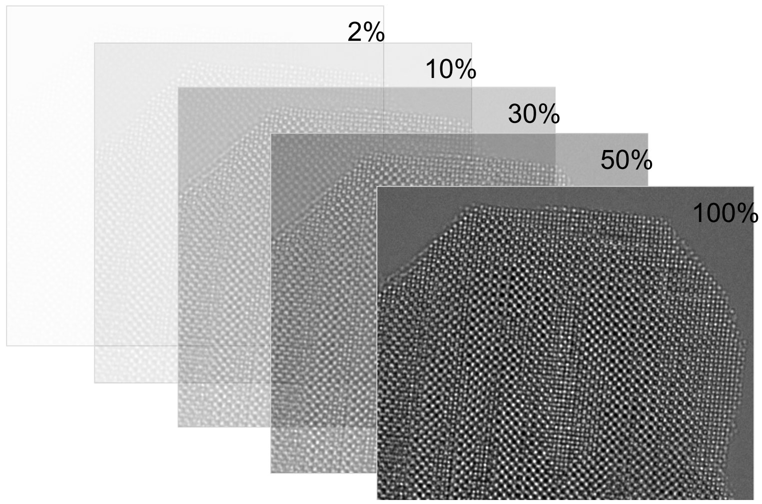
What are the Challenges?

If you can't Detect it then you can't Measure it!

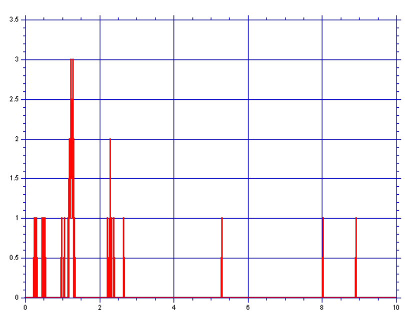


$$Intensity = \Gamma_{scatteringprobability} \bullet N_{atoms} \bullet \eta_{electrons} \bullet \tau_{time} \bullet \Omega_{efficiency}$$

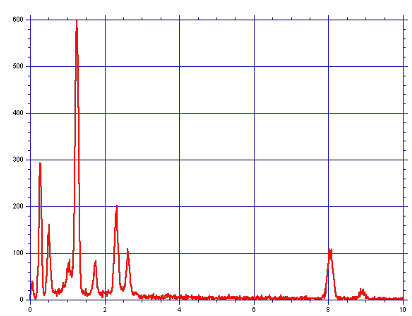
1

One of the important limiting factors in
Imaging or Spectroscopy is Signal

100 µsec



100 sec

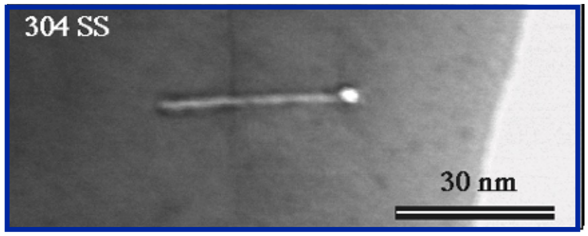


$$Intensity = \Gamma_{scatteringprobability} \bullet N_{atoms} \bullet \eta_{electrons} \bullet \tau_{time} \bullet \Omega_{efficiency}$$

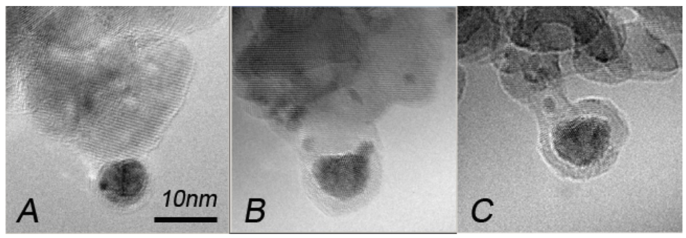
2

Electron Damage can take many forms
depending upon the material and the probe conditions

Focussed
Probe



Broad
Beam

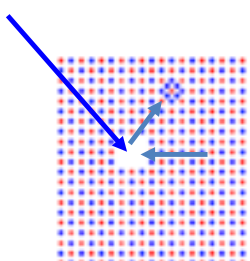


Au NP / ZnO

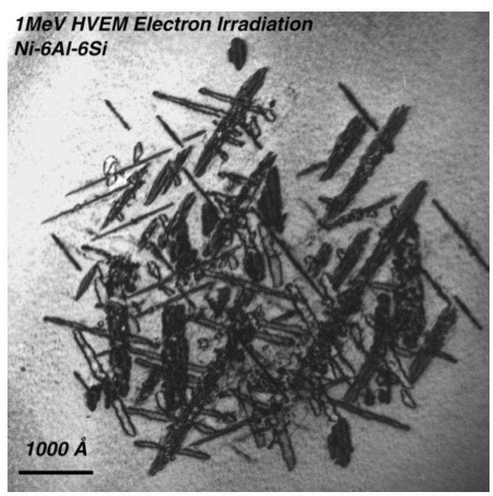
3

Displacement Damage in Crystalline Materials

Damage Creation Event/Process



Mobile
Vacancy & Interstitials
Created



4

Two **mechanisms** of irradiation damage:

Knock-on displacement (due to elastic scattering)

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

Disappears for beam energy < **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)

5

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

Grays = C/cm^2 X [E_{av}(eV) / IMFP(nm)] [10^4/ ρ(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

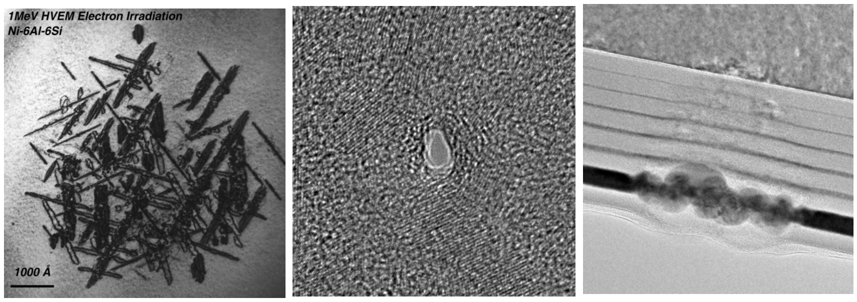
Critical or characteristic dose D_c:

Amino acid (l-valine): 0.002 C/cm^2 = 5 MGy

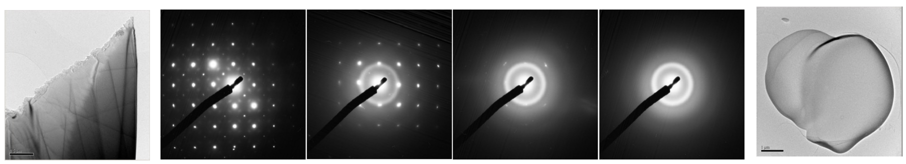
Chlorinated Cu-phalocyanine: 30 C/cm^2 = 75,000 MGy

6

Radiation Damage in Hard vs Soft Materials
Displacement versus Ionization



Atomic Displacement — Sputtering — Melting

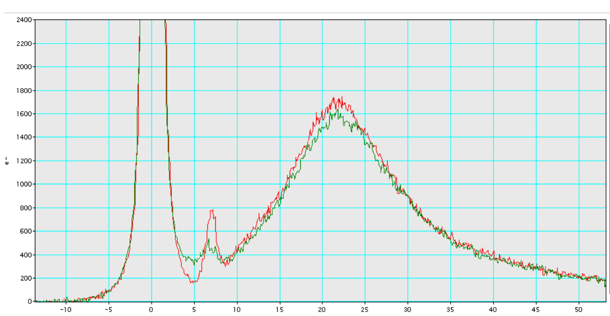


$0.0\ D_c$ — $0.4\ D_c$ — $0.8\ D_c$ — $1.0\ D_c$

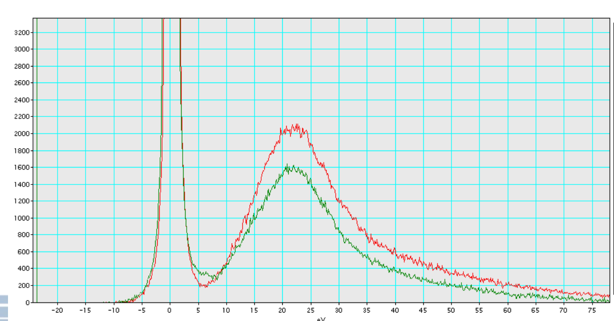
Amorphization

7

Polystyrene : Radiation Damage Effects on 7 eV Loss Peak



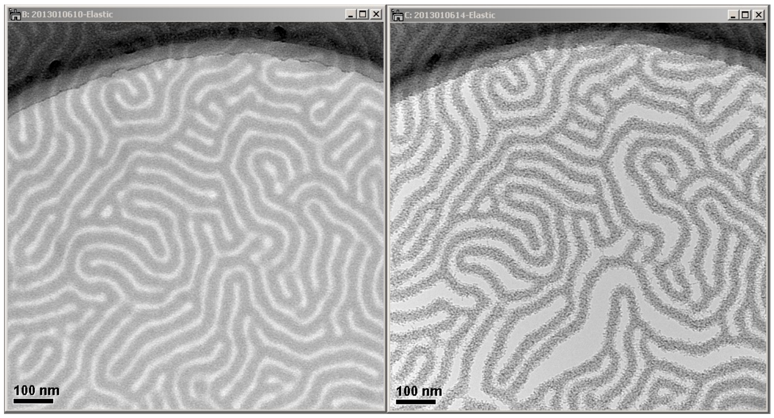
PMMA: Radiation Damage Effects on Low Loss "Plasmon" Peak



Start Spectrum
End Spectrum

8

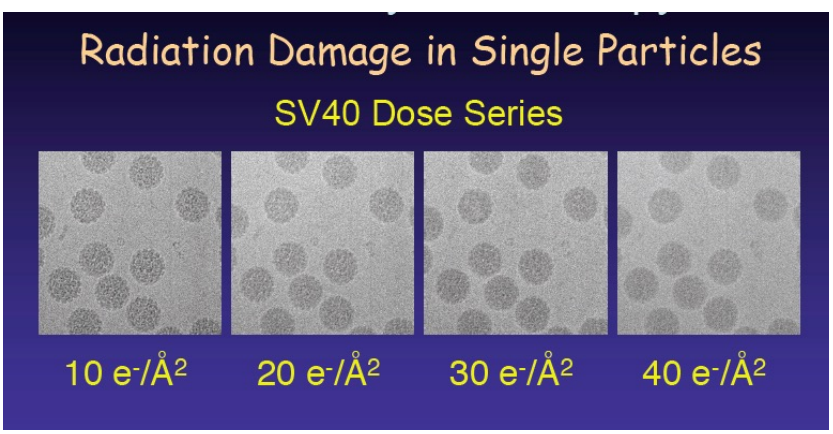
Radiolysis of Soft/Organic Matter



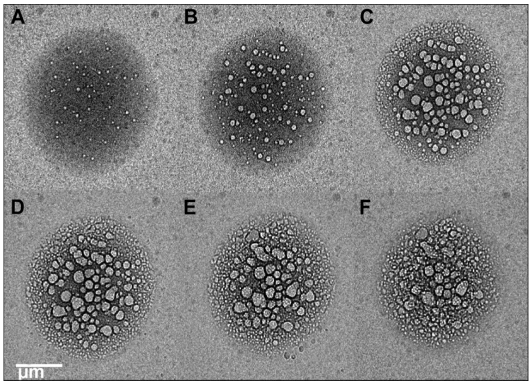
Soft Matter Imaging Limit ~ few tens, to hundreds, to few thousand e/Å^2

100 keV @ 1 e/Å^2 ~ 4 MGrey

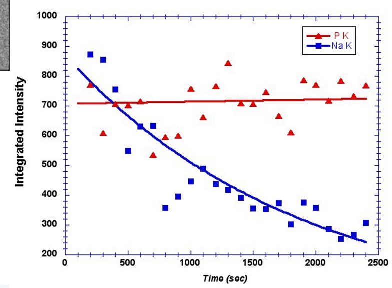
9



10



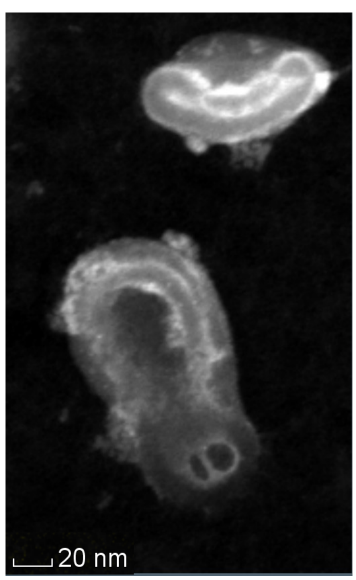
Sodium Phosphate on SiN

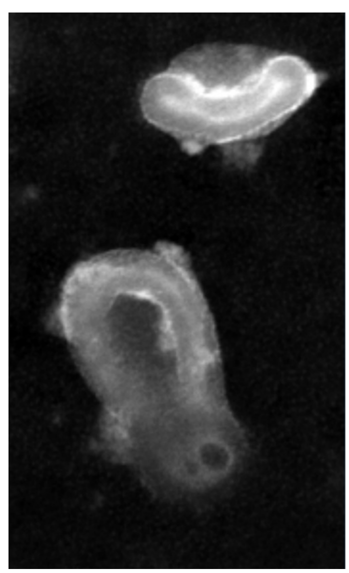


100 sec ~7.7 x 10^4 e^-/nm^2 (~770 $e^-/Å^2$).

11

Polyamide Filtration Nanomembranes



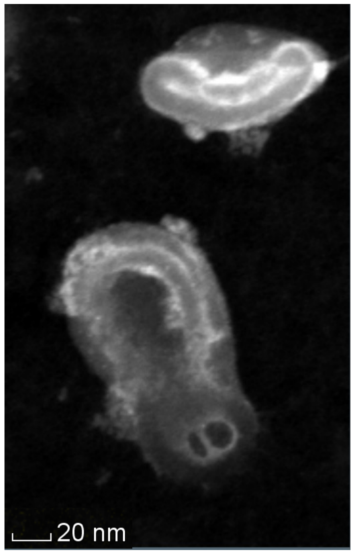


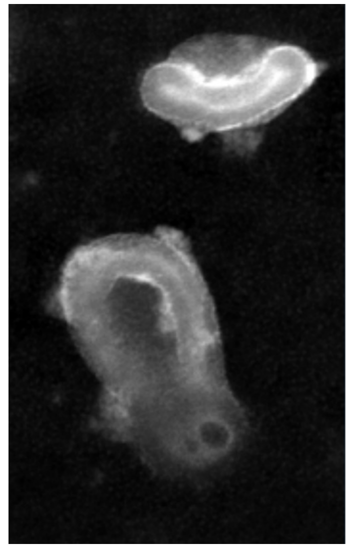
t = 0 @ 100 usec/pixel
~300 $e^-/Å^2$

Δt = 33 msec/pixel
~$1.05 \times 10^5 e^-/Å^2$

12

Polyamide Filtration Nanomembranes





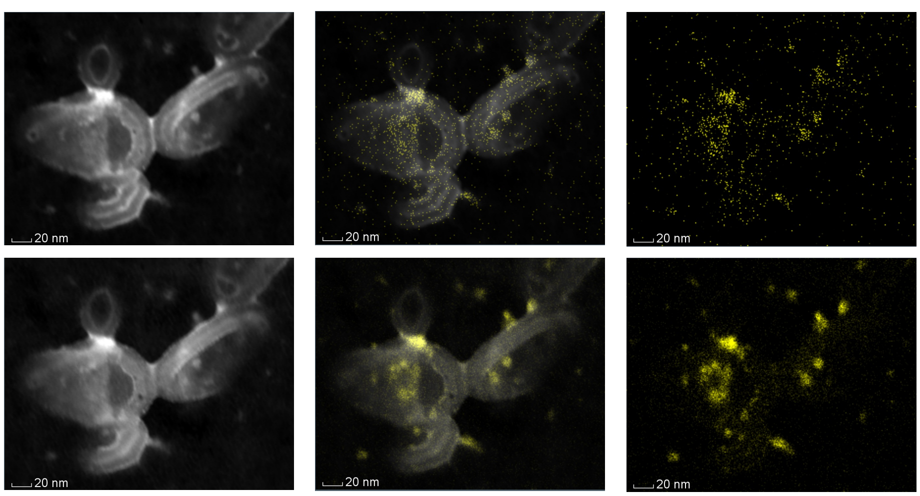
t=0
~300 $e^-/Å^2$

t = 33 msec/pixel
~$1.05x10^5 e^-/Å^2$

~ 2nm / 0.2nA
100usec/pix
333 frames

13

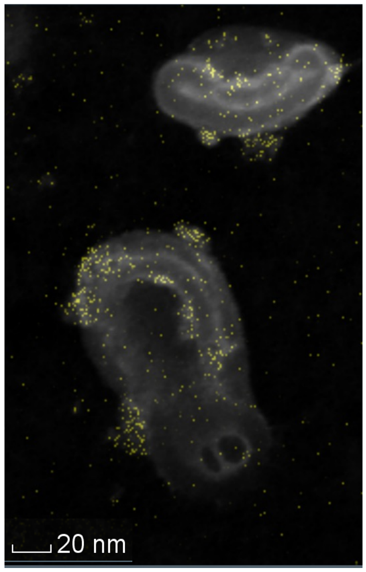
Polyamide Filtration Nanomembranes

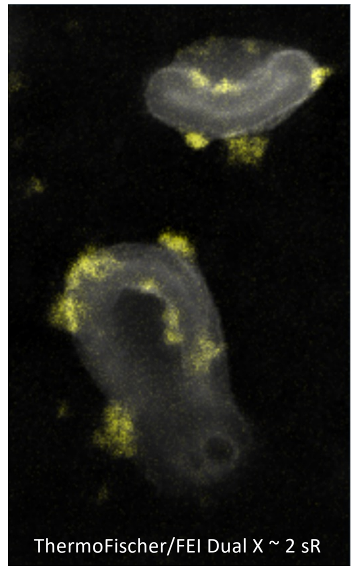


14

Polyamide Filtration Nanomembranes

Hyperspectral Imaging *+ Spatial Temporal Event Spectroscopy (X,Y,E,t)*



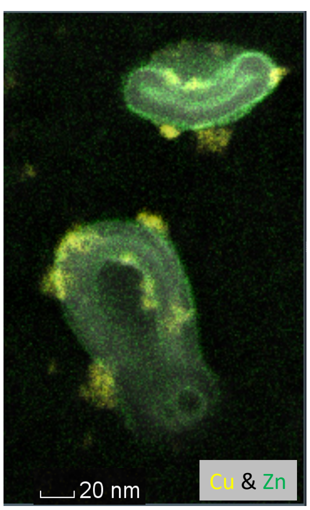


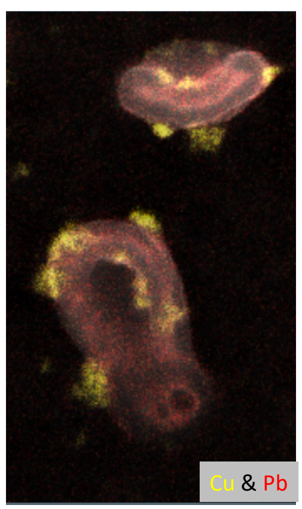
$\triangle$t = 1 msec/pixel

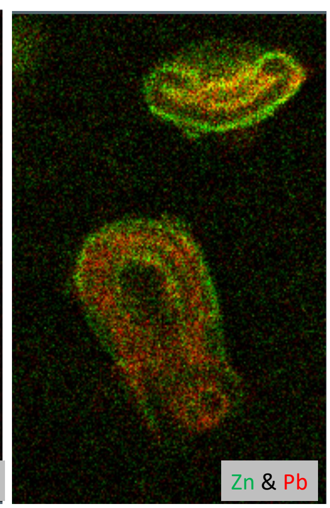
$\triangle$t = 33 msec/pixel

15

Polyamide Filtration Nanomembranes



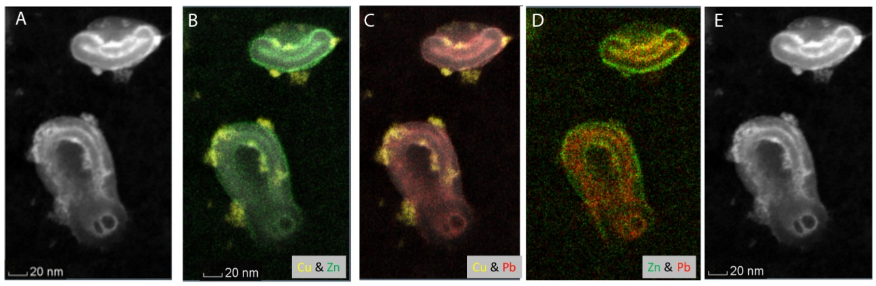




$\triangle$t = 33 msec/pixel

16

Polyamide Filtration Nanomembranes



Localization of Heavy Metals to
Site specific Membrane features

17

Radiation Damage vs Microanalysis

Comparison of
Characteristic Signal Generation
and Displacement Rates

$\frac{\text{Ionizations}}{\text{sec}}$ $\quad N_i = Q * J * C \frac{N_o \rho}{A}$

$\frac{\text{Displacements}}{\text{sec}}$ $\quad N_d = \sigma_d * J * \phi(f) * C \frac{N_o \rho}{A}$

$\frac{\text{Detected X-rays}}{\text{sec}}$ $\quad N_i = Q*[\omega_X \Gamma_X \varepsilon_X \Omega_X] J * C \frac{N_o \rho}{A}$

$\frac{\text{Detected EEL}}{\text{sec}}$ $\quad N_i = Q *[\omega_E \Gamma_E \varepsilon_E \Omega_E] J * C \frac{N_o \rho}{A}$

$\omega_E \sim \Gamma_E \sim \varepsilon_E \sim 1$

18

Radiation Damage vs Microanalysis

Energy Transfered by an Incident Electron to an Atomic Nucleus

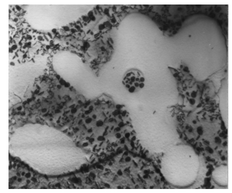
$$T_T = \frac{2*T_o*(T_o+2*m_oc^2)*\sin^2(\frac{\phi}{2})}{Mc^2}$$

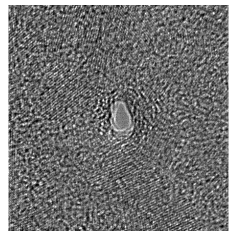
To = eVo, M= nuclear mass, mo = electron mass, f = scattering angle

Comparison of Maximum Transferable Kinetic Energy for Selected Elements with Displacement and Sputtering Energies (all values in eV)

Element	<------------ --	-----------	-T_T--------- -	------------ >	T_d[1]	T_s[2]
	100 kV	200 kV	300 kV	400 kV		
Al	8.93	19.5	31.6	45.3	16	3.5-7.0
Ti	5.00	11.0	17.8	25.5	15	4.9-9.8
V	4.73	10.3	16.72	24.0	29	5.3-10.6
Cr	4.63	10.1	16.38	23.5	21	4.1-8.2
Fe	4.31	9.40	15.25	21.8	16	4.3-8.6
Co	4.08	8.91	14.45	20.7	23	4.4-8.8
Ni	4.10	8.94	14.5	20.8	21	4.5-9.0
Cu	3.79	8.26	13.4	19.2	18	3.5-7.0
Zn	3.69	8.03	13.03	18.7	16	1.4-2.8
Nb	2.59	5.65	9.17	13.2	24	7.5-15.0
Mo	2.51	5.47	8.88	12.7	27	6.8-13.6
Ag	2.23	4.87	7.90	11.3	28	3.0-6.0
Cd	2.14	4.67	7.58	10.9	20	1.2-2.4
Ta	1.33	2.90	4.71	6.75	33	8.1-16.2
Pt	1.23	2.69	4.37	6.26	33	5.9-11.8
Au	1.22	2.67	4.32	6.2	36	3.8-7.6

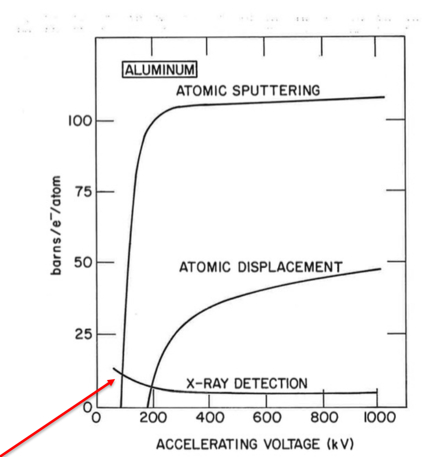
Td = Displacement Threshold (Bulk) Energy
Ts = Sputtering Threshold (Surface) Energy





19

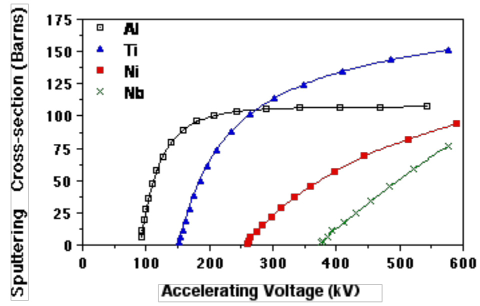
Is there ever a "safe" zone?

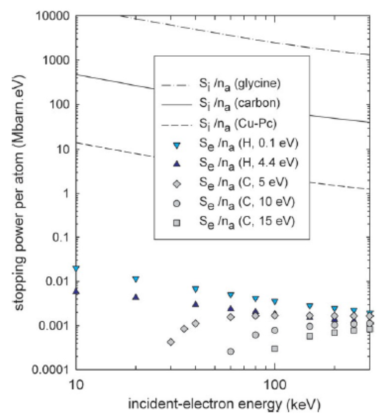


Damage is Material and Dose Dependant
XEDS – additionally Instrument Dependent

20

Calculated Cross-Sections & Stopping Power

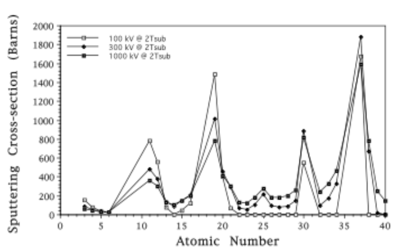


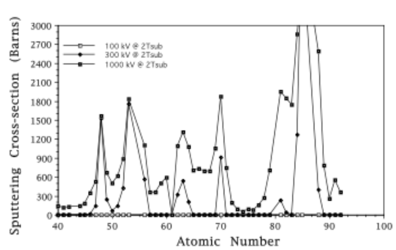


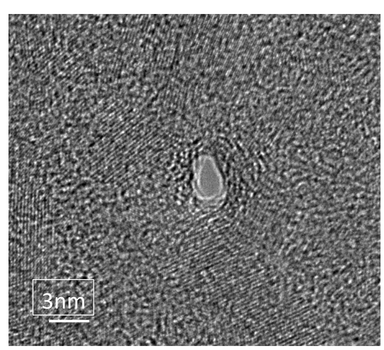
Egerton 2012

21

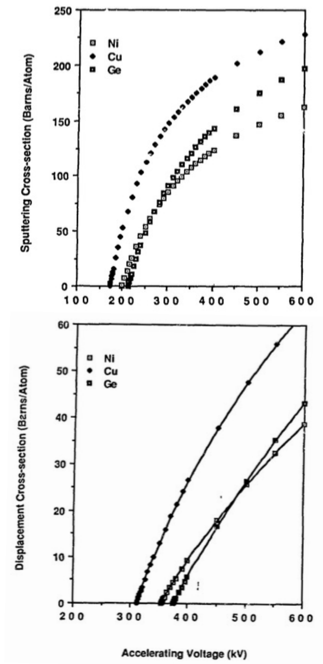
Calculated Sputtering Cross-

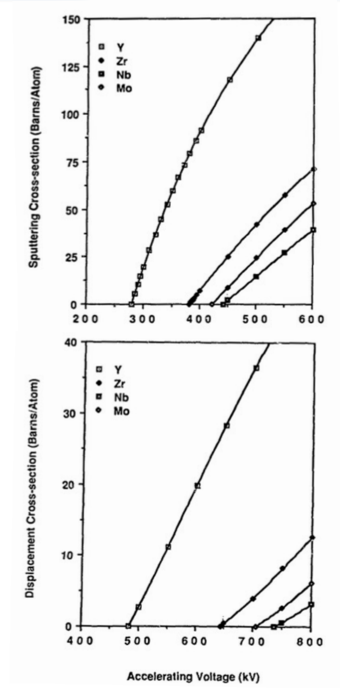




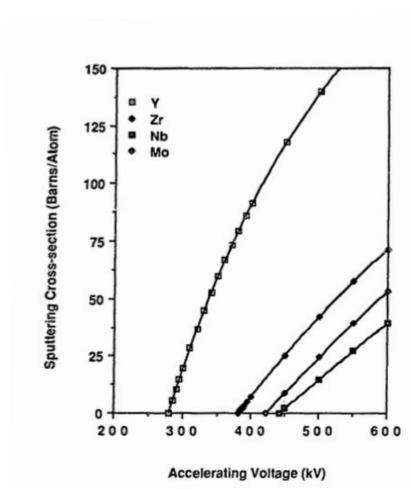


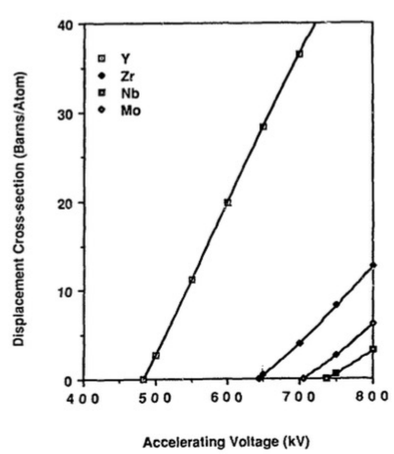
22


Ni
Cu
Ge
Sputtering Cross-section (Barns/Atom)
Displacement Cross-section (Barns/Atom)
Accelerating Voltage (kV)


Y
Zr
Nb
Mo
Sputtering Cross-section (Barns/Atom)
Displacement Cross-section (Barns/Atom)
Accelerating Voltage (kV)

23


Y
Zr
Nb
Mo
Sputtering Cross-section (Barns/Atom)
Accelerating Voltage (kV)


Y
Zr
Nb
Mo
Displacement Cross-section (Barns/Atom)
Accelerating Voltage (kV)

24

TABLE 1
THRESHOLD ACCELERATING VOLTAGES

Atomic Number	Element	Atomic Mass	Sublimation Energy (E_S) eV	Threshold Accel. Voltage at E_S	Threshold Accel. Voltage at $2E_S$	Threshold Accel. Voltage at 4Es	Threshold Accel. Voltage at $5E_S$
3	Li, Lithium	6.939	1.670	5.3	10.5	20.7	25.7
4	Be, Beryllium	9.012	3.360	13.6	26.9	52.5	64.9
5	B, Boron	10.811	6.030	28.9	56.3	107.5	131.6
6	C, Carbon	12.010	7.430	39.2	75.7	142.7	173.7
11	Na, Sodium	22.990	1.120	11.6	22.9	44.9	55.6
12	Mg, Magnesium	24.312	1.520	16.6	32.6	63.4	78.2
13	Al, Aluminum	26.980	3.420	40.4	78.1	147.0	178.9
14	Si, Silicon	28.090	4.680	56.7	108.3	200.3	242.1
15	P, Phosphorus	30.974	3.440	46.4	89.3	166.9	202.6
16	S, Sulfur	32.060	2.870	40.3	77.9	146.6	178.4
19	K, Potassium	39.100	0.929	16.3	32.1	62.4	76.9
20	Ca, Calcium	40.080	1.850	32.7	63.6	120.8	147.6
21	Sc, Scandium	44.956	3.920	74.8	141.1	256.7	308.4
22	Ti, Titanium	47.900	4.860	96.9	180.3	322.5	385.1
23	V, Vanadium	50.942	5.330	111.5	205.9	364.7	434.1
24	Cr, Chromium	51.996	4.110	89.5	167.3	300.9	360.0
25	Mn, Manganese	54.938	2.940	68.9	130.5	238.6	287.2
26	Fe, Iron	55.847	4.310	99.9	185.6	331.3	395.3
27	Co, Cobalt	58.933	4.440	107.8	199.5	354.1	421.9
28	Ni, Nickel	58.710	4.460	107.9	199.6	354.3	422.1
29	Cu, Copper	63.546	3.500	92.9	173.3	310.8	371.5
30	Zn, Zinc	65.380	1.350	38.7	74.9	141.3	172.1
31	Ga, Gallium	69.72	2.840	83.4	156.5	282.7	338.8
32	Ge, Germanium	72.590	3.880	115.3	212.5	375.4	446.5
33	As, Arsenic	74.922	3.140	97.8	182.0	325.2	388.3
34	Se, Selenium	78.960	2.350	78.5	147.7	267.9	321.5
37	Rb, Rubidium	85.470	0.850	32.1	62.4	118.6	144.9
38	Sr, Strontium	87.620	1.700	63.9	121.3	222.8	268.7
39	Y, Yttrium	88.906	4.400	154.8	279.8	483.8	571.5
40	Zr, Zirconium	91.220	6.310	216.4	381.8	643.6	754.3

25

TABLE 1
THRESHOLD ACCELERATING VOLTAGES

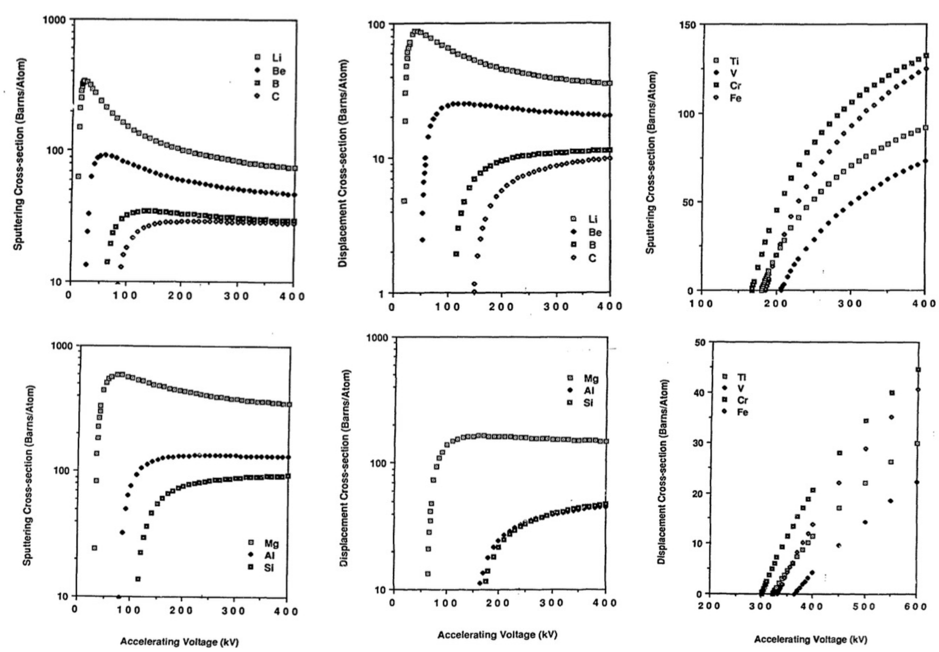
Atomic Number	Element	Atomic Mass	Sublimation Energy (E_S) eV	Threshold Accel. Voltage at E_S	Threshold Accel. Voltage at $2E_S$	Threshold Accel. Voltage at 4Es	Threshold Accel. Voltage at $5E_S$
41	Nb, Niobium	92.906	7.480	253.6	442.0	736.1	859.7
42	Mo, Molybdenum	95.940	6.810	240.9	421.5	704.7	823.9
44	Ru, Ruthenium	101.070	6.740	249.5	435.3	725.8	848.0
45	Rh, Rhodium	102.905	5.770	222.2	391.2	658.1	770.9
46	Pd, Palladium	106.400	3.900	163.0	293.7	505.8	596.8
47	Ag, Silver	107.868	2.950	128.7	235.6	413.0	489.9
48	Cd, Cadmium	112.400	1.160	56.3	107.5	198.9	240.4
49	In, Indium	114.820	2.520	118.2	217.4	383.4	455.8
50	Sn, Tin	118.690	3.130	147.9	268.1	465.2	550.1
51	Sb, Antimony	121.750	2.740	134.3	245.1	428.4	507.7
52	Te, Tellurium	127.600	2.040	107.3	198.6	352.7	420.2
53	I, Iodine	126.904	1.110	60.6	115.3	212.5	256.5
56	Ba, Barium	137.340	1.840	104.4	193.5	344.3	410.5
57	La, Lanthanum	138.906	4.335	224.9	395.6	664.8	778.5
58	Ce, Cerium	140.120	4.380	228.5	401.5	673.9	788.9
59	Pr, Praeseodymium	140.908	3.689	198.3	352.2	597.7	701.9
60	Nd, Neodymium	144.240	3.325	185.0	330.3	563.4	662.7
61	Pm, Promethium	145.000	3.035	171.7	308.1	528.6	622.8
62	Sm, Samarium	150.350	2.140	130.0	237.8	416.5	494.1
63	Eu, Europium	151.960	1.890	117.4	216.0	381.2	453.2
64	Gd, Gadolinium	157.250	2.241	141.1	256.6	446.8	528.9
65	Tb, Terbium	158.925	3.121	190.5	339.3	577.5	678.9
66	Dy, Dysprosium	162.500	3.087	192.3	342.4	582.3	684.4
67	Ho, Holmium	164.930	3.251	203.7	361.0	611.4	717.5
68	Er, Erbium	167.800	3.290	208.8	369.4	624.4	732.5
69	Tm, Thullium	168.934	2.514	166.4	299.3	514.7	606.9
70	Yb, Ytterbium	173.040	1.580	112.2	207.1	366.7	436.4
71	Lu, Lutetium	174.967	3.312	217.6	383.8	646.7	757.9
72	Hf, Hafnium	178.490	6.420	380.4	641.5	1036.6	1200.3
73	Ta, Tantalum	180.948	8.100	460.3	764.1	1218.4	1405.5

26

TABLE 1
THRESHOLD ACCELERATING VOLTAGES

Atomic Number	Element	Atomic Mass	Sublimation Energy (E_S) eV	Threshold Accel. Voltage at E_s	Threshold Accel. Voltage at $2E_S$	Threshold Accel. Voltage at 4Es	Threshold Accel. Voltage at $5E_s$
74	W, Tungsten	183.850	8.810	496.6	819.2	1299.4	1496.9
75	Re, Rhenium	186.200	8.020	467.0	774.2	1233.2	1422.2
76	Os, Osmium	190.200	8.150	480.4	794.6	1263.2	1456.1
77	Ir, Iridium	192.200	6.940	428.2	715.0	1145.9	1323.7
78	Pt, Platinum	195.090	5.860	379.7	640.4	1035.0	1198.5
79	Au, Gold	196.967	3.820	270.9	469.7	778.3	907.7
81	Tl, Thallium	204.370	1.890	153.0	276.9	479.2	566.2
82	Pb, Lead	207.200	2.020	164.3	295.8	509.1	600.5
83	Bi, Bismuth	208.981	2.170	176.2	315.7	540.5	636.5
84	Po, Polonium	209.000	1.444	122.7	225.3	396.3	470.7
85	At, Astatine	210.000	0.936	82.8	155.4	280.9	336.8
88	Ra, Radium	226.025	1.678	150.6	272.8	472.6	558.6
89	Ac, Actinium	227.028	3.988	315.2	539.8	884.4	1028.1
90	Th, Thorium	232.038	5.962	440.4	733.7	1173.5	1354.9
91	Pa, Protactinium	231.036	4.769	368.8	623.5	1009.9	1170.1
92	U, Uranium	238.029	5.460	419.7	702.0	1126.5	1301.9

27

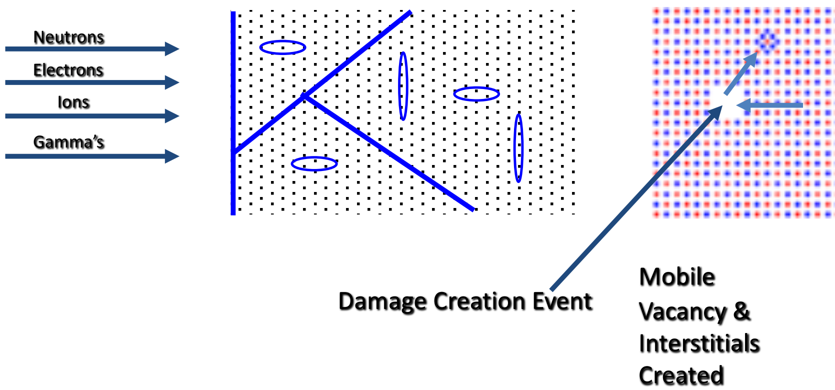


28

Radiation Induced Segregation

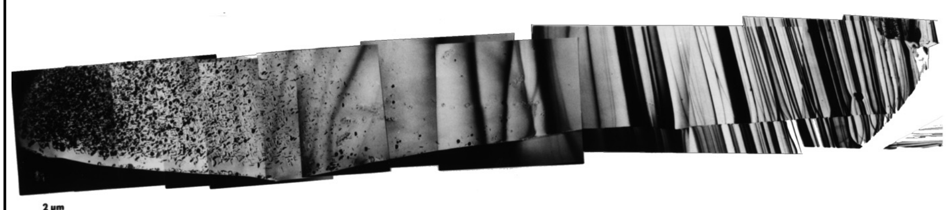
Migrating defects preferentially transport elements in initially homogeneous alloys, changing local compositions near defect sinks.

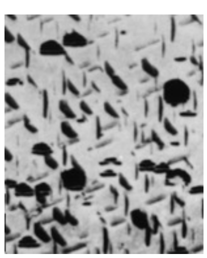
Surfaces, Grain Boundaries, Dislocations

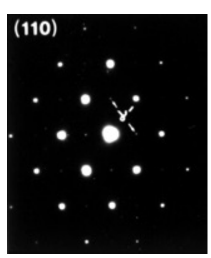


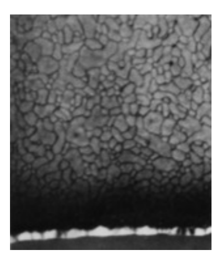
29

Radiation Induced Segregation





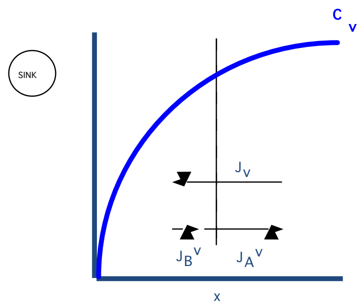




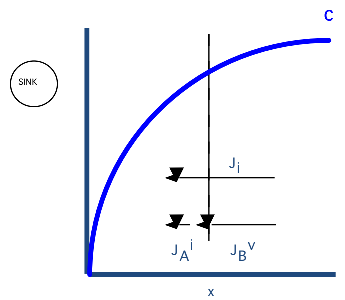
30

Radiation Induced Segregation

Inverse Kirkendall Effect Results in Preferential Solute Transport to Defect Sinks



$$\frac{J_A^v}{J_B^v} = \frac{D_A^v C_A}{D_B^v C_B}$$



$$\frac{J_A^i}{J_B^i} = \frac{D_A^i C_A}{D_B^i C_B}$$

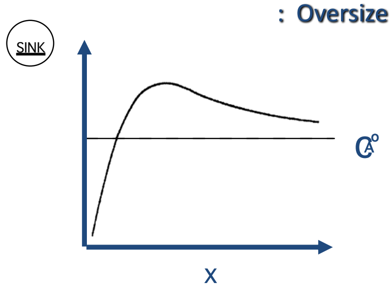
Journal of Nuclear Materials: 83 (1979) Okamoto & Rehn

31

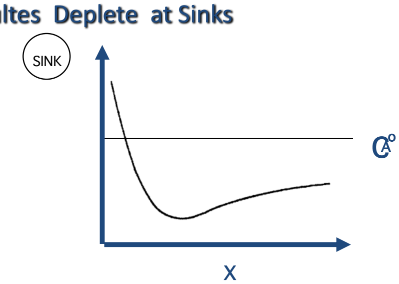
Radiation Induced Segregation

- Concentration Gradiants = Function of Diffusion Coefficients
- Solute Size Effects : Undersize Solutes Enrich at Sinks

  : Oversize Soultes Deplete at Sinks



$$\frac{D_A^V}{D_B^V} > \frac{D_A^i}{D_B^i}$$

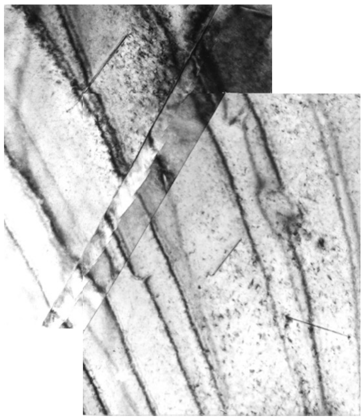


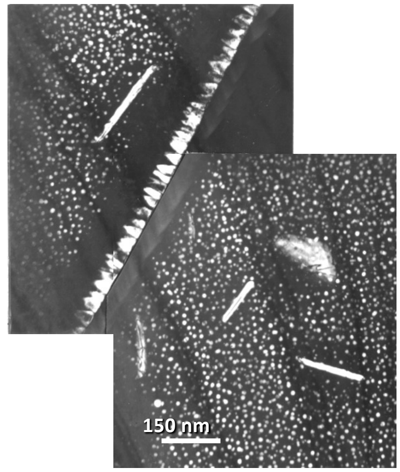
$$\frac{D_A^V}{D_B^V} < \frac{D_A^i}{D_B^i}$$

Journal of Nuclear Materials: 83 (1979) Okamoto & Rehn

32

Radiation Induced Segregation

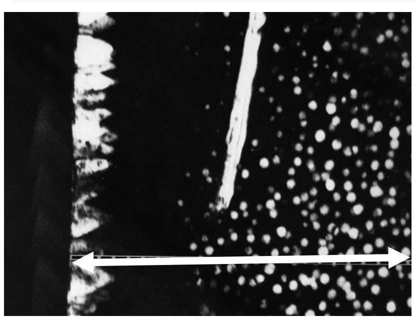


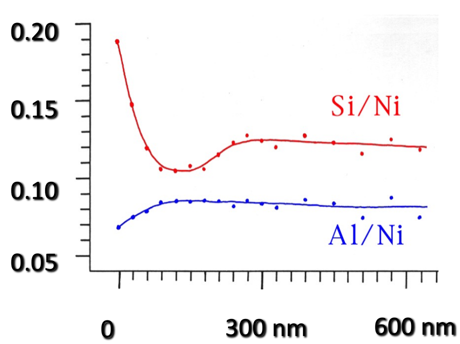


Ni - 6Al - 6 Si
3 MeV Nickel Ion Irradiation- 3 dpa

33

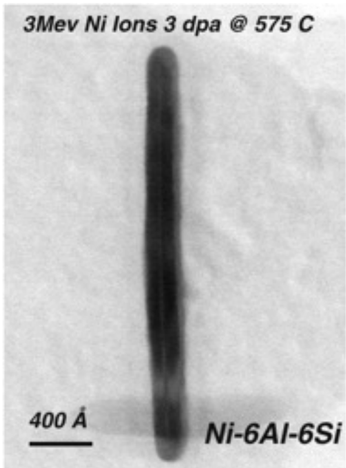
Radiation Induced Segregation

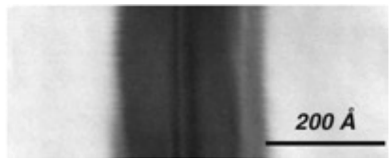


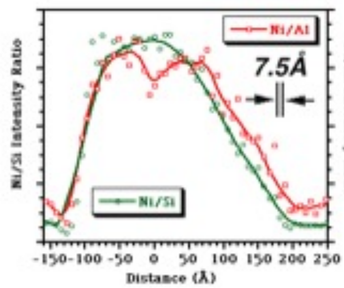


34

Radiation Induced Segregation

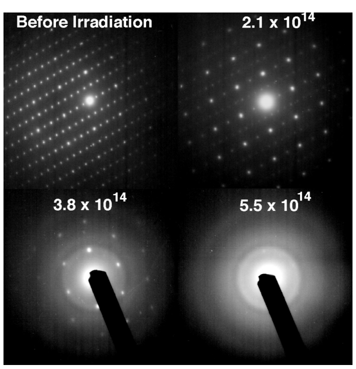


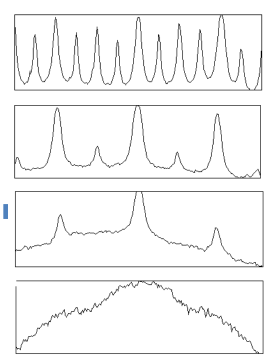


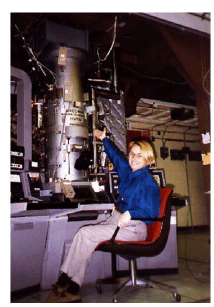


35

Radiation Damage v. Dose
monitored using the HVEM-Tandem at ANL







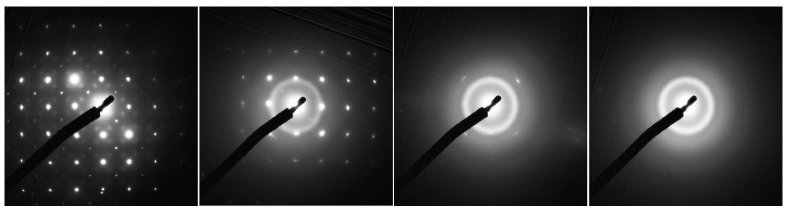
Selected area diffraction patterns of individual grains are recorded as a function of dose to establish the critical dose for amorphisation (Dc).

36

IVEM-Tandem Irradiation experiments

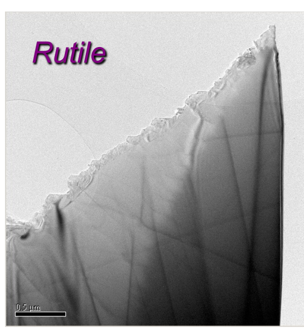
Selected area electron diffraction patterns as a function of irradiation dose

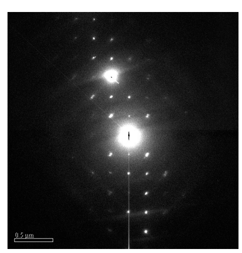
D_c – critical dose, dosage of radiation required to amorphise the sample



0.0 D_c 0.4 D_c 0.8 D_c 1.0 D_c

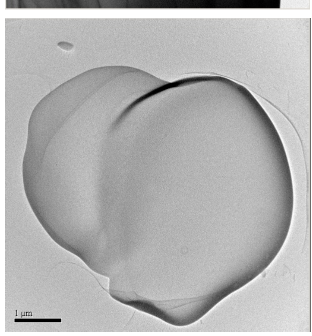
37

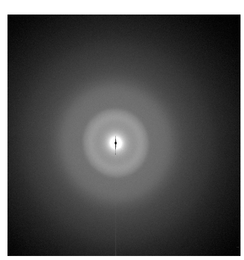




Typical Specimen used in the EELS work

Dc = 0
Native
State





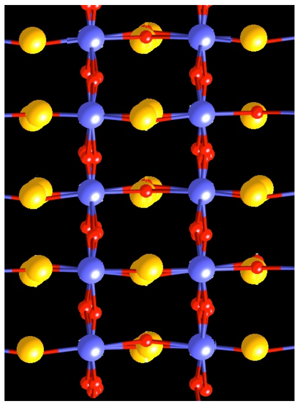
Dc = 5
Fully
Amorphized
State

38

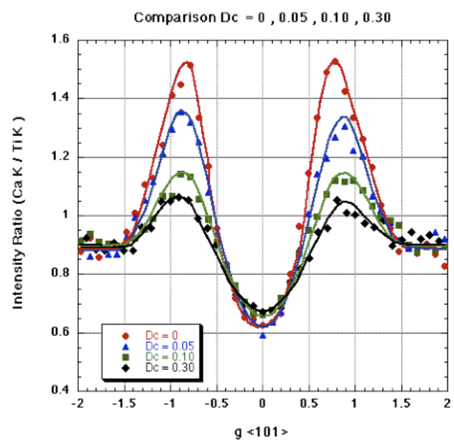
38

HARECXS of radiation damaged perovskite

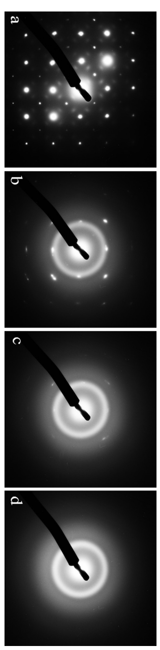
$CaTiO_3$



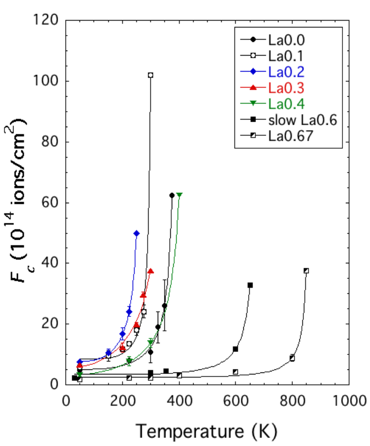
Orthorhombic Pcmn

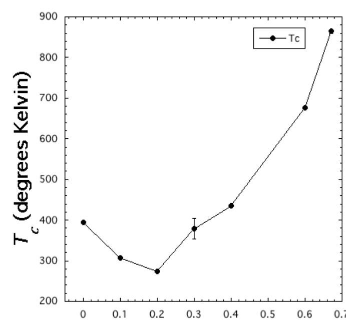


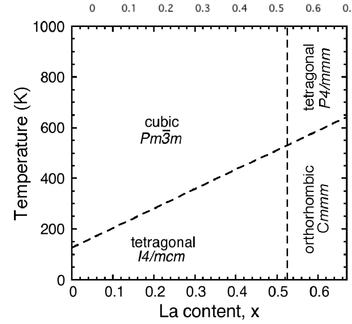
39



IVEM-Tandem Results for $La_xSr_{1-3x/2}TiO_3$







T_c – temperature above which no amorphization can occur

40

EELS Measurements

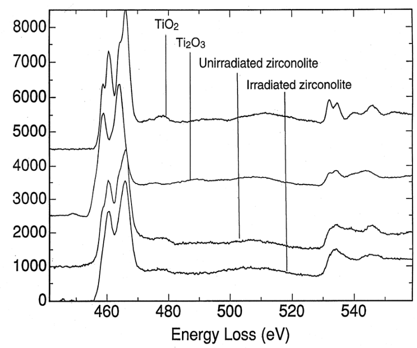


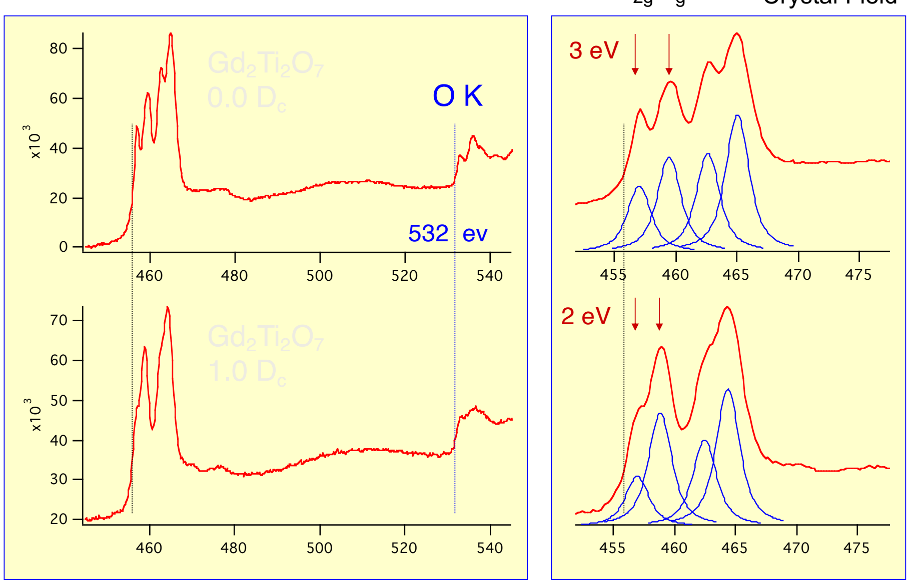
Figure 2. The Ti L edges of undoped zirconolite before and after ion irradiation, and two Ti standards (TiO_2 and Ti_2O_3)

41

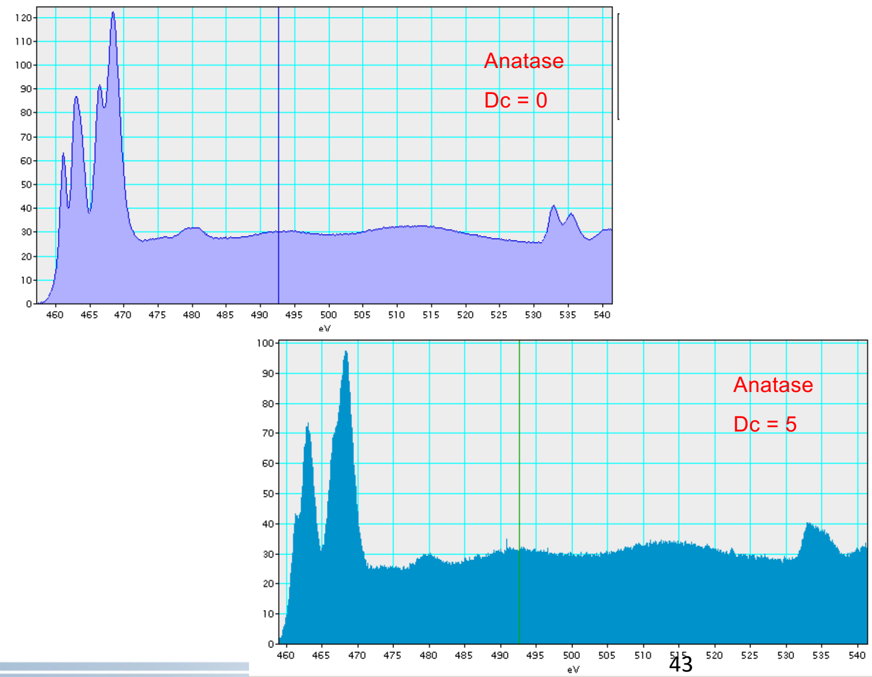
Example Ti $L_{2,3}$ ELNES

L_3 L_2 ← Spin Orbit

t_{2g} e_g ← Crystal Field



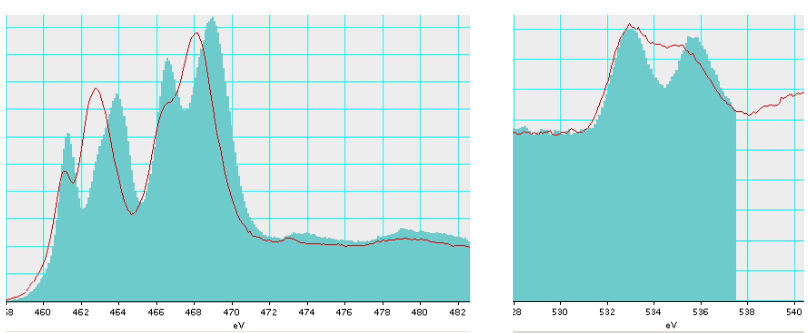
42



43

43

Rutile Comparison Dc = 0 / 5



TiL

OK

44

44