Amorphous materials

similarities and differences to crystalline materials

PV-lab
IMT NEUCHATEL

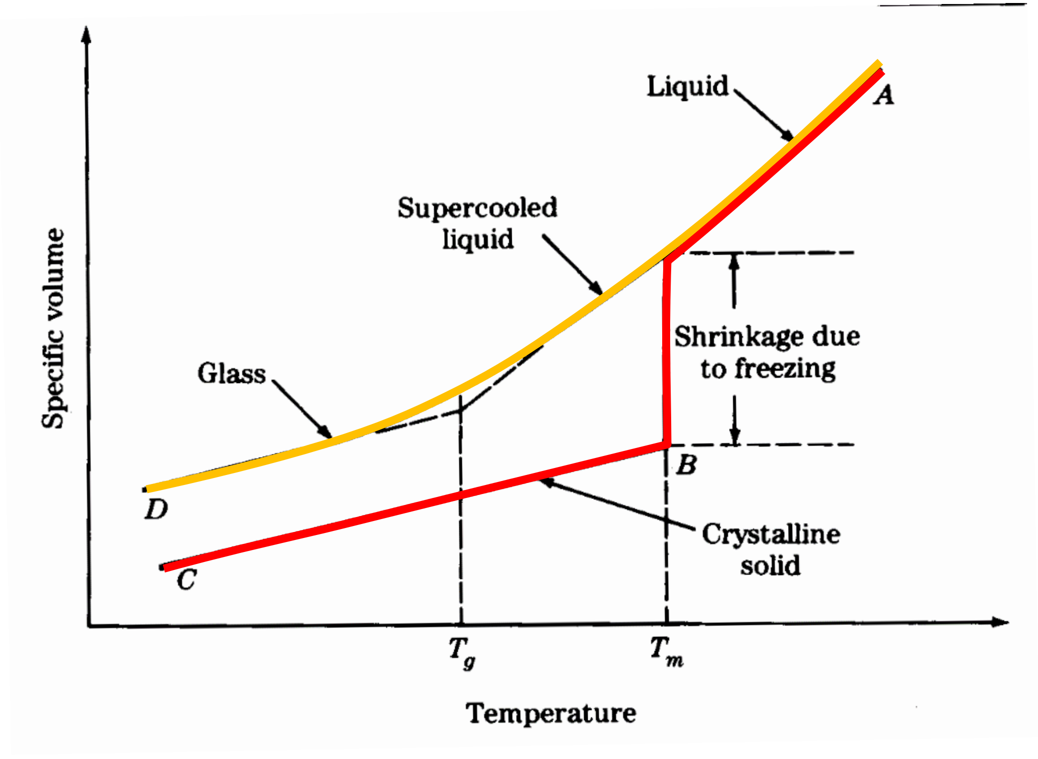
Well known amorphous material: glass

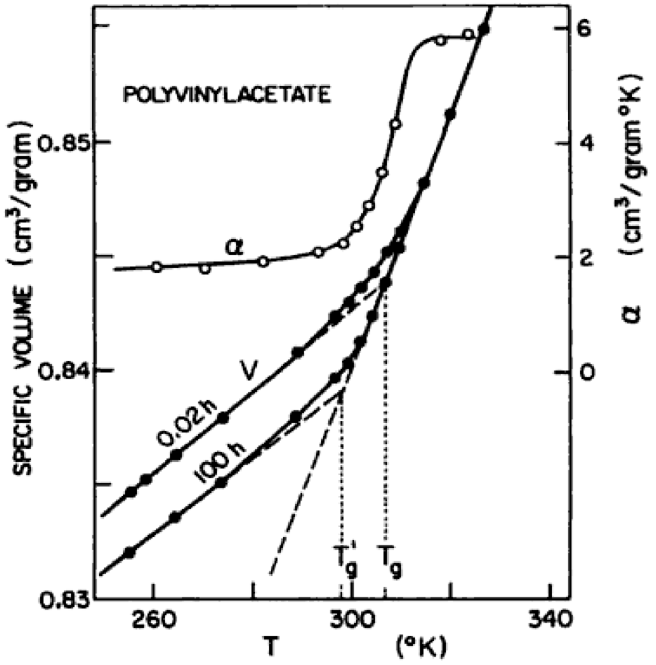
volcanic glass (obsidian) is probably among the oldest used materials (preceded by wood and bone)

modern glass:

- obtained by cooling from melt of quartz (SiO_2) and fluxing agent (Na_2O)
- glass transition at ca. 550°C
- typically $(SiO_2)_{0.8}(Na_2O)_{0.2}$, other ingredients for special properties (K_2O, Fe_2O_3, B_2O_3, PbO, etc.)

The glass transition





- solidification without crystallization
- continuous volume change, but sharp change in expansion coefficient
- freezing of liquid state, no far range order among molecules or atoms
- metals require ultra-fast cooling, few bulk metallic glasses exist

Common amorphous materials

Material		Applications	Advantageous properties
Oxide glasses	$(SiO_2)_{0.8}(Na_2O)_{0.2}$	Window glass...	Transparency, resistance, large sheets fabrication
fused Quartz	SiO_2	Optical fibers	High transparency
Organic polymers	polystyrene, polyethylene, etc.	Plastic	Mechanical resistance, low weight
Chalcogenides	Se, As_2Se_3	Xerography	photoconductivity, Large area thin films (copy machine drums)
Tetravvalent semiconductors	a-Si:H	thin film transistors	Large area, photoconductive
	a-C	Protective coatings	Hardness, low friction
Metallic glasses	$Fe_{0.8}B_{0.2}$	Non-adhesive layer, electrical transformer	Ferromagnetic, low magnetic hysteresis, ribbon fabrication
amorphous oxides	$InGaZnO_4$	emerging TFT channel materials	transparency, stability

From order to disorder

Tetravalent bonding in the fcc structure

Silicon:

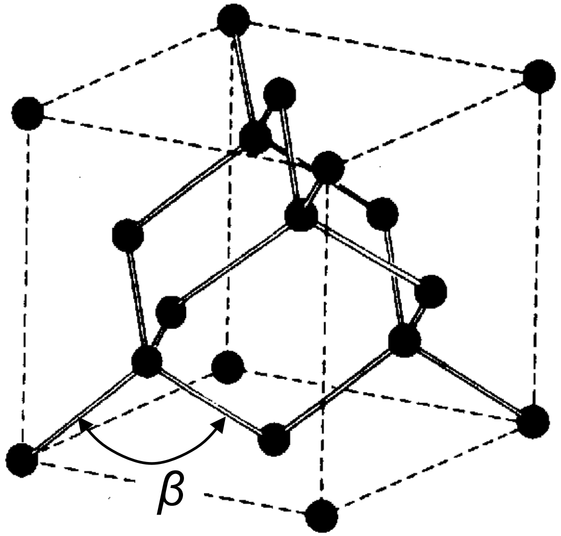
Specific weight: 2.329 g/cm^3

Lattice parameter 5.43095 Å
eight r atoms in unit cell
=> atomic density: 5x10^{22} 1/cm^3

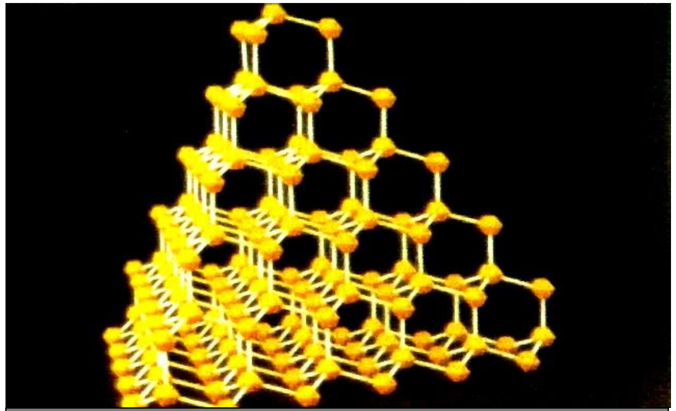
Next neighbour (quarter cube diagonal: 2.35 Å
Second neighbour (half face diagonal): 3.83 Å

Bond angle β: 109°
(can be determined from 1st and 2nd shell radii)

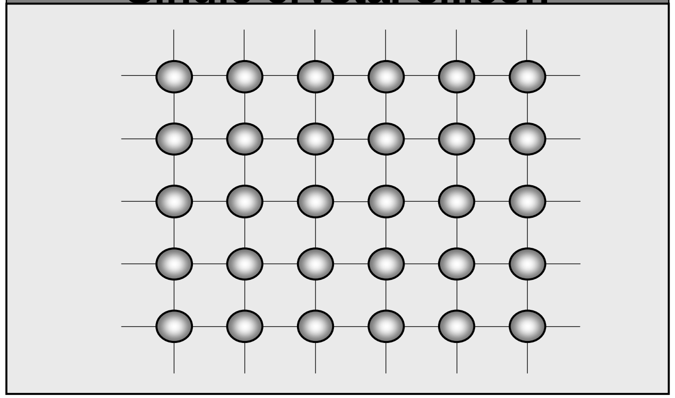
diamond structure:
fcc lattice with basis

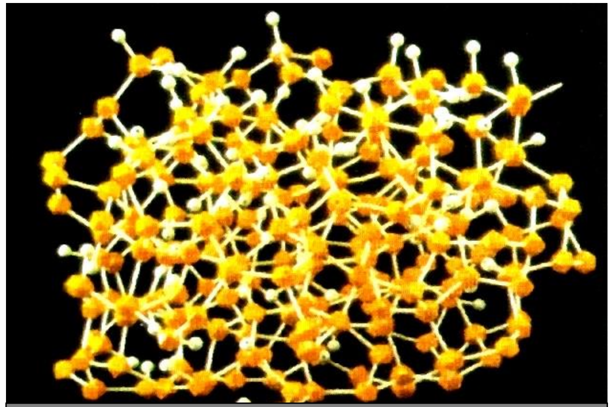


Model atomic structure of c-Si and a-Si:H

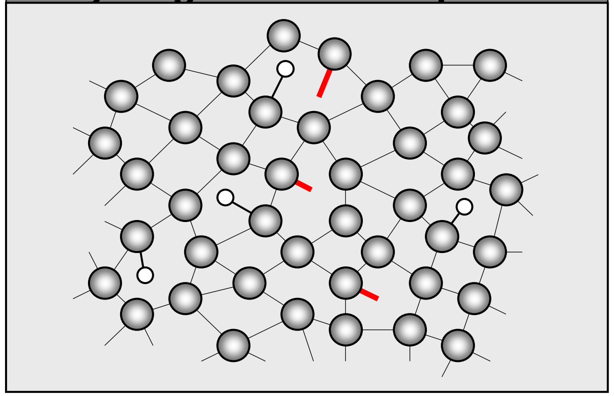


Single crystal silicon





Hydrogenated amorphous



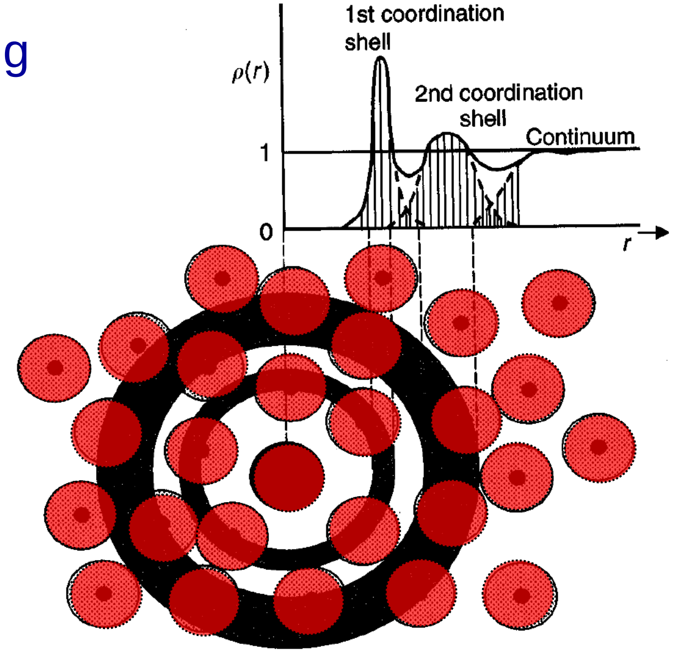
Ball and stick models are illustrative, BUT:
one “defect” in a model with 1000 atoms: defect density of ~10^{19} 1/cm^3 !
we can build bigger models, but calculating them is almost impossible!

Probing the atomic structure

XRD (X-ray diffraction) => crystallographic structure (none in amorphous solid)
SAXS (small angle X-ray scattering) => near neighbours, voids
XAFS (X-ray absorption fine structure) => nearest neighbour information

alternative to X-rays: neutron scattering

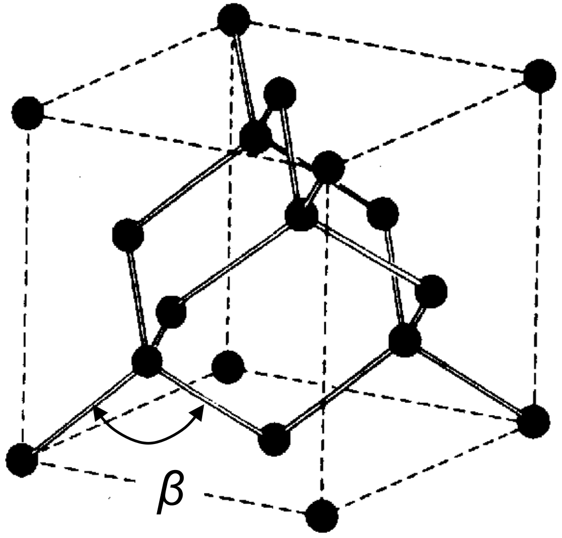
Experimental access to
short range order:
radial distribution function



other methods: IR and Raman scattering => vibrational properties

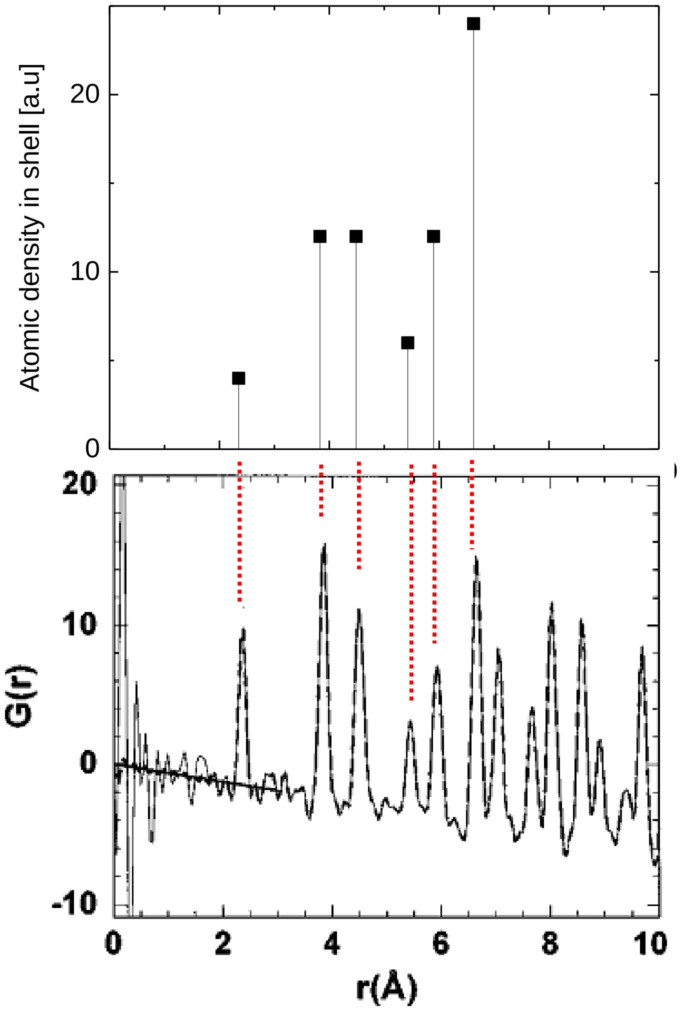
Nearest neighbours in the fcc lattice

High energy X-ray scattering



Bond angle

$$\sin\beta/2=\frac{d(2^{nd})/2}{d(1^{st})}$$

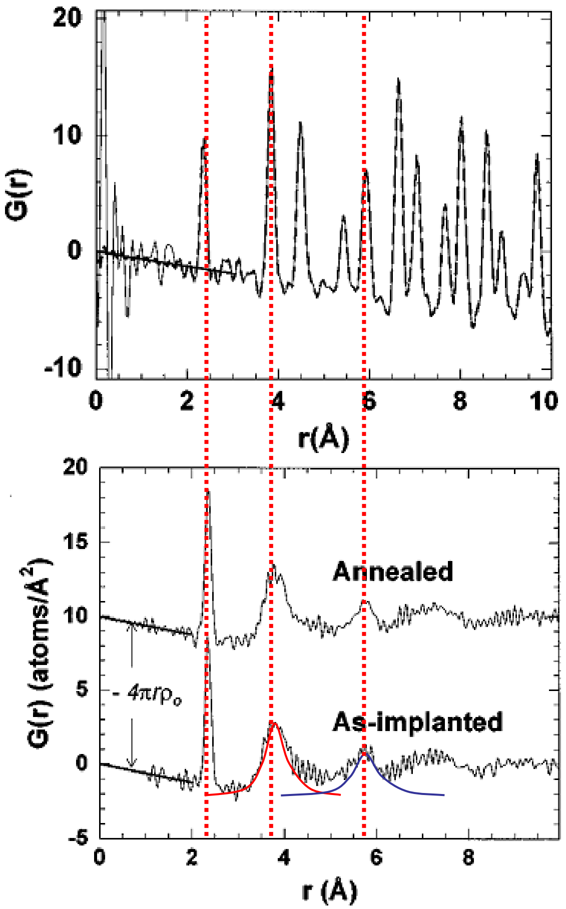


Laaziri, PRB 60(19), 13520 (1999)

Nearest neighbours in a-Si (H-free)

powder c-Si

a-Si (H-free)



Coordination:
c-Si: 4
a-Si: 3.8-3.9 (vacancies)

a-Si: first and second shell radii:
2.35 Å and 3.8 Å (same as c-Si)
=> bond angle $\beta \approx 108°$

a-Si shows tetrahedral bonding on short range, bonding is disordered

Note: hydrogen cannot be probed by XRD

Laaziri, PRB 60(19), 13520 (1999)

Effect of hydrogen on structure?

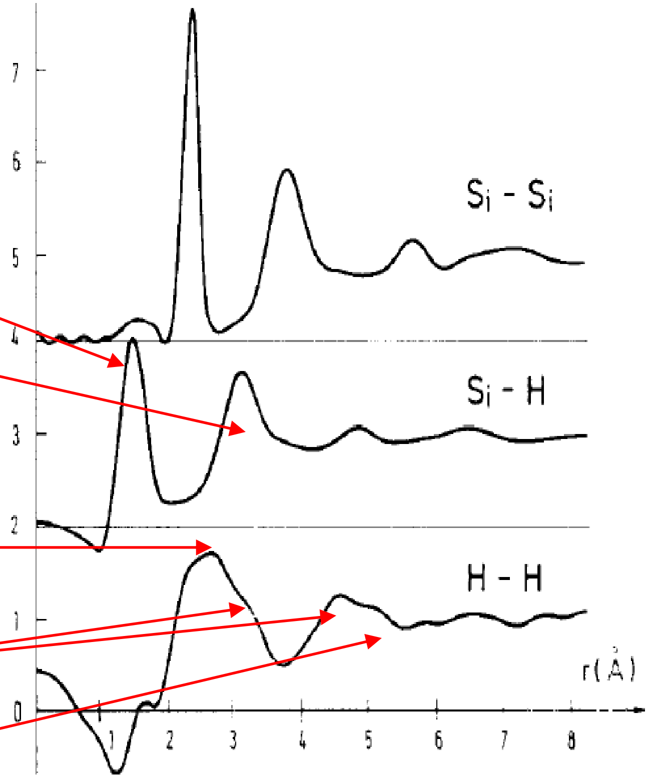
Neutron scattering: very sensitive to hydrogen (similar mass)
additional information by isotope exchange with D and component analysis

SiH-bonds:

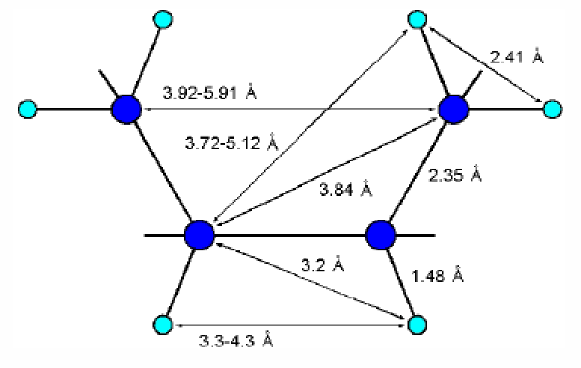
- Si-H hydride
  0.148 nm
- Si-Si-H
  0.32 nm

H-H correlation

- di-hydride
  0.241 nm
- H-Si-Si-H
  0.33-0.43 nm
- H-Si…Si-H
  0.39-0.51 nm



Interpretation:



Hydrogen incorporation does not change the tissue;
same Si-Si distances and angles

Wright, J. Phys. 19,45109 (2007)

Hydrogen incorporation into a-Si:H

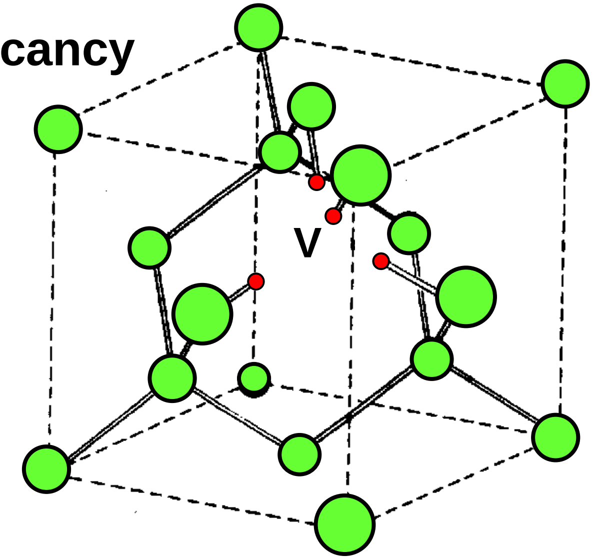
Small angle X-ray scattering (SAXS) and lattice vibrations (IR absorption):
presence of voids with radii ~3.3 to 4.0 Å

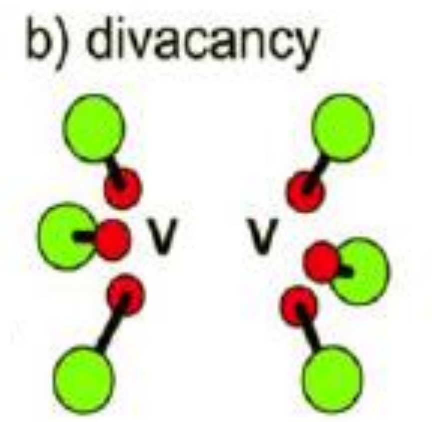
- Si-H bonds at void surfaces
- some H_2 molecules (30 to 50) trapped in (large) voids

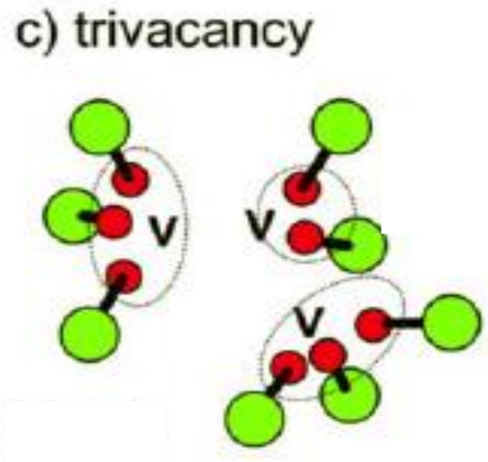
Mahan, Solar Cells 27, 465 (1989)

Smallest H-terminated void configurations:

a) monovacancy




b) divacancy

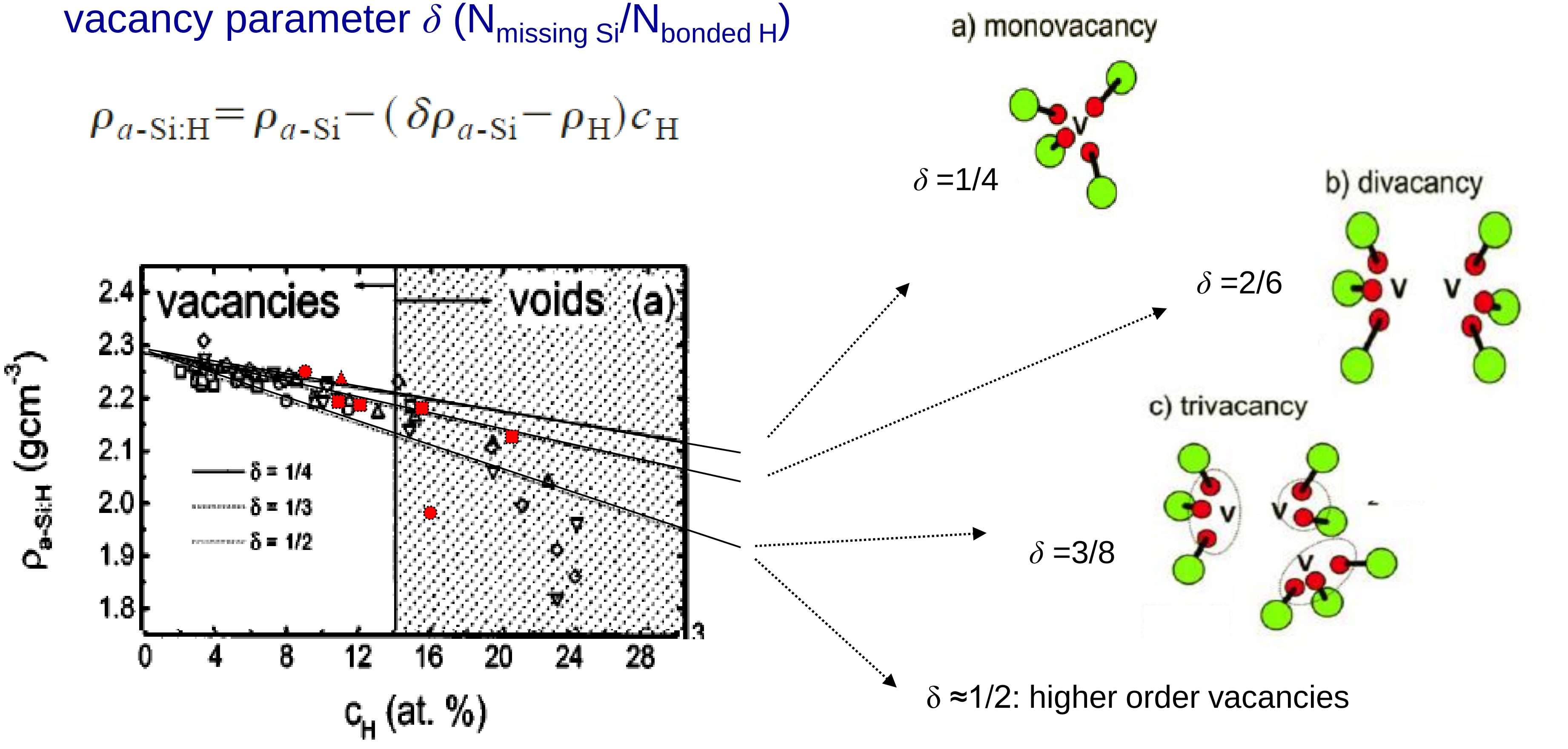

c) trivacancy

Smets, PRB 76, p073202 (2007)

Hydrogenated voids and specific weight

Dependence of mass density ρ on
vacancy parameter δ ($N_{\text{missing Si}}/N_{\text{bonded H}}$)

$$\rho_{a\text{-Si:H}} = \rho_{a\text{-Si}} - (\delta\rho_{a\text{-Si}} - \rho_{\text{H}})c_{\text{H}}$$



δ =1/4

δ =2/6

δ =3/8

δ ≈1/2: higher order vacancies

device grade   porous

Smets, PRB 76, p073202 (2007)

Summary: How disordered is a-Si?

- atomic structure of a-Si and a-Si:H is NOT completely random!
- On short range, the chemical covalent bonding nature of Si is conserved in a network of silicon atoms
- The translational invariance over long ranges (the lattice) is lost
- Disorder arises from bond length and bond angle distribution as well as from lower coordination
- Local order (average of four bonds, average bond angle of 109°) gives similar high energy absorption and preserves the overall semiconductor nature of the material