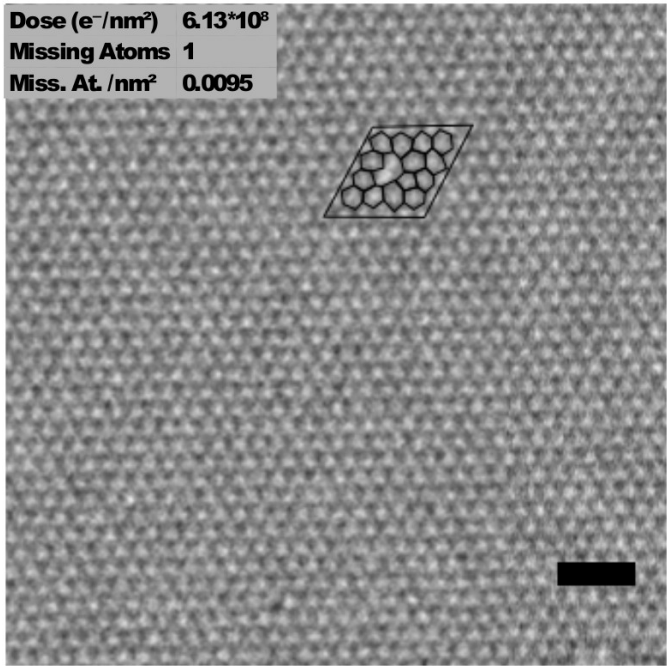
Better, phonon DOS:

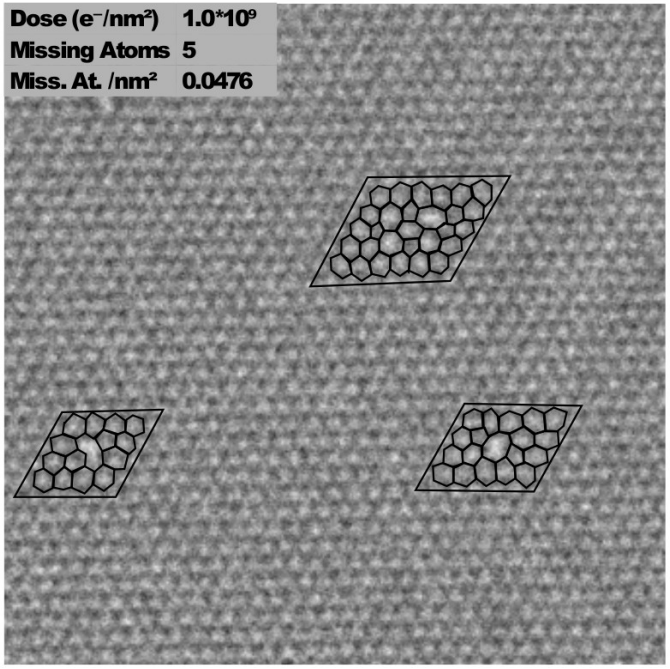


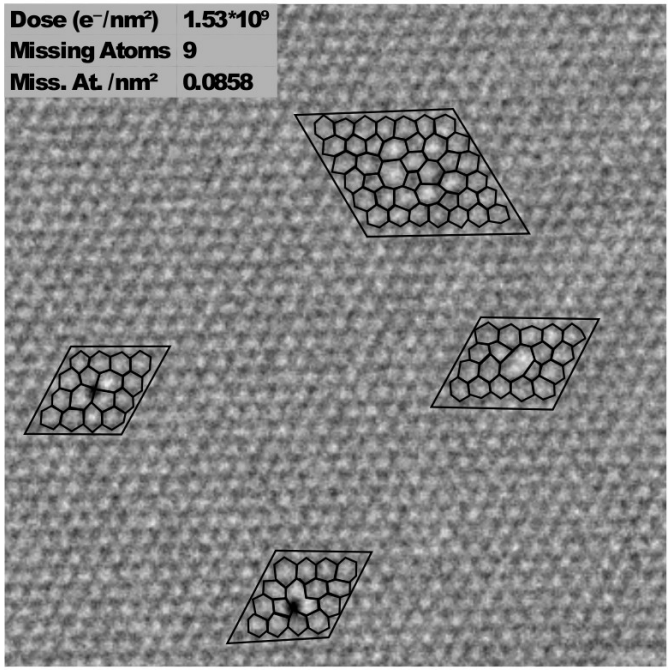
$$\overline{v_z^2}(T) = U_z/(2M) = \frac{\hbar}{2M}\int_0^{\omega_z} g_z(\omega)\left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega/(kT)) - 1}\right]\omega\,\mathrm{d}\omega$$

Susi, ..., JK, Nat. Commun. 7, 13040 (2016)

Graphene @ 90 kV, TEM

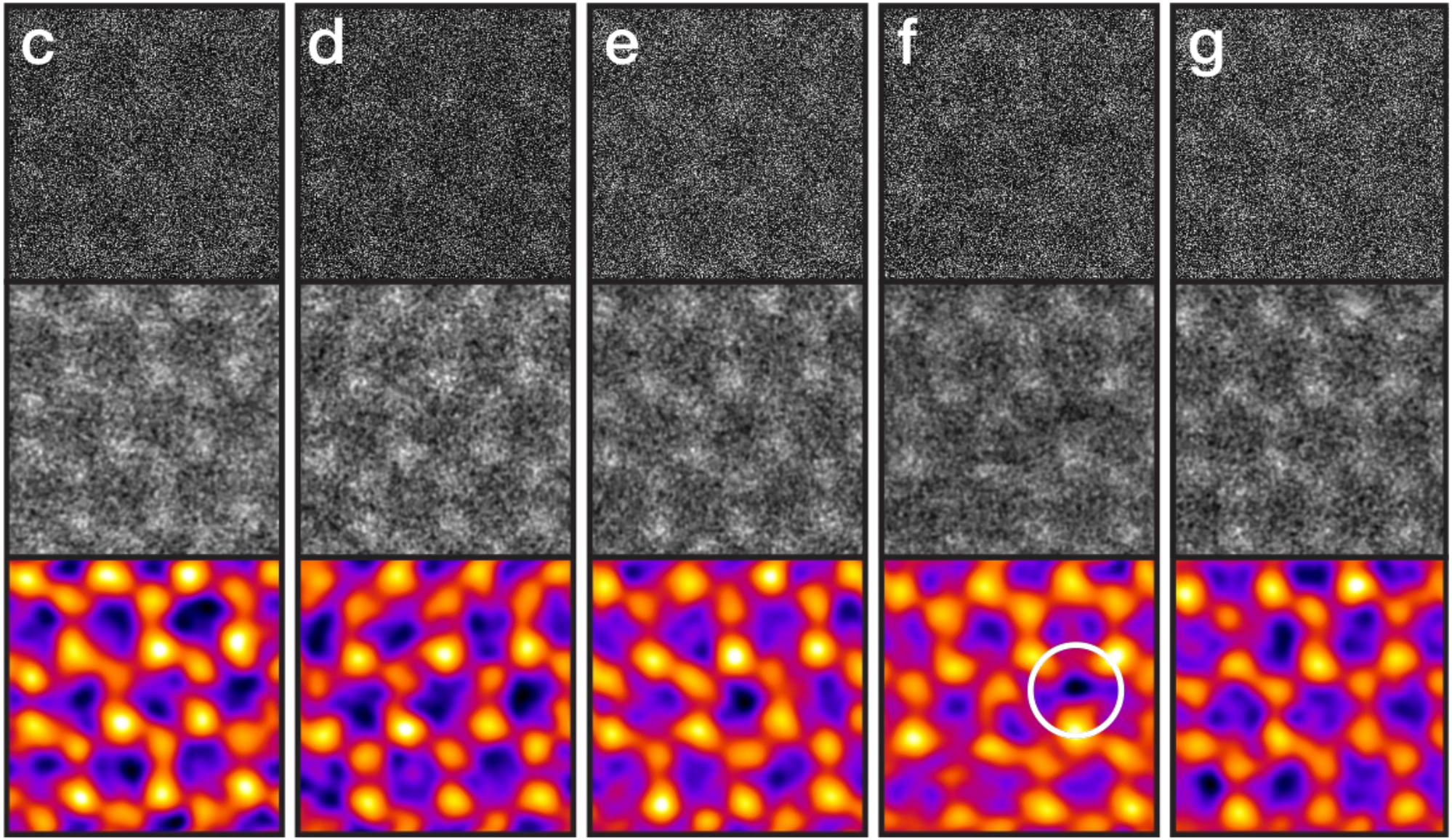






Meyer, JK et al., Phys. Rev. Lett. (2012)

Graphene @ 95 kV, STEM



Susi, ..., JK, Nat. Commun. 7, 13040 (2016)

Displacement Cross Section

Coulomb Interaction: $$V(\mathbf{r}) = \frac{-e^2 Q_1 Q_2}{4\pi\varepsilon_0 \; r}$$

Nucleus: $Q_2 = Z$

Electron: $Q_1 = 1$

Rutherford scattering: $$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 \alpha(\hbar c)}{4 E_K \sin^2 \frac{\Theta}{2}} \right)^2$$ (valid for charges at low energies)

Extended for spin and relativistic electrons by *Mott* & approximated by *McKinley* and *Feshbach*:

$$\sigma(\theta) = \sigma_R \left[1 - \beta^2 \sin^2(\theta/2) + \pi \frac{Ze^2}{\hbar c} \beta \sin(\theta/2)(1 - \sin(\theta/2)) \right]$$

Electron scattering angle

Using $$T(\theta) = T_{max} \sin^2(\theta/2)$$

one gets $$\sigma(T) = \left(\frac{Ze^2}{4\pi\varepsilon_0 2 m_0 c^2} \frac{T_{max}}{T} \right)^2 \frac{1-\beta^2}{\beta^4} \left[1 - \beta^2 \frac{T}{T_{max}} + \pi \frac{Ze^2}{\hbar c} \beta \left(\sqrt{\frac{T}{T_{max}}} - \frac{T}{T_{max}} \right) \right]$$

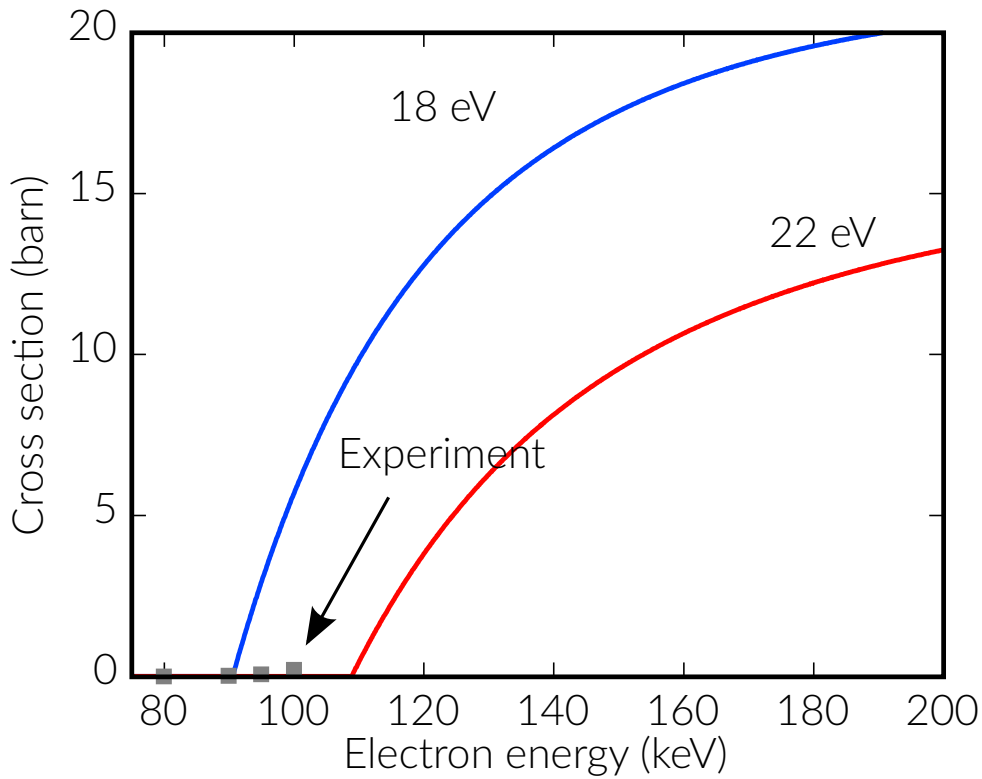
Energy of nucleus after scattering

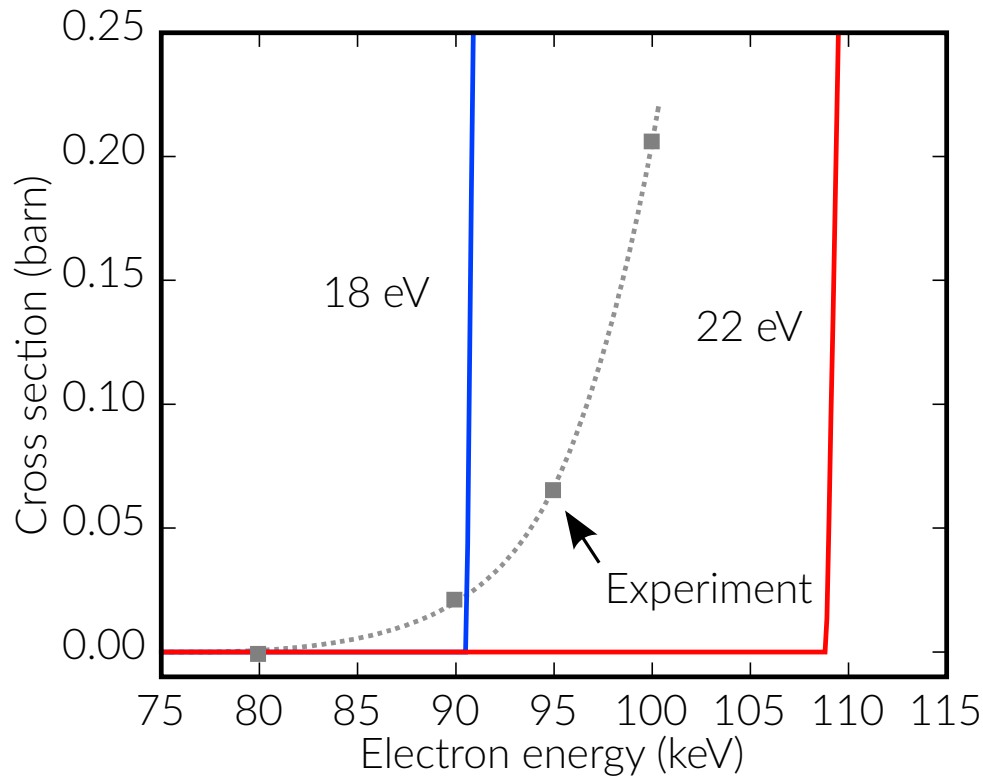
Assuming isotropic displacement threshold E_d and integrating over $T > E_d$ leads to:

$$\sigma_d = 4\pi \left(\frac{Ze^2}{4\pi\varepsilon_0 2 m_0 c^2} \right)^2 \frac{1-\beta^2}{\beta^4} \left\{ \frac{T_m}{E_d} - 1 - \beta^2 \ln\left(\frac{T_m}{E_d}\right) + \pi \frac{Ze^2}{\hbar c} \beta \left[2\left(\frac{T_m}{E_d}\right)^{1/2} - \ln\left(\frac{T_m}{E_d}\right) - 2 \right] \right\}$$

See: Zobelli et al., Phys. Rev. B 75, 245402 (2007)
McKinley and H. Feshbach, Phys. Rev. 74, 1759 (1948)

Theory vs. experiment



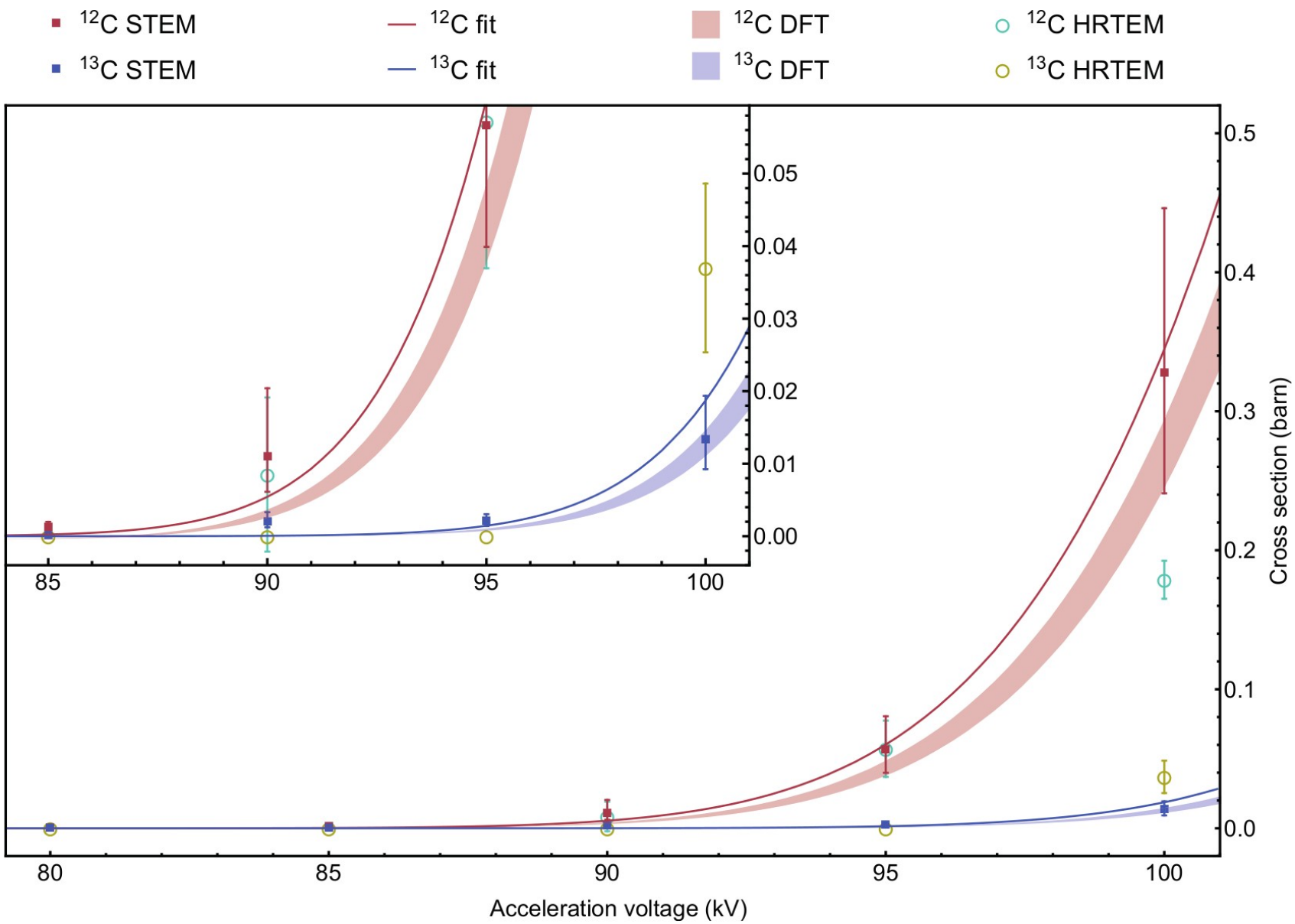


$$\sigma_d = 4\pi\left(\frac{Ze^2}{4\pi\varepsilon_0 2m_0c^2}\right)^2 \frac{1-\beta^2}{\beta^4}\left\{\frac{T_m}{E_d} - 1 - \beta^2 \ln\left(\frac{T_m}{E_d}\right) + \pi\frac{Ze^2}{\hbar c}\beta\left[2\left(\frac{T_m}{E_d}\right)^{1/2} - \ln\left(\frac{T_m}{E_d}\right) - 2\right]\right\}$$

Meyer, JK, et al., Phys. Rev. Lett. 108, 196102 (2012)

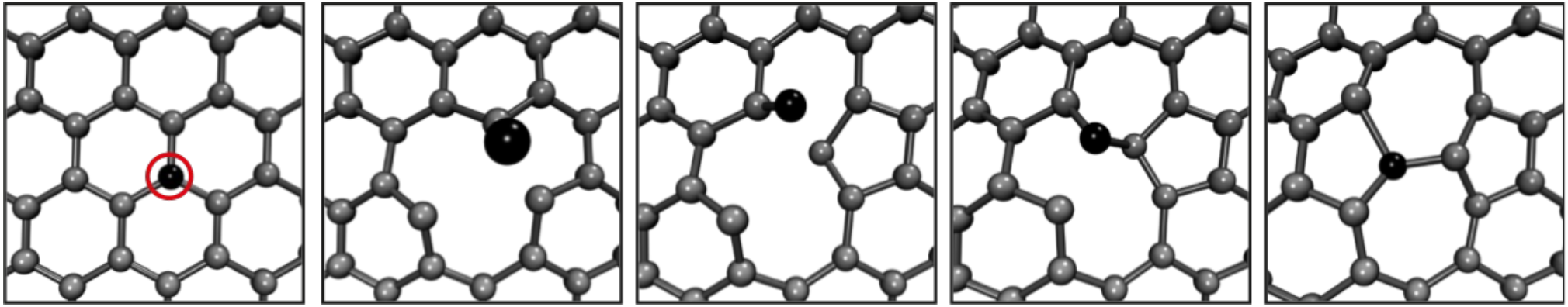
Extended model: $$\sigma(T, E_e) = \int_{E_{max}(v,E_e) \geq T_d} P(v,T)\,\sigma(E_{max}(v,E_e))\,\mathrm{d}v$$

Velocity distribution of nuclei

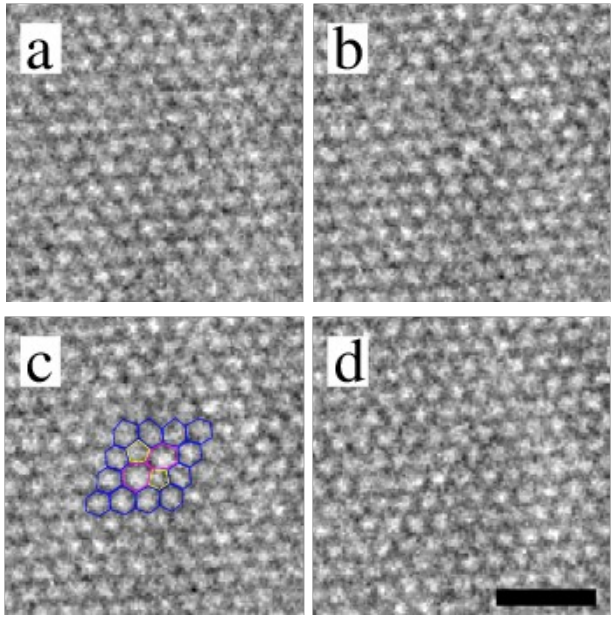


Susi, ..., JK, Nat. Commun. 7, 13040 (2016)

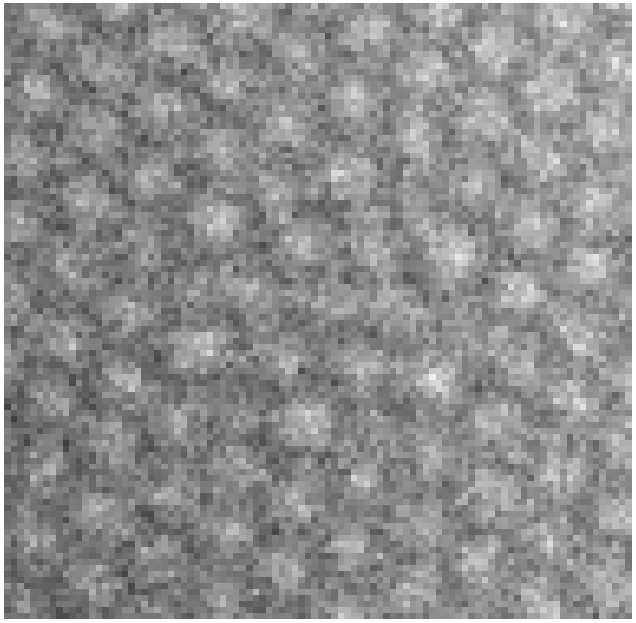
Sub-threshold Knock-On Effects



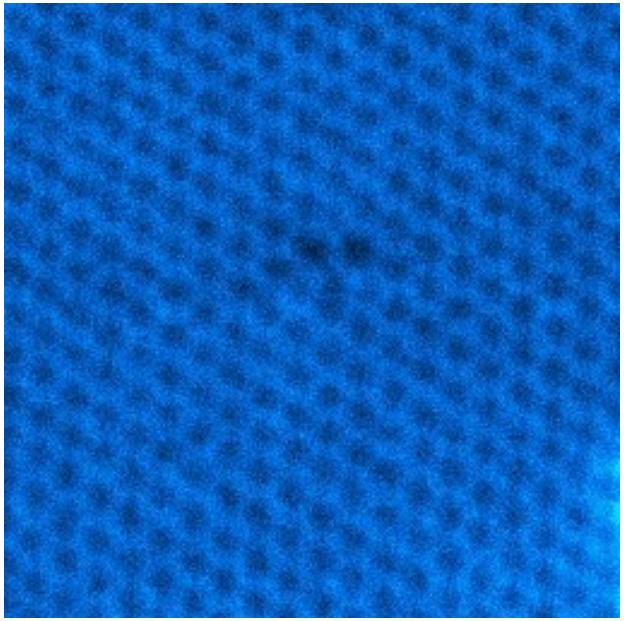
Dynamical process due to an impact on one atom



Stone-Wales



„Flower defect“

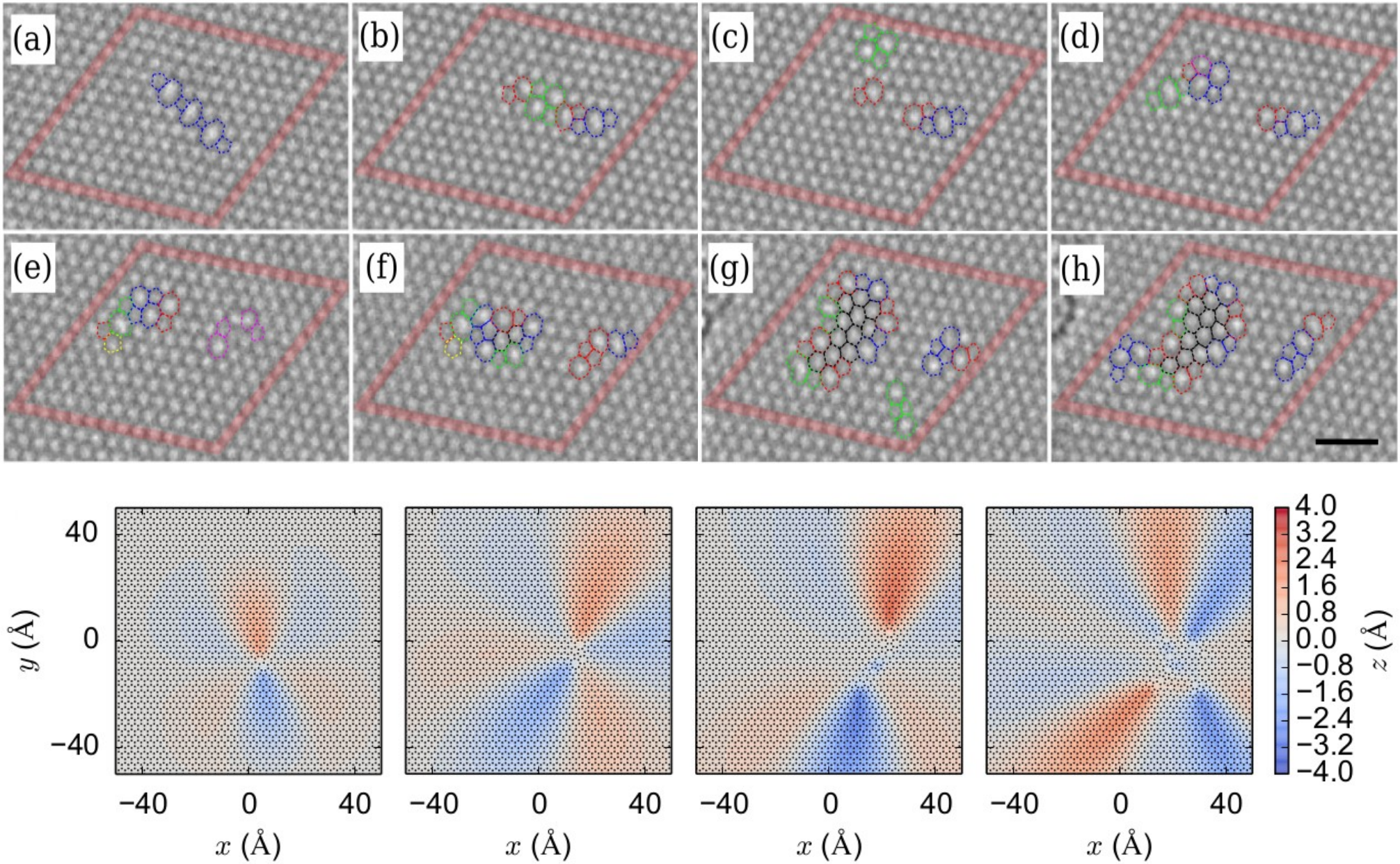


Divacancy

JK et al., Phys. Rev. B 83, 245420 (2011) — Susi, ..., JK, 2D Mater. 4, 042004 (2017)
Kurasch, JK, et al., Nano Lett. 12, 3168 (2012) — JK et al., Nat. Commun. 5, 4991 (2014)

From Single- to Multivacancies

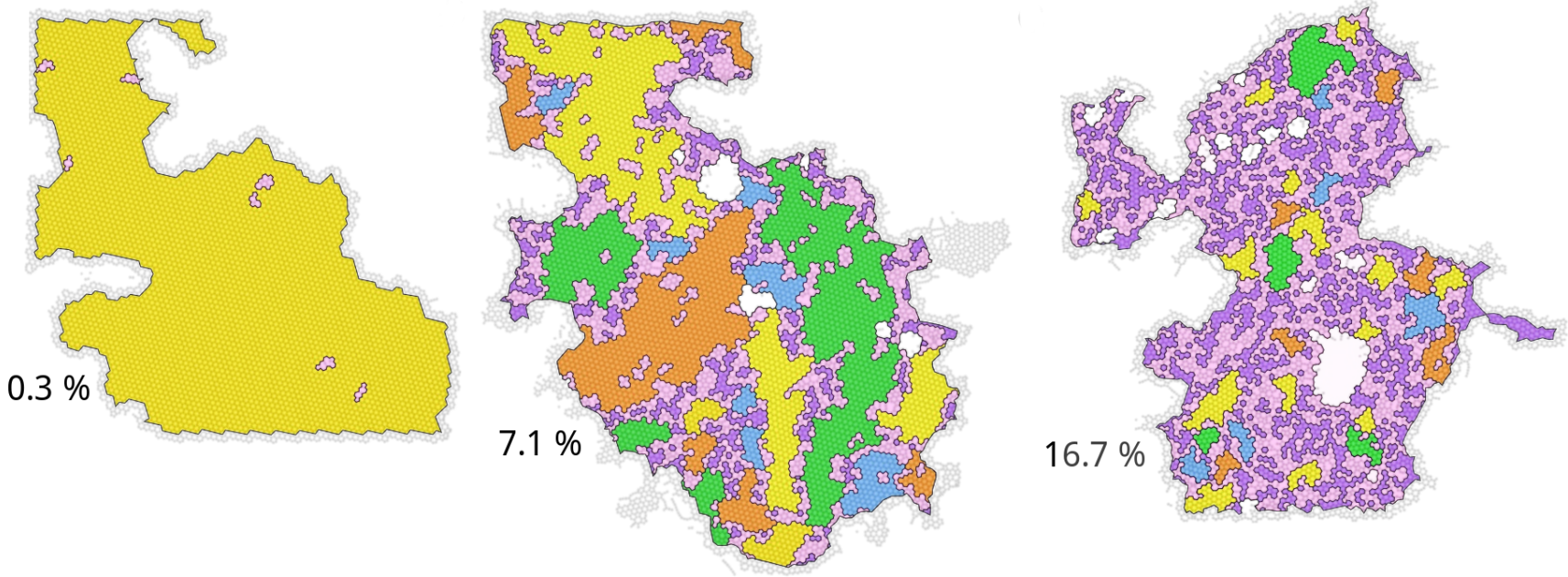
@ 100 kV

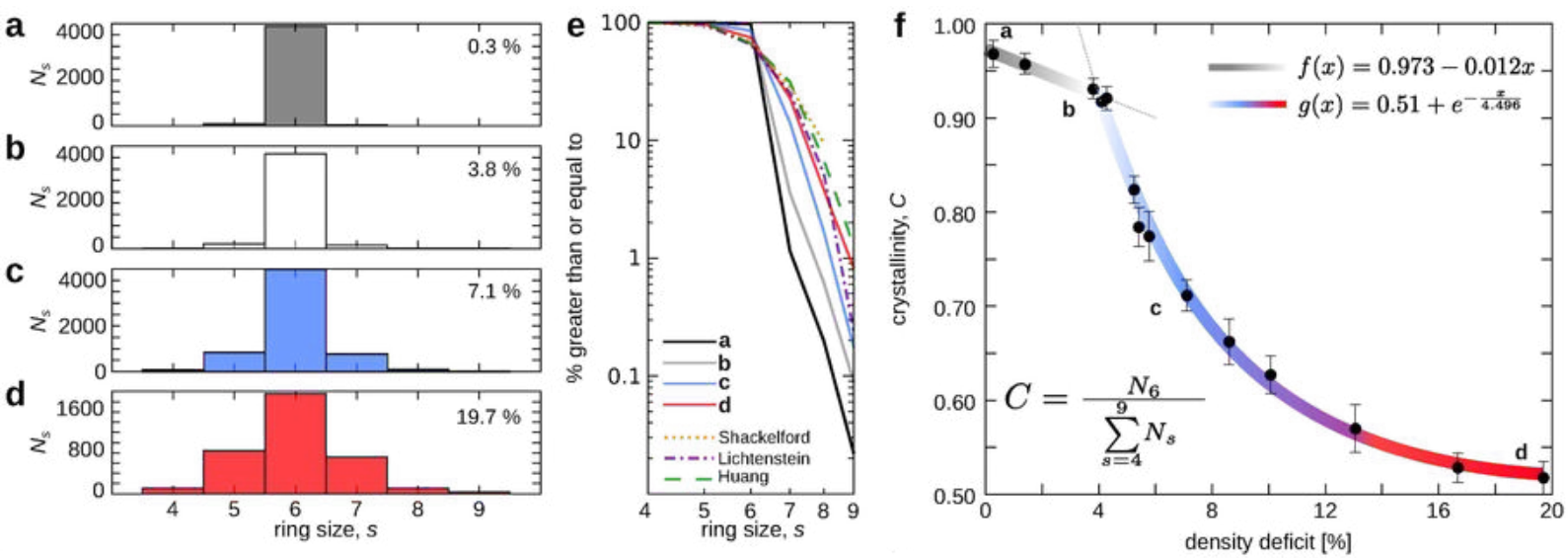


Kotakoski et al., Phys. Rev. Lett. 106, 105505 (2011) & Kotakoski et al., Phys. Rev. B 89, 201406 (2014)

… and to Amorphous 2D Carbon

@ 100 kV





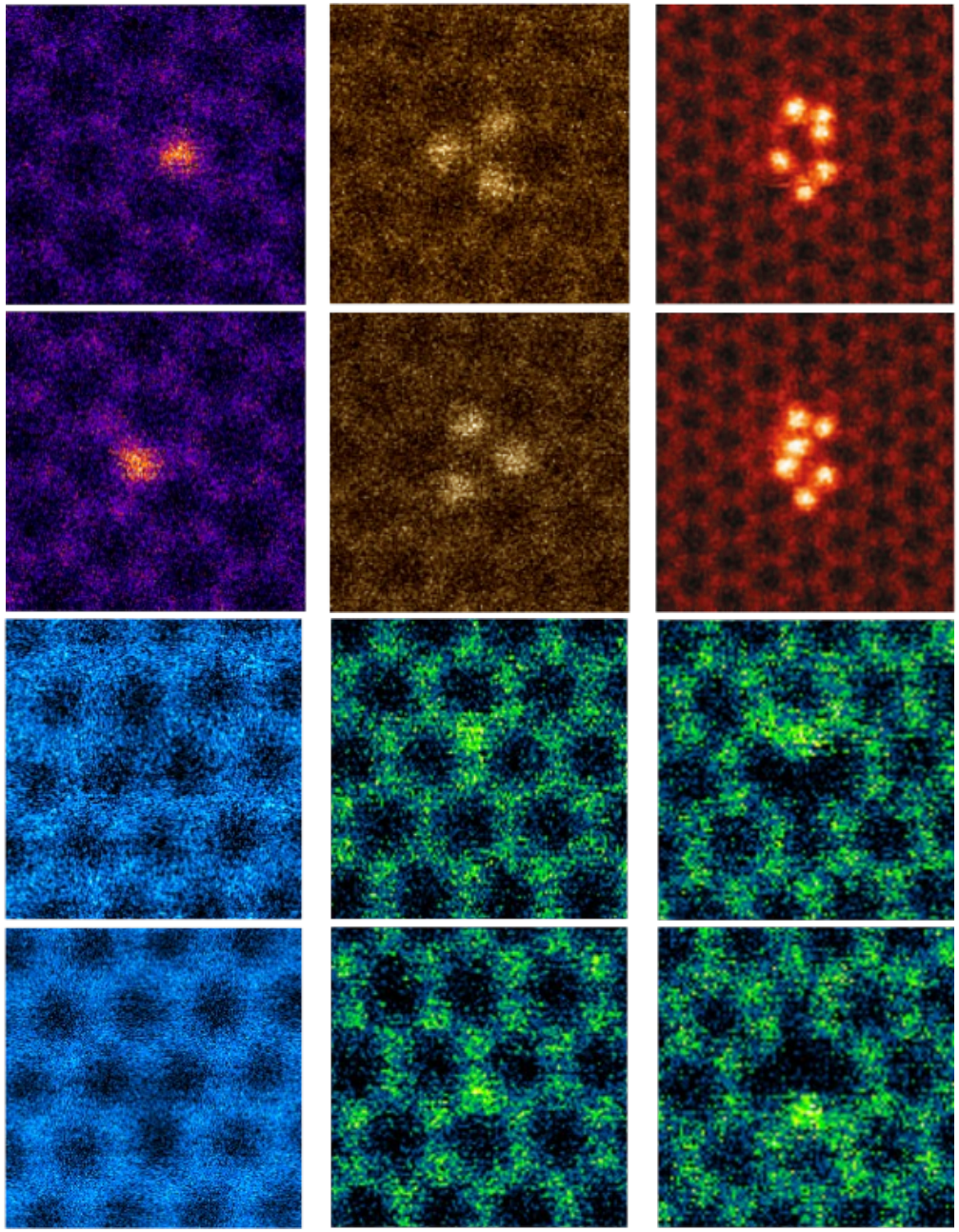
Kotakoski et al., Phys. Rev. Lett. 106, 105505 (2011) & Eder, JK et al., Sci. Rep. 4, 4060 (2014)

Impurity Atom Dynamics

Observed dynamics

Atom	Event	T_d^{exp}	T_d^{sim}
^{12}C	KO	21.14	21.9
^{13}C	KO	21.14	21.9
N_{sub}	KO	>20.4	19.1
$C@N_{sub}$	KO	17.5	19.2
$C@N_{sub}$	Jump	15.9	—
$C@N_{pyr}$	Jump	9.7	—
B	KO	15.9	18
C@B	KO	15.1	19.6
C@B	Jump	14.8	18.5
Si	KO	>10.0	13.3
C@Si	KO	12.8	16.9
C@Si	Jump	13.0	14.8

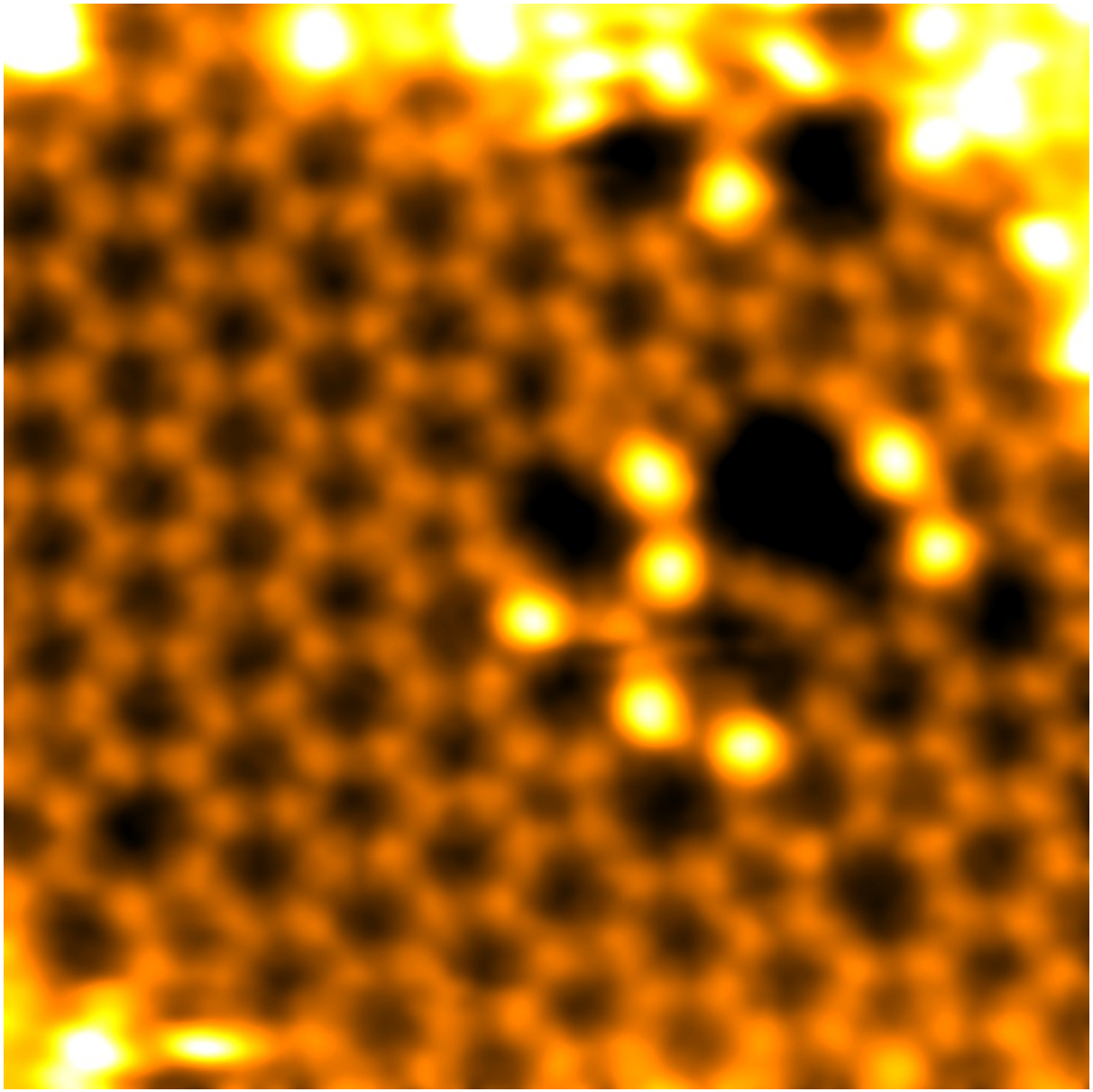
Susi, ..., JK, 2D Mater. 4, 042004 (2017)



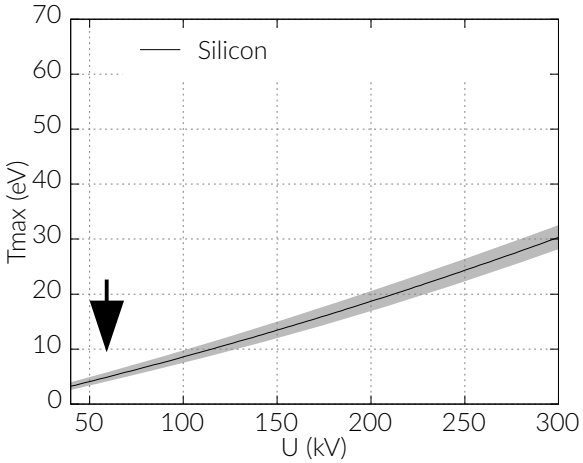
Susi, JK, et al. Phys. Rev. Lett. 113, 115501 (2014), Yang et al., Angewandte Chemie 126, 9054 (2014), Lee et al., Nature 4, 1650 (2013), Lin et al., Nano Letters 15, 74087413 (2015), Kepaptsoglou et al., ACS Nano 9, 11398 (2015)

Hints Towards 2D Silicon Carbide?

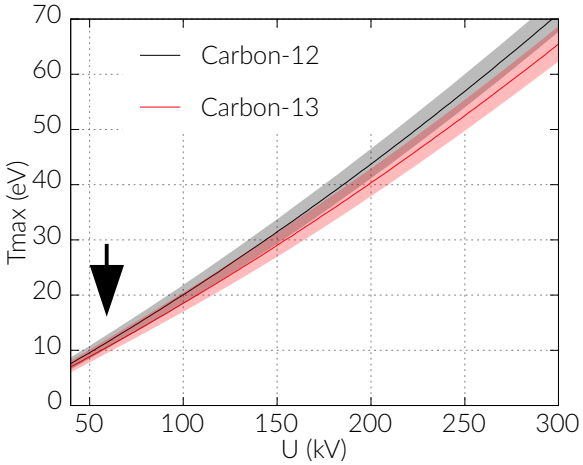
Sample: reduced graphene oxide
Imaging: Nion UltraSTEM 100 @ 60 kV, ca. 30 pA @ 10^{-9} mbar



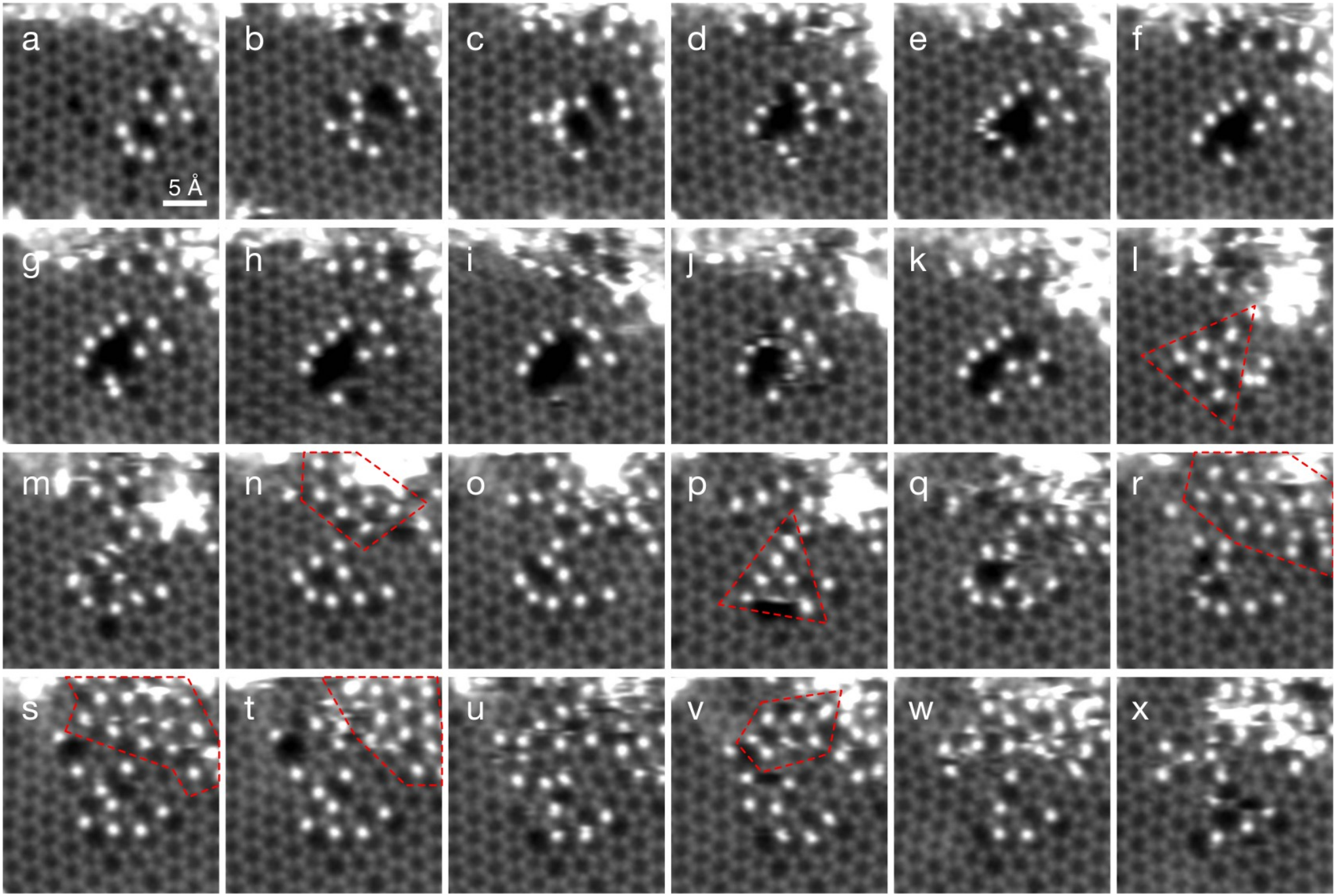
14
Si
Silicon
28.09



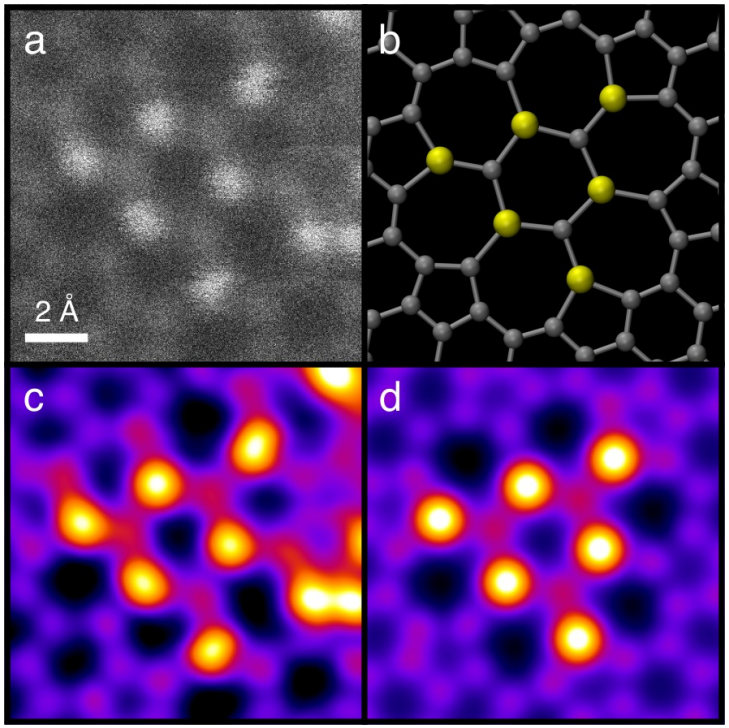
@ 60 kV ~ 4–6 eV (Si)
~ 10–13 eV (C)

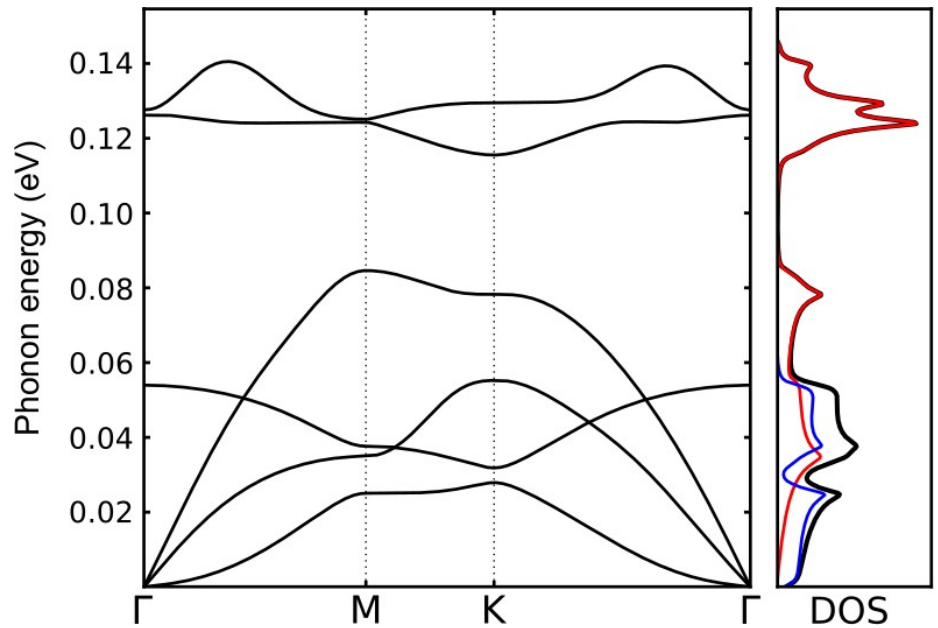


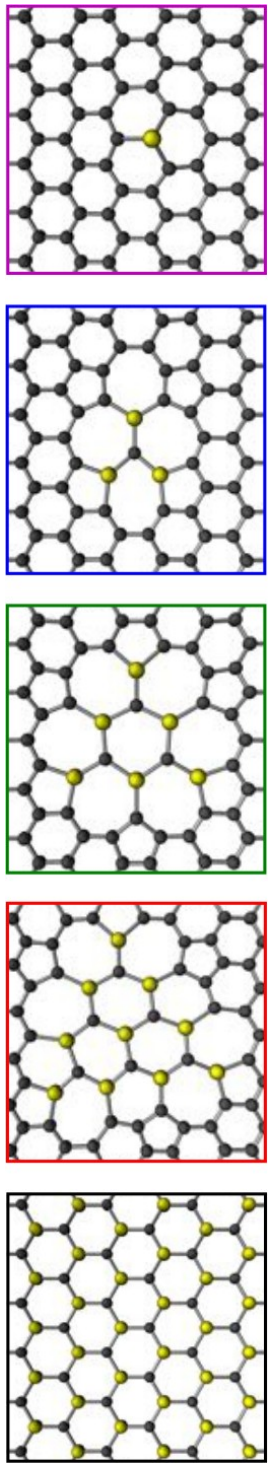
Susi, JK, et al. ,Sci. Rep. 7, 4399 (2017)



Susi, JK, et al. ,Sci. Rep. 7, 4399 (2017)







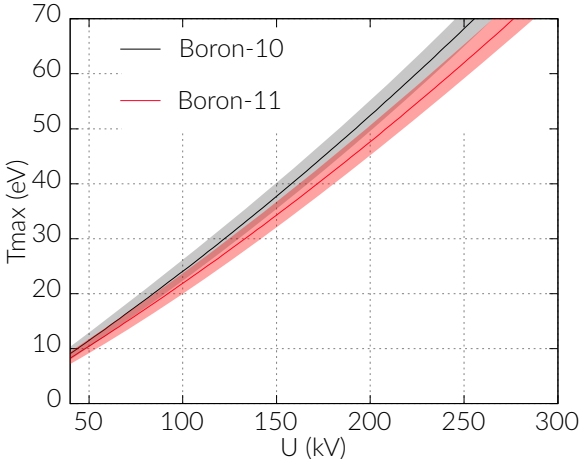
Polytype	2D-SiC	6H (α)	4H	3C (β)
Symmetry	hexagonal	hexagonal	hexagonal	cubic
In-plane lattice constant (Å)	3.104	3.0810	3.0730	4.3596
Si-C bond length (Å)	1.792	1.89	1.89	1.89
Bandgap (eV)	2.58	3.05	3.23	2.36
Bulk modulus (GPa)	98.3	220	220	250
Optical phonon energy (meV)	127	102.8	104.2	104.2
C 1s – Si 2p (eV)	182.19	181.9[45]	182.3[46]	182.17[47]

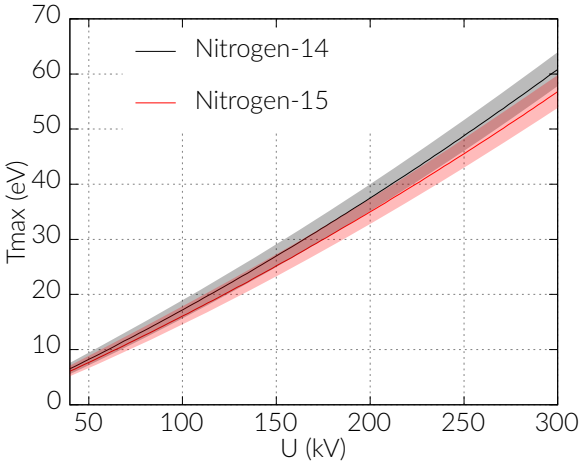
Susi, JK, et al. ,Sci. Rep. 7, 4399 (2017)

Knock-On vs. Ionization, or Both?

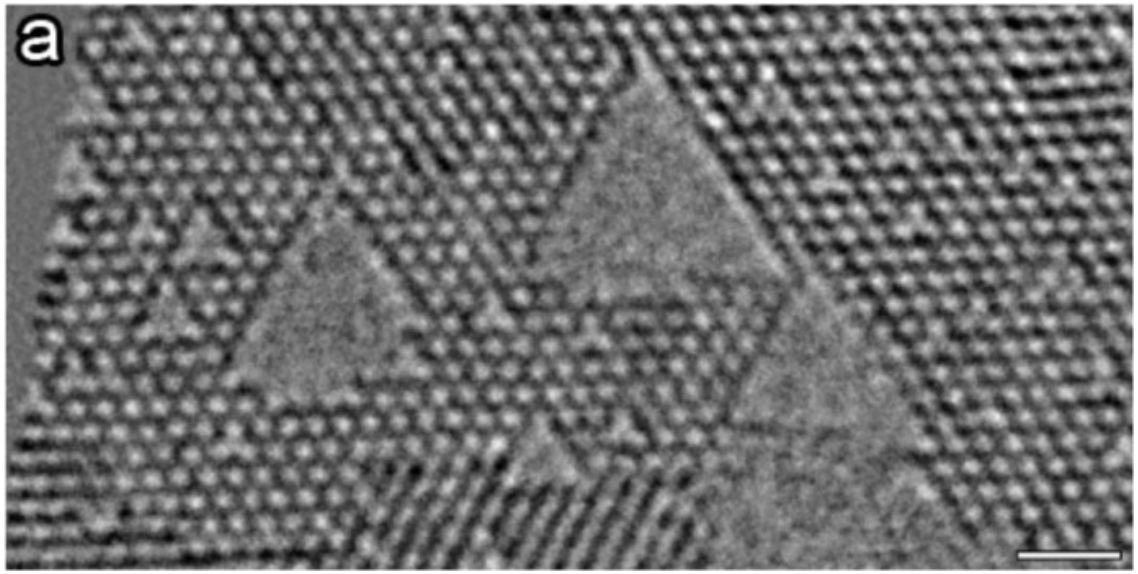
Electron irradiation of hBN

5	7
B	N
Boron	Nitrogen
10.01, 11.01	14.00, 15.00



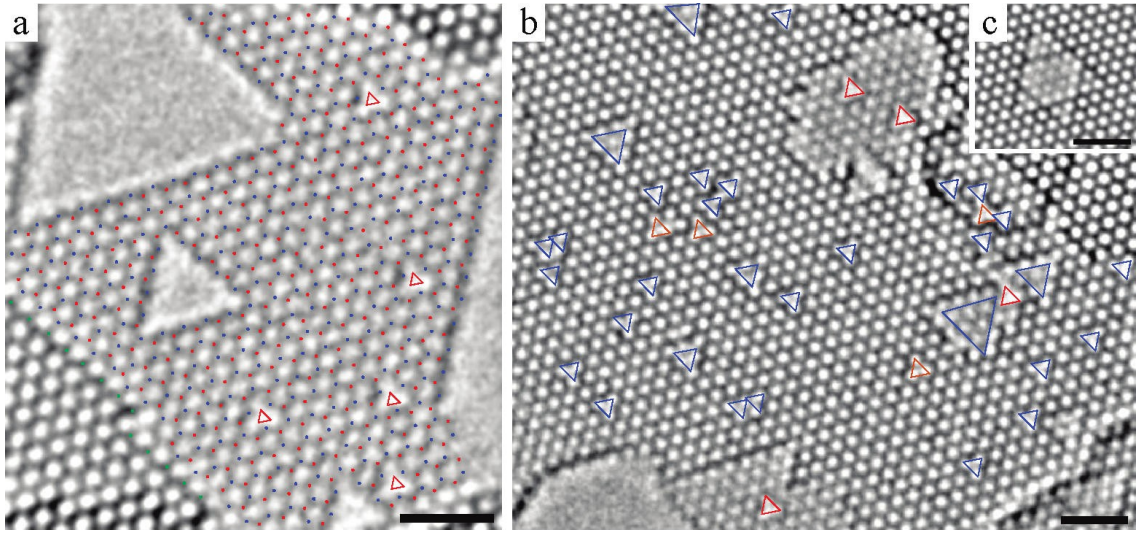


@ 120 kV

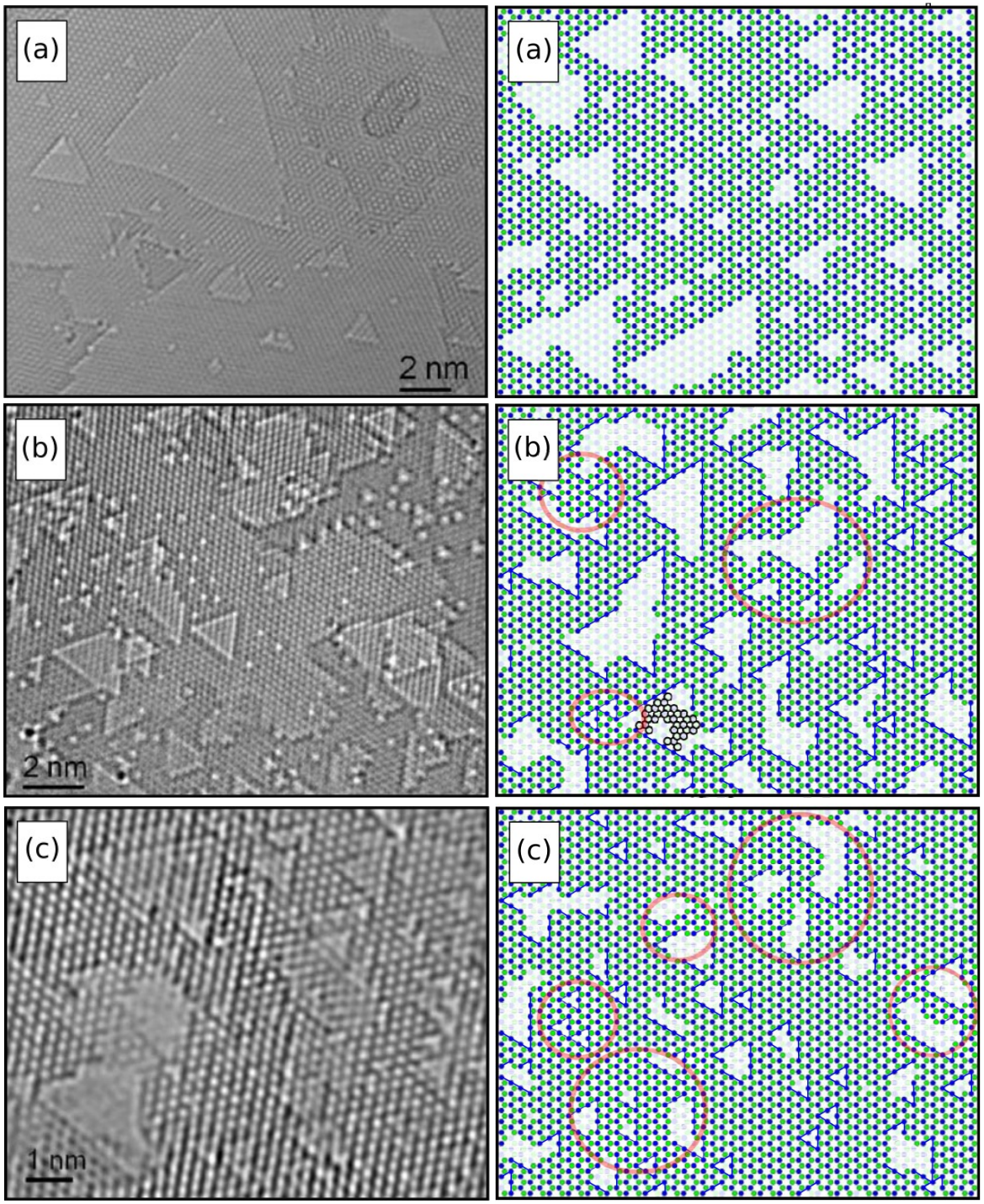


Jin et al., Phys. Rev. Lett. 102, 195505 (2009)

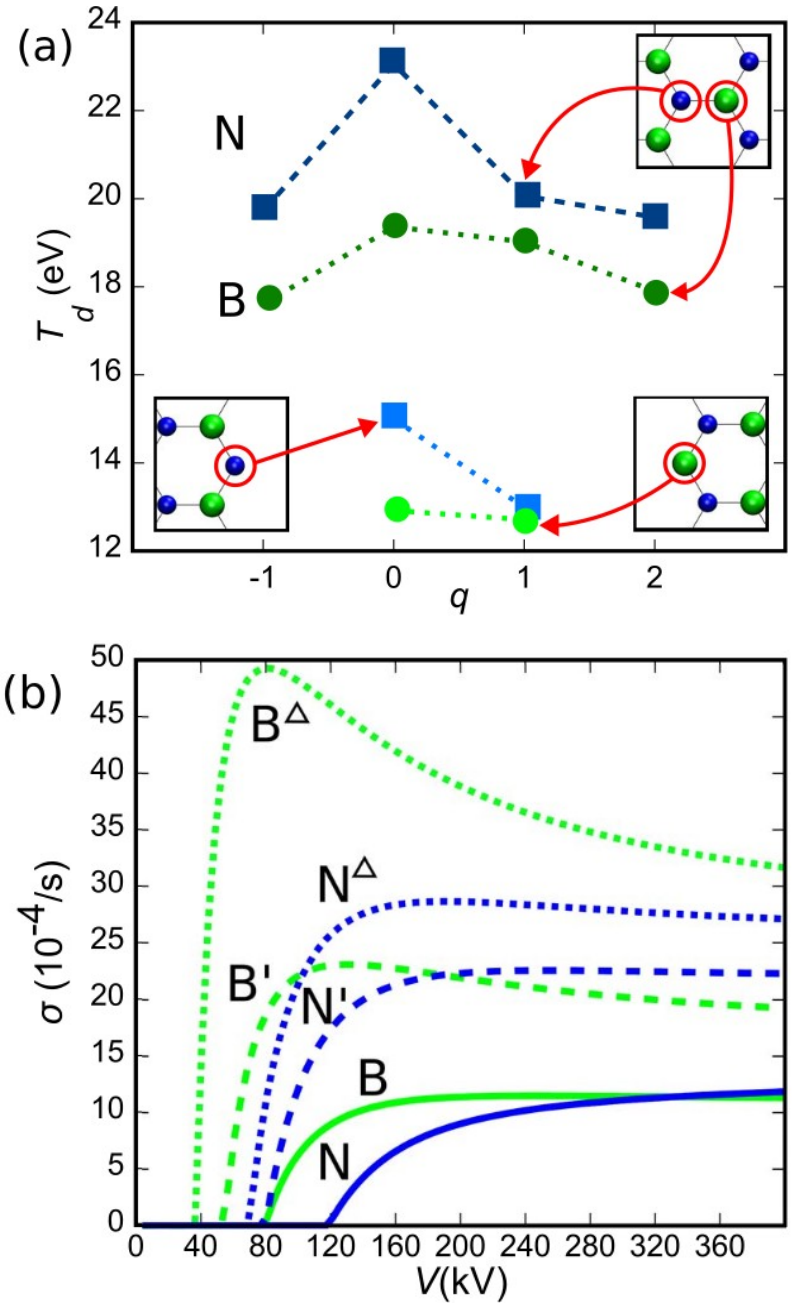
@ 80 kV



Meyer et al., Nano Lett. 9, 2683 (2009)



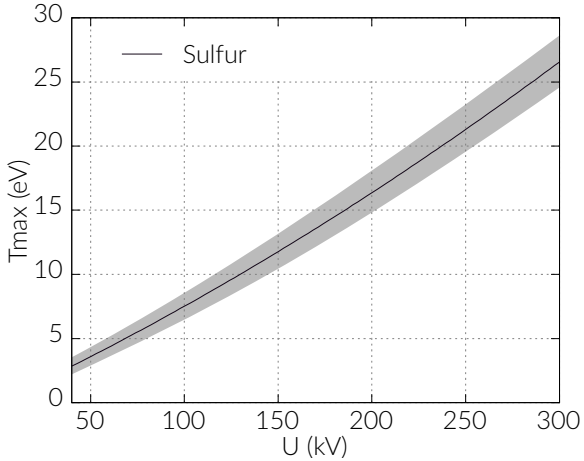
(a) 80 kV (b) 120 kV (c) 200 kV

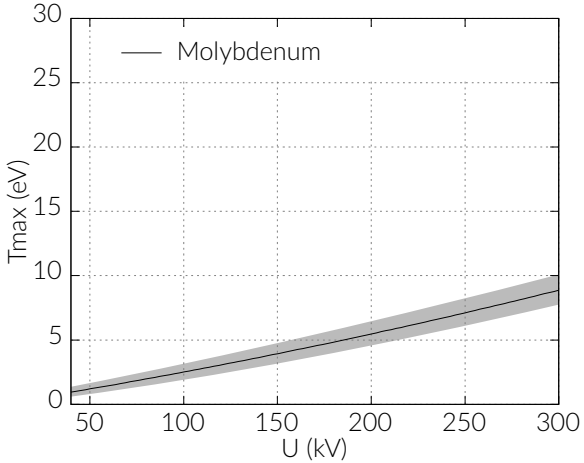


Kotakoski et al., Phys. Rev. B 82, 113404 (2010)

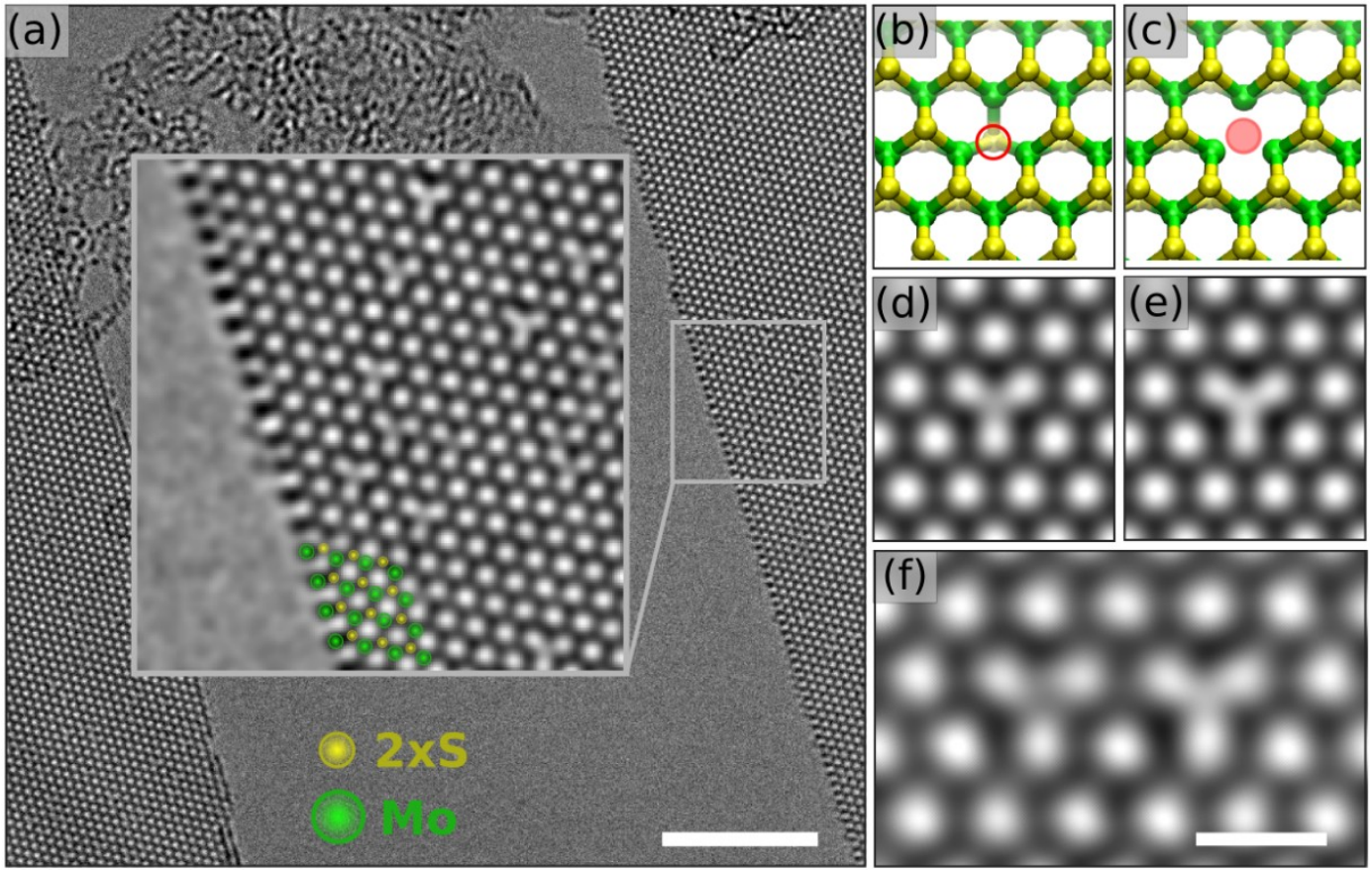
Sulfur Vacancies in MoS_2

16	42
S	**Mo**
Sulfur	Molybdenum
32.06	95.95



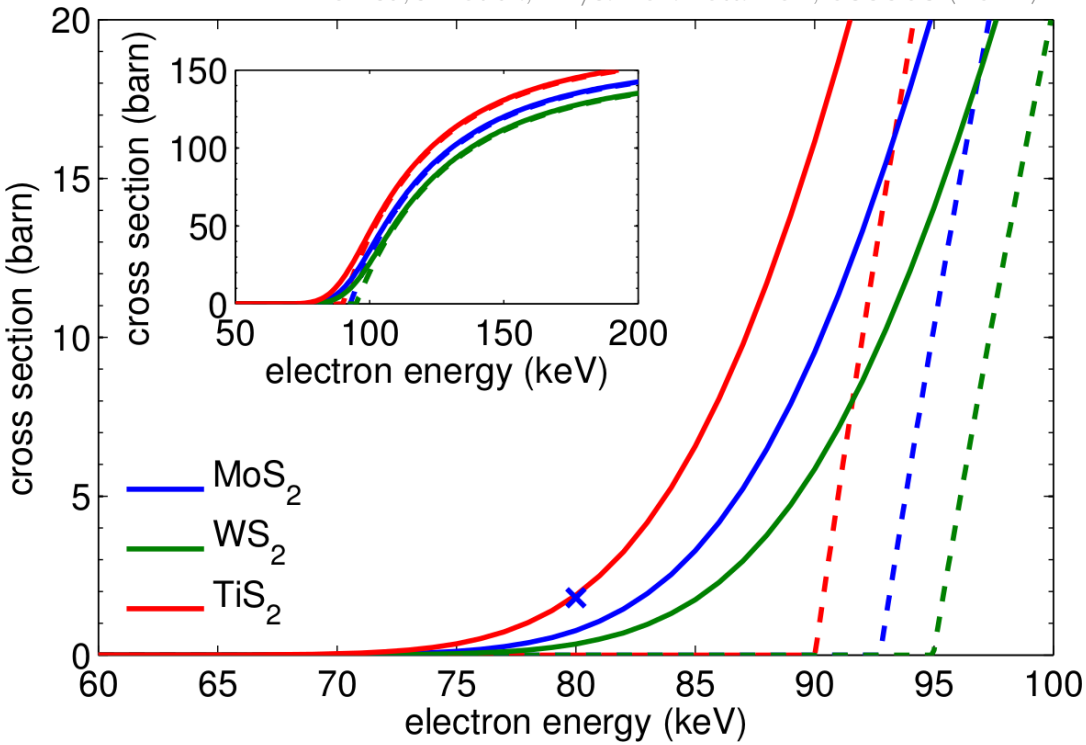


@ 80 kV

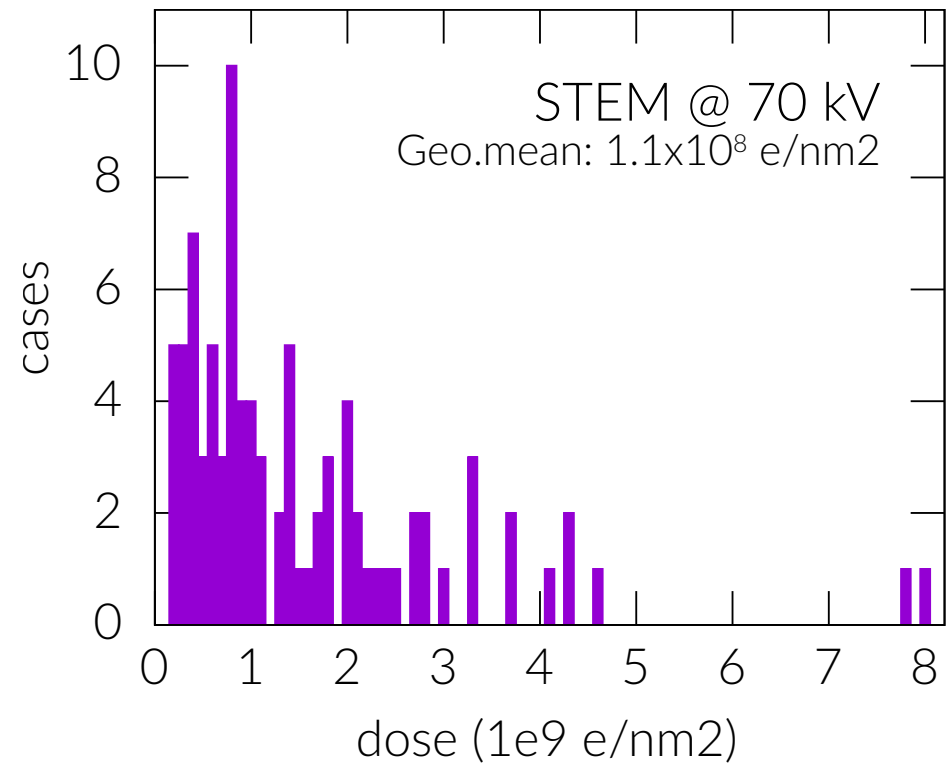


Komsa, JK et al., Phys. Rev. Lett. 109, 035503 (2012)

Komsa, JK et al., Phys. Rev. Lett. 109, 035503 (2012)



× MoS_2, HRTEM



From Knock-On to Ionization

Heavier TMDs: $MoTe_2$

Kuc, Chemical Modelling 11, 1-29 (2014)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

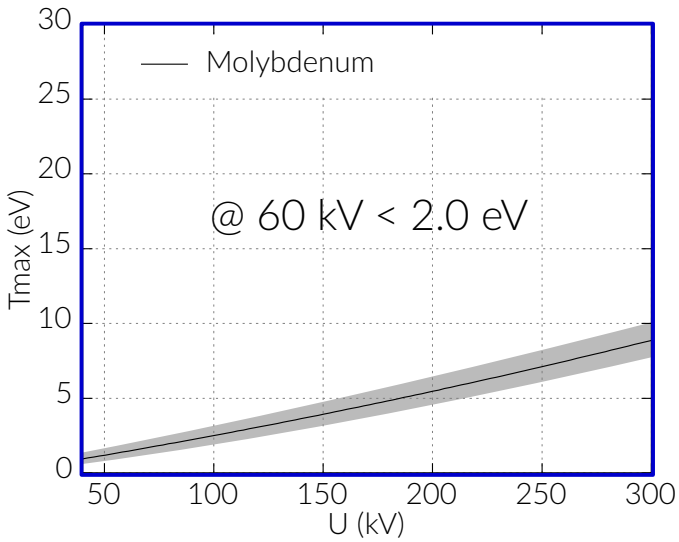
42
Mo
Molybdenum
95.95

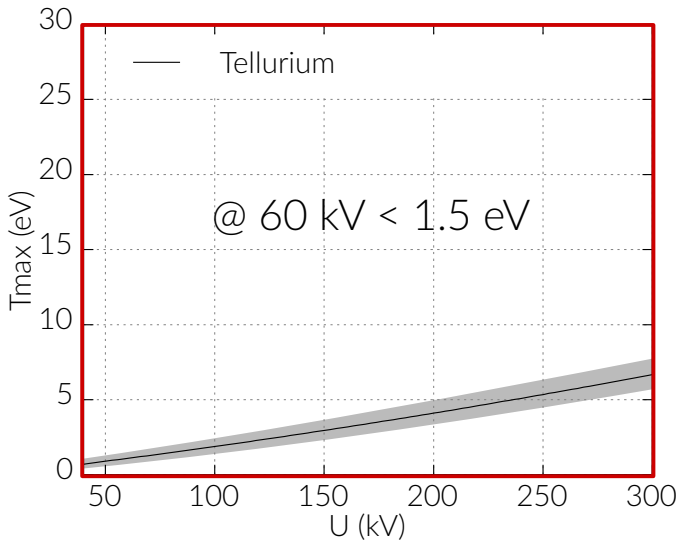
74
W
Tungsten
183.84

16
S
Sulfur
32.06

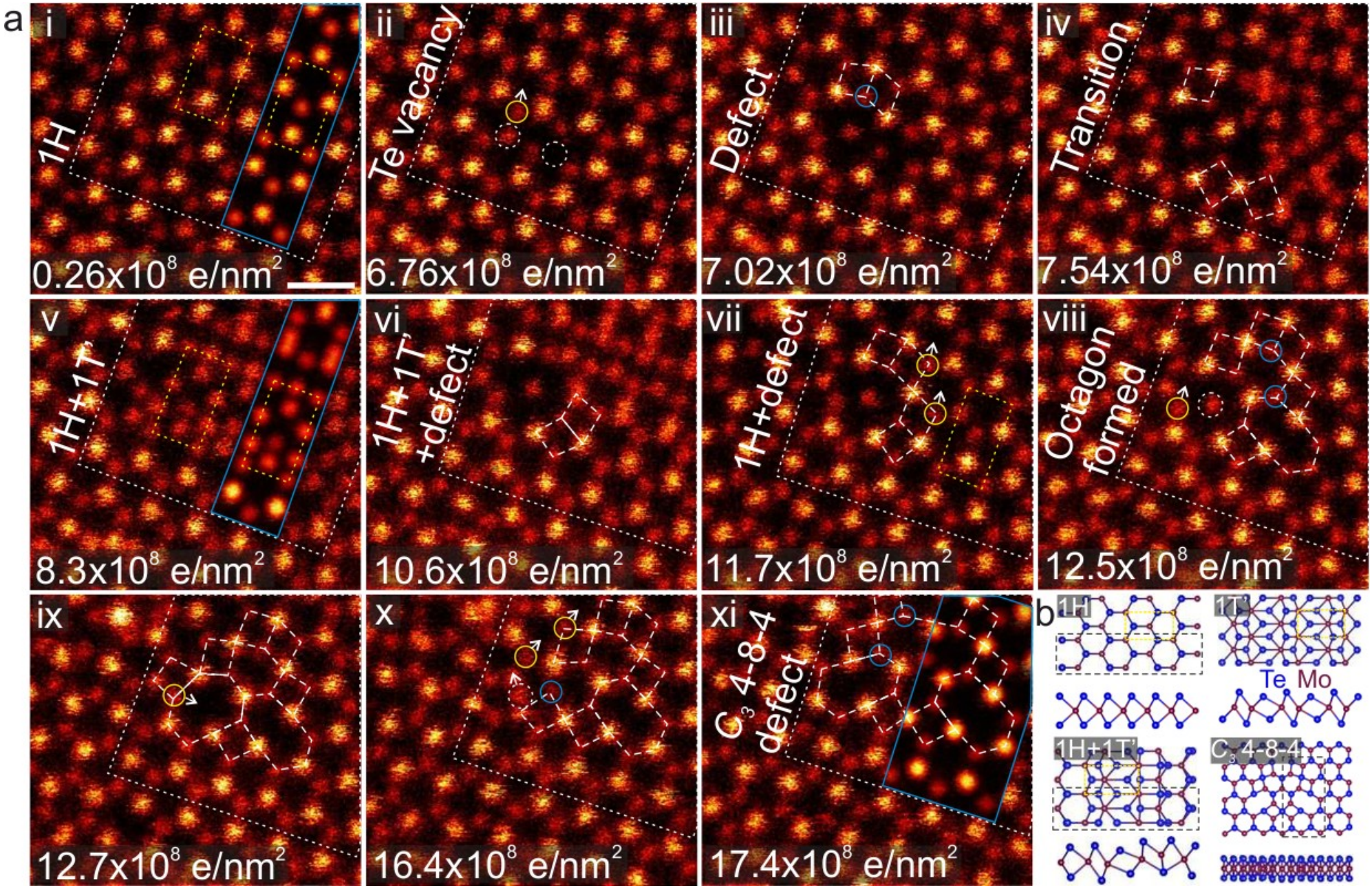
34
Se
Selenium
78.971

52
Te
Tellurium
127.60

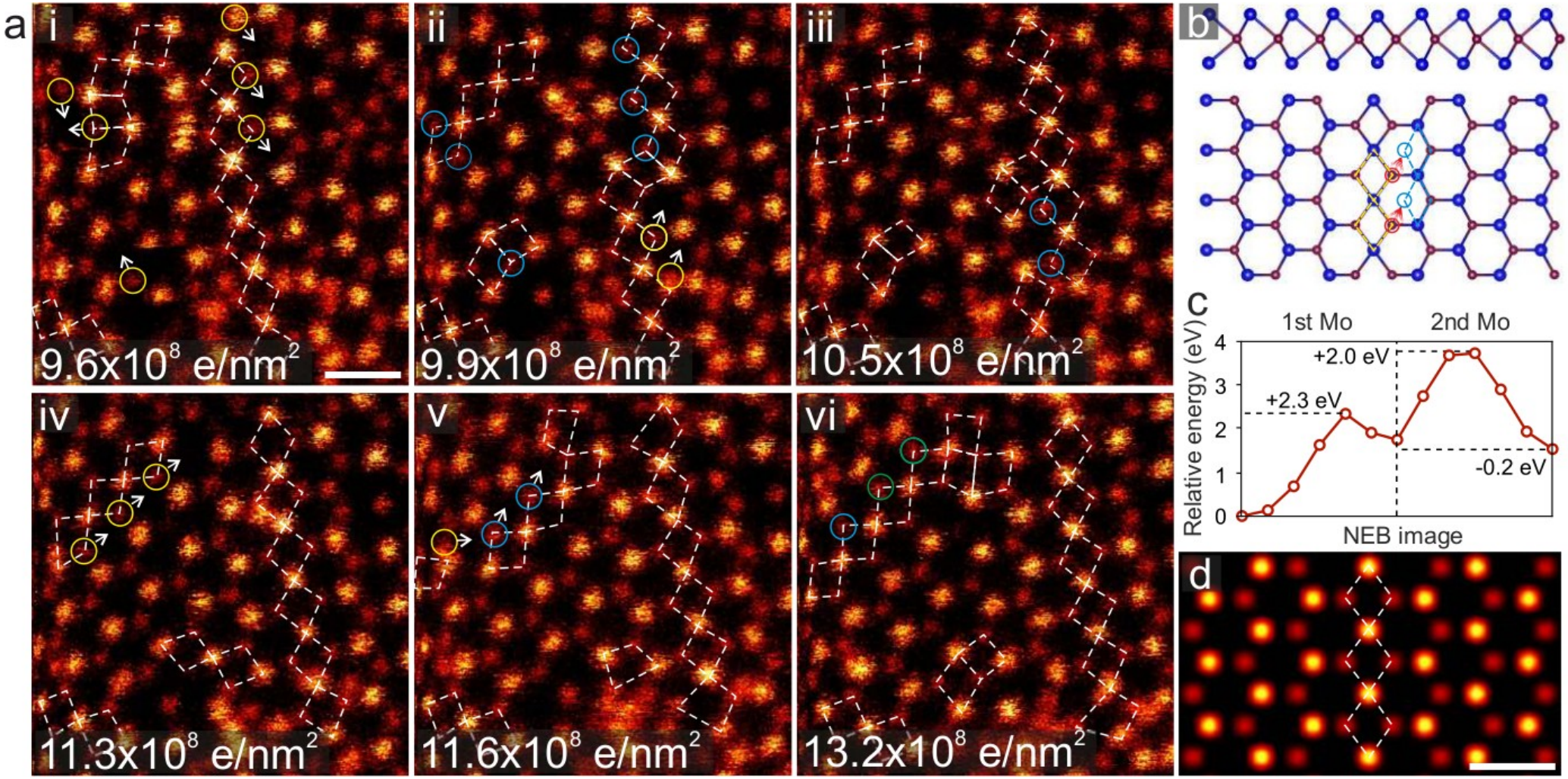




Non-knock-on dynamics

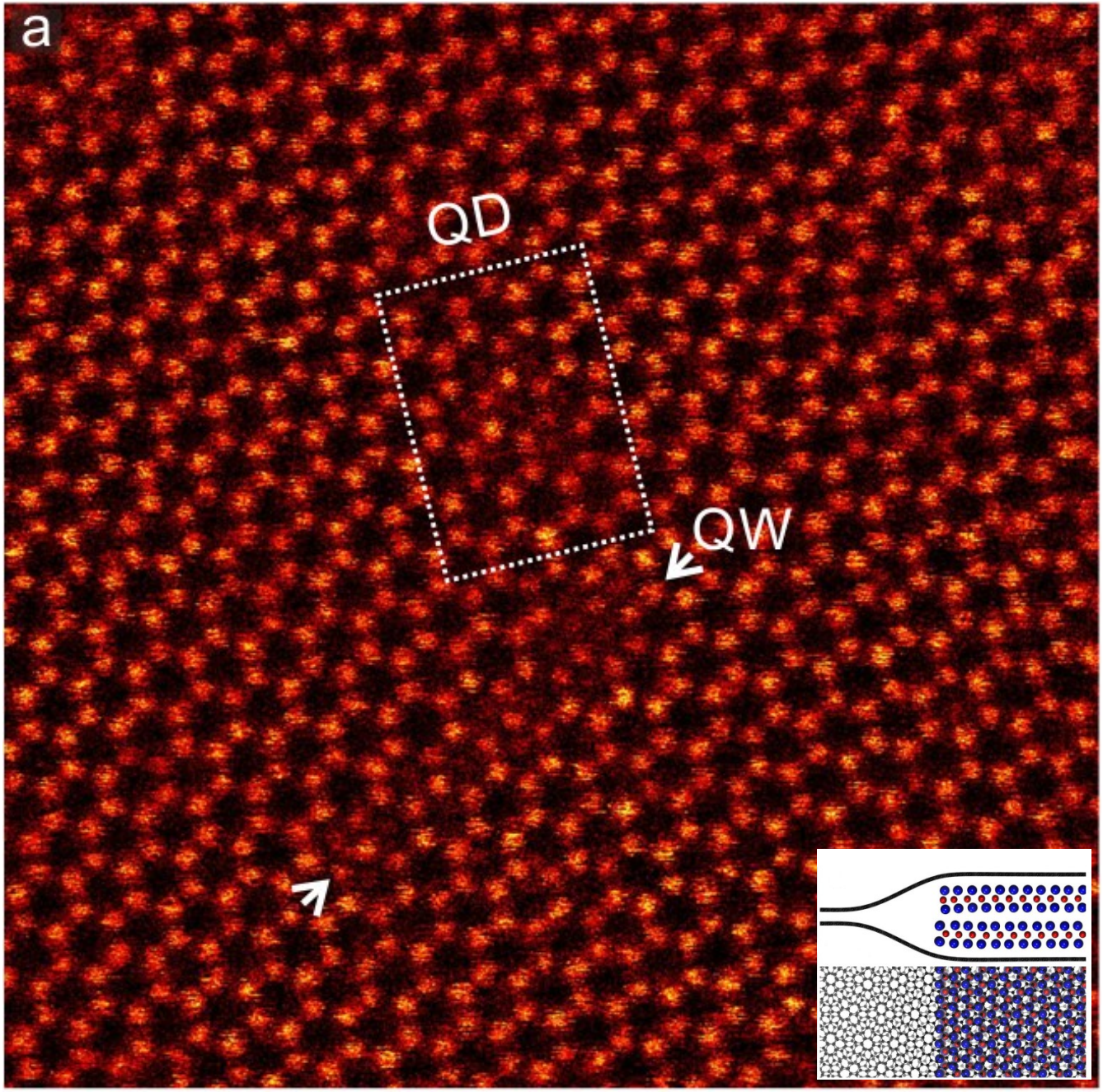


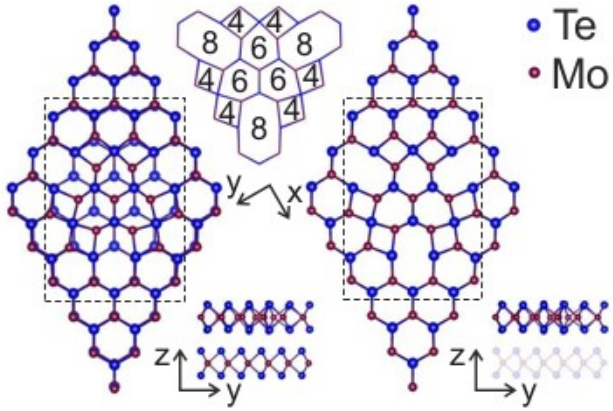
Elibol, ... , JK, Chem. Mater. 30, 1230 (2018)

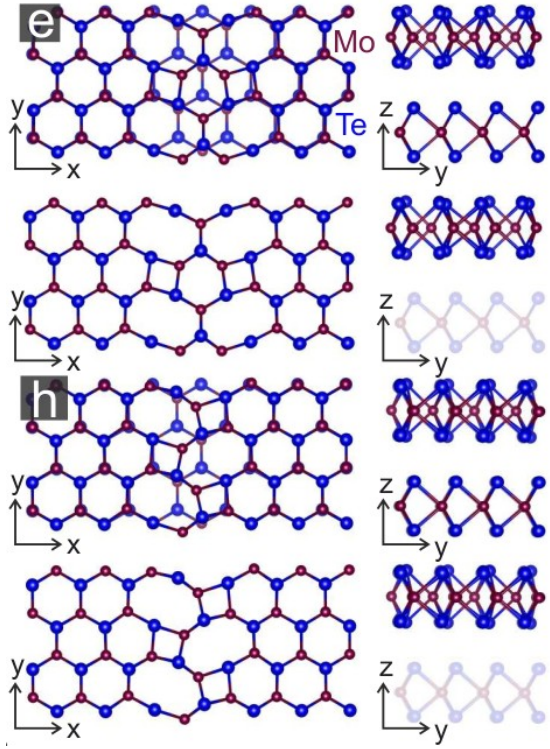


Elibol, ... , JK, Chem. Mater. 30, 1230 (2018)

Intrinsic defects





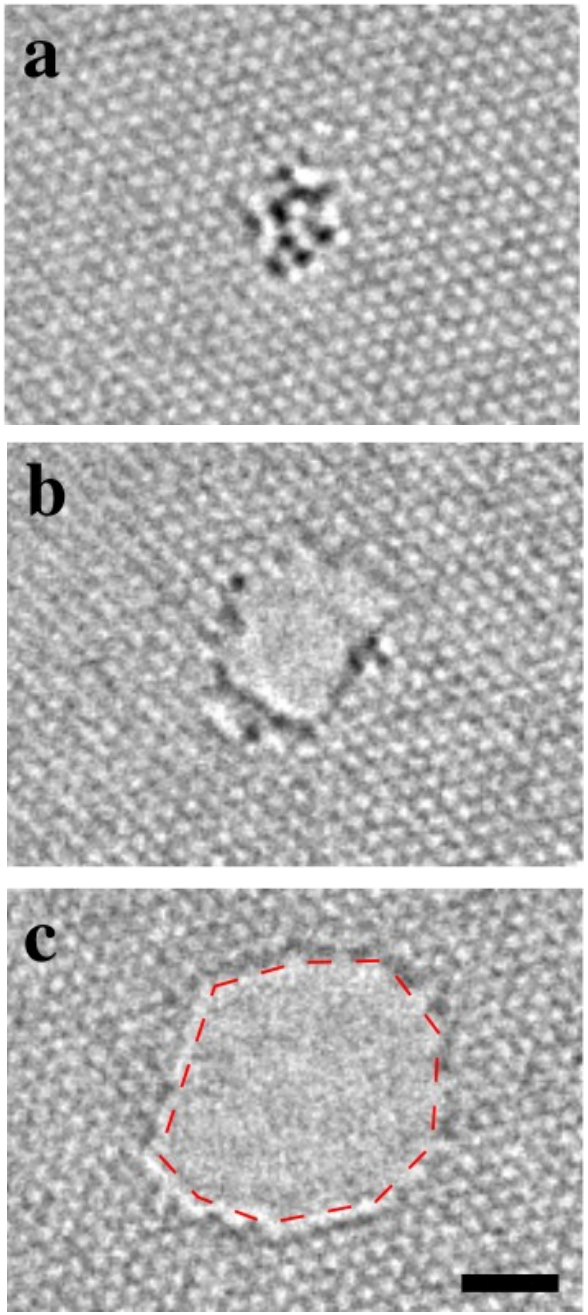


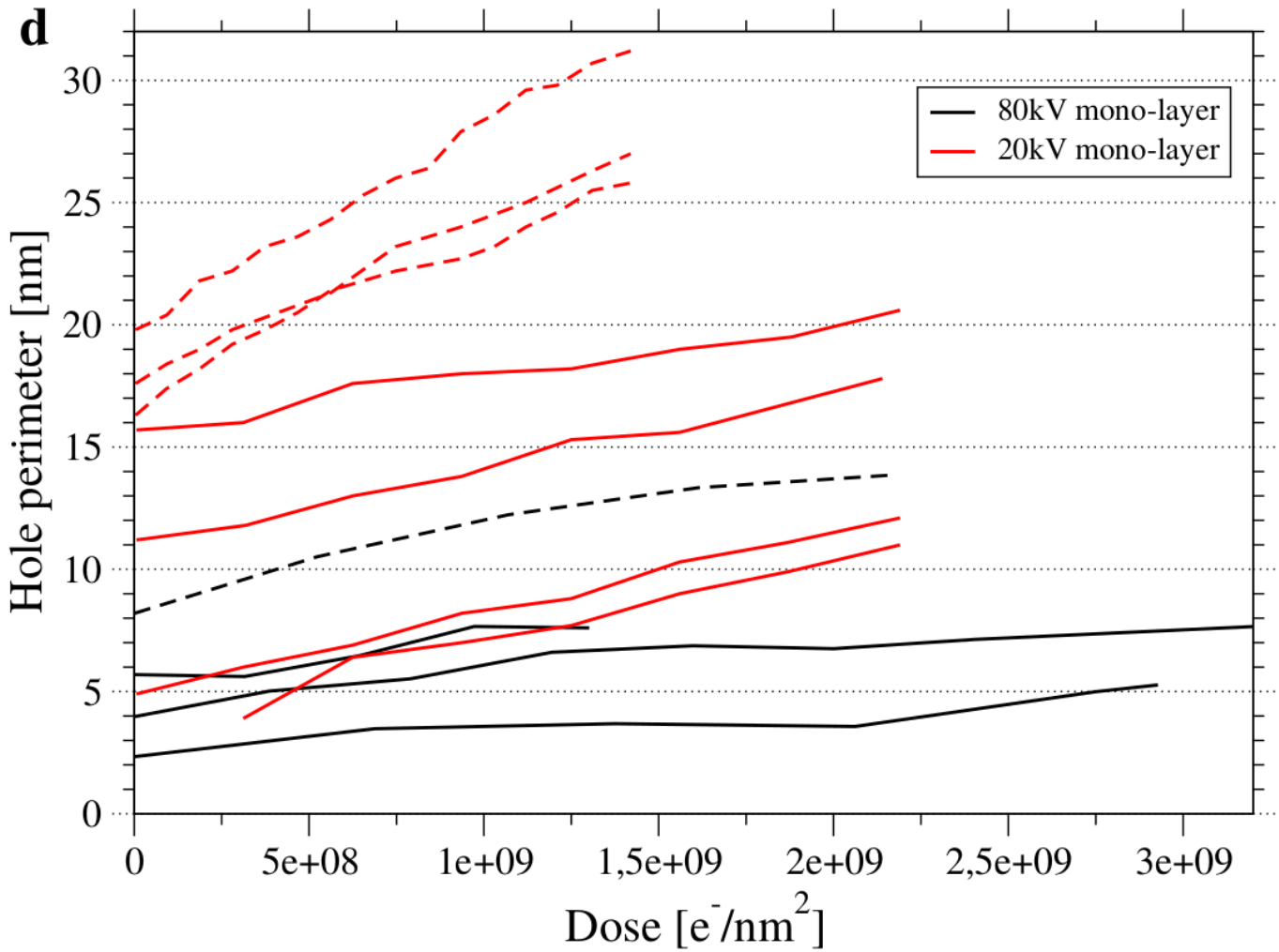
TMD-protection through sandwiching:
Algara-Siller et al., Appl. Phys. Lett. 103, 203107 (2013)

Elibol, … , JK, Chem. Mater. 30, 1230 (2018)

Graphene Edges under the Electron Beam

Typical Results in a HRTEM: Growing Holes

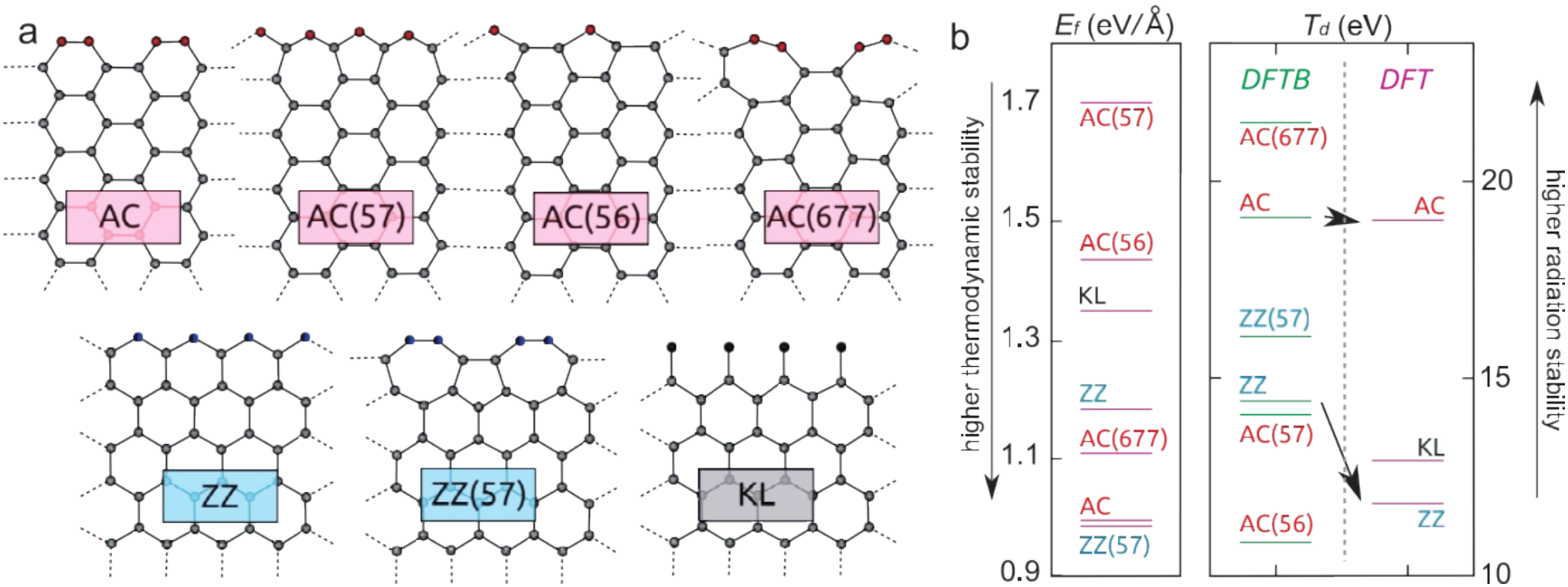




Meyer, JK, et al., Phys. Rev. Lett. 108, 196102 (2012)
See also: Girit et al., Science 323, 1705 (2009)

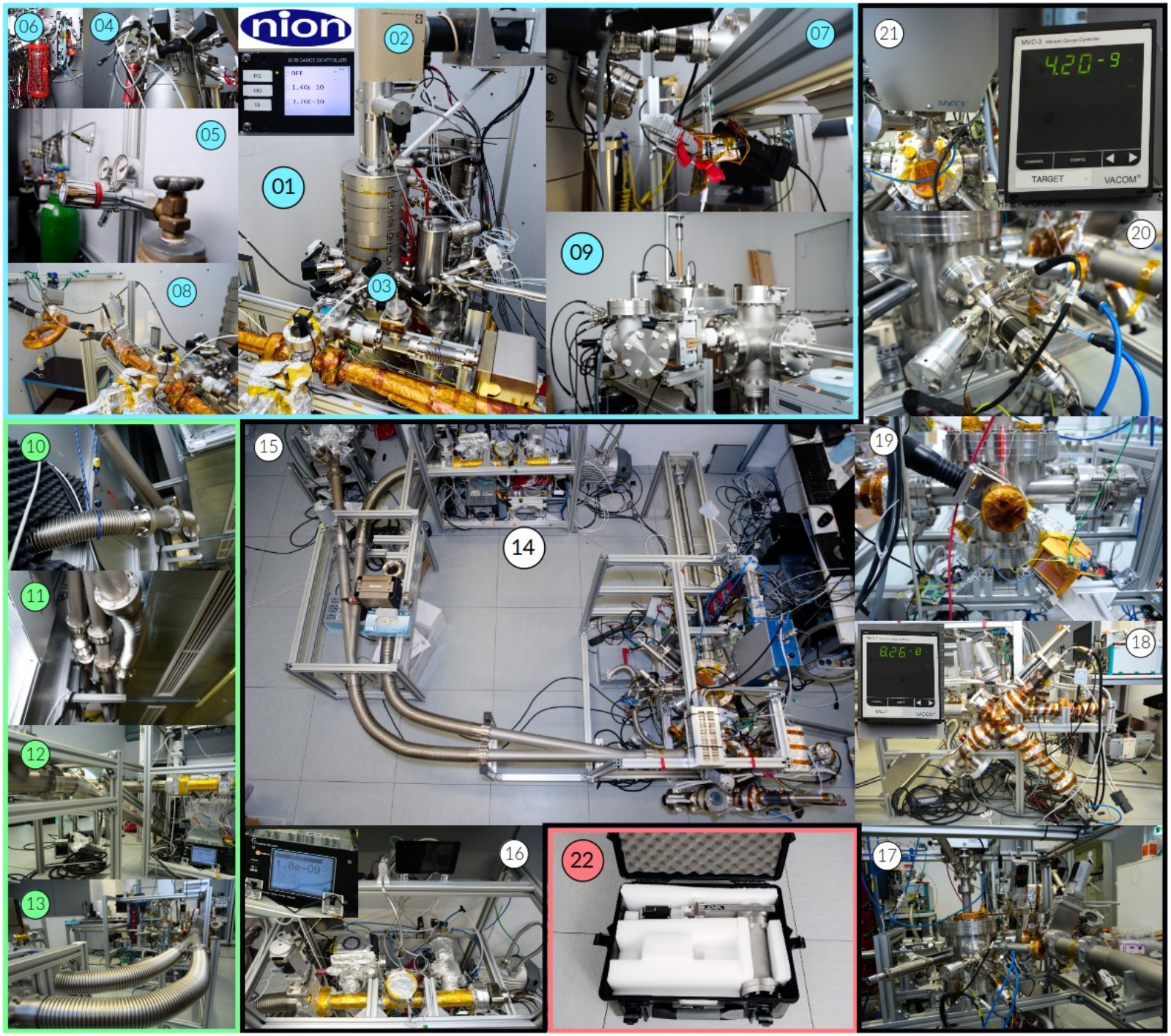
What Should We Expect?

Knock-on damage at various edges



Kotakoski et al., ACS Nano 6, 671 (2012)

Experimental setup in Vienna



1st FLOOR

01 - **Nion UltraSTEM 100**

02 - EELS
Gatan PEELS 666 spectrometer
Andor iXon 897 EMCCD

03 - Customized objective area
04 - Leak valve
05 - Gas distribution line
06 - Non-evaporating getter (NEG)
Pressure @ sample: 1.4e-10 mbar
07 - 6W diode laser (445 nm)
08 - Custom UHV sample entry

09 - **Getec self-sensing AFSEM**
(installation to finish in 2018)

TRANSFER

10 Line out from microscope room
11 To AFM and 2nd floor
12 Entry to 2nd floor
13 To loadlock and manipulation

2nd FLOOR

14 **2nd floor setup**

15 Storage for samples

16 Load lock and bake (150°C)

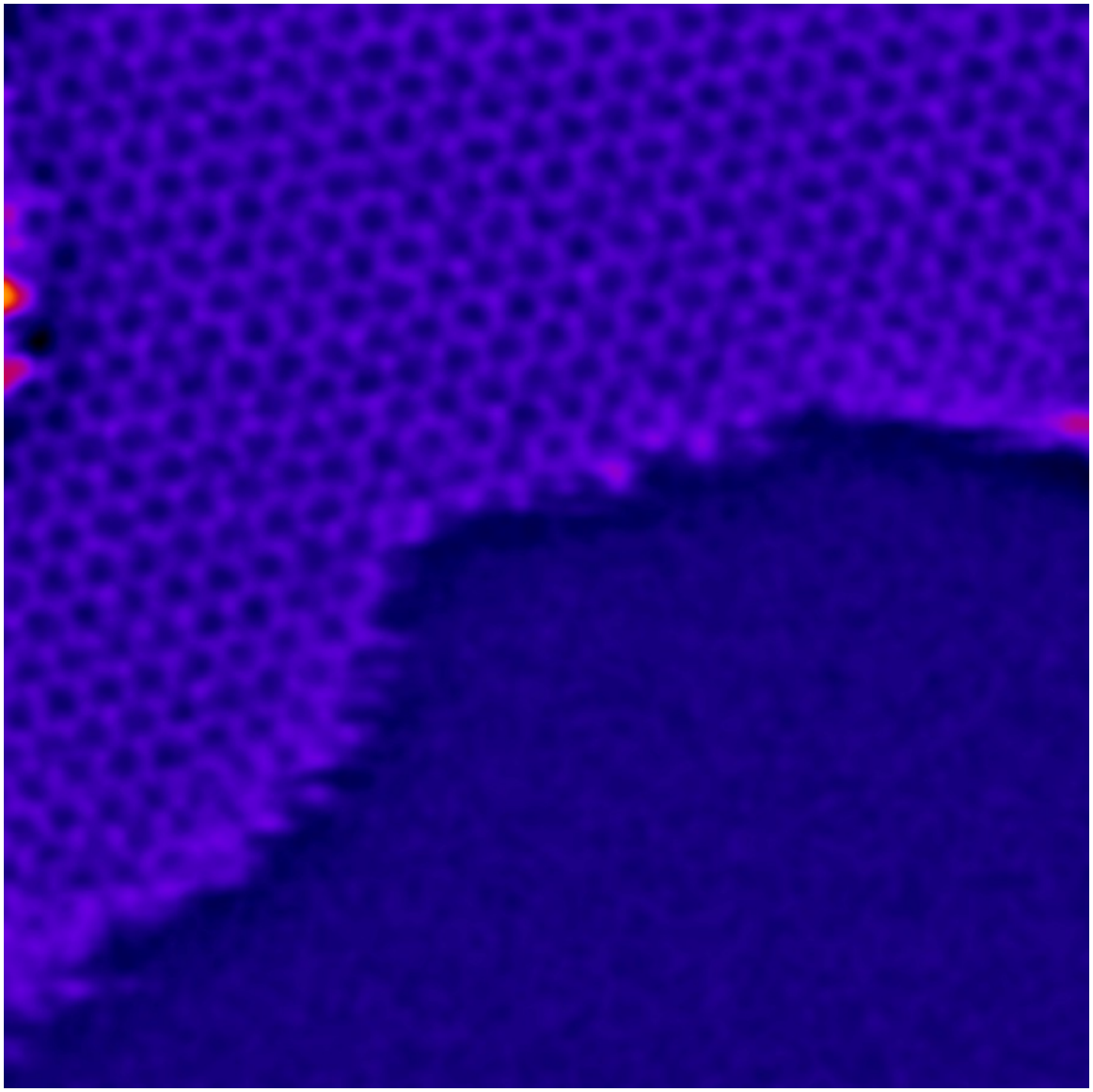
17 Manipulation system
18 Knudsen evaporation cell
19 Ion beam entry & 6W diode laser
(ion beam to arrive in 2018)
20 e-beam evaporator
21 Plasma ion source

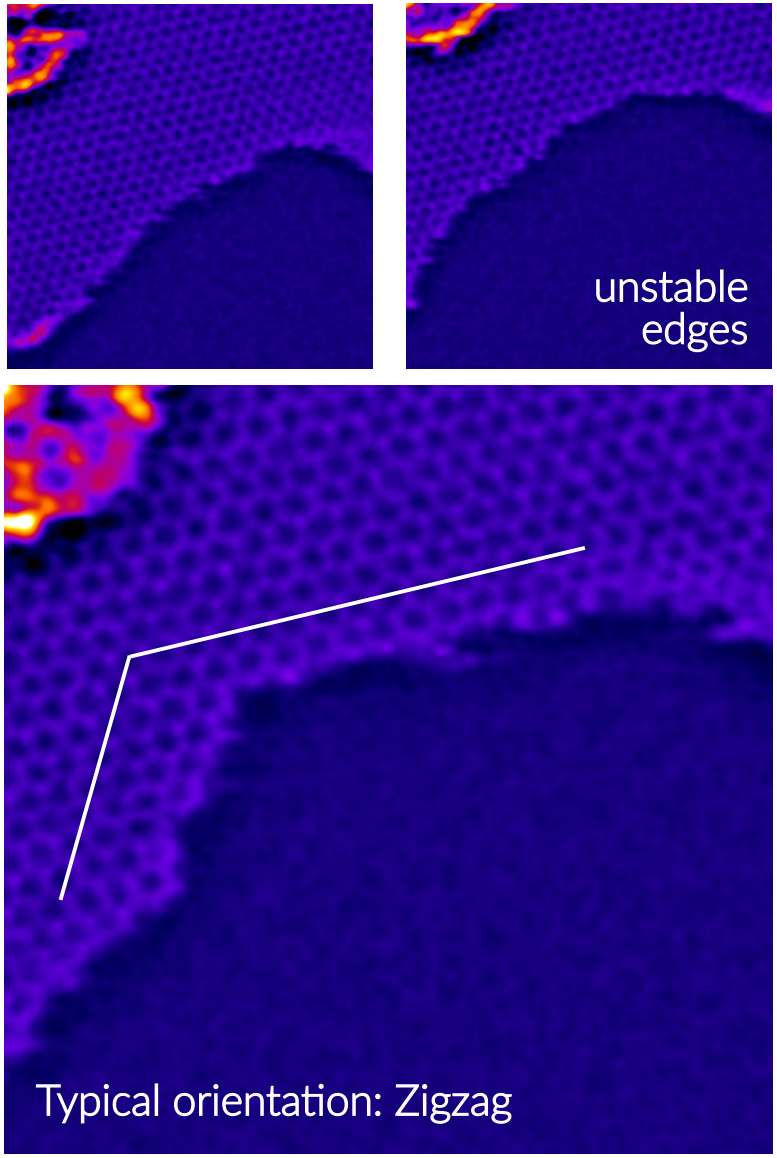
SUITCASE

22 **Ar+ suitcase** (sample transfer)

… in a STEM at 10^{-7} to 10^{-6} mbar (O_2)

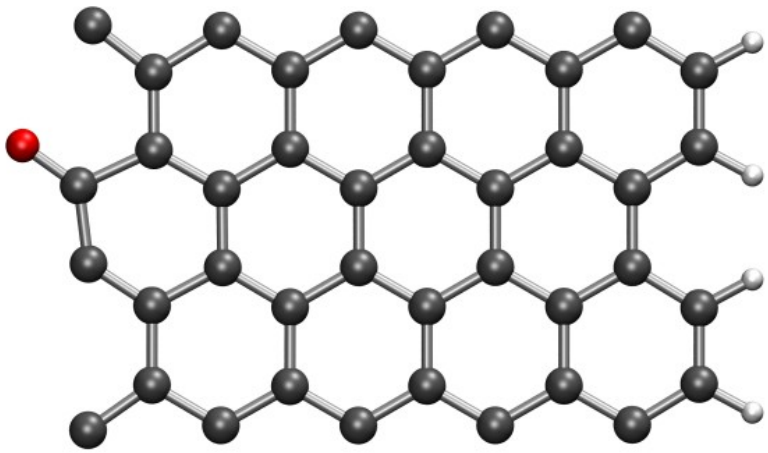
STEM imaging at 60 kV

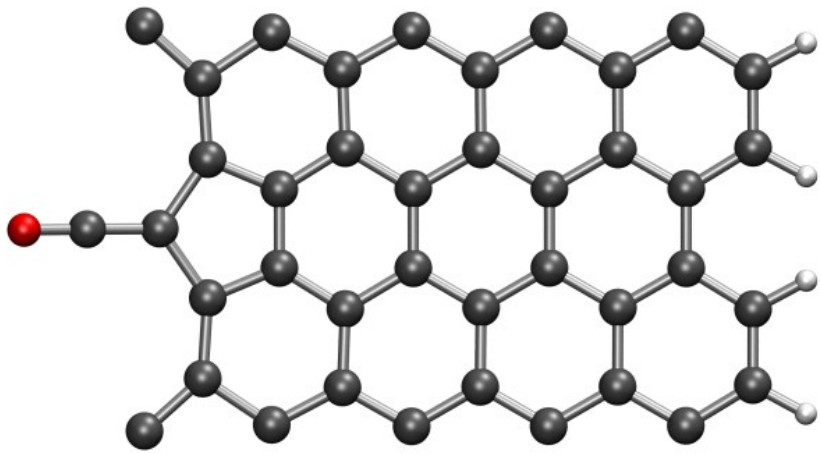




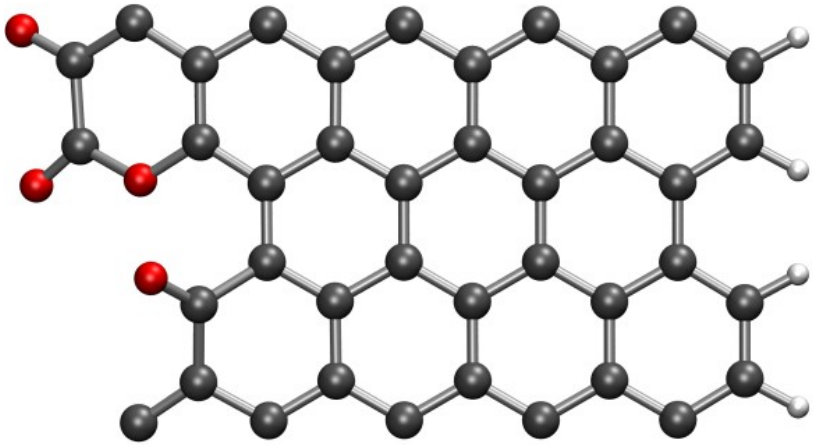
Leuthner et al., in preparation

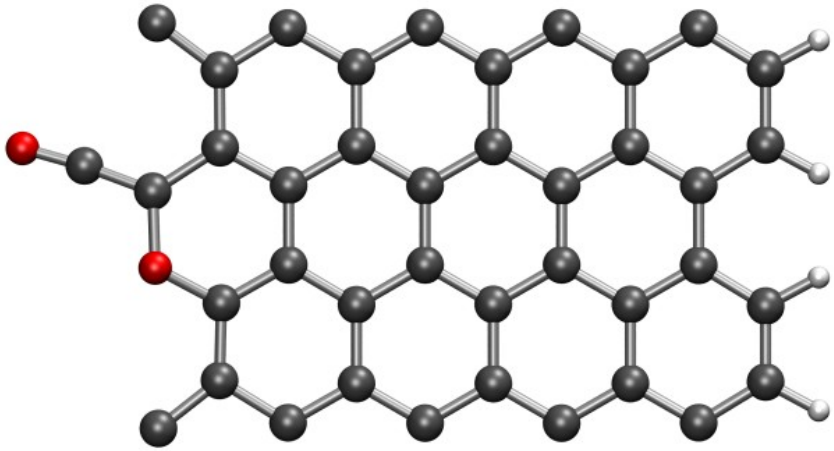
Near-barrierless reconstruction





Absorbing more O atoms on C–C bridges…



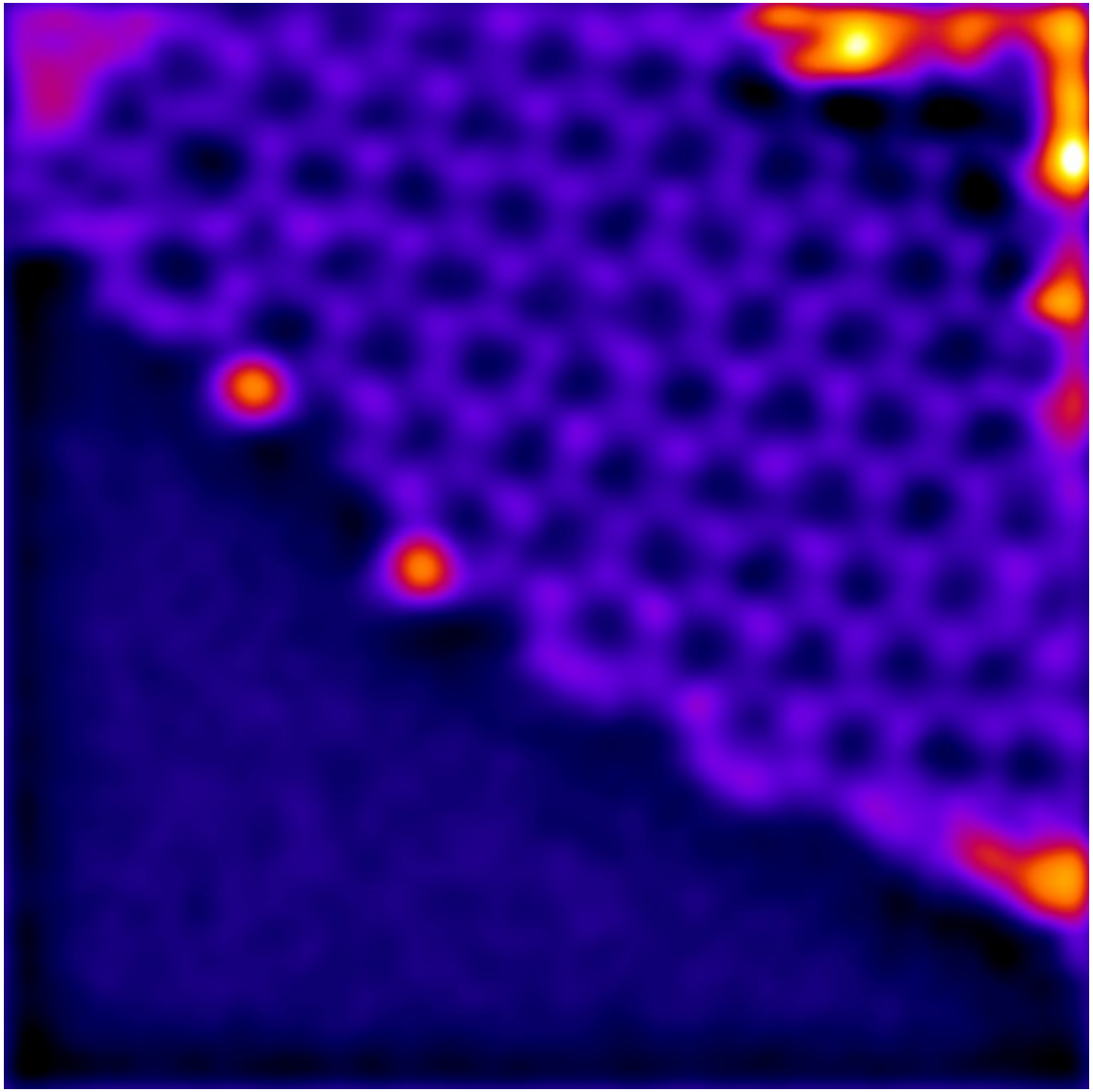


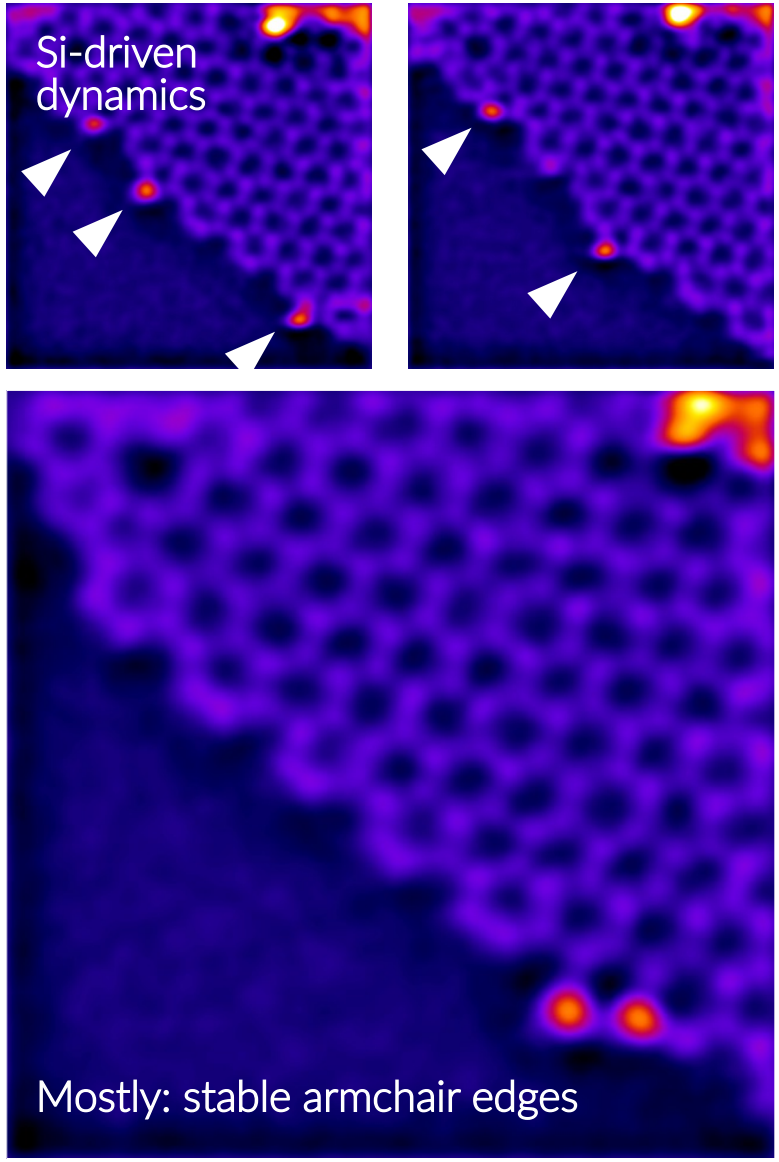
…leads to the edge unraveling with no barrier

Leuthner et al., in preparation

How About in UHV?

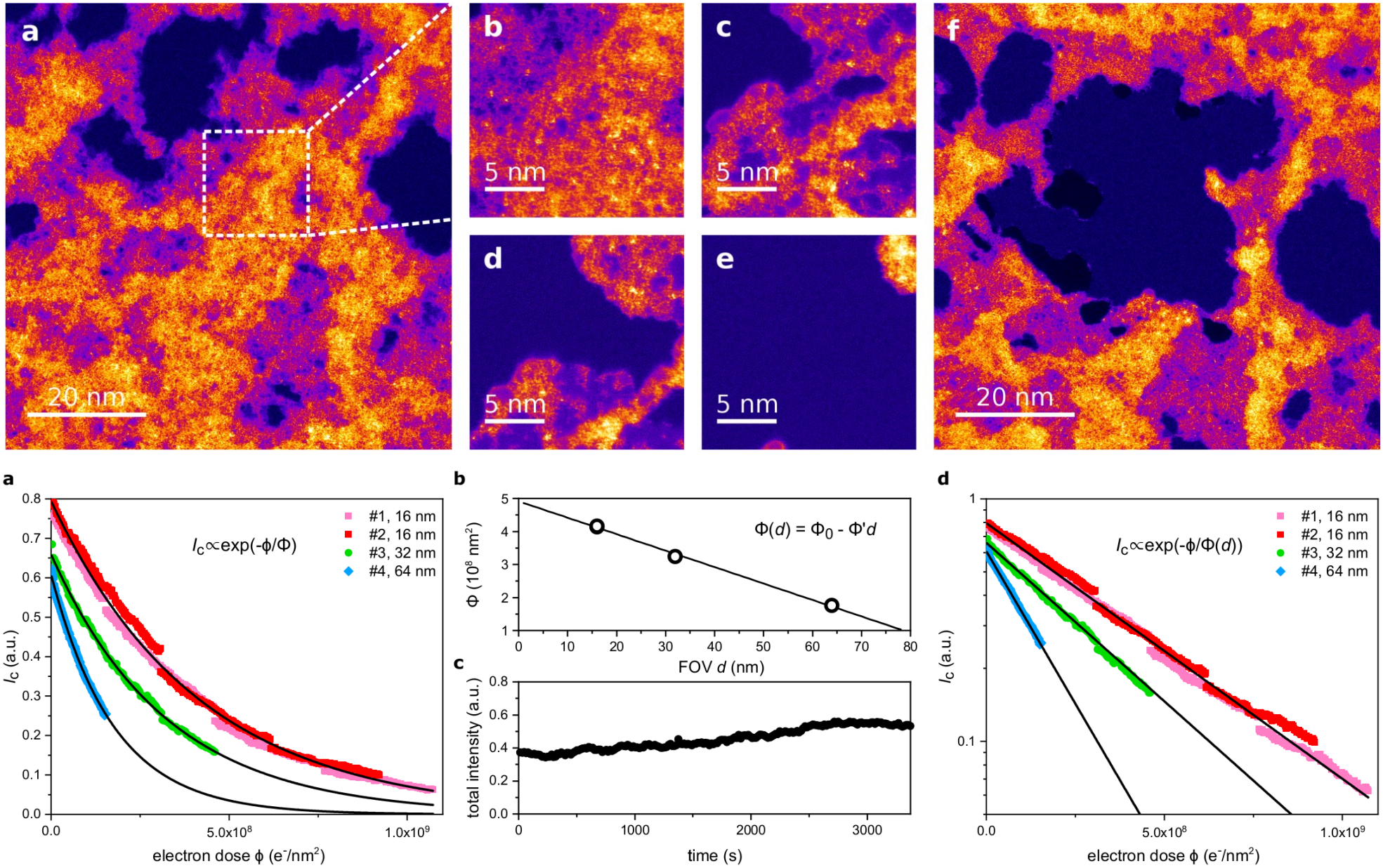
STEM imaging at 60 kV and ca. 2×10^{-10} mbar





Leuthner et al., in preparation

Etching-Induced Cleaning @ 10^{-7} mbar (Air)



Leuthner et al., in preparation

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