Università degli Studi di Trieste
Dipartimento di Ingegneria ed Architettura

Scienza e tecnologia dei materiali ceramici

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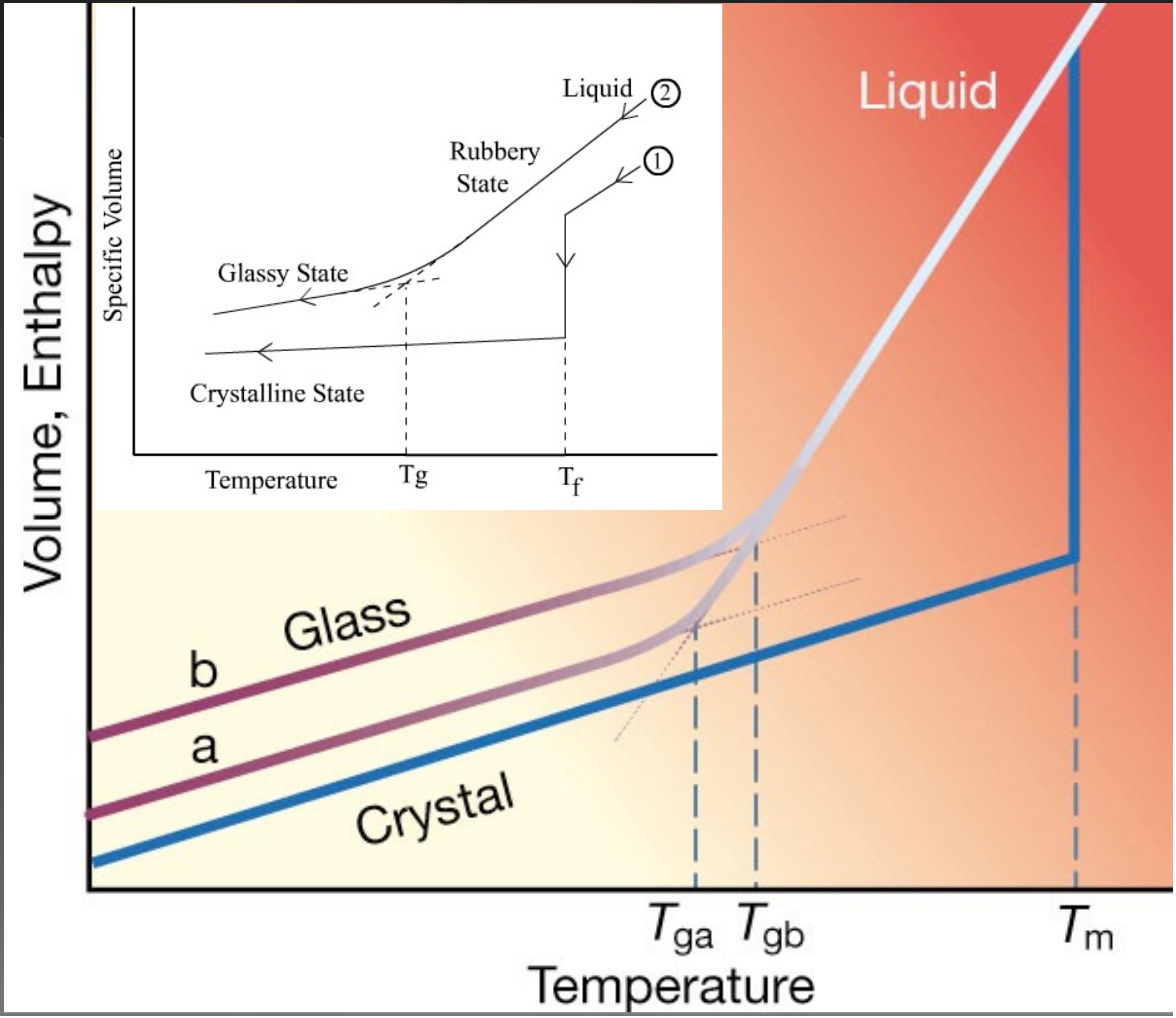
Glass theory

- Glasses lack the periodic (long range) order of a crystal
- •
- Infinite unit cell (no repeating large scale structures)
- •
- 3D network lacking symmetry and periodicity
- •
- ISOTROPIC: same average packing and properties in all directions
- •
- Crystals in different directions(see above):
- •
- different atom packing and so different properties



Liquid
Rubbery State
Glassy State
Crystalline State
Specific Volume
Temperature
Tg
Tf
Liquid
Glass
b
a
Crystal
Volume, Enthalpy
Tga
Tgb
Tm
Temperature

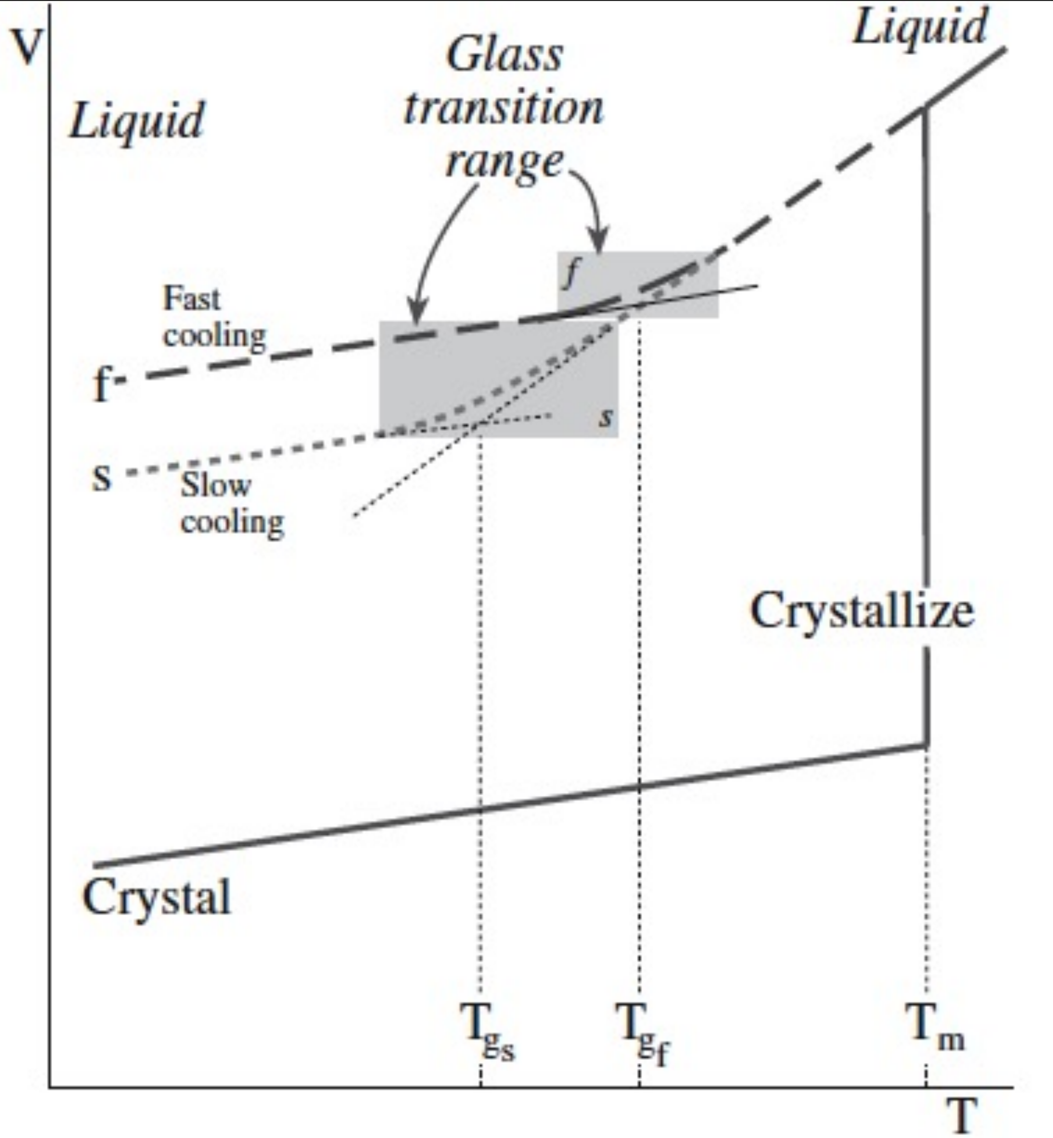
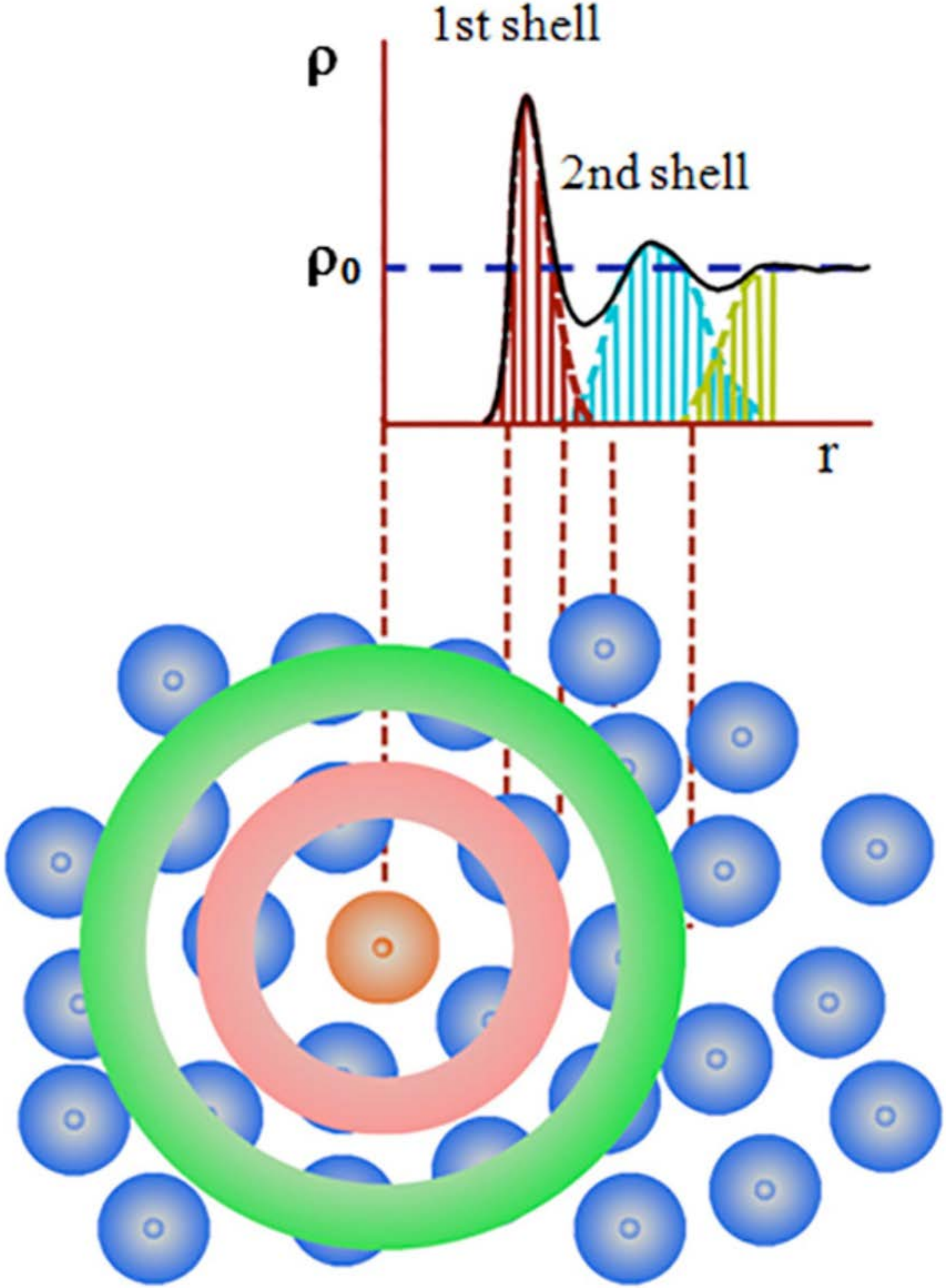
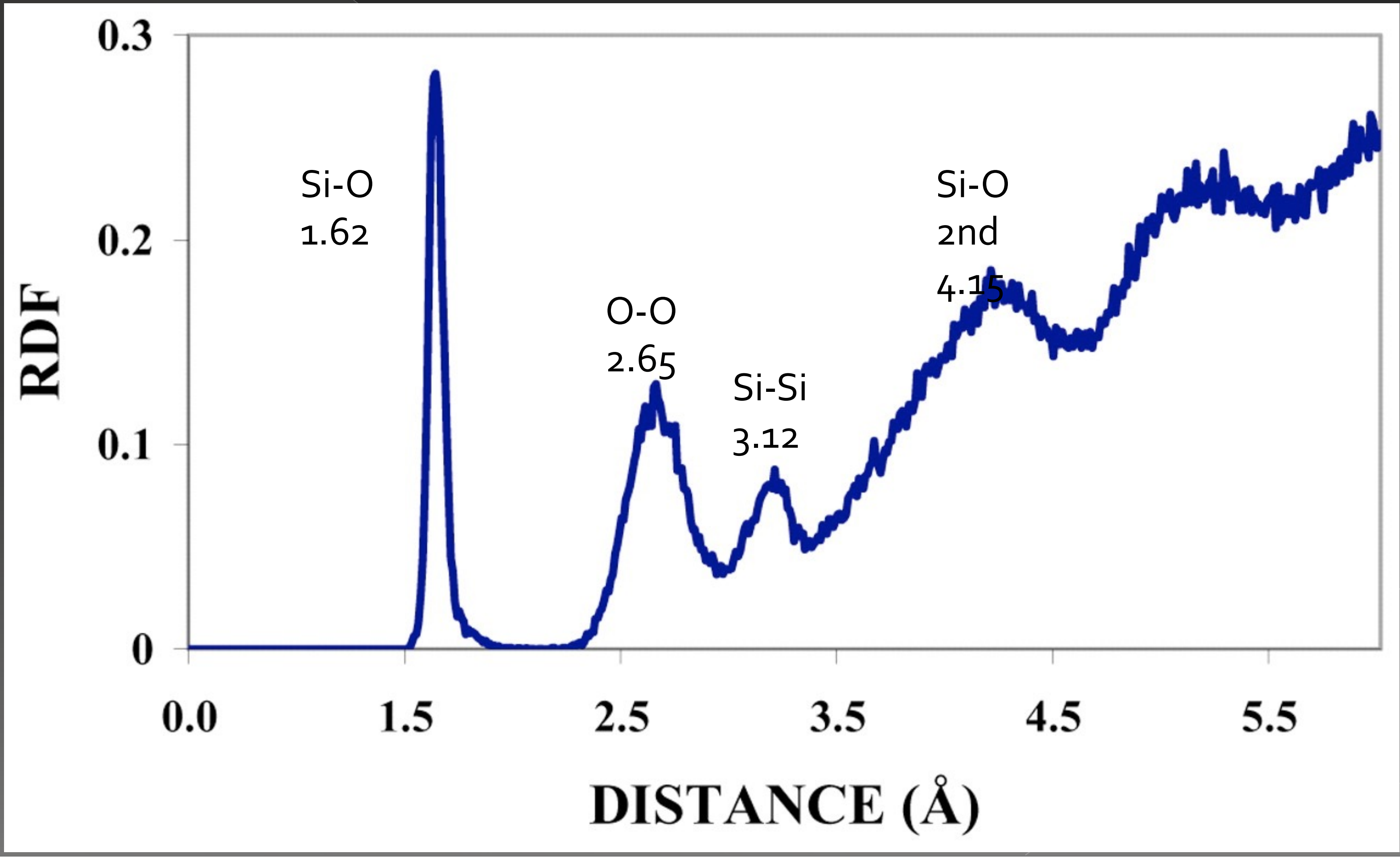


FIGURE 21.1 Plot of volume versus temperature for a liquid that forms a glass on cooling and one that forms a crystalline solid. The glass transition temperature, T_g, depends on the cooling rate and is not fixed like T_m.

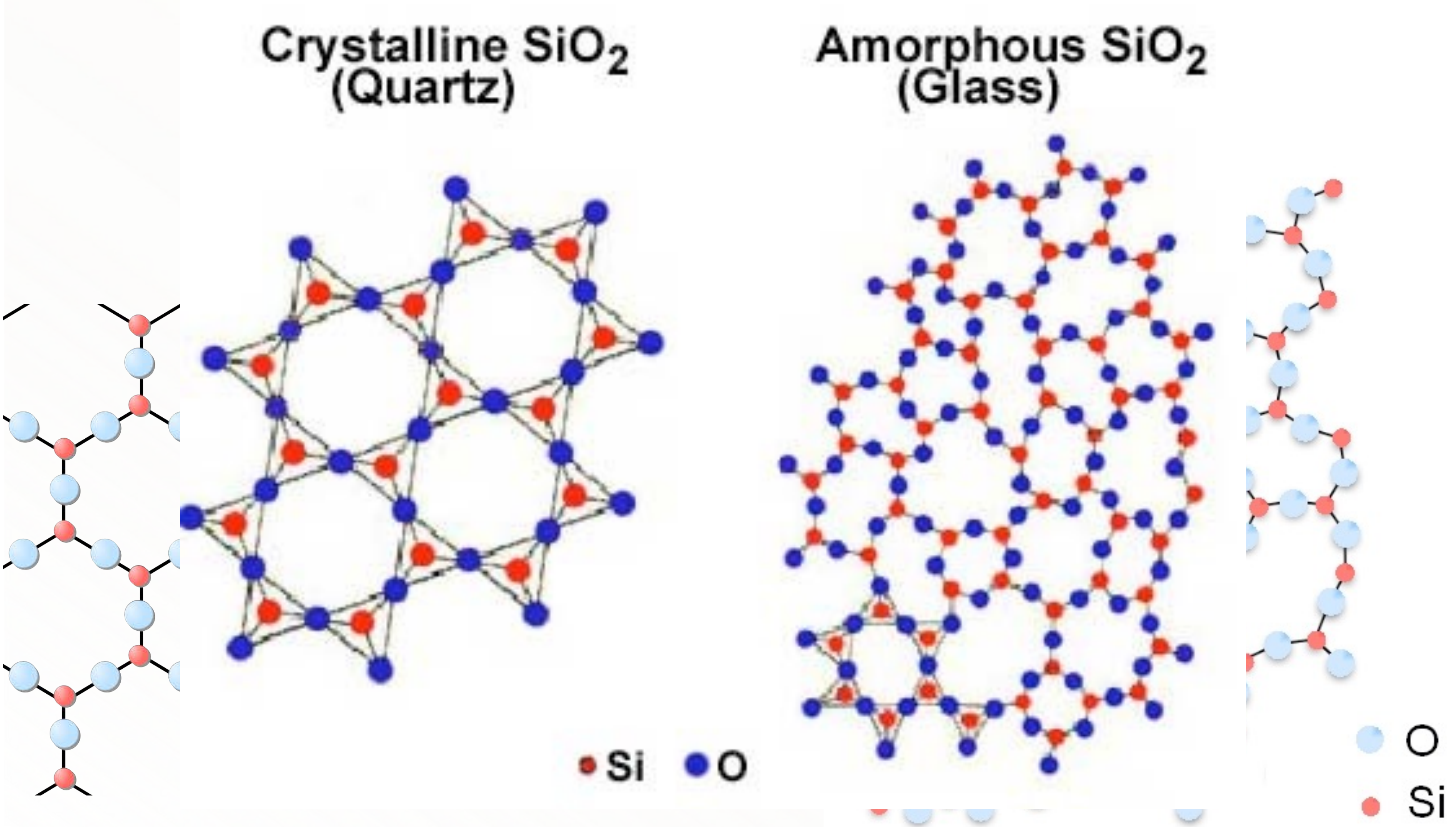
Pair distribution function of SiO2 glass

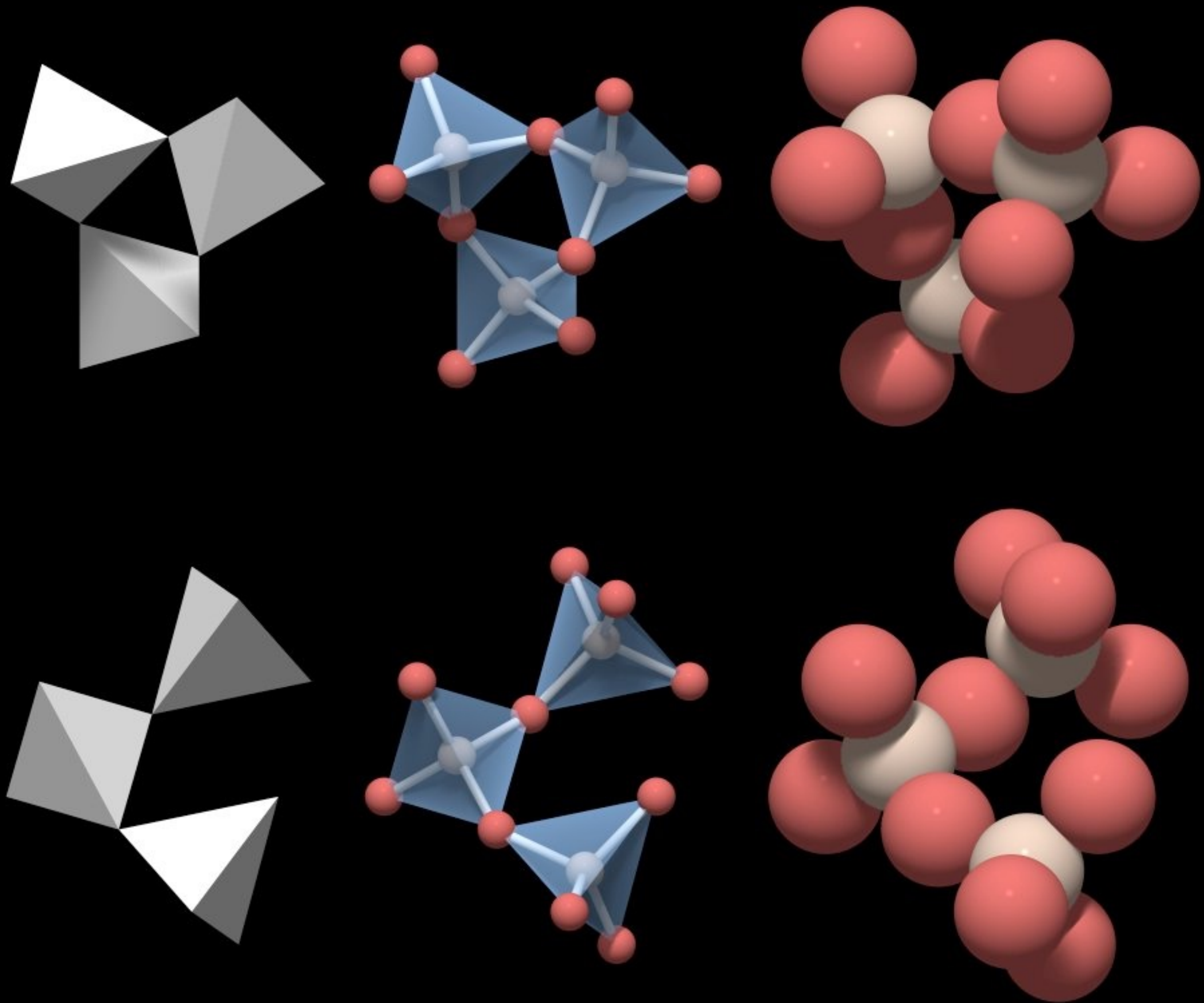


Radial distribution function for SiO_2



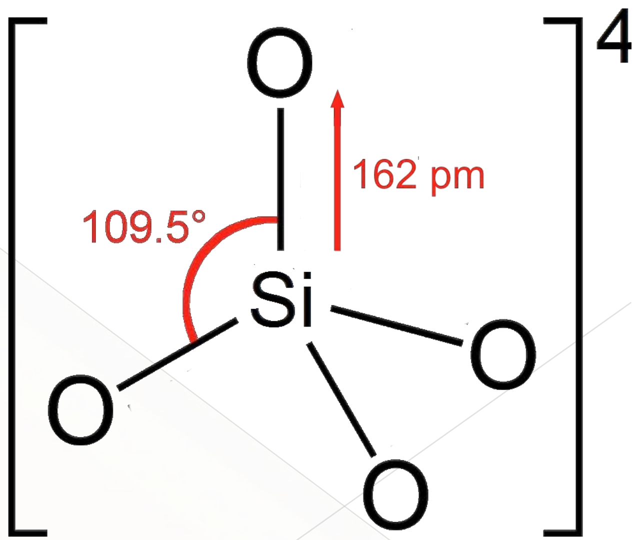
Glass structure:
SiO2 quartz compared to SiO2 glass





Zachariasen rules for glass A_mO_n

1) An oxygen atom is linked to no more than two glass-forming atoms A.
2) The number of oxygen atoms around each glass-forming atom A is small, perhaps 3 or 4.
3) Among the oxygen-containing polyhedra, a polyhedron cation A shares corners, but no sides or faces.
4) For three-dimensional networks of oxygen-containing polyhedra, at least three corners must be shared.



In general, all four rules should be satisfied for glass formation to occur.

Low coordination numbers, corner-sharing rules imply that glass formation is more likely with open, low density polyhedral structures.

1. Consider Silica:
    - covalent Si-O bond: sp^3 hybrid
        - tetrahedral bonding
- Pauling's packing rule:

$$\frac{r(Si^{4+})}{r(O^{2-})} = \frac{0.40}{1.40} \approx 0.29$$ *prefers tetrahedral bonding*

- satisfies Zachariasen's rule #2.

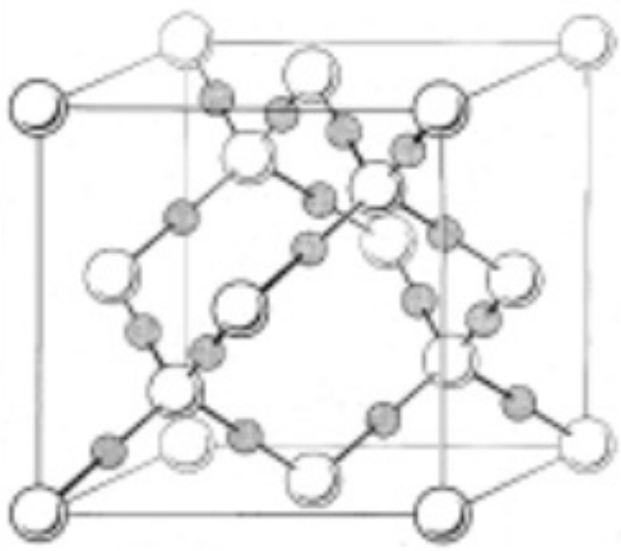
$$\frac{charge(Si^{4+})}{CN(Si^{4+})} = \frac{4}{4} = \frac{charge(O^{2-})}{CN(O^{2-})} = \frac{2}{2}$$ $CN(O^{2-})$ *is* 2.

- satisfies Zachariasen's rule #1.

Crystal structure: sharing four corners:

All Rules are Satisfied: SiO_2 forms a glass.

β-cristobalite (SiO_2)



Cation CN:Anion CN = 4:2

2. Consider Magnesia (MgO):

- ionic Mg-O bond
  - Pauling's packing rule:

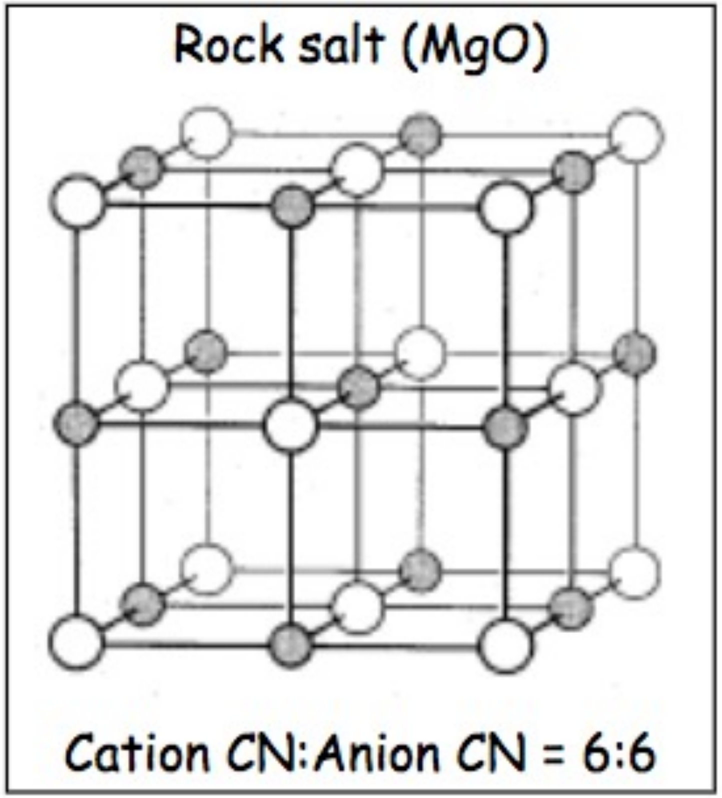
$$\frac{r(Mg^{2+})}{r(O^{2-})} = \frac{0.72}{1.40} \approx 0.51 \quad \textit{prefers octahedral bonding}$$

  - violates Zachariasen's rule #2.

$$\frac{charge(Mg^{2+})}{CN(Mg^{2+})} = \frac{2}{6} = \frac{charge(O^{2-})}{CN(O^{2-})} = \frac{2}{6} \quad CN(O^{2-}) \textit{ is } 6.$$

  - violates Zachariasen's rule #1.

Crystal structure: edge-sharing polyhedra;
Rules are Not Satisfied: MgO does not form a glass.



3. Consider Alumina (Al_2O_3):

- Pauling's packing rule:

$$\frac{r(Al^{3+})}{r(O^{2-})} = \frac{0.53}{1.40} \approx 0.38 \quad \textit{octahedral / tetrahedral boundary}$$

- octahedral CN preferred in Al_2O_3.

$$\frac{charge(Al^{3+})}{CN(Al^{3+})} = \frac{3}{6} = \frac{charge(O^{2-})}{CN(O^{2-})} = \frac{2}{4} \quad CN(O^{2-}) \textit{ is } 4.$$

- violates Zachariasen's rule #1.

Al_2O_3 does not form a glass.

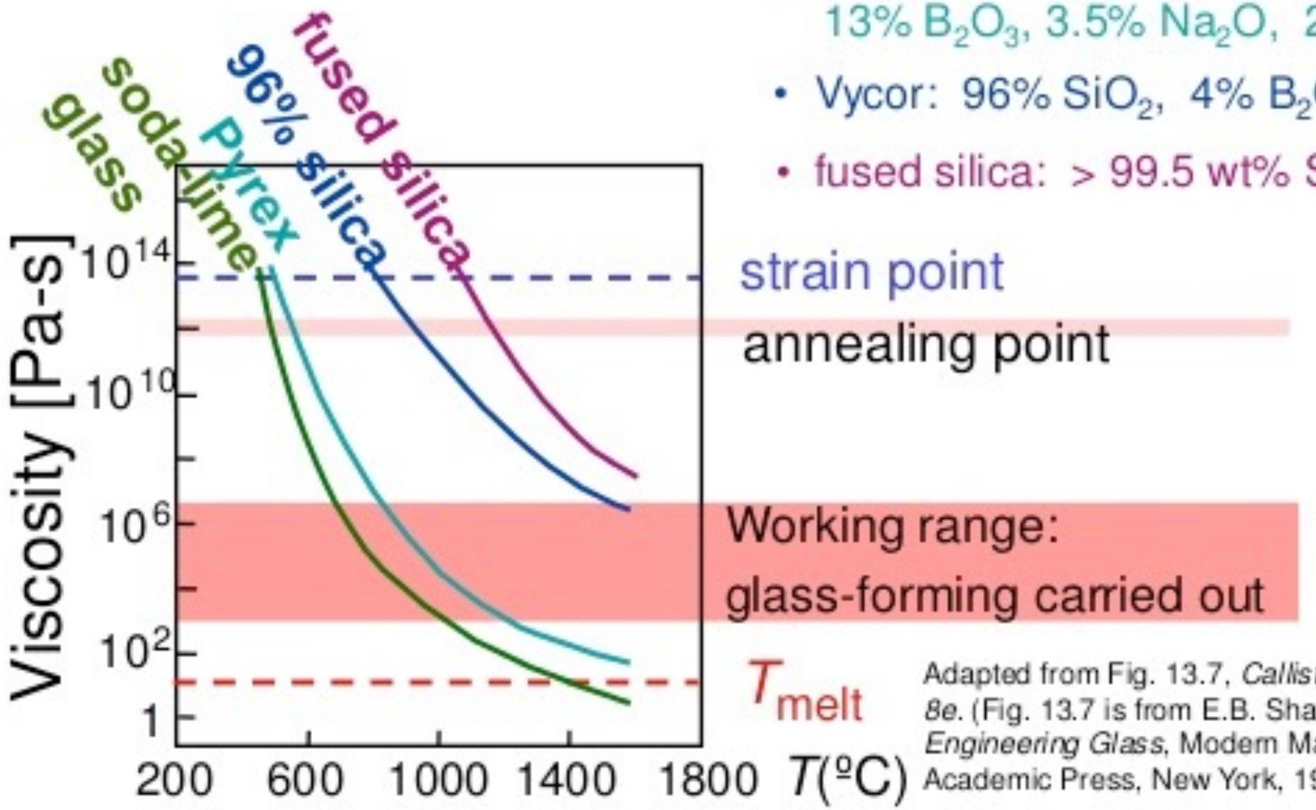
Elements for glass formation

Formers	Modifiers	Intermediate
B	Sc	Ti
Si	La	Zr
Ge	Na	Pb
Al	K	Al
V	Rb	Th
As	Cs	

Log Glass Viscosity vs. Temperature

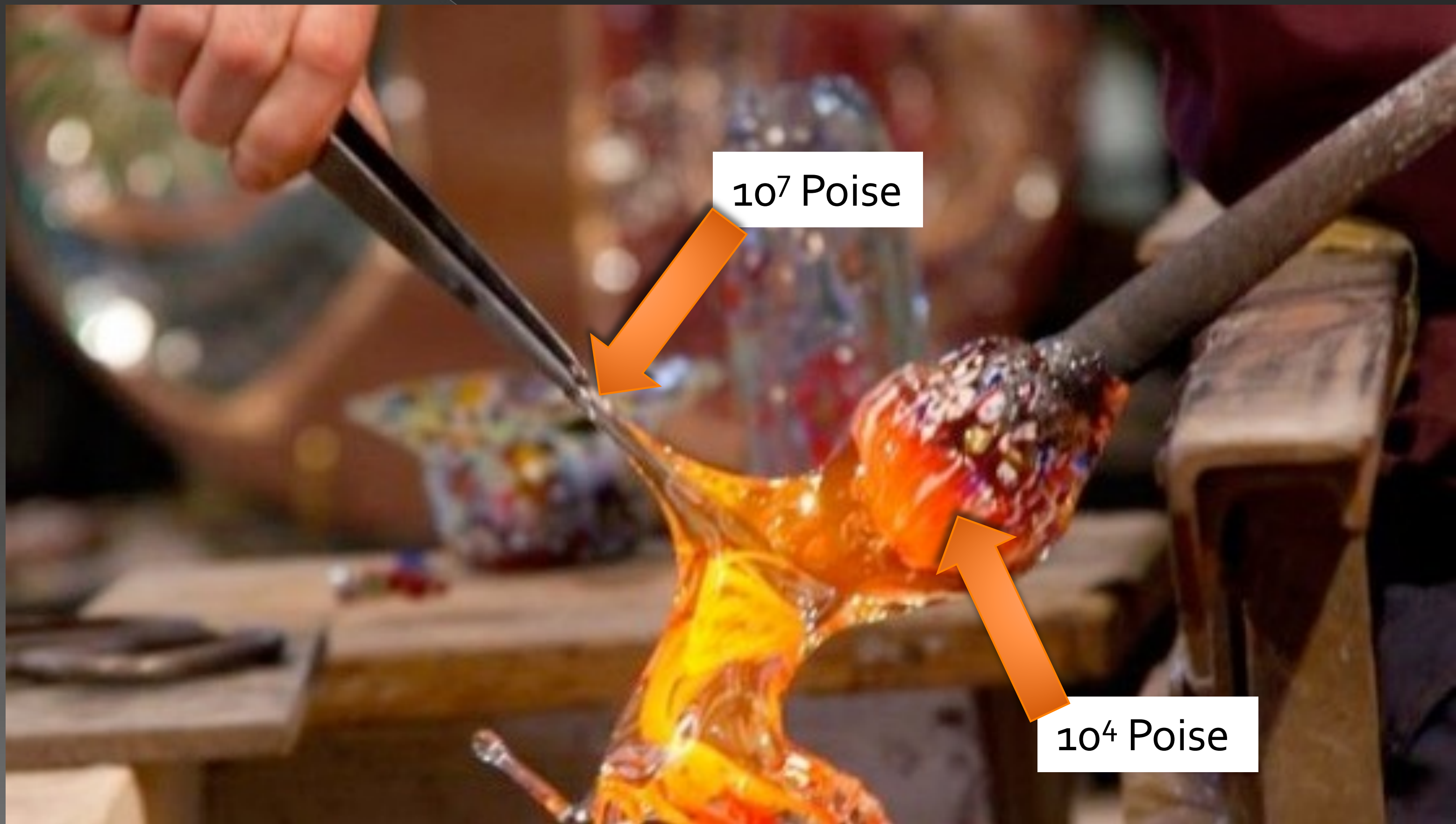
- Viscosity decreases with *T*

- soda-lime glass: 70% SiO_2 balance Na_2O (soda) & CaO (lime)
- borosilicate (Pyrex): 13% B_2O_3, 3.5% Na_2O, 2.5% Al_2O_3
- Vycor: 96% SiO_2, 4% B_2O_3
- fused silica: > 99.5 wt% SiO_2

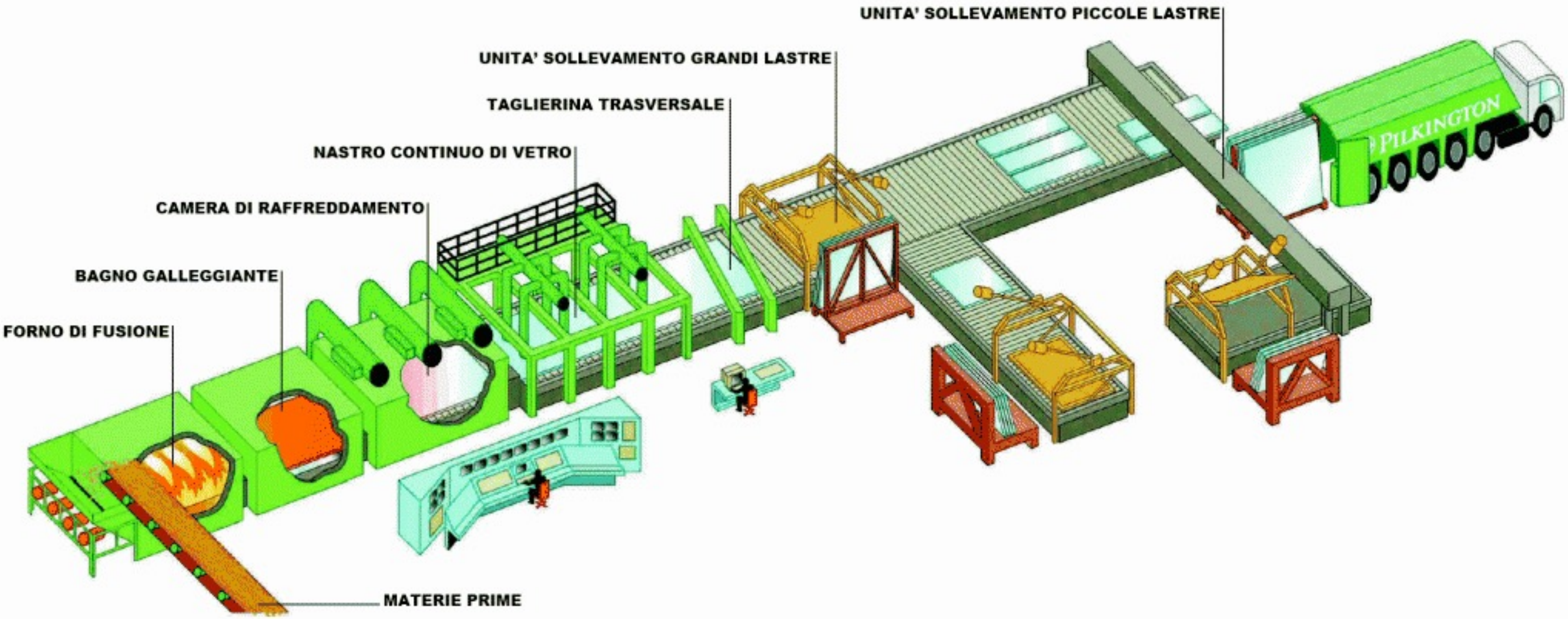


Adapted from Fig. 13.7, *Callister & Rethwisch 8e*. (Fig. 13.7 is from E.B. Shand, *Engineering Glass*, Modern Materials, Vol. 6, Academic Press, New York, 1968, p. 262.)

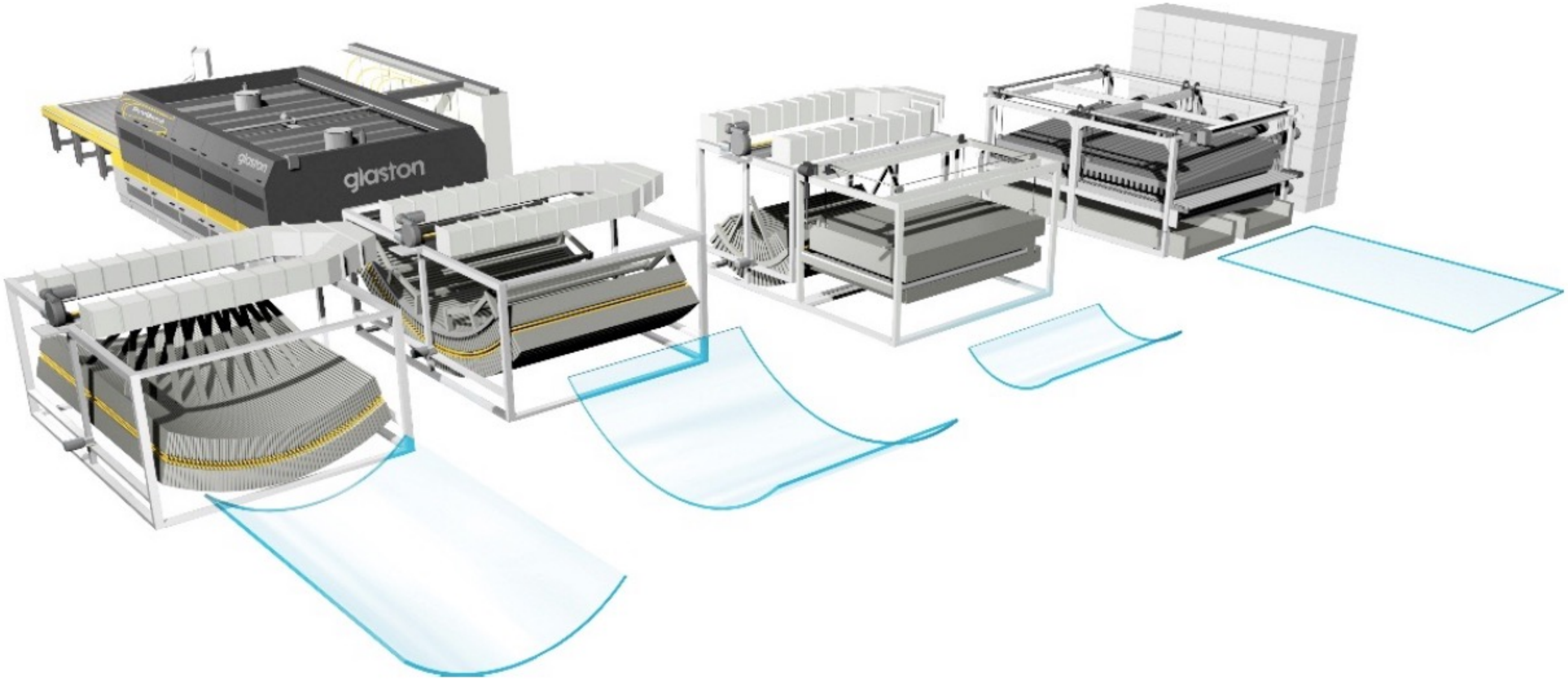
Glass Viscosity and Workability

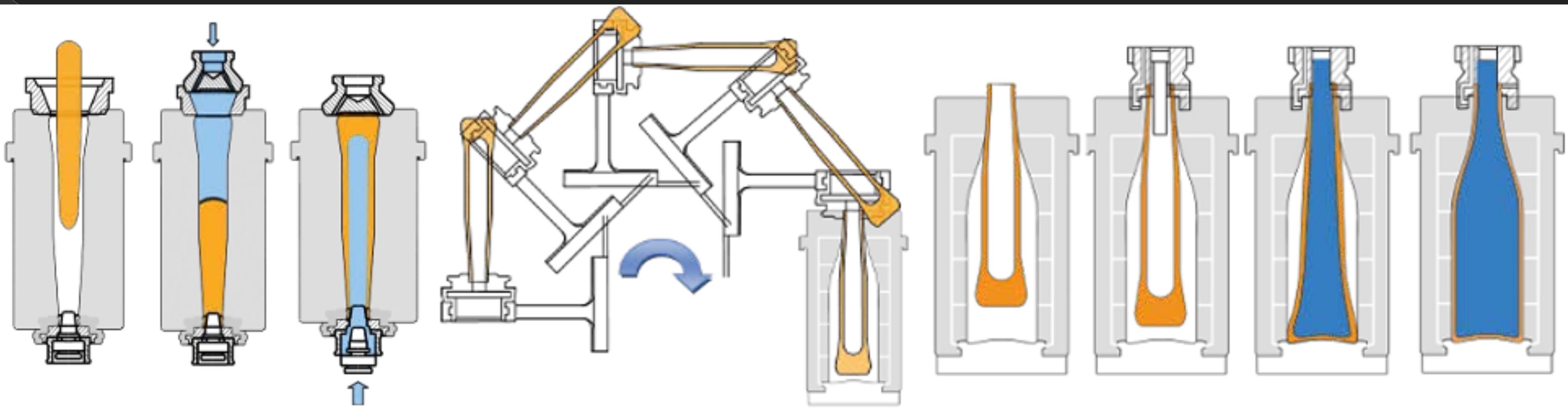


Pilkington process



Glass bending





Bottle production line
://www.youtube.com/watch?v=k8MmEuvugG4

Dielectrics

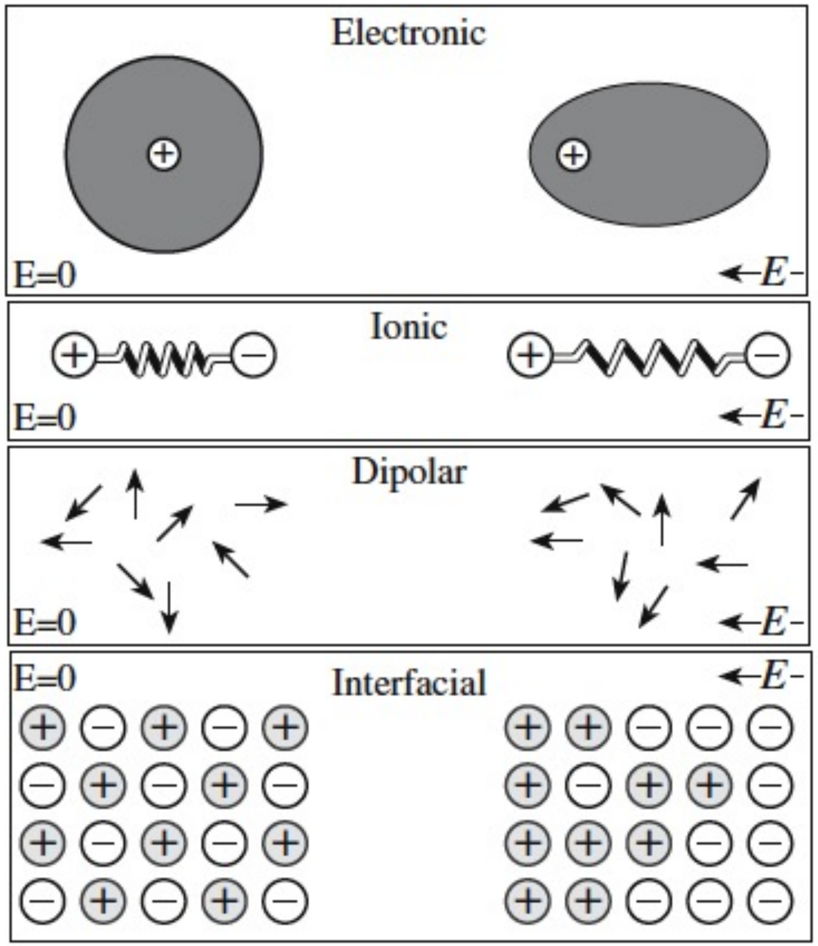


FIGURE 31.1 Illustration of the different polarization mechanisms in a solid.

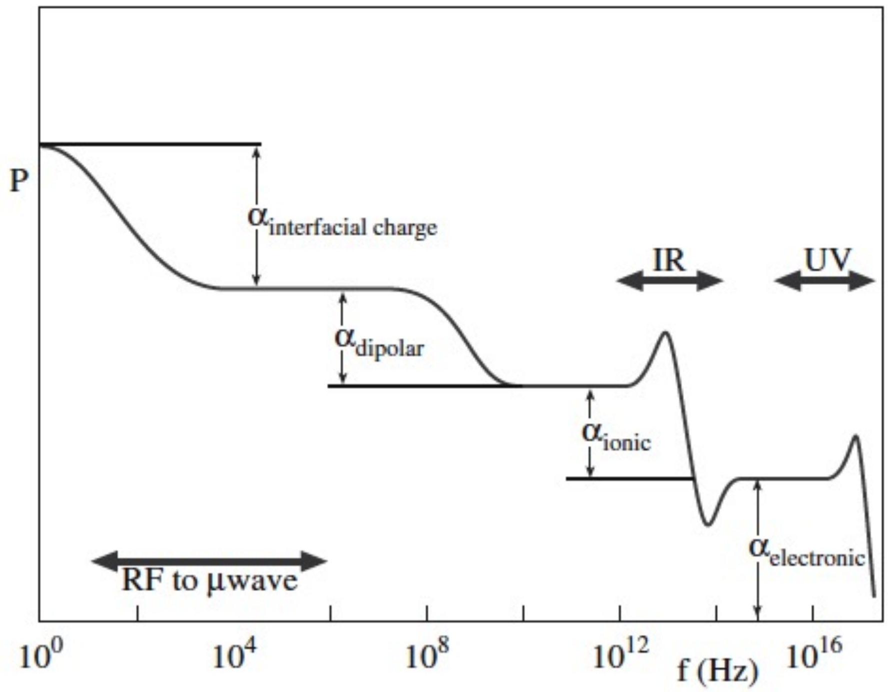


FIGURE 31.2 Frequency dependence of polarization.

TABLE 31.2 Dielectric Constants of Various Ceramics

Material	*κ at 1 MHz*	*Material*	*κ at 1 MHz*
Diamond	5.5–6.6	Al_2O_3	8.8
SiO_2	3.7–3.8	MgO	9.6
NaCl	5.9	$BaTiO_3$	3000
Mica	5.4–8.7	Pyrex glass	4.0–6.0
Soda-lime glass	7.0–7.6	TiO_2	14–110
Steatite (SiO_2 + MgO + Al_2O_3)	5.5–7.5	Forsterite ($2MgO \cdot SiO_2$)	6.2
Cordierite (SiO_2 +MgO + Al_2O_3)	4.5–5.4	Mullite	6.6
High-lead glass	19		

TABLE 31.4 Dielectric Strengths for Various Ceramics

Material	*Dielectric strength (MV/cm at 25°C)*
Al_2O_3 (99.5%)	0.18
Al_2O_3 (94.0%)	0.26
High-voltage porcelain	0.15
Steatite porcelain	0.10
Lead glass	0.25
Lime glass	2.5
Borosilicate glass	5.8
Fused quartz	6.6
Quartz crystal	6.0
NaCl [100], [111], [110]	2.5, 2.2, 2.0
Muscovite mica	10.1

Non destructive testing Techniques

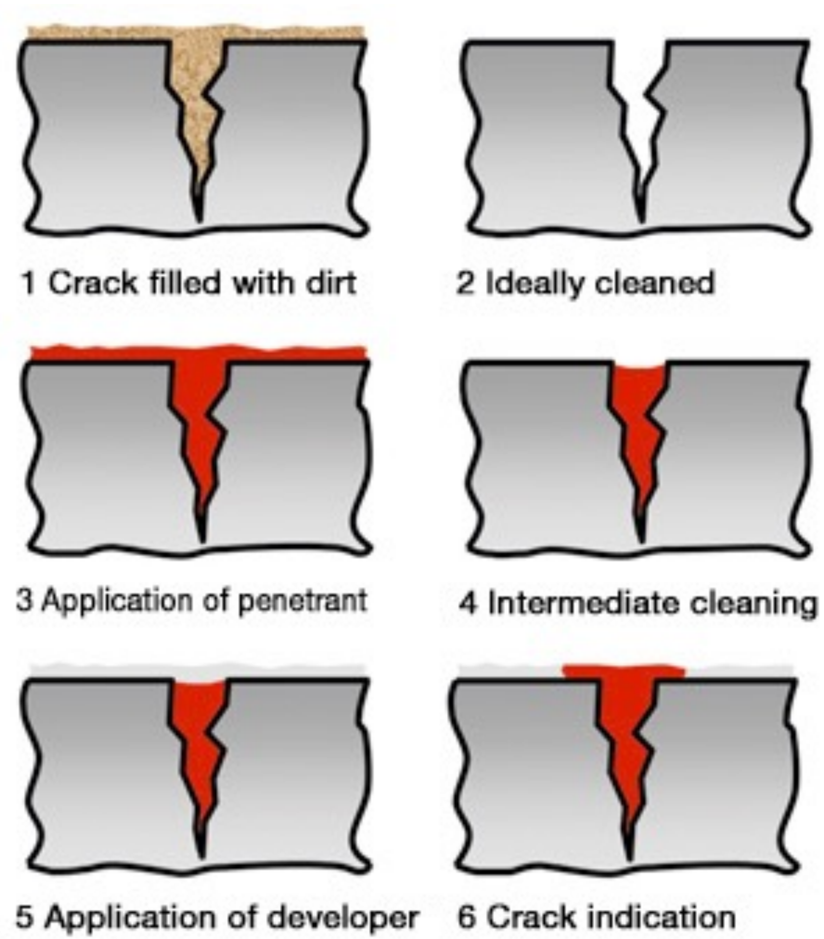
- Visual inspection
- Penetrant dyes
- Ultrasonic testing
- Radiographic testing
- Magnetoscopic testing
- Eddy currents

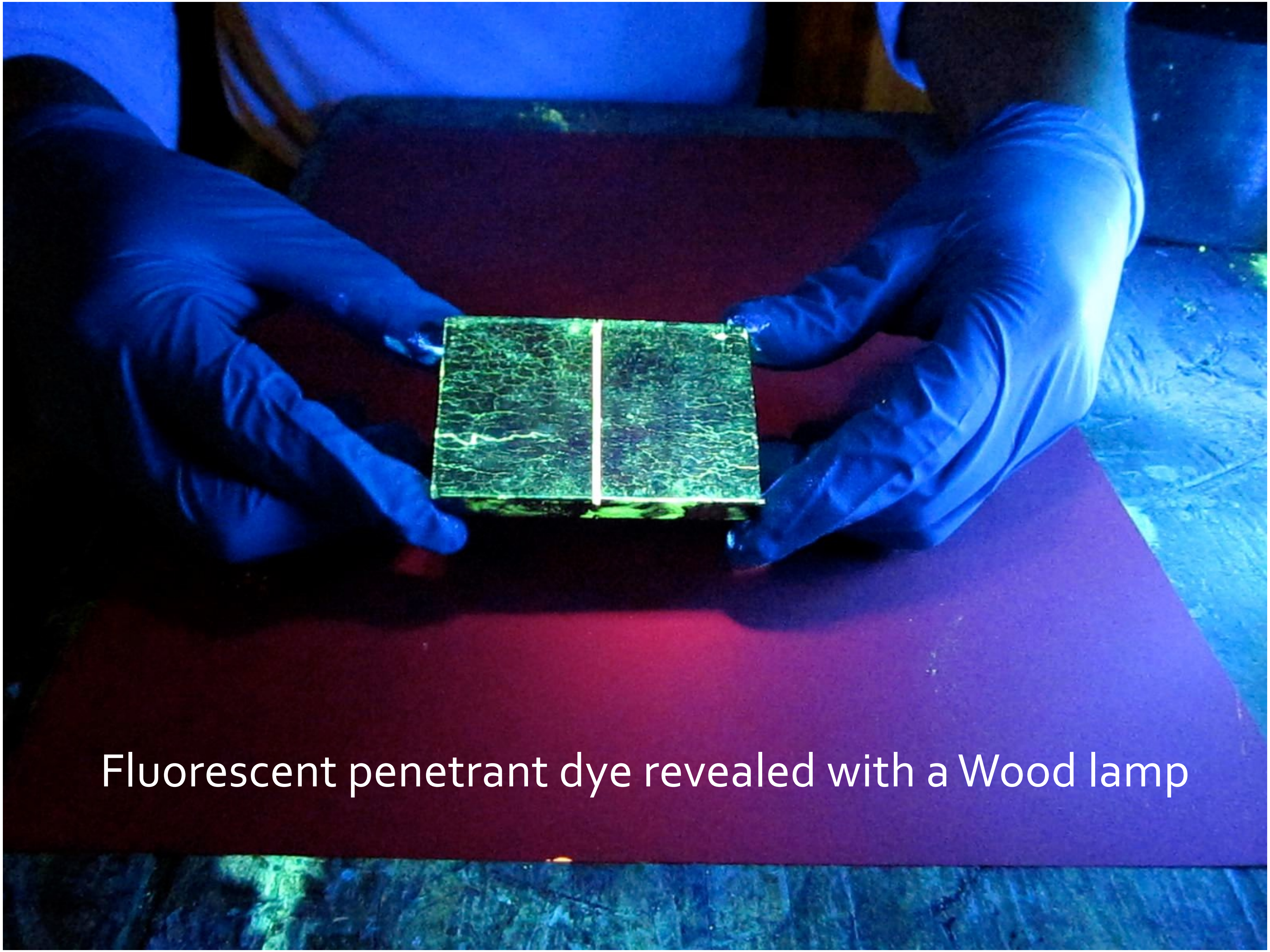
Proof testing:

1) load configuration as similar as possible to service condiction

2) one single test slightly above load/stress values in service

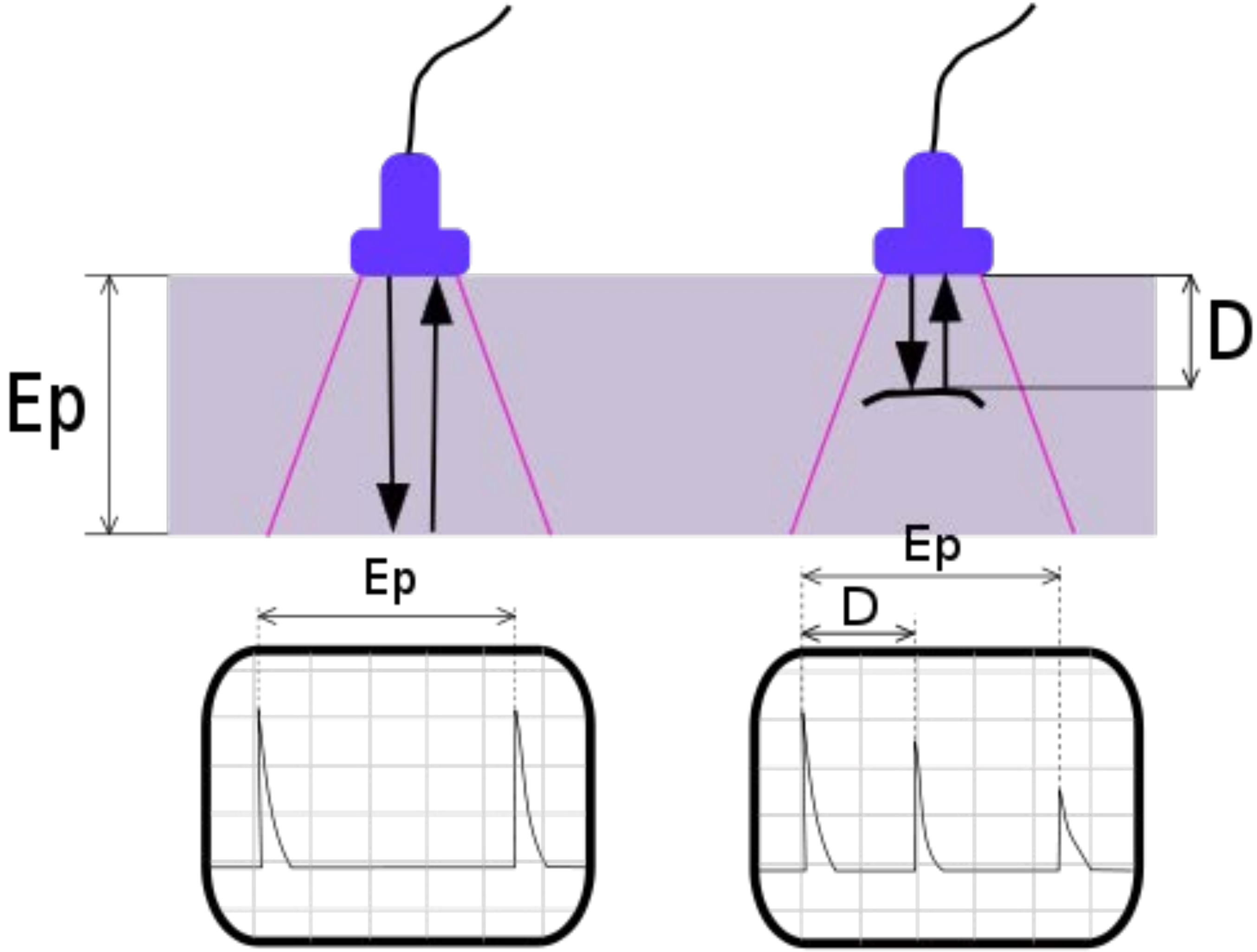
Liquid penetrant dyes





Fluorescent penetrant dye revealed with a Wood lamp

Ultrasonic testing



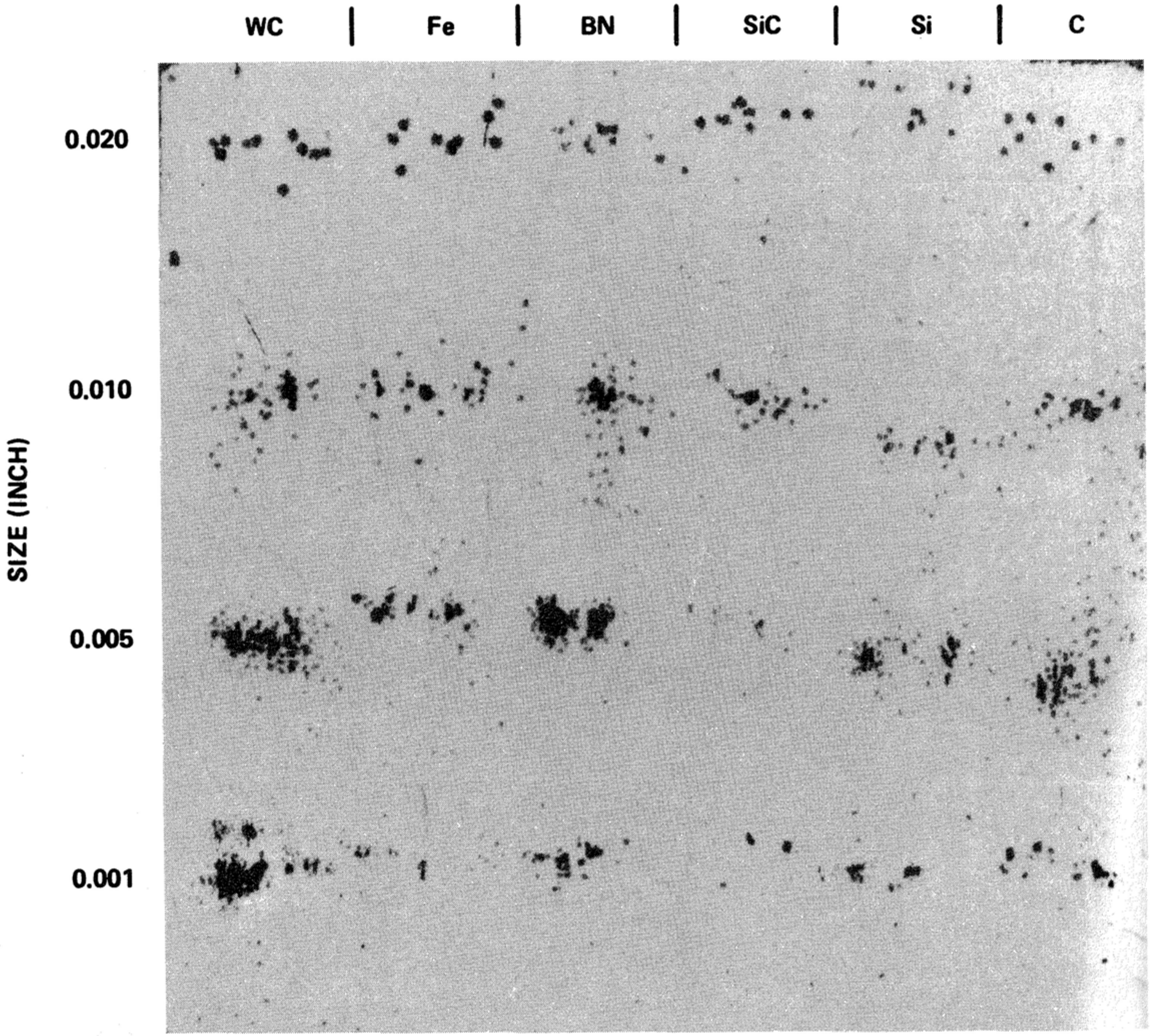
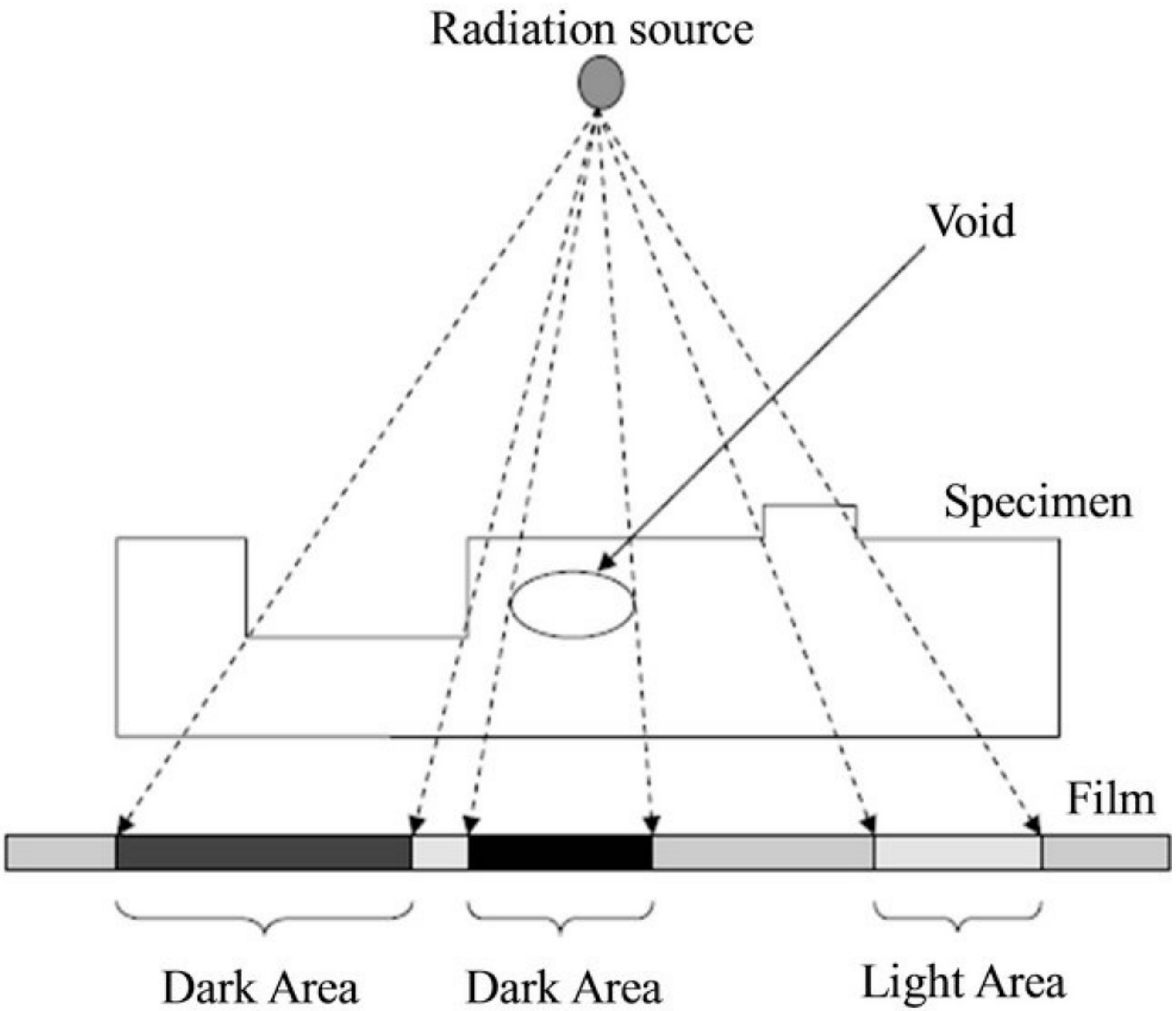
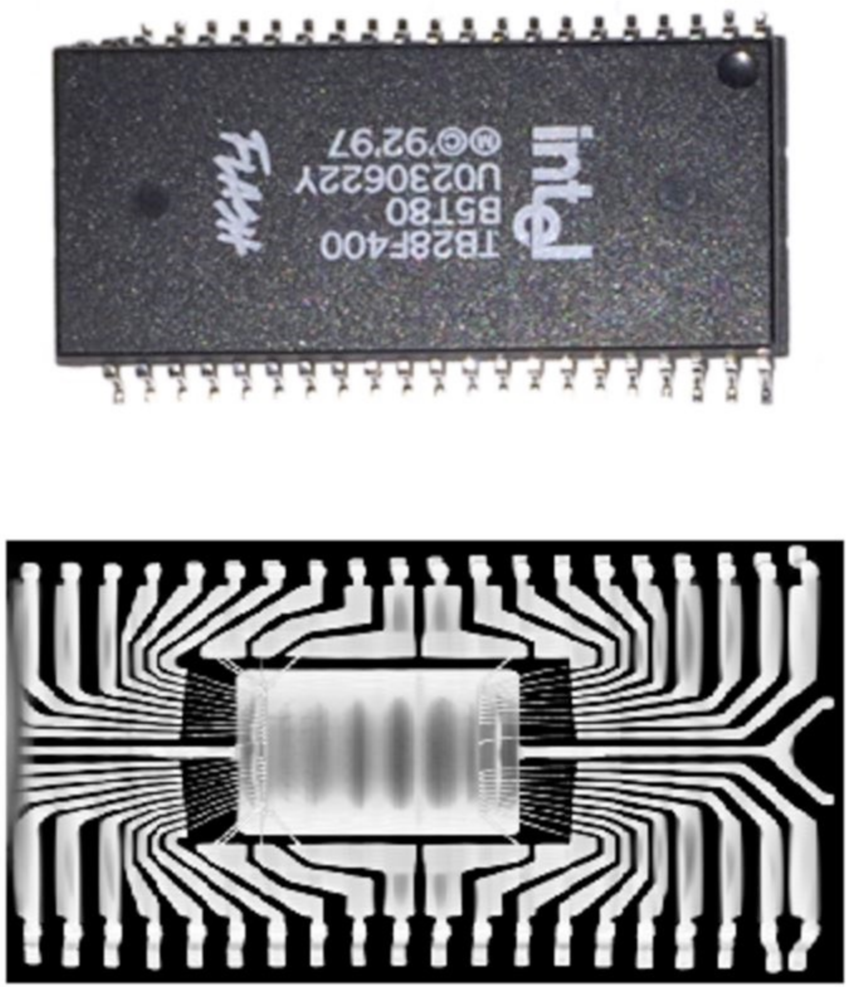


Figure 13.10 Ultrasonic C-scan with a 25-MHz transducer of a 0.64-cm (0.25-in.)-thick hot-pressed Si_3N_4 plate. (Courtesy Garrett Turbine Engine Company, Phoenix, Ariz., Division of Allied-Signal Aerospace.)

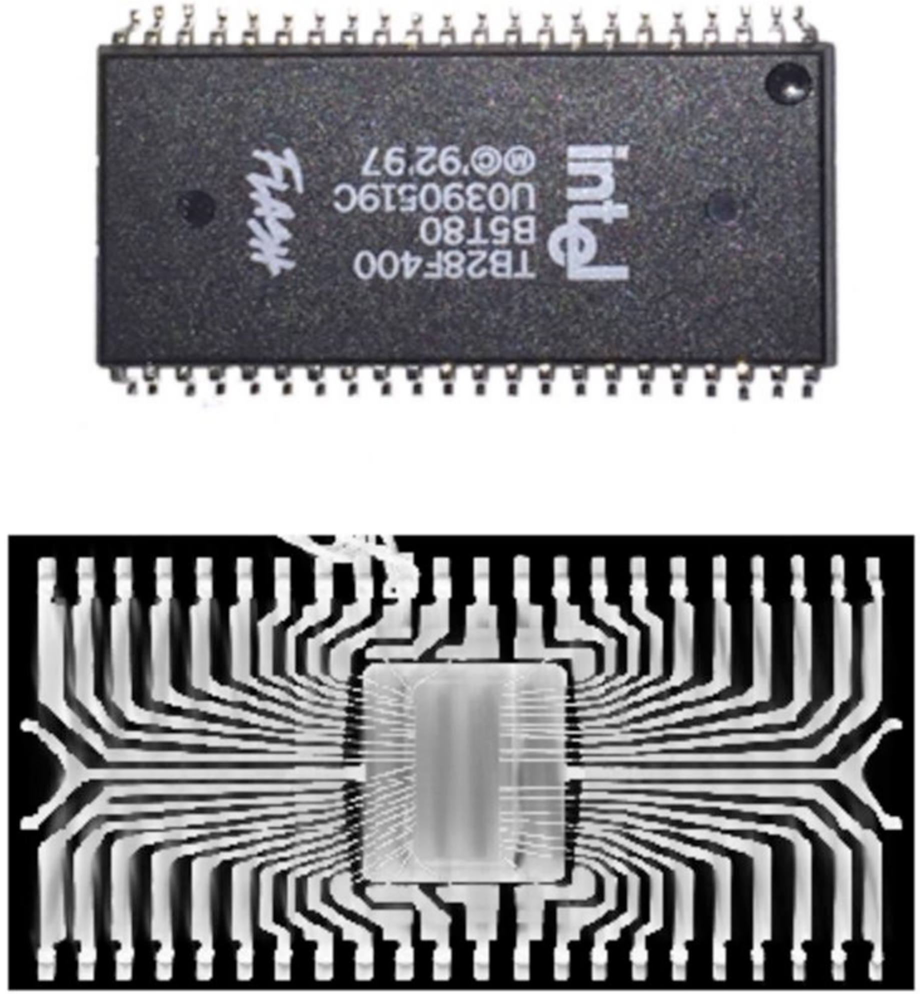
Radiographic testing



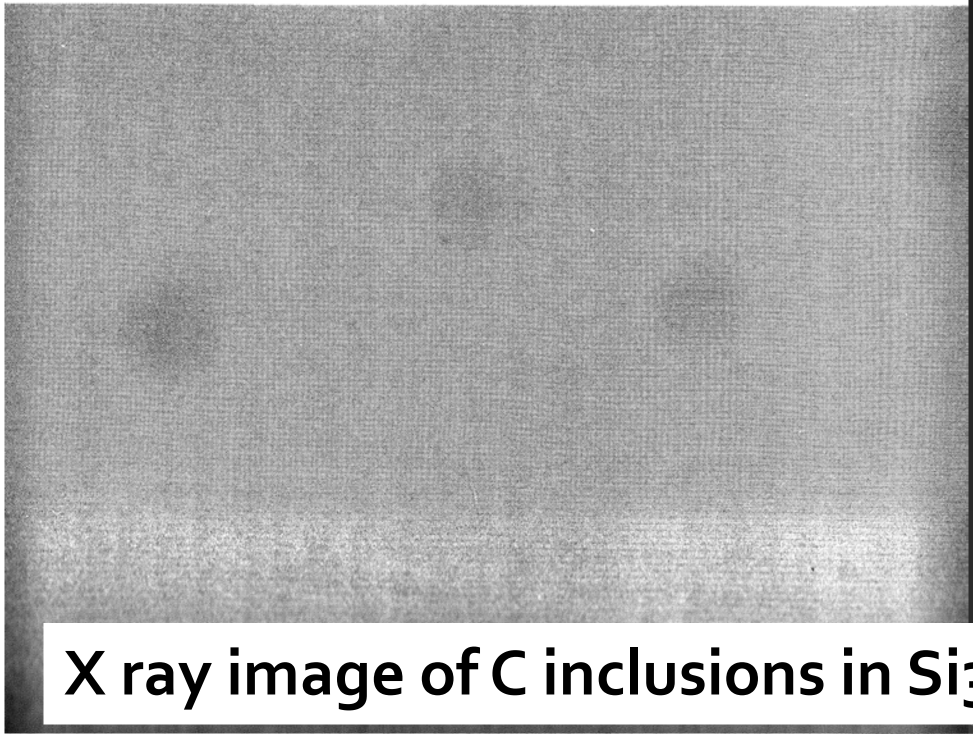
Radiographic testing of two chips

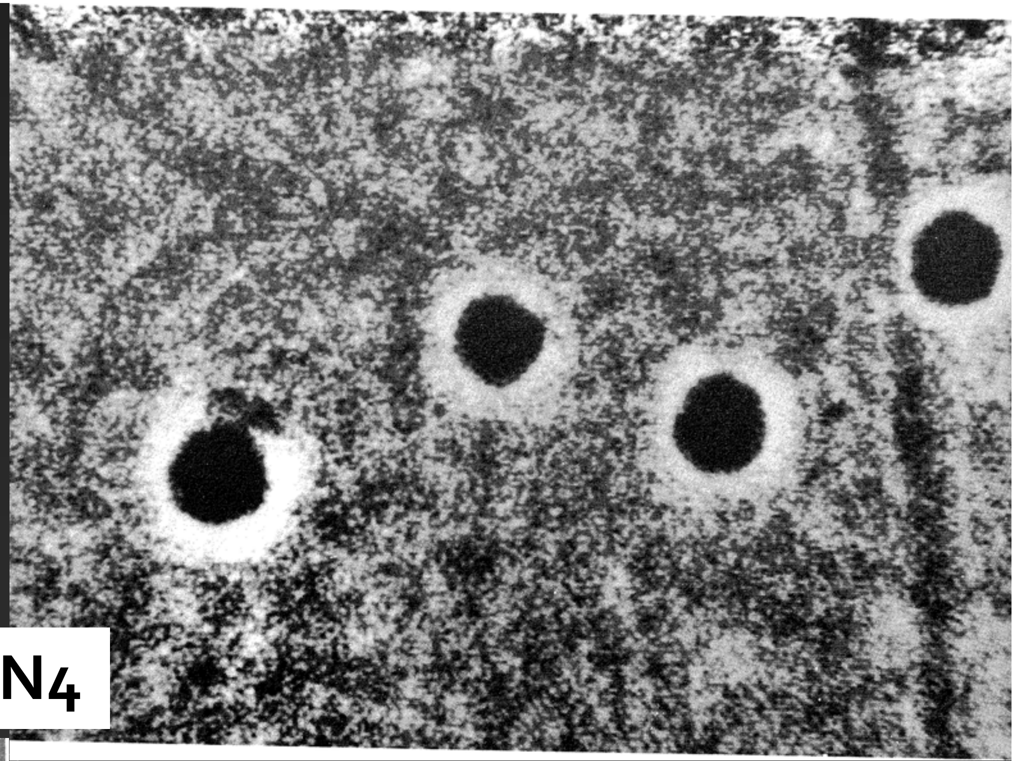


Counterfeit

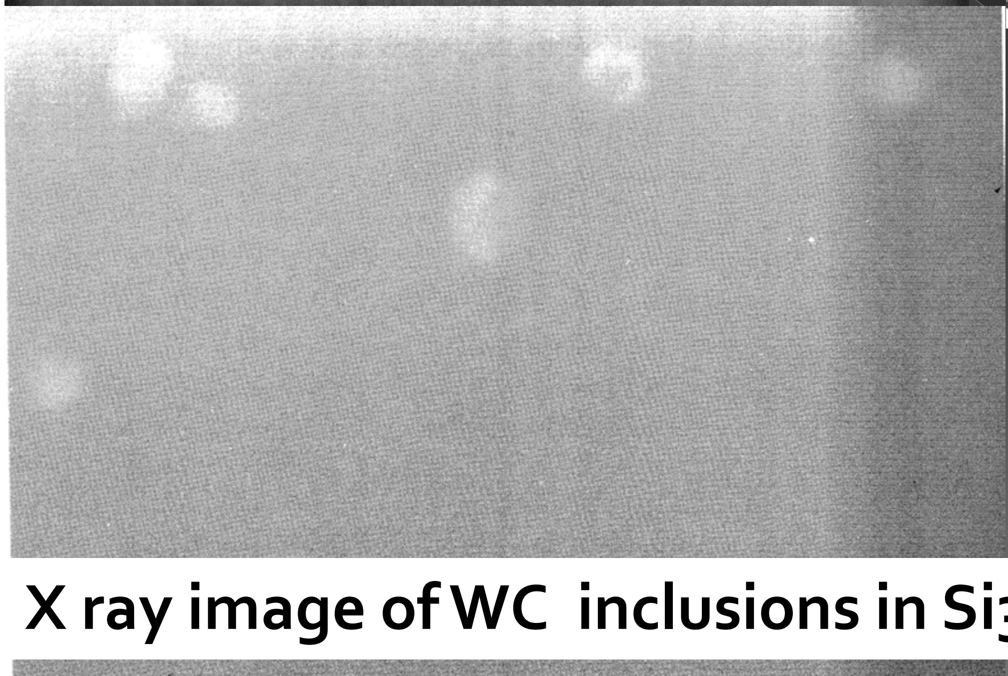


Authentic





X ray image of C inclusions in Si3N4



X ray image of WC inclusions in Si3N4

Magnetoscopic testing

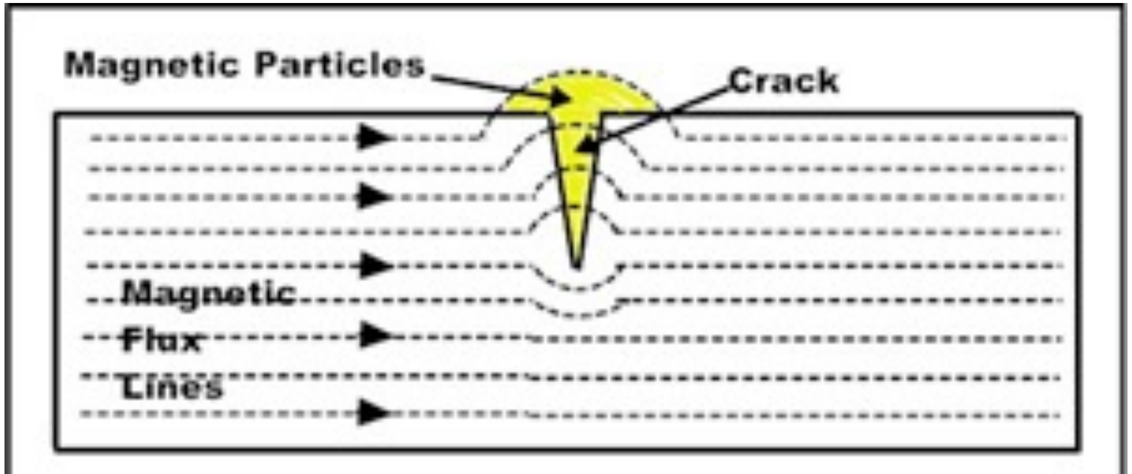
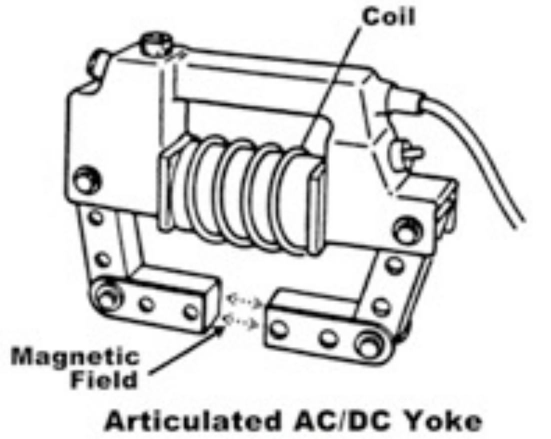
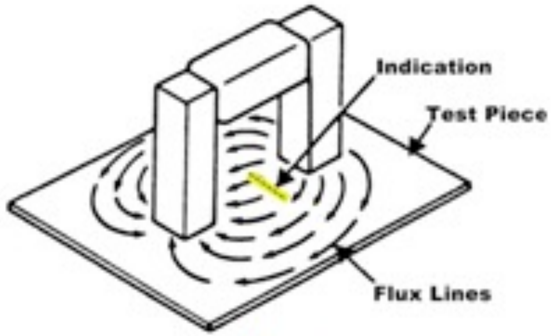


Figure 1



(a)



(b)

Figure 2

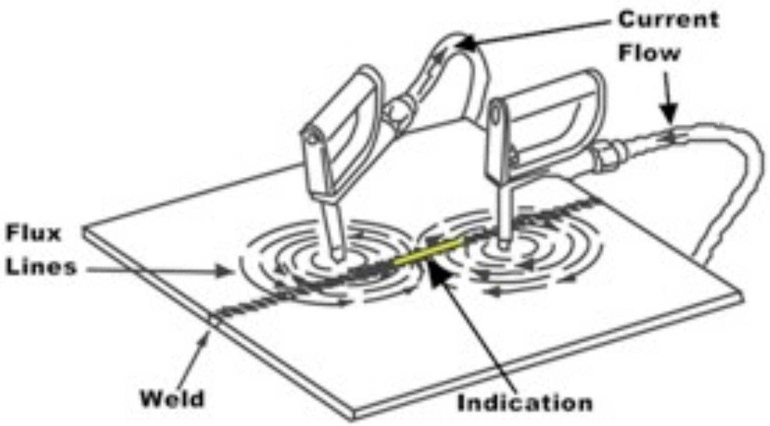


Figure 3

Eddy current testing

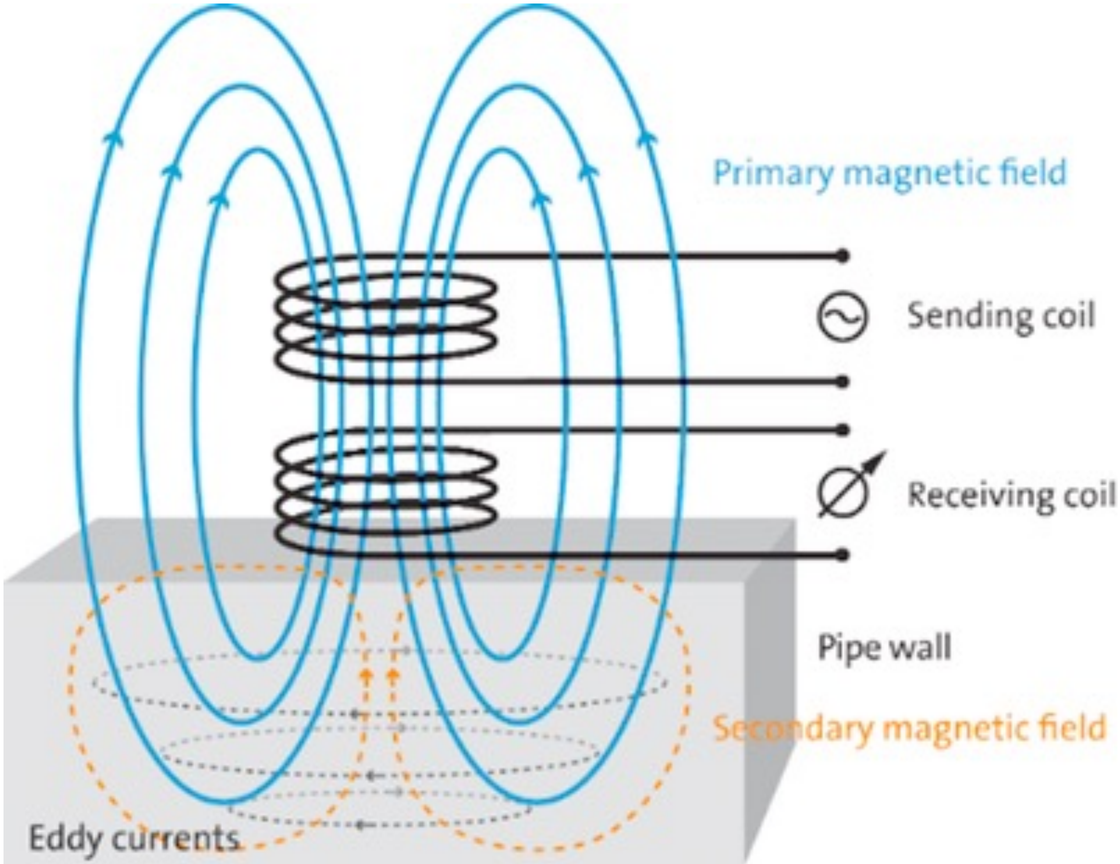


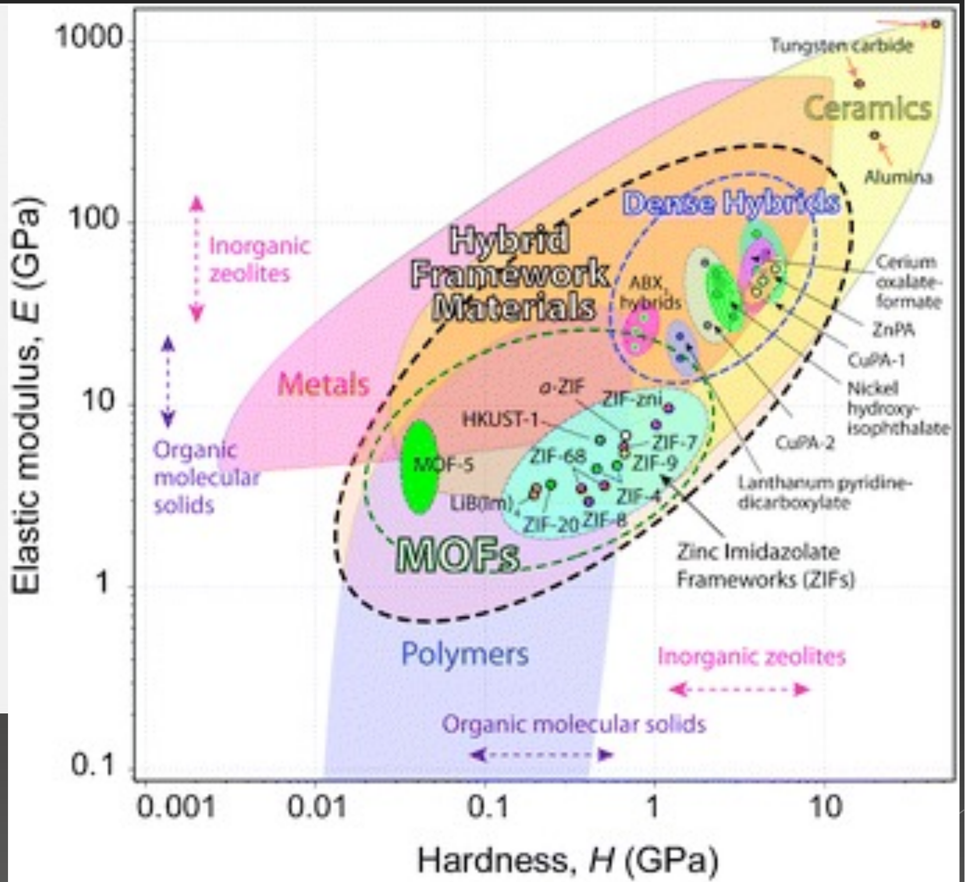
Table 14.2 Examples of Design Requirements of Various Applications and Ceramics with Properties Which Match the Requirements

Application	Requirements of the applications	Candidate ceramics	Key properties
Seal			
Turbine stator			
Heating element			
Rotary heat exchanger			
Heat sink for IC and transistor devices			
Furnace insulation			
Miniature capacitor			
High-speed, high-load bearing			
Segments of watch band			

SiC Heat exchanger

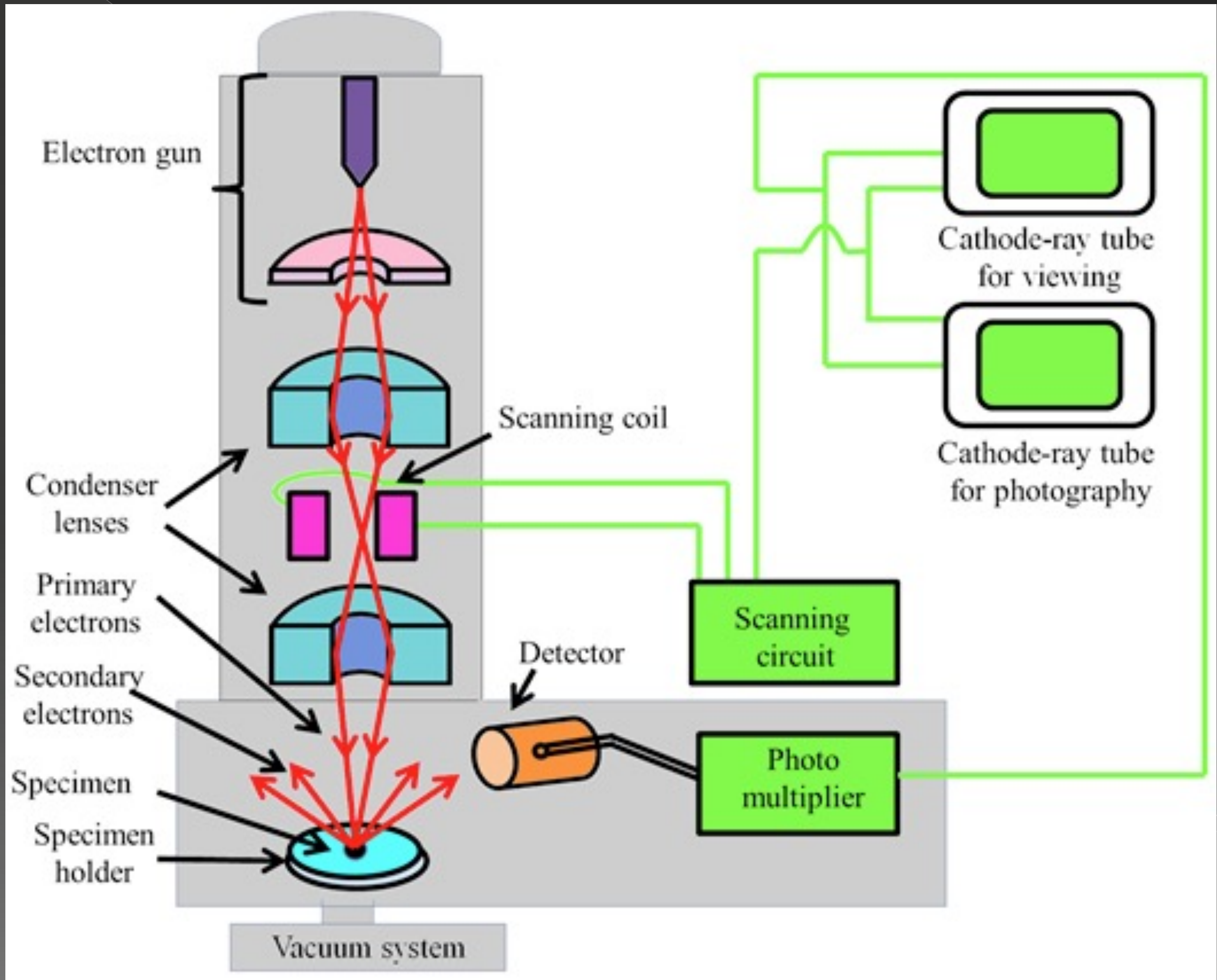
Ceramic seal for taps

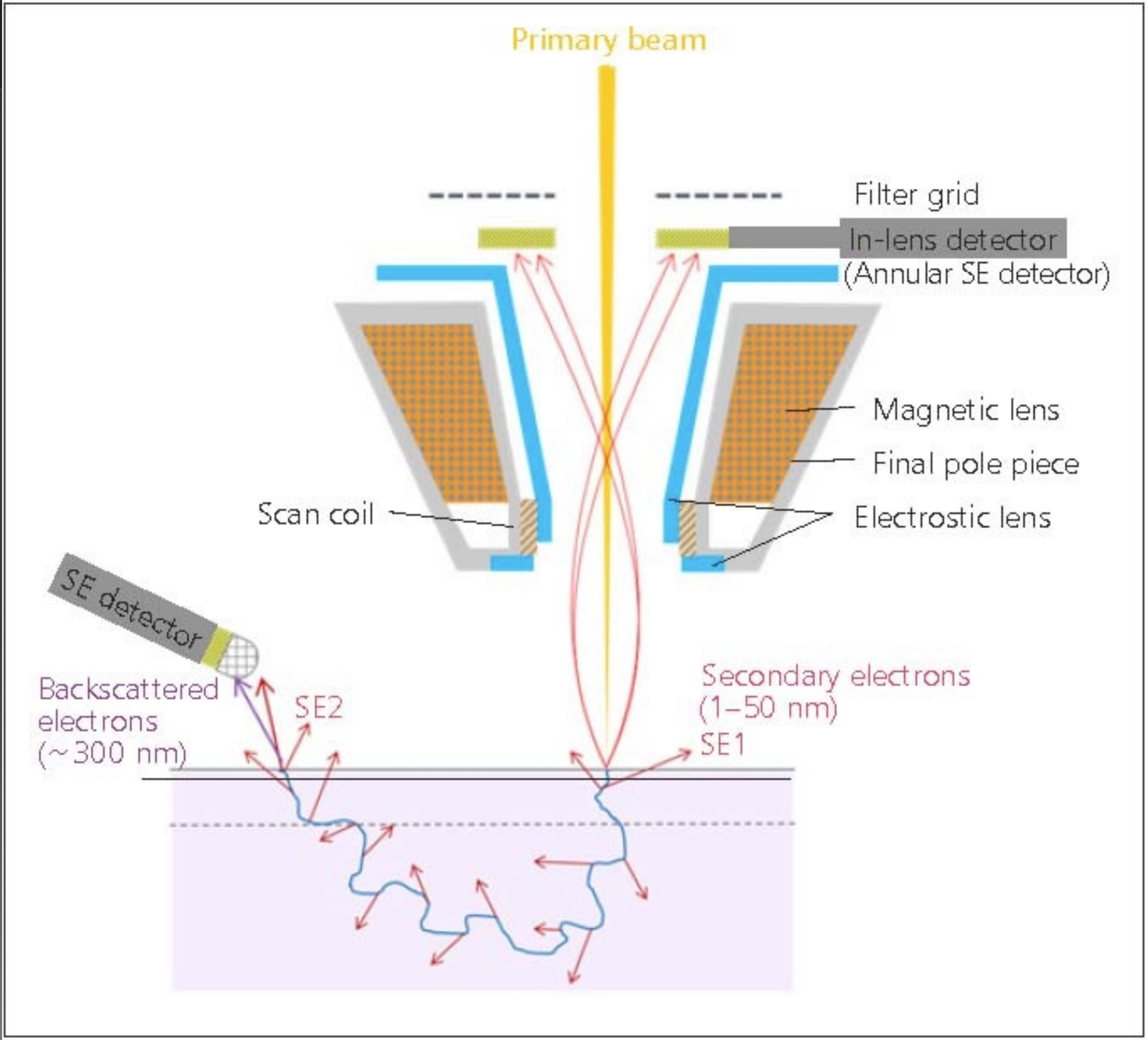
Sandblast nozzles



Rado watches

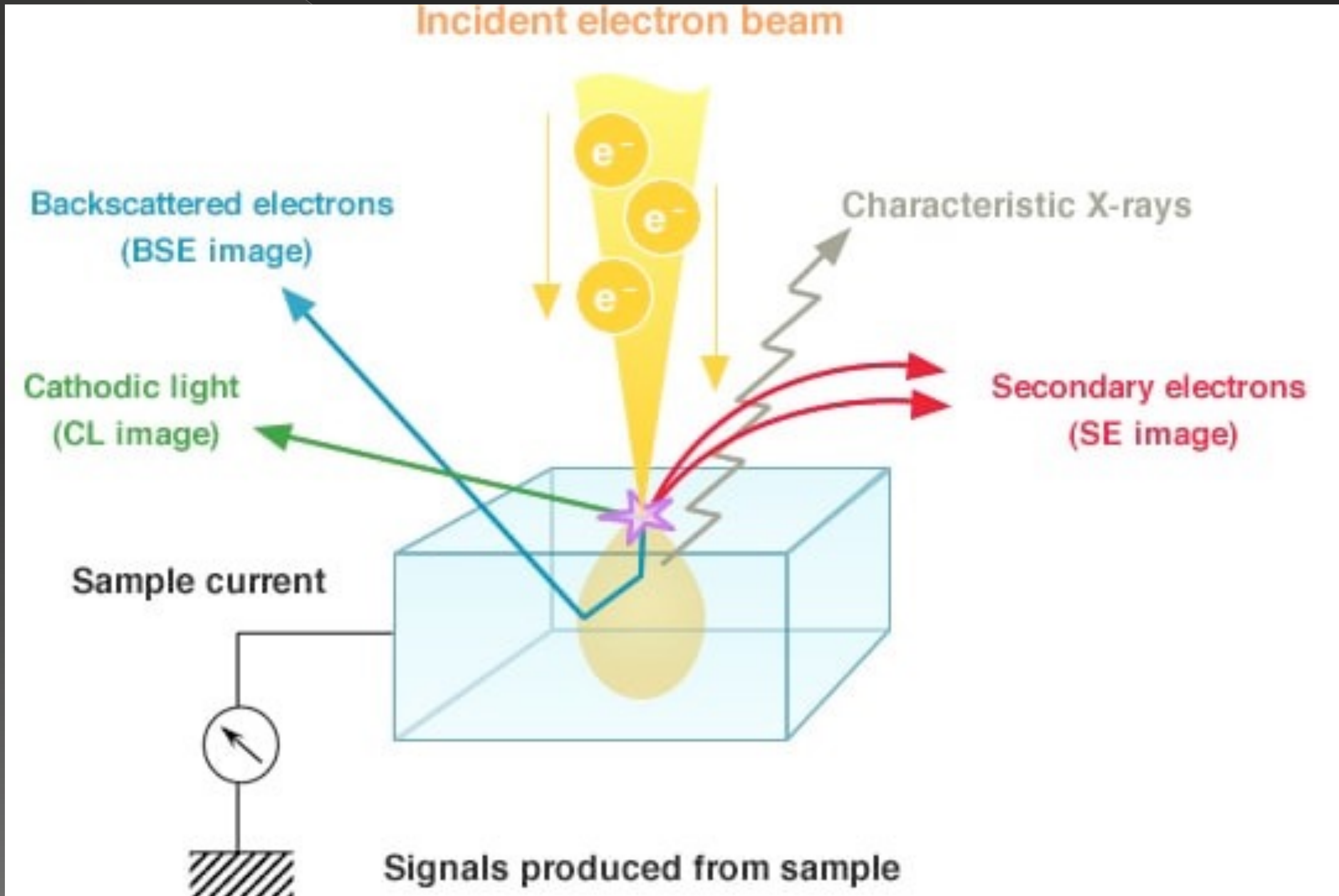
SEM fundamentals

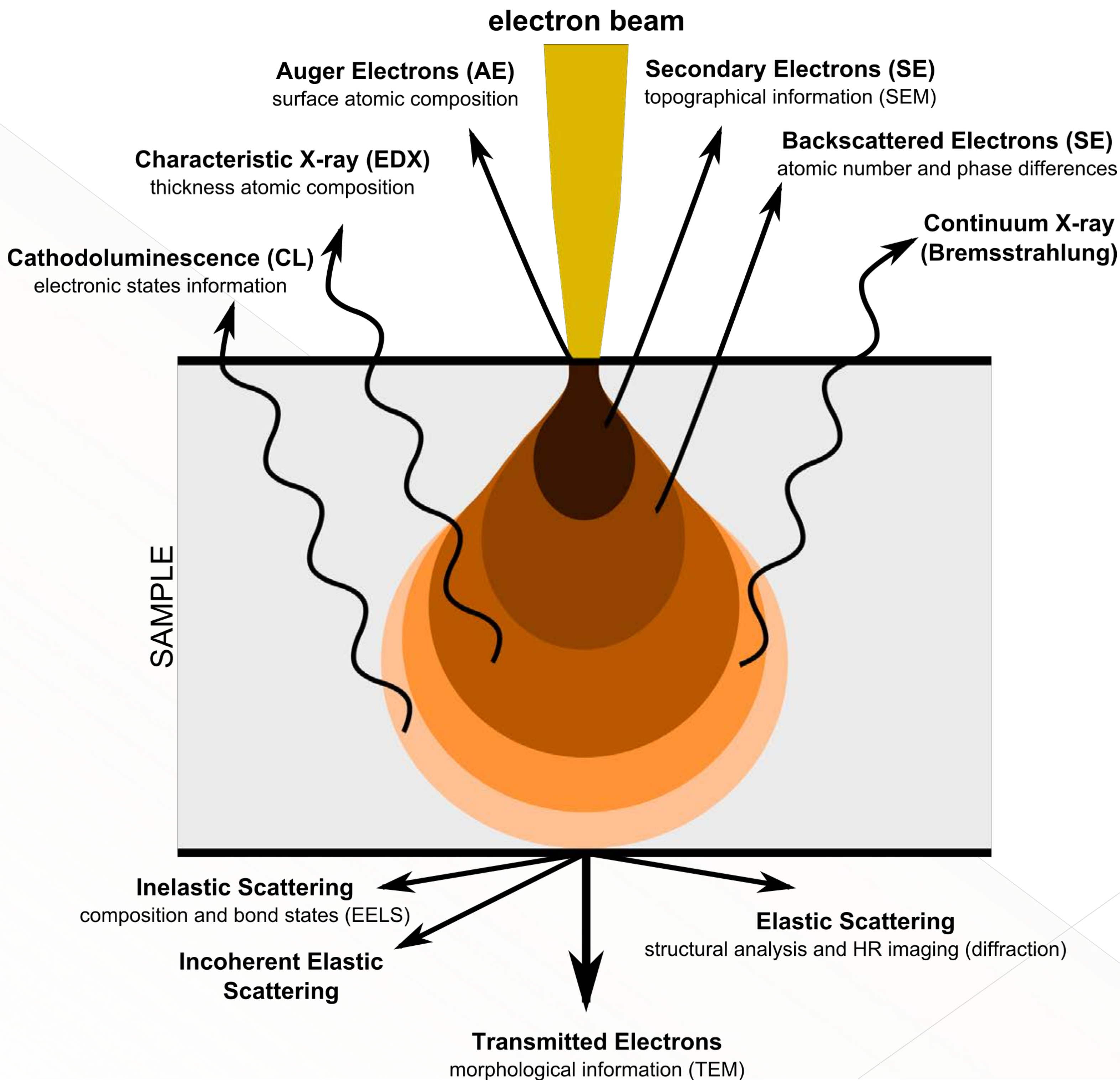


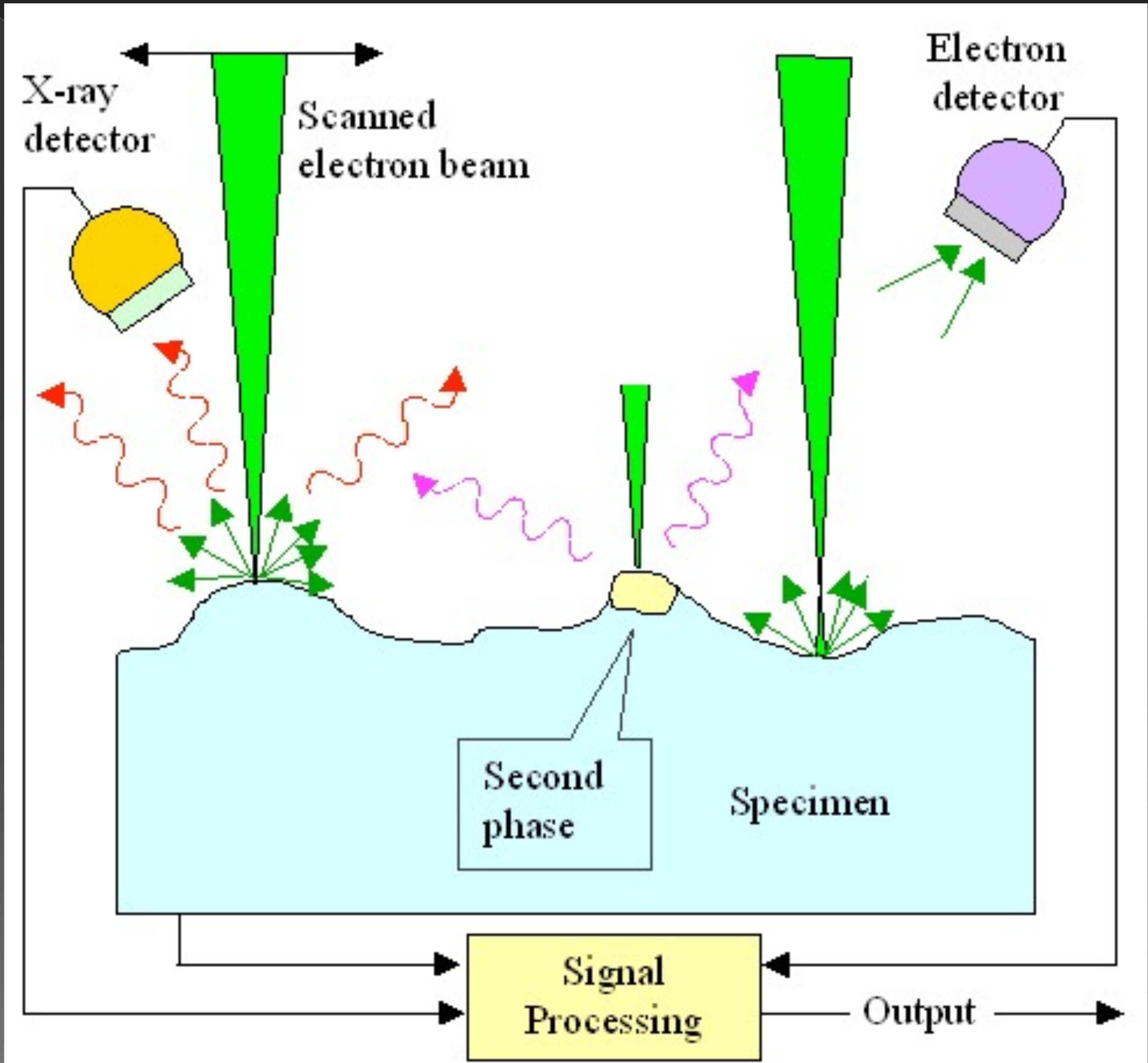


Primary beam
Filter grid
In-lens detector
(Annular SE detector)
Magnetic lens
Final pole piece
Scan coil
Electrostic lens
SE detector
Backscattered
electrons
(~300 nm)
SE2
Secondary electrons
(1–50 nm)
SE1

E-beam sample intercation




electron beam
Auger Electrons (AE)
surface atomic composition
Secondary Electrons (SE)
topographical information (SEM)
Backscattered Electrons (SE)
atomic number and phase differences
Characteristic X-ray (EDX)
thickness atomic composition
Continuum X-ray
(Bremsstrahlung)
Cathodoluminescence (CL)
electronic states information
SAMPLE
Inelastic Scattering
composition and bond states (EELS)
Incoherent Elastic
Scattering
Elastic Scattering
structural analysis and HR imaging (diffraction)
Transmitted Electrons
morphological information (TEM)


X-ray detector
Scanned electron beam
Electron detector
Second phase
Specimen
Signal Processing
Output

Compositional contrast

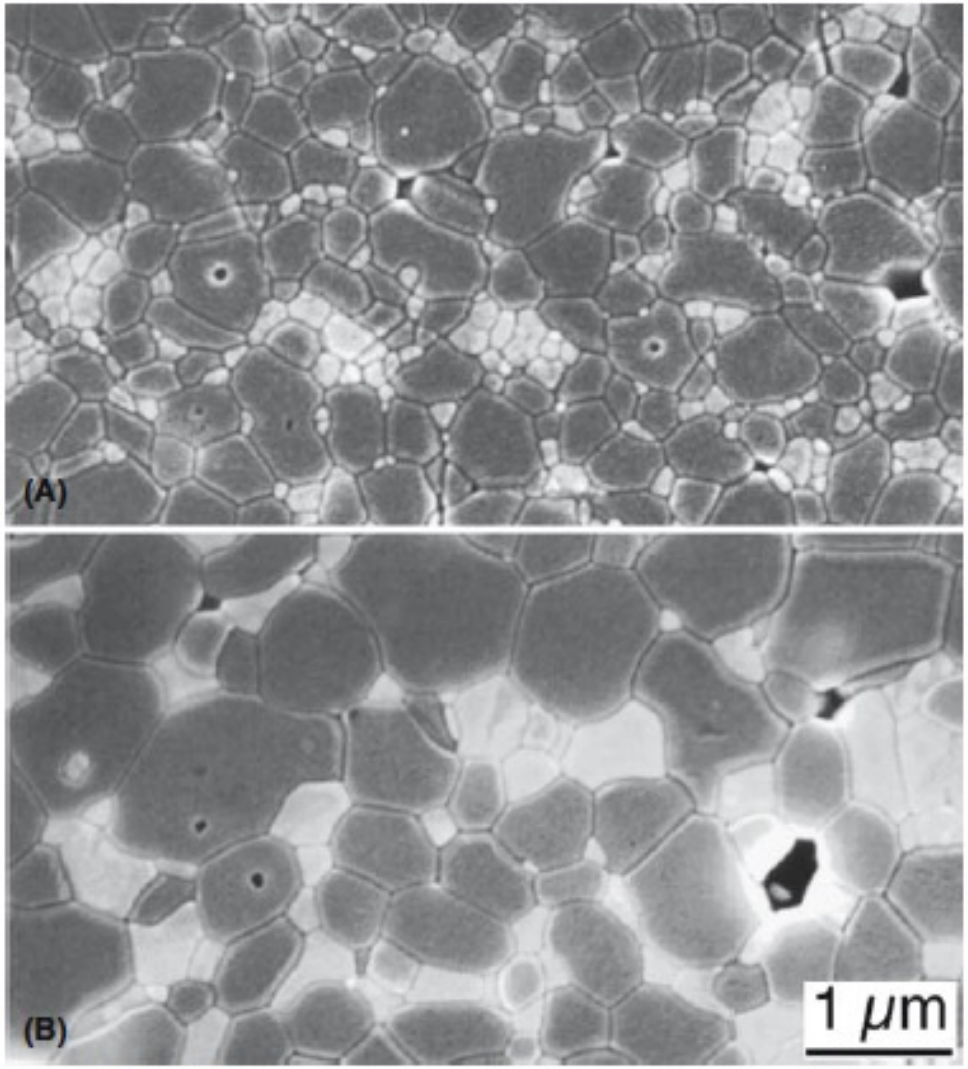
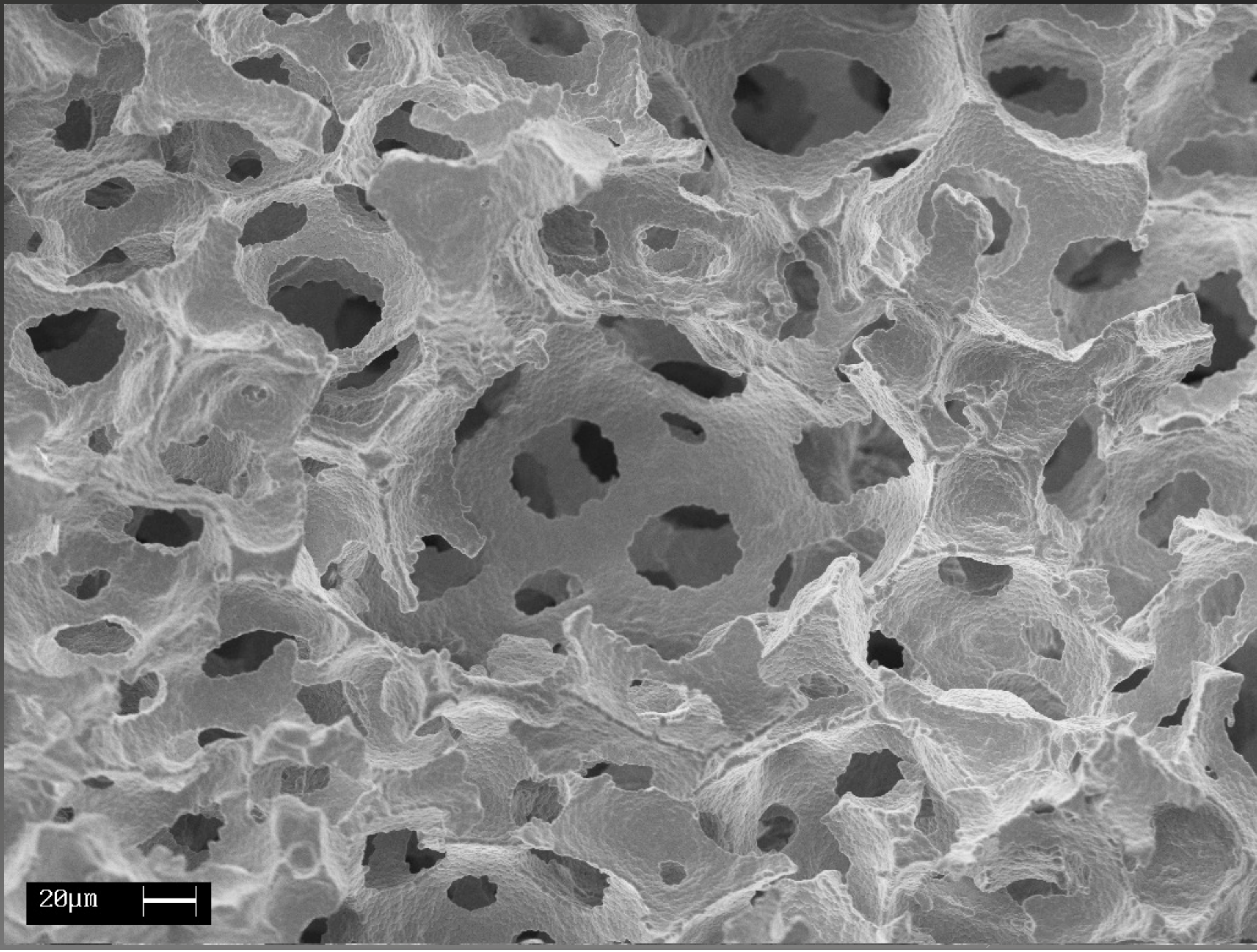
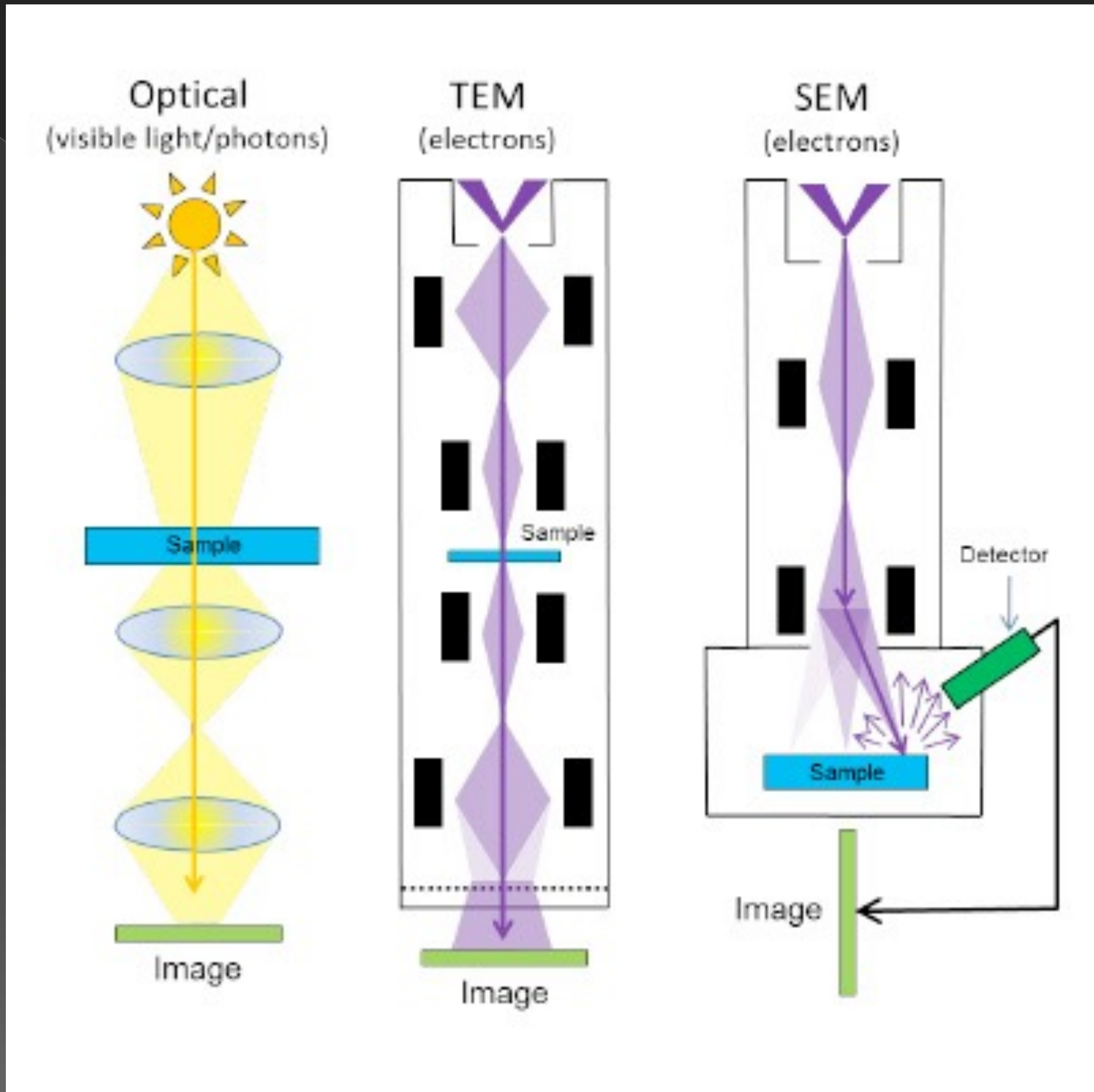


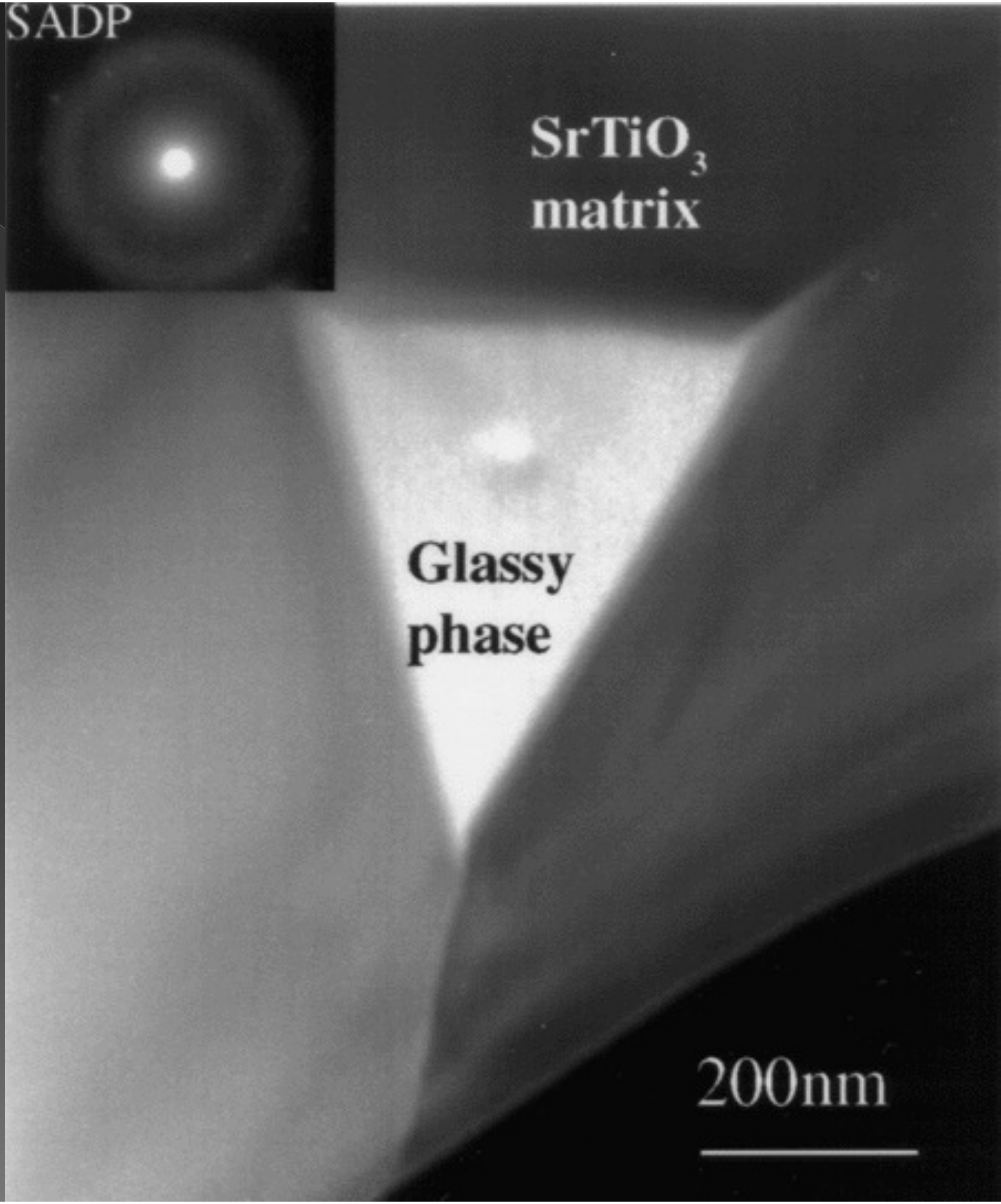
FIGURE 24.27 Two-phase ceramics. (a) As sintered and (b) heat treated at 1600°C for 30 hours. ZTA 30% (zirconia-toughened alumina with 30 vol% YSZ containing 10 molar% yttria).

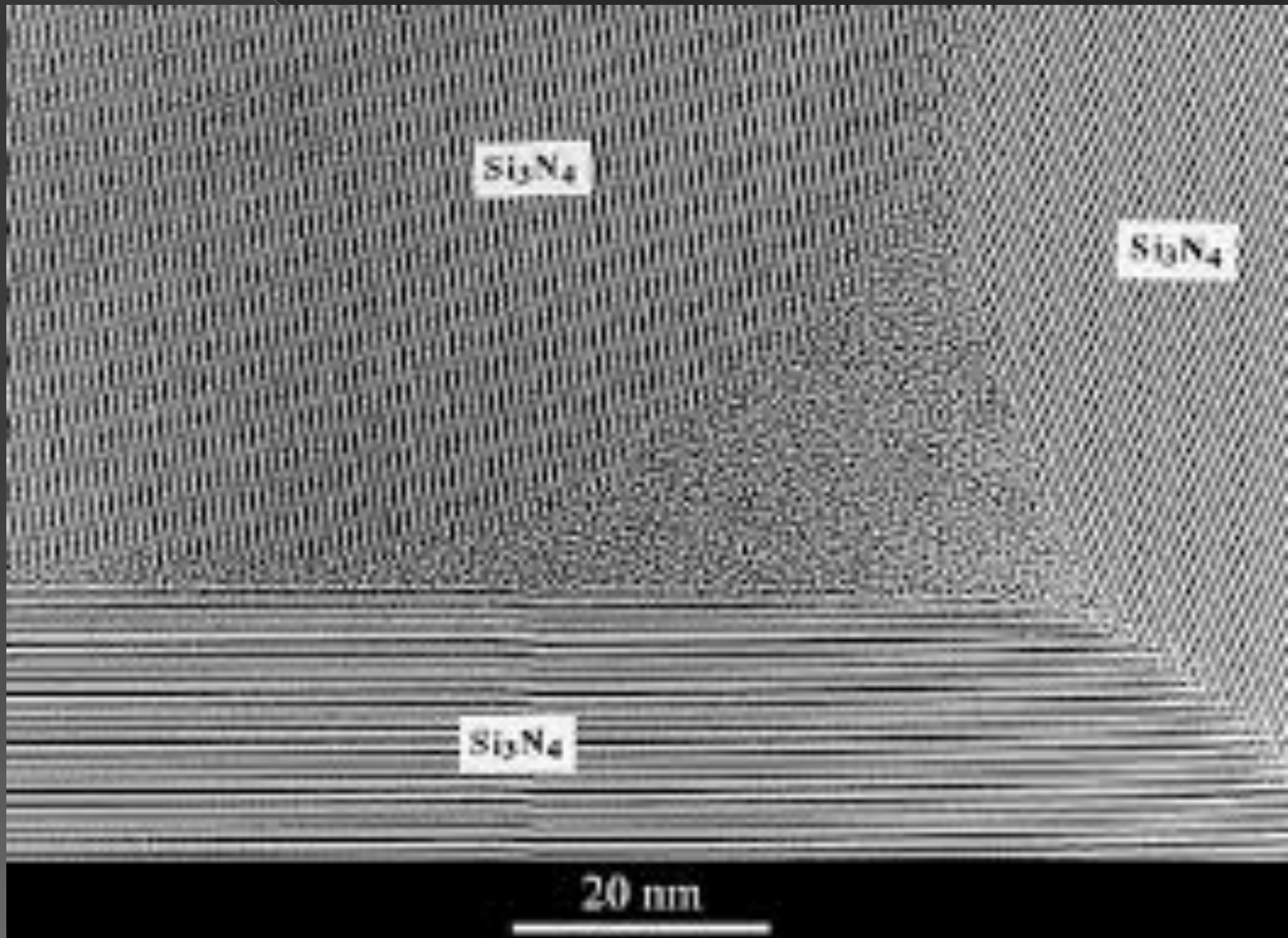
Topographycal contrast



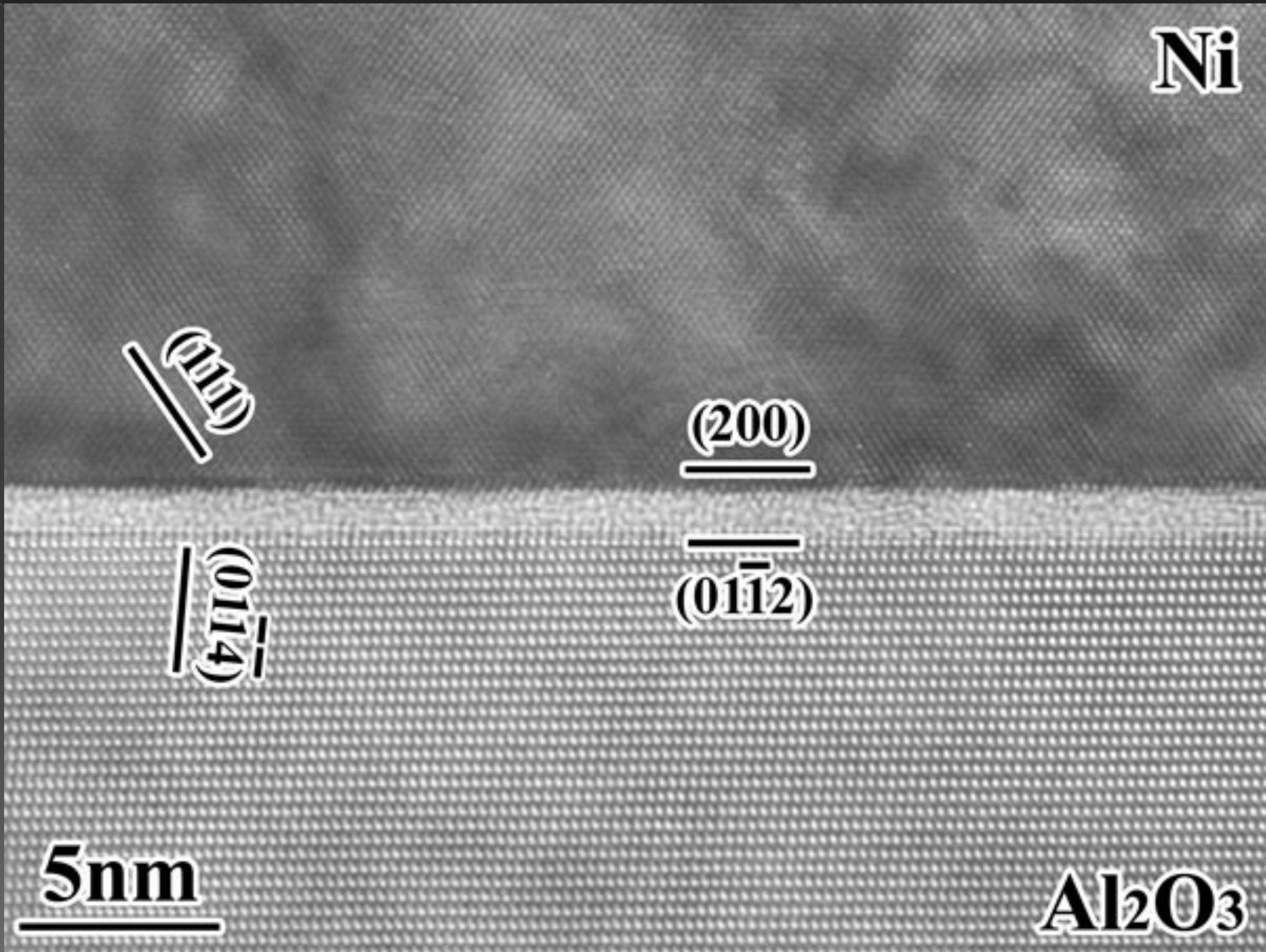


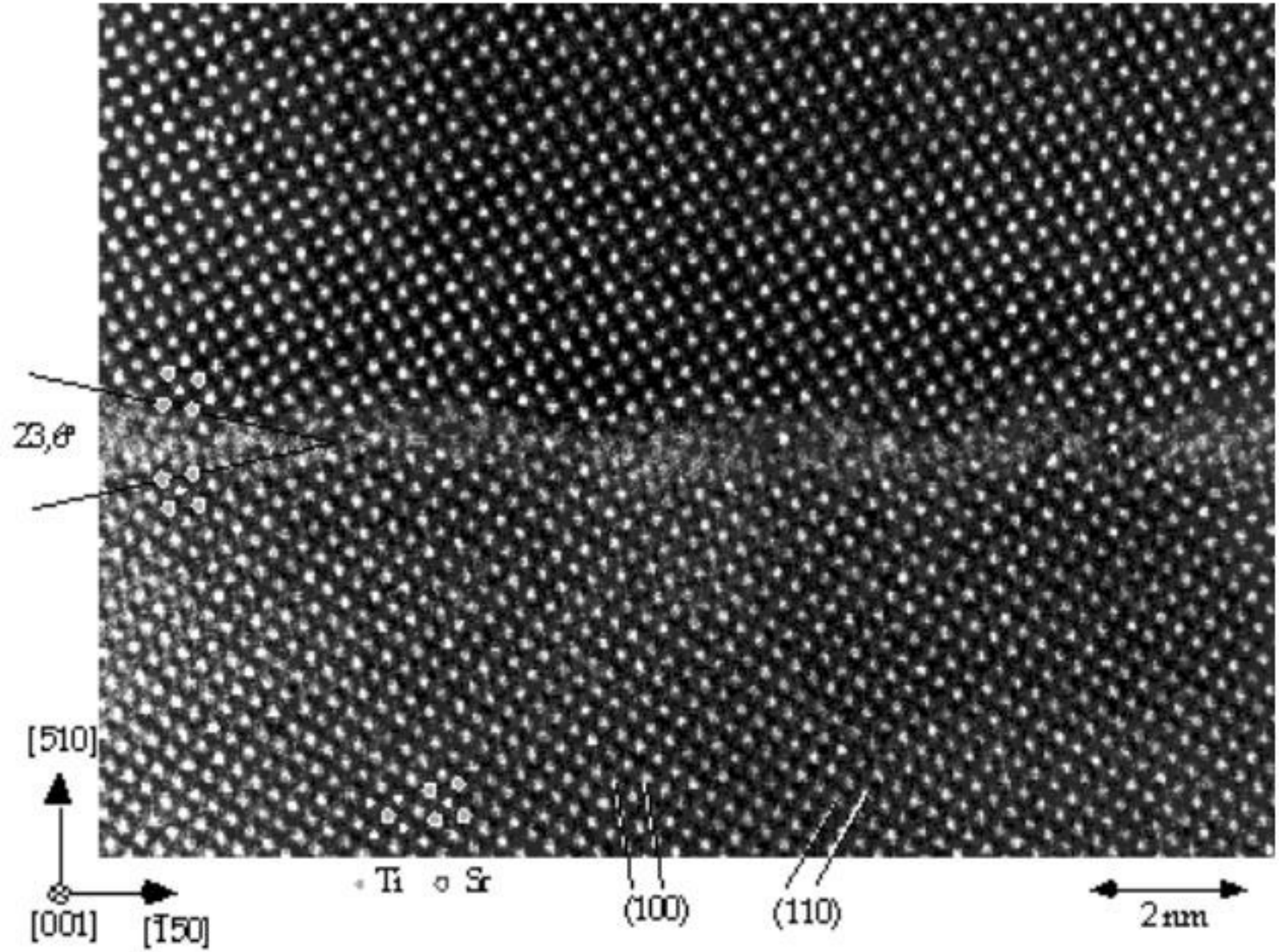
Optical
(visible light/photons)
TEM
(electrons)
SEM
(electrons)
Sample
Sample
Detector
Sample
Image
Image
Image


SADP
SrTiO3 matrix
Glassy phase
200nm

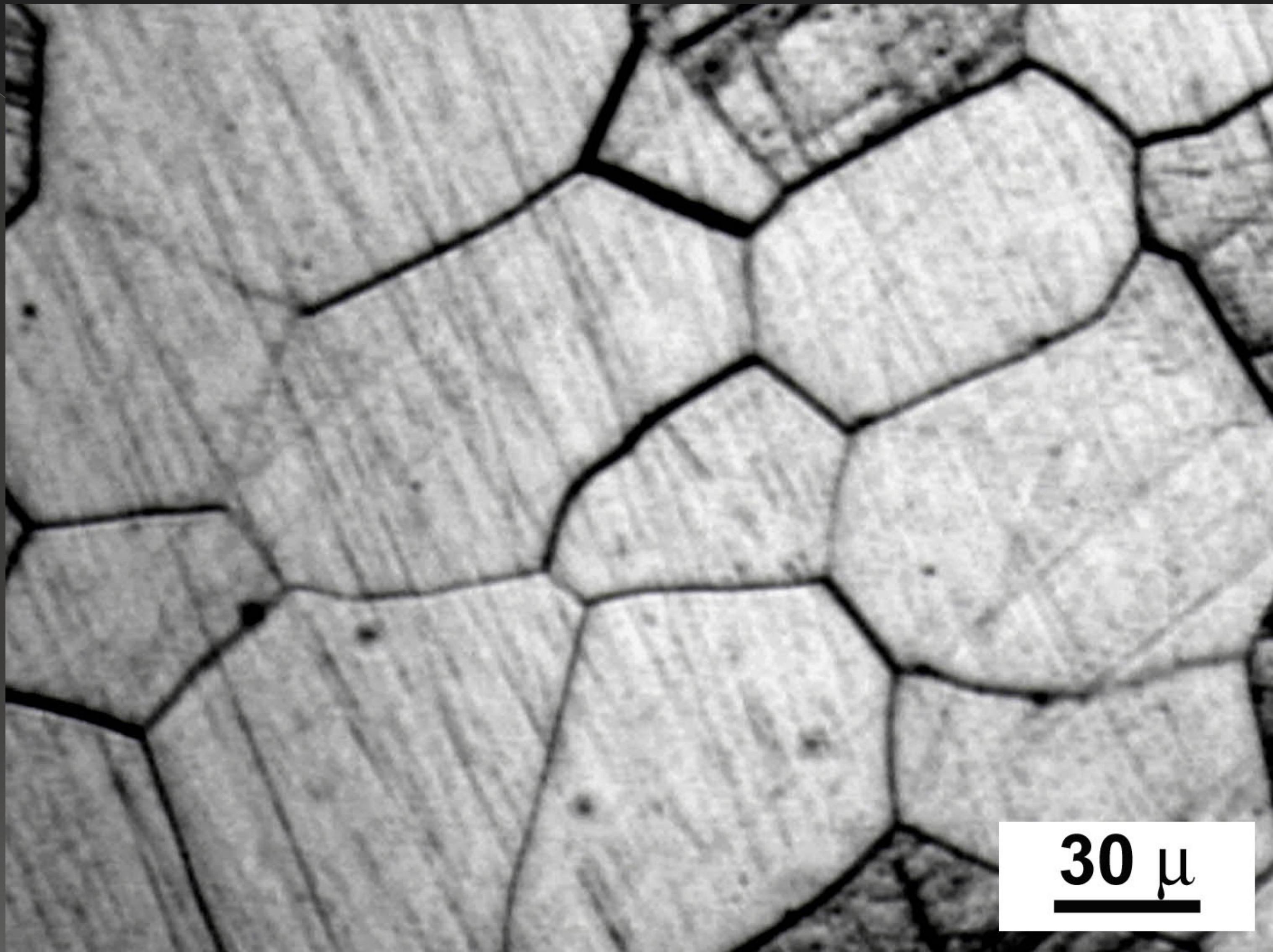


Si3N4
Si3N4
Si3N4
20 nm


Ni
(200)
(01̄12)
5nm
Al2O3



23,6°
[510]
[001]
[1̄50]
Ti
Sr
(100)
(110)
2 nm


30 μ