7

Diffraction

Diffraction

Chapters on diffraction

Physics of Surfaces and Interfaces
H. Ibach
Springer

Surface Science - An Introduction
K.Oura, V. G. Lifshits, A. A. Saranin, A.V. Zotov, M. Katayama
Springer

Introduction to Surface and Thin Film Processes
J. A. Venables
Cambridge University Press

More specific

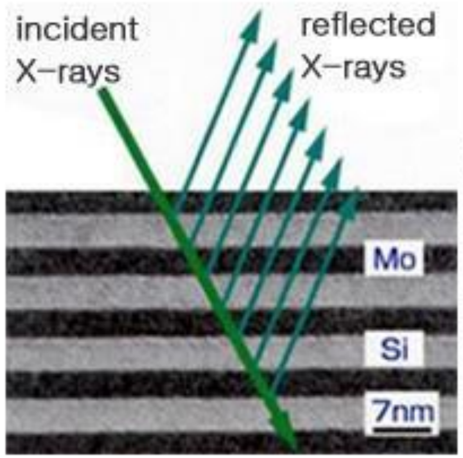
Surface Structure Determination by LEED and X-rays
W. Moritz and M. A. Van Hove
Cambridge University Press

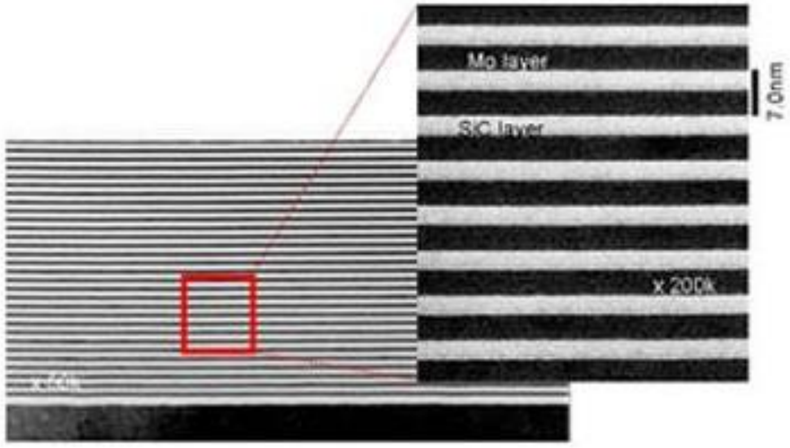
Reflection high-energy electron diffraction
A. Ichimiya and Ph. I. Cohen
Cambridge University Press

Thin films: Control of thickness and crystallinity

Electronic devices (FET, FGT, ...), created by successive processes (lithography, etching, growth, implantation, ...) are composed of many “layers”

Creation of mirrors and masks for EUV-lithography
(thickness, interface roughness...)





Magnetic tunnel junction (spintronics): increased by improving and controlling the crystallographic order at the interfaces

Control of surface and thin film quality (crystallinity), of film thickness, of interfaces is needed
→
Diffraction

Diffraction: Choice of probing particles

Different probes can be used, given an appropriate the de Broglie wavelenght: x-rays, electrons, He-atoms, neutrons ...

Examples:

X-ray:

$$E = h\upsilon = \frac{hc}{\lambda} \longleftrightarrow \lambda = \frac{hc}{E}$$

$$\lambda \approx 1\,\mathring{A} \Rightarrow \boxed{E \approx 12\,\text{k eV}}$$

Electrons:

$$\lambda \approx 1\,\mathring{A} \qquad m_e = 9.1\ 10^{-31}\ \text{kg}$$

$$p = \hbar k = \frac{h}{\lambda} \longleftrightarrow \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \Rightarrow \boxed{E \approx 150\ \text{eV}}$$

Neutrons:

$$\lambda \approx 1\,\mathring{A} \qquad m_n = 1.6749\ 10^{-27}\ \text{kg}$$

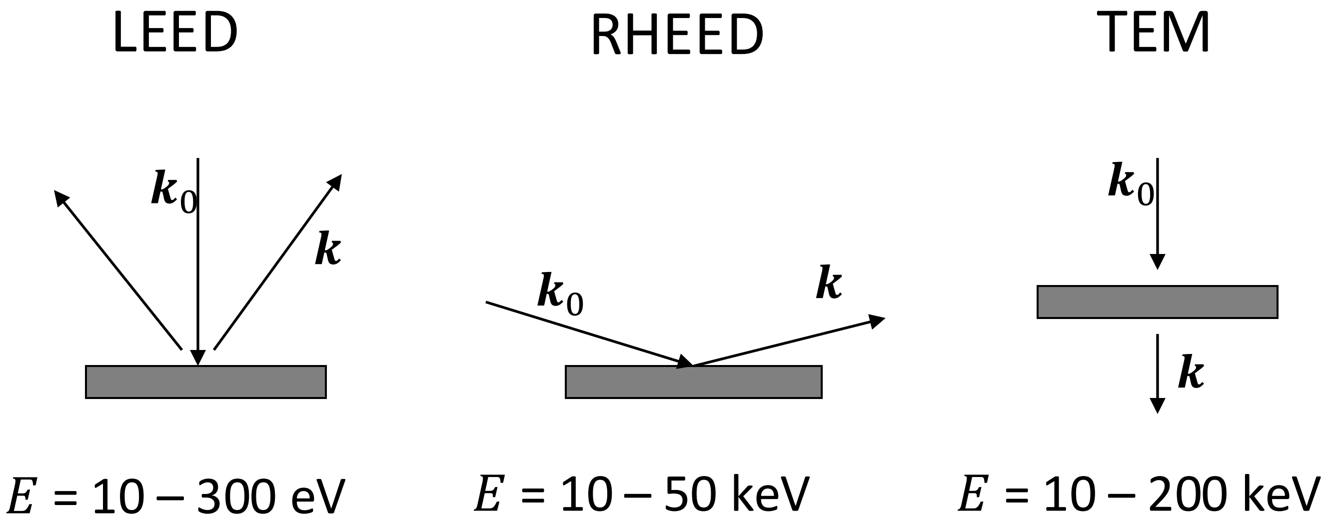
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \Rightarrow \boxed{E \approx 0.08\ \text{eV}}$$

Here we focus on electrons (surface sensitivity, easy to integrate into other setups)

The interpretation is not as straightforward as for x-rays: electrons interact strongly with matter, dynamic theory should be used, but useful information can be deduced from simple descriptions

Structural analysis: Electron diffraction

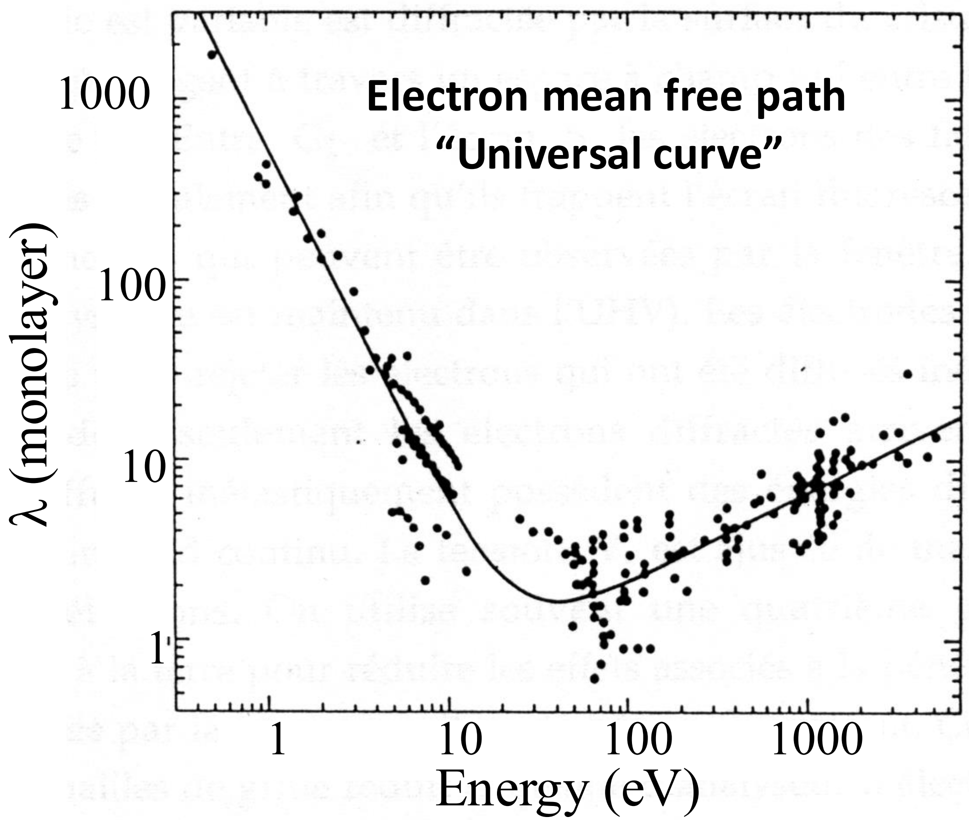
LEED: Low Energy Electron Diffraction
RHEED: Reflection High Energy Electron Diffraction
TEM: Transmission Electron Microscopy



E = 10 – 300 eV

E = 10 – 50 keV

E = 10 – 200 keV


Electron mean free path
"Universal curve"

Electron energy and geometry are chosen considering
the electron mean free path
and
the spatial resolution

Note: Electron energy = 2 eV → Wavelength = 8.5 Å
The hypothetical "RLEED" would have low resolution

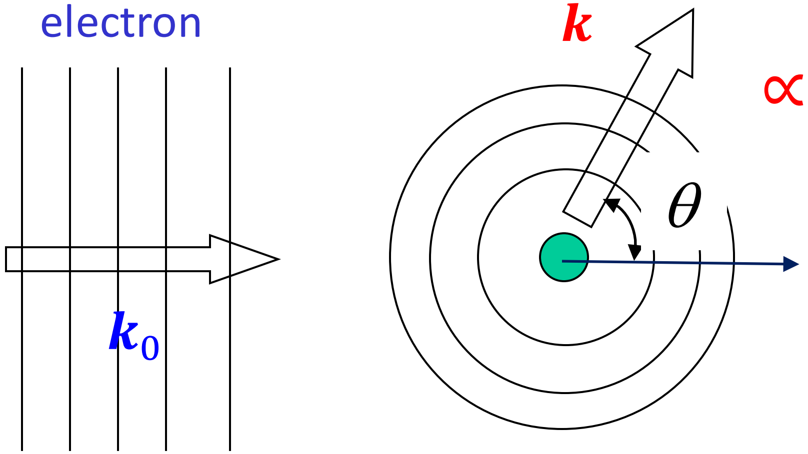
Plane wave scattering

Single scatterer

$$\boldsymbol{p}_0 = \hbar \boldsymbol{k}_0$$

incoming electron

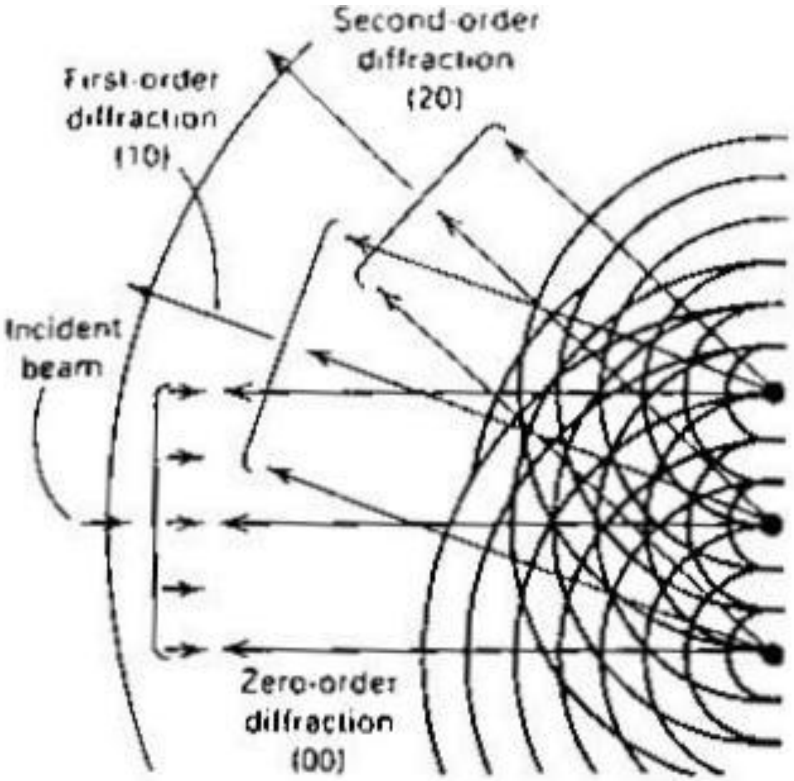
scattered electron



$$\propto e^{i\boldsymbol{k}_0 \cdot \boldsymbol{r}}$$

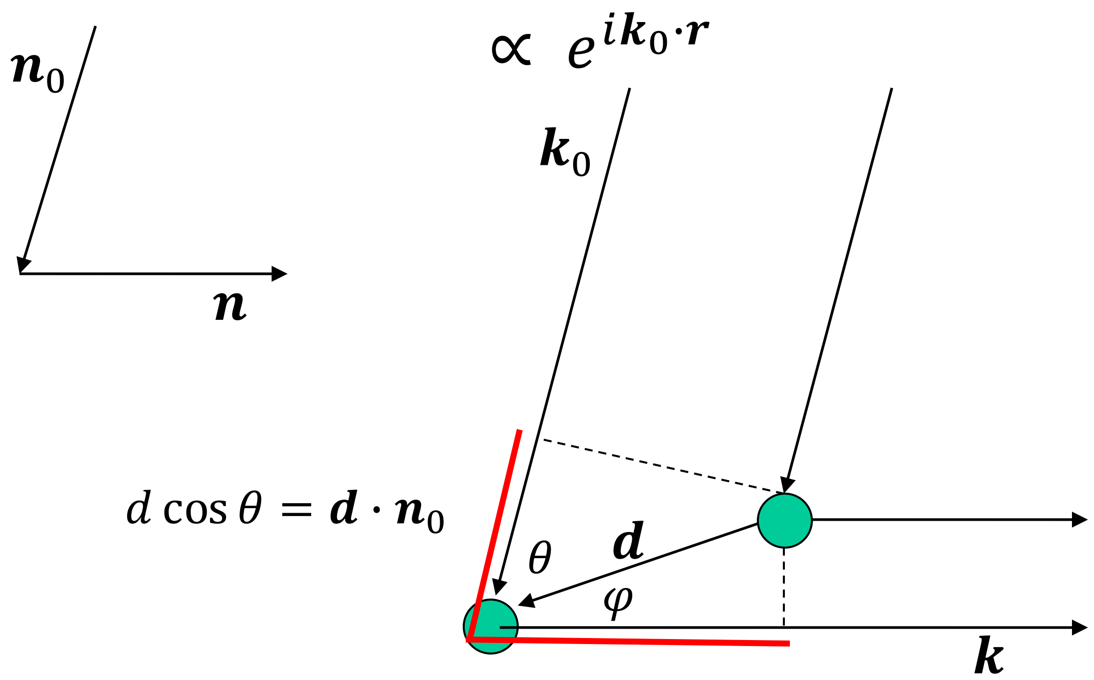
$$\propto f(\theta, r)\frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{r}$$

$f(\theta, r)$ is the atomic form factor:
it reflects the atomic electron density



In the case of many scatter points, diffraction spots are the result of the interference pattern generated by the spherical waves scattered by the atoms in the crystal lattice

Two scatterers, Laue description



$d\cos\theta = \boldsymbol{d}\cdot\boldsymbol{n}_0$

$d\cos\varphi = -\,\boldsymbol{d}\cdot\boldsymbol{n}$

$$\boldsymbol{k}_0 = \frac{2\pi}{\lambda}\boldsymbol{n}_0$$

$$\boldsymbol{k} = \frac{2\pi}{\lambda}\boldsymbol{n}$$

1) Elastic scattering:

incident and reflected rays have the same wavelength λ

$|\boldsymbol{k}| = |\boldsymbol{k}_0|$

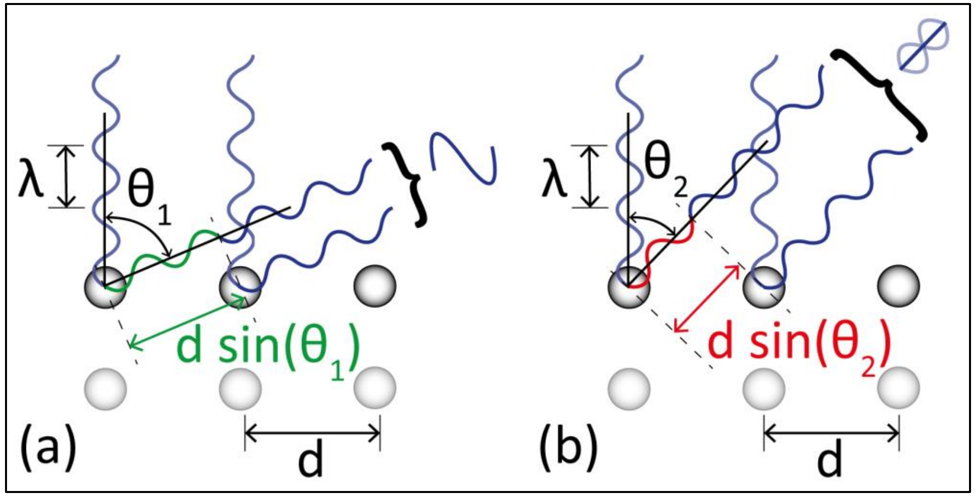
2) Constructive interference:

difference in path length = multiple of wavelength

$d\cos\theta + d\cos\varphi = \boldsymbol{d}\cdot(\boldsymbol{n}-\boldsymbol{n}_0) = m\lambda$

or

$\boldsymbol{d}\cdot(\boldsymbol{k}-\boldsymbol{k}_0) = 2\pi m \qquad m \in \mathbb{Z}$



3D Bravais lattice, Laue condition

Constructive interference verified by all the lattice points

$\boldsymbol{R} \cdot (\boldsymbol{k} - \boldsymbol{k}_0) = 2\pi m$

with $\boldsymbol{R}$ Bravais lattice vector, $m \in \mathbb{Z}$

➡

$\boldsymbol{k} - \boldsymbol{k}_0 = \boldsymbol{G}$

$\boldsymbol{G}$ is a reciprocal lattice vector

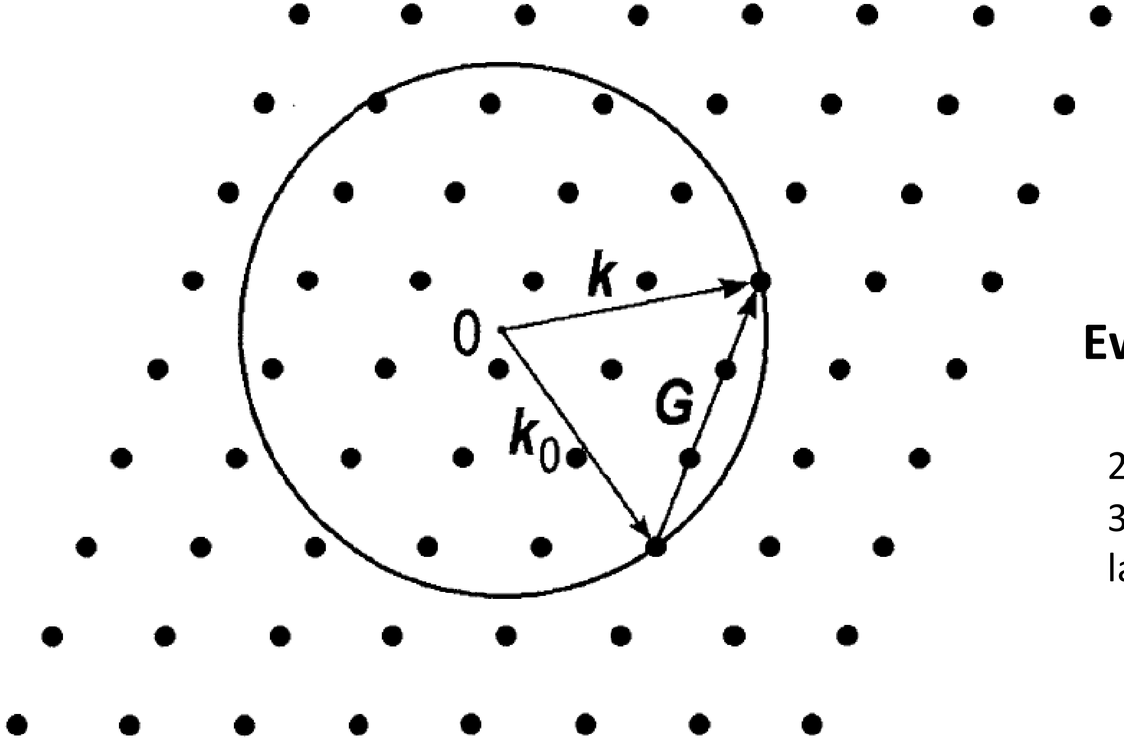
$\boldsymbol{G} = \sum_i m_i \boldsymbol{a}_i^*, \qquad \boldsymbol{a}_1^* = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3}$

$\boldsymbol{a}_i \cdot \boldsymbol{a}_j^* = 2\pi\, \delta_{ij}$

Laue diffraction condition

$$|\boldsymbol{k}| = |\boldsymbol{k}_0|$$

$$\boldsymbol{k} - \boldsymbol{k}_0 = \boldsymbol{G}$$



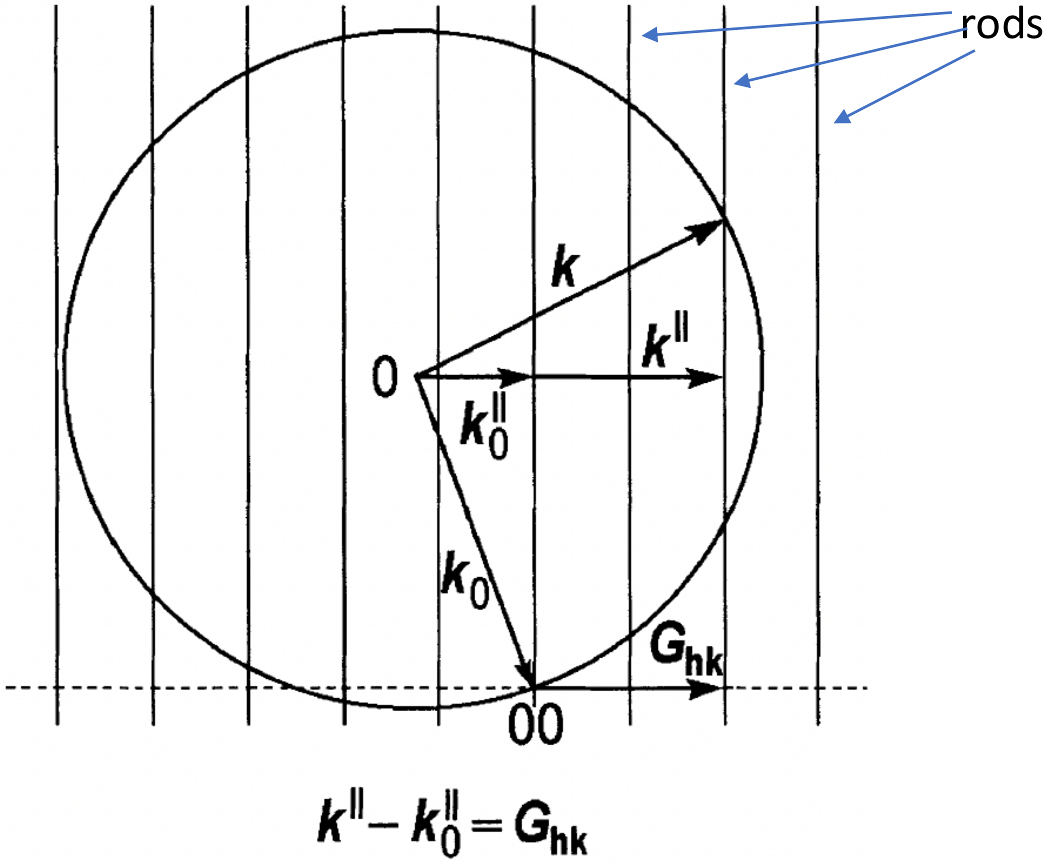
Ewald sphere

2D plane in a
3D reciprocal
lattice

2D case: surface diffraction

At the surface, the bulk periodicity is truncated, and the Laue equation (3 equations, one for each direction) reduces to 2 equations concerning the components of the incident and scattered wave vectors parallel to the surface.

In contrast to the 3D reciprocal lattice points, reciprocal lattice **rods** perpendicular to the surface are attributed to every 2D reciprocal lattice point. (An ideal 2D lattice can be conceived as a 3D lattice with infinite periodicity in the normal direction. This will lead to infinitely dense reciprocal lattice points along the normal direction, thus forming rods.)



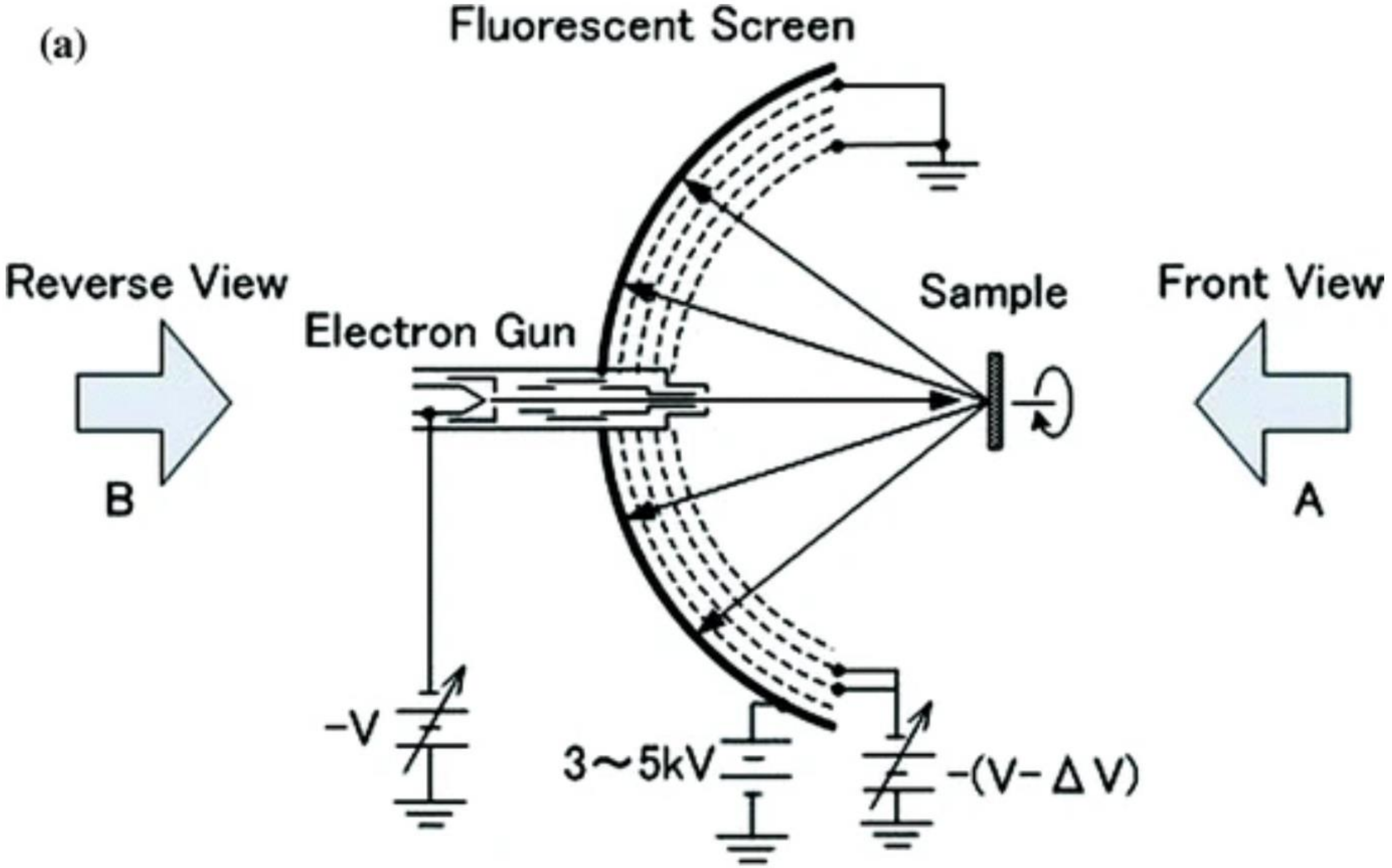
- Scattering from a surface lattice leads to diffracted beams for all incident wave vectors
- Intensity will be higher in correspondence of the points of the bulk reciprocal lattice (actually rods are “modulated”)

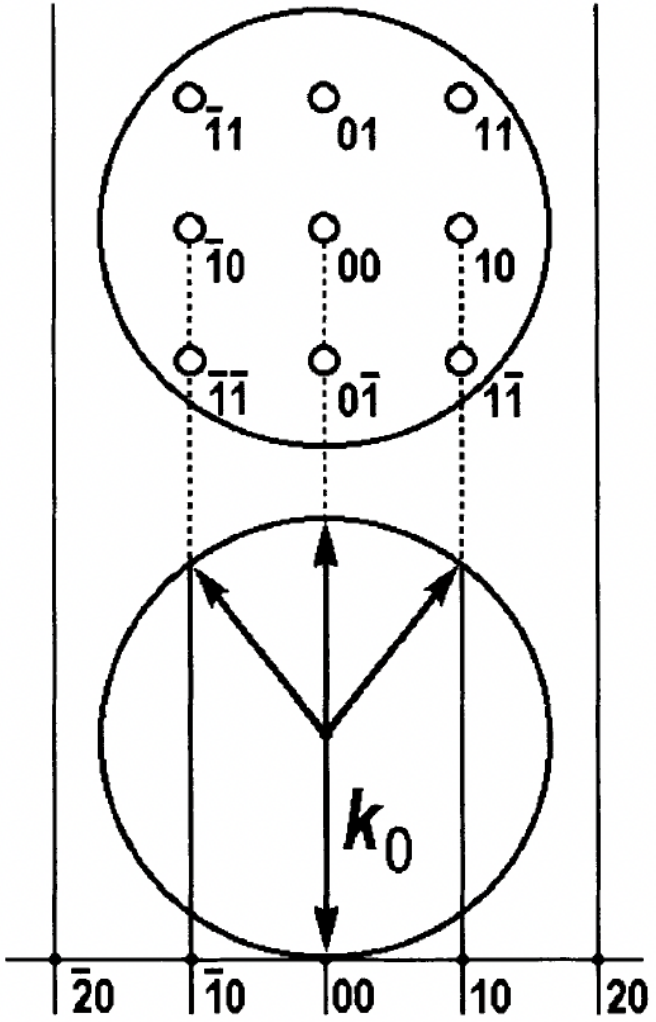
$$\boldsymbol{k}_{\parallel} - \boldsymbol{k}_{\mathbf{0}\parallel} = \boldsymbol{G}_{\mathrm{hk}}$$

with $\boldsymbol{G}_{\mathrm{hk}}$ a vector of the 2D reciprocal lattice

The diffraction pattern is a map of the 2D reciprocal lattice

LEED setup

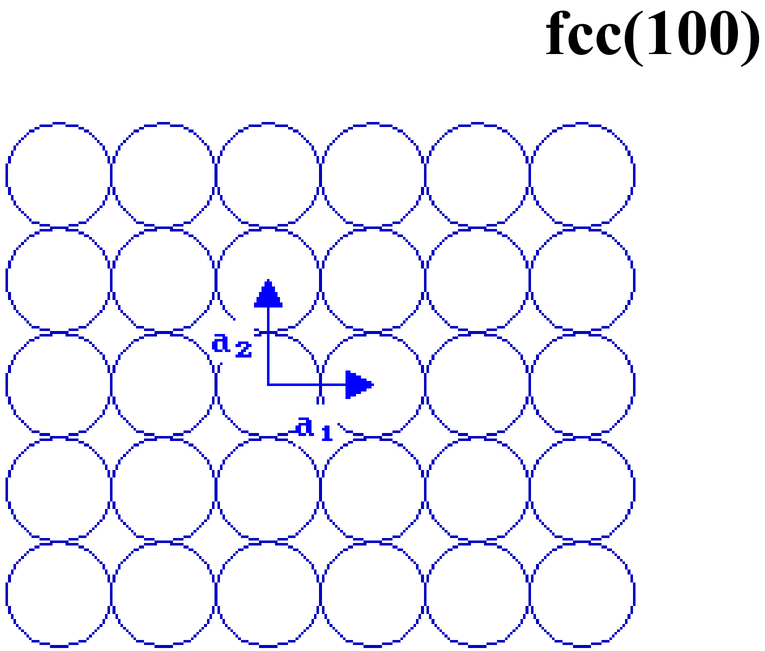


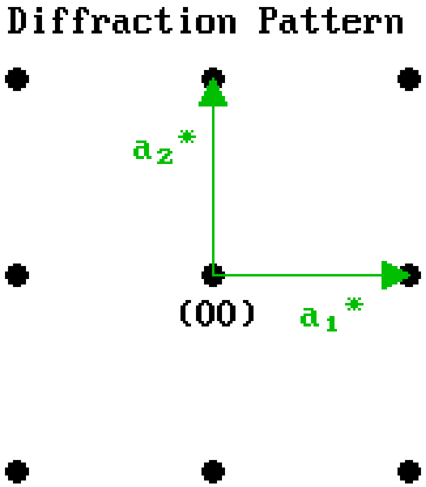


spot labeling →

hk indexes as for reciprocal lattice vectors

Examples: fcc (100)





$\boldsymbol{a}_1^*$ and $\boldsymbol{a}_2^*$ are the primitive vectors in the reciprocal space

$$\boldsymbol{a}_i \cdot \boldsymbol{a}_j^* = 2\pi\, \delta_{ij}$$

$$\boldsymbol{a}_1^* = \frac{2\pi}{a_1} \frac{\boldsymbol{a}_1}{a_1}$$

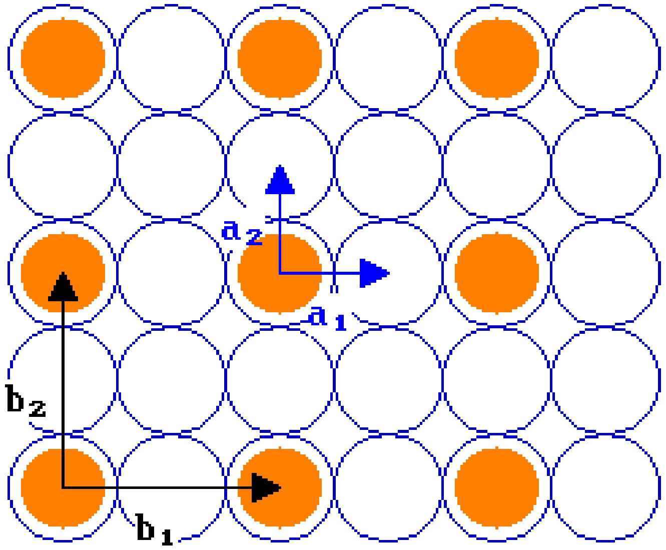
$$\boldsymbol{a}_2^* = \frac{2\pi}{a_2} \frac{\boldsymbol{a}_2}{a_2}$$

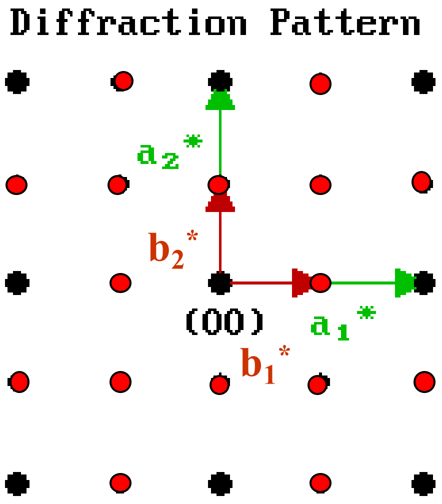
$\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the primitive vectors in real space

(0,0) corresponds the reflected beam along the surface normal

Examples: fcc (100)

fcc(100) (2x2)





The LEED pattern provides information on the periodicity, but not on the “internal” structure of the superstructure unit cell, or on the position of the orange atoms in the unit cell.
More sophisticated measurements and analysis are needed
(Spot-Profile LEED, simulations)

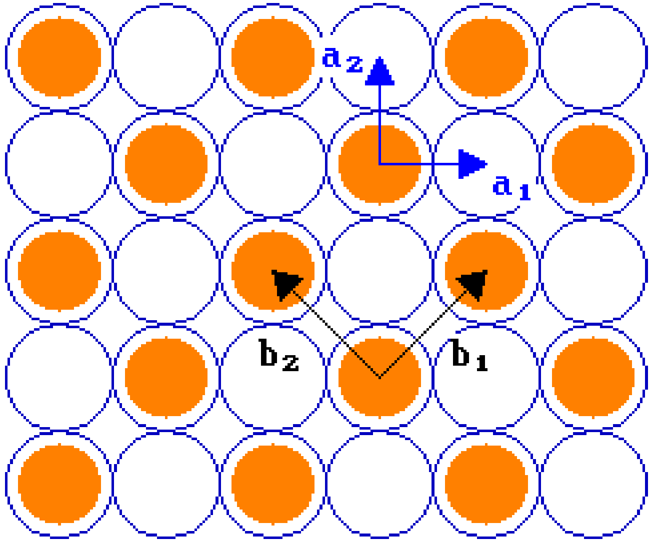
Orange disks represents adsorbate atoms: their periodicity is responsible of the red spots in the diffraction pattern

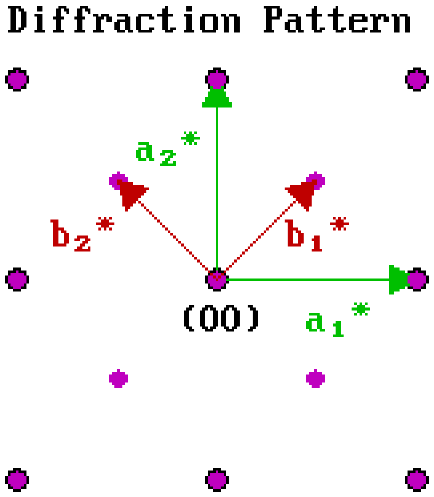
2x2 means that the adsorbates have a double periodicity in both directions with respect to the substrate

Examples: fcc (100)

Exercises 7.1 – 7.4

fcc(100) c(2x2)





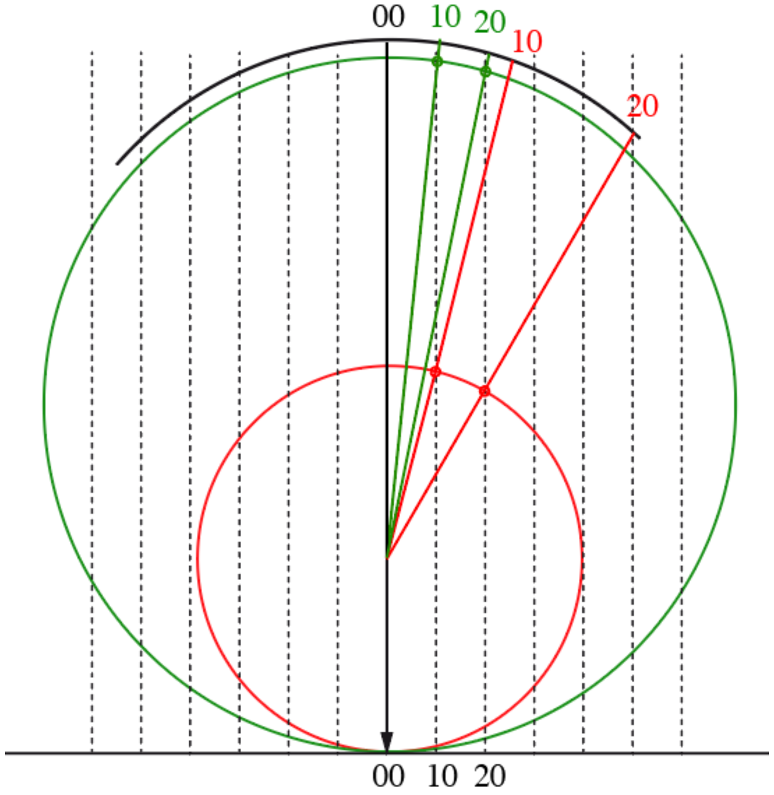
The surface unit cell is rotated by 45° with respect to the substrate one:
$\sqrt{2}$ x$\sqrt{2}$ R45°

However, it is usual to describe this structure as c(2x2), where "c" stays for "centered" to indicate that there is an additional atom in the center of the 2x2 cell. (This kind of nomenclature is used especially for structures with square or rectangular symmetry).

LEED movie

diffraction pattern recorded as a function of the energy of the incident electrons (increasing energy)

$$E = \frac{\hbar^2 k^2}{2m}$$



https://www.ocivm.com/_low_energy_electron_diffraction.html

graphene/Ir(111)

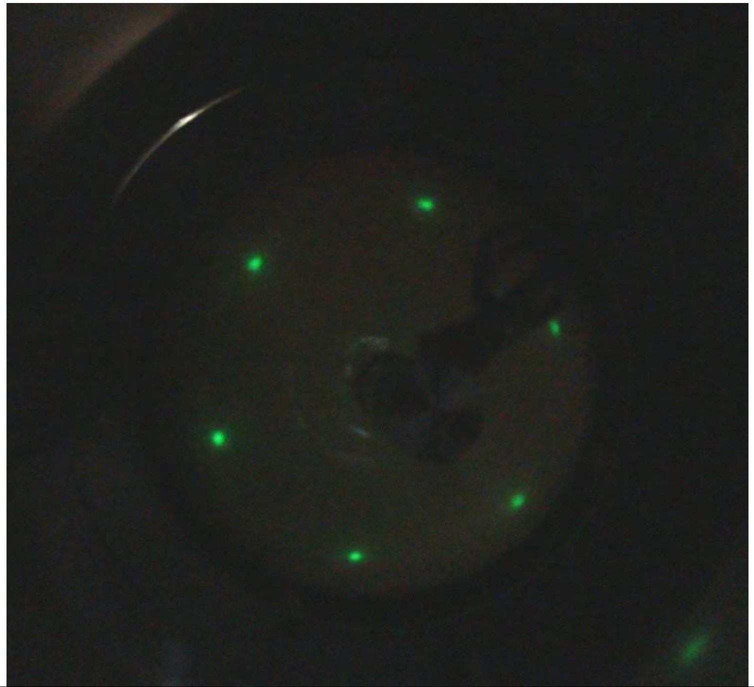
Ir(111)

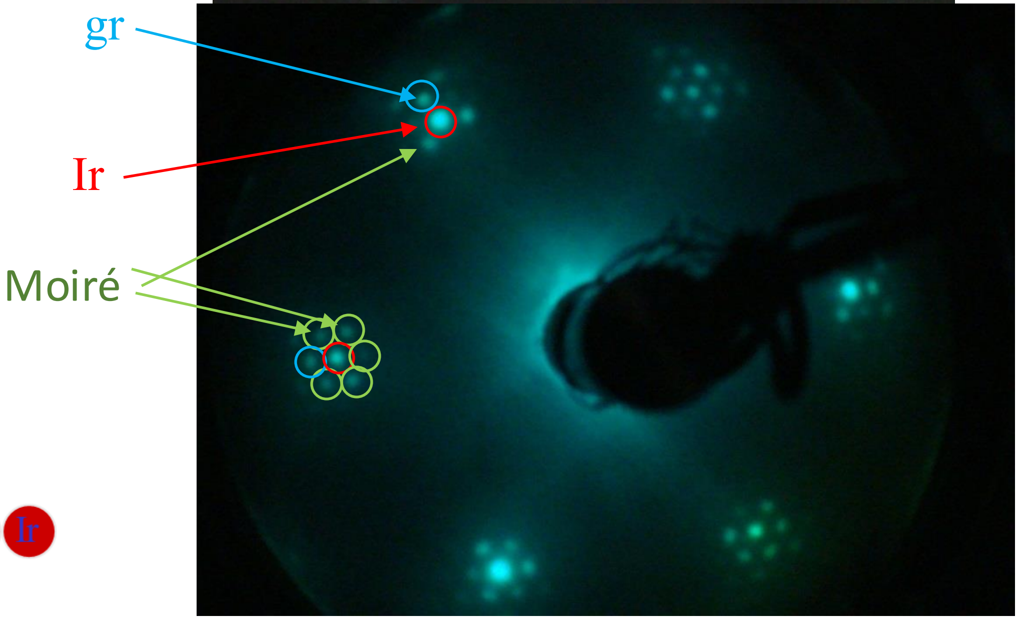
graphene/Ir(111): modulated surface

Electrons scattered by
the potential due to :

1) Ir atoms
2) C atoms
3) C-Ir bond formed at sites with minimum C-Ir separation (Moiré periodicity)

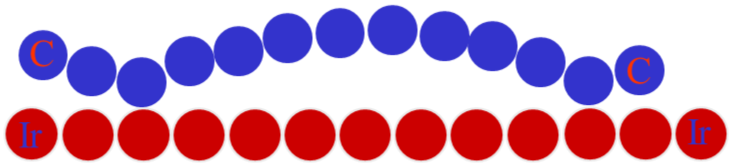
satellite reflections
(only the reflections
surrounding the main
reflections are visible)



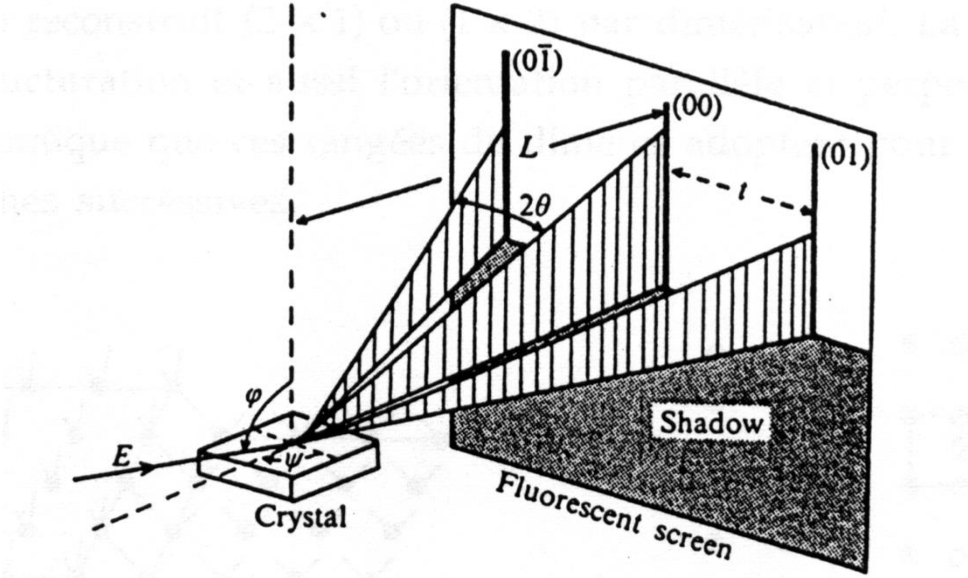


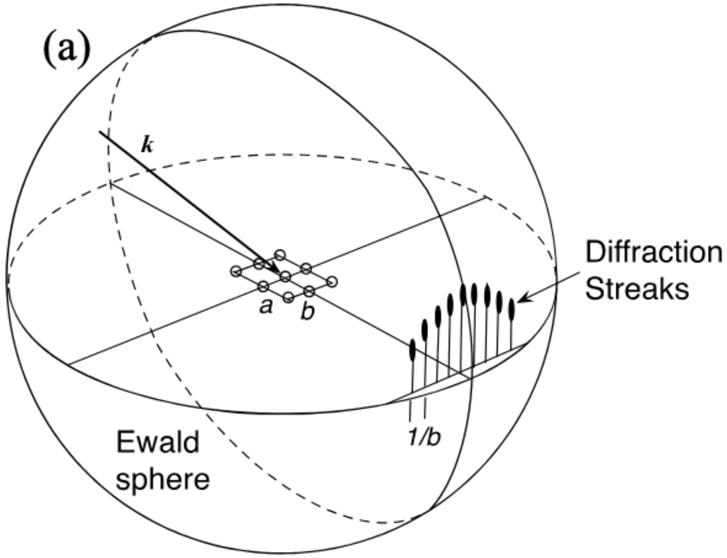
10 x 10 C atoms over
9 x 9 Ir atoms

$a_{Ir} = 0.27$ nm
$a_c = 0.245$ nm



RHEED





- (0,0) is the specular bar
- Lateral bars are the diffraction ones

Electron penetration depth $\lambda =$ 10 – 30 nm at 40 keV for normal incidence

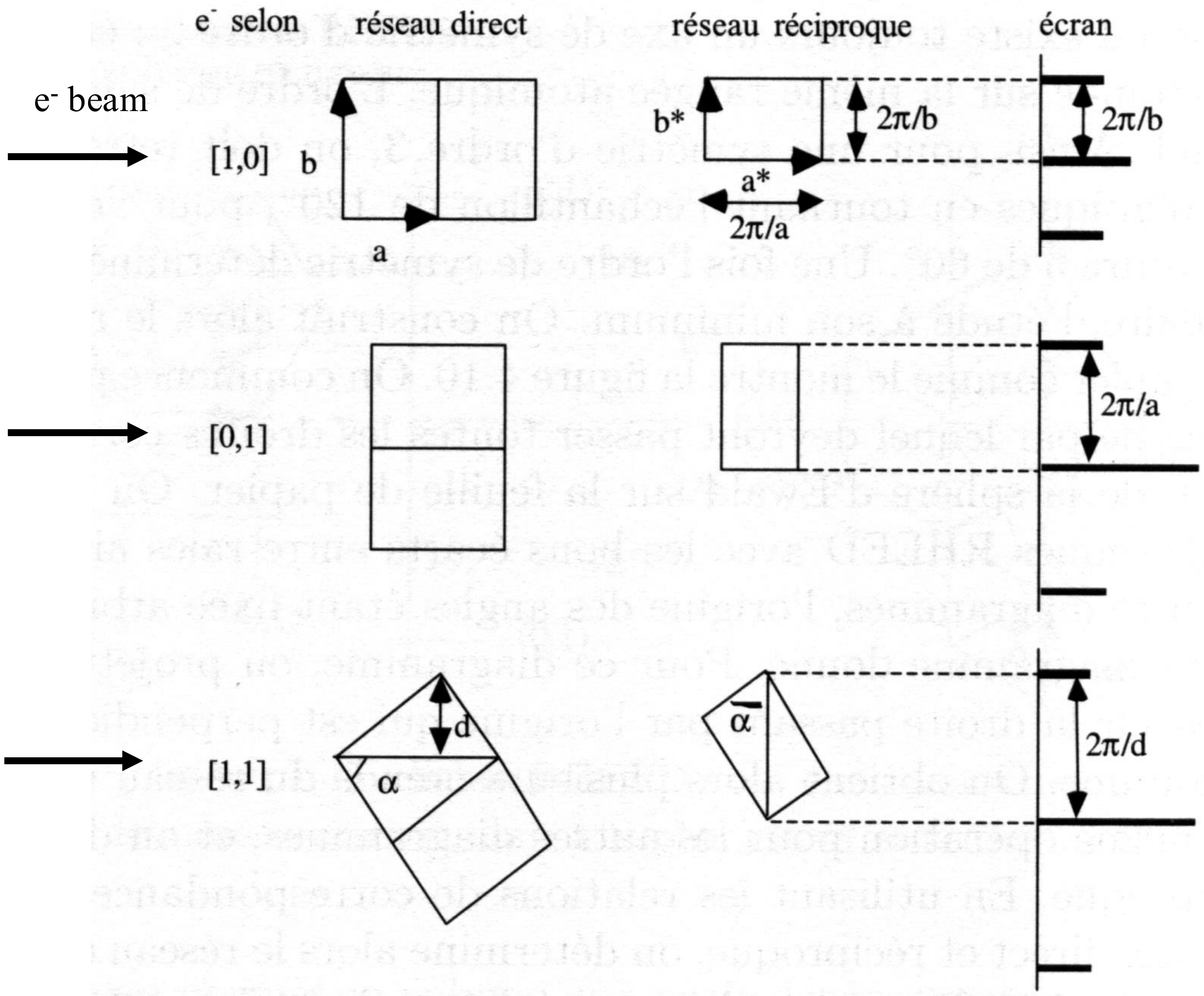
Surface sensitivity if $\cos\varphi = d/\lambda$ with d = 1-2 atomic layers
or
φ about 89°

Due to the grazing incidence, the surface is seen as continuous along the incidence direction (no diffraction) and consequently only the periodicity perpendicularly to the incidence direction is detected

For an overview see also doi.org/10.1533/9780857094957.1.3

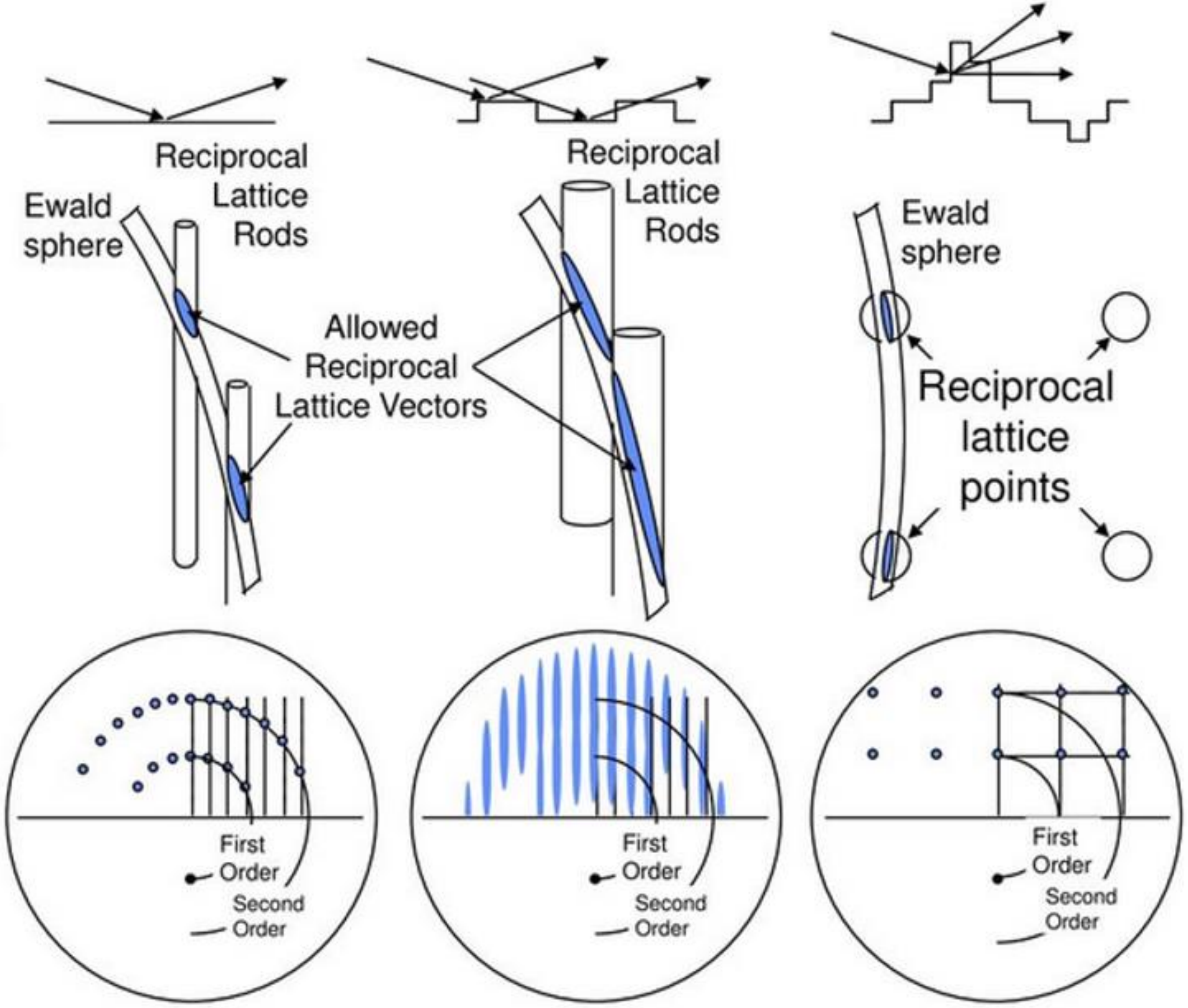
RHEED: 2D reciprocal lattice

Exercise 7.5



At least measurements at two different angles are needed to get the 2D reciprocal lattice

RHEED: qualitative pattern interpretation

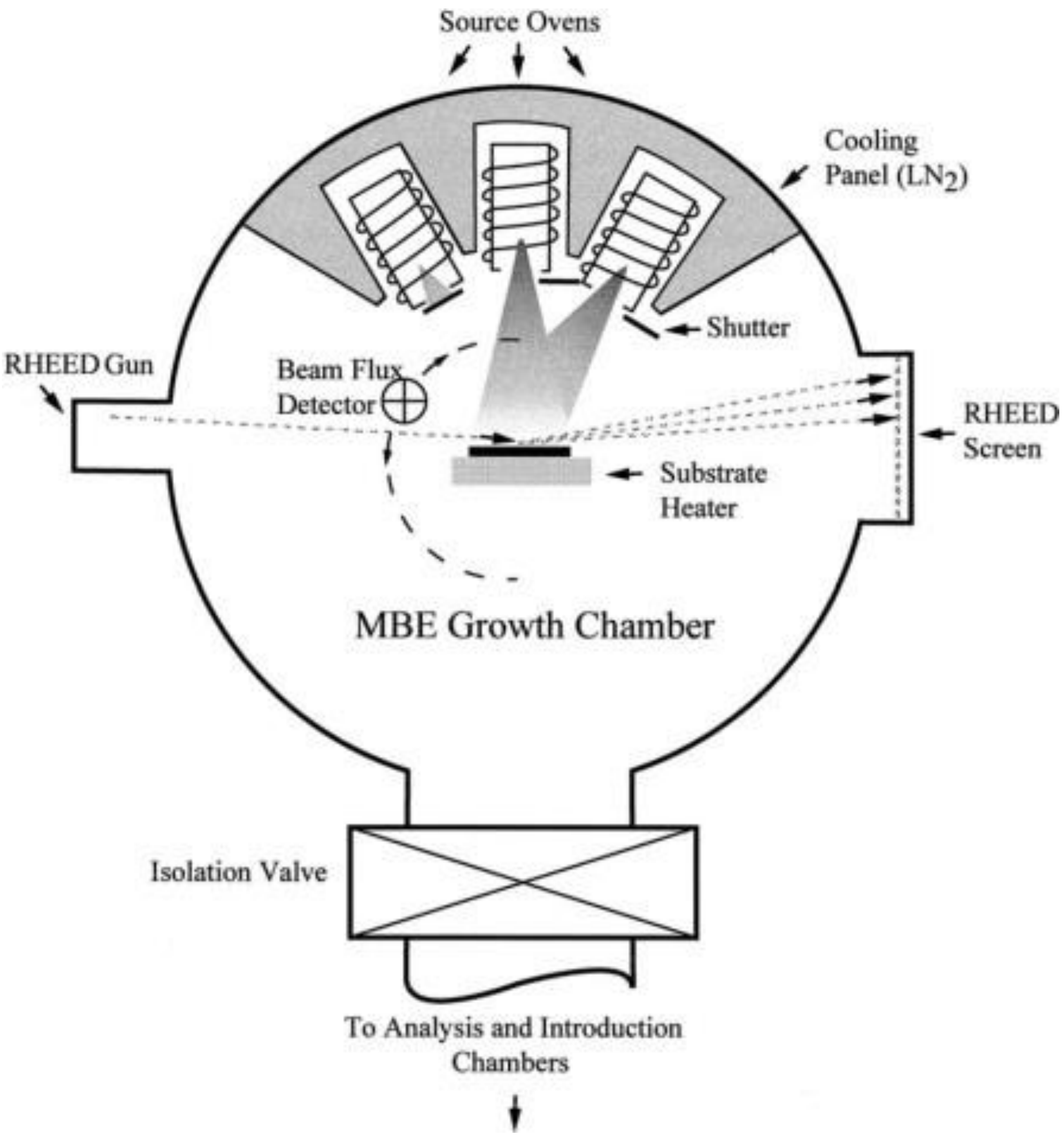


Perfectly flat surface
Reciprocal rods have
no width

Surface with
monolayer roughness.
Broadened rods.

Surface with large
roughness.
Transmission features.

RHEED for real-time growth control

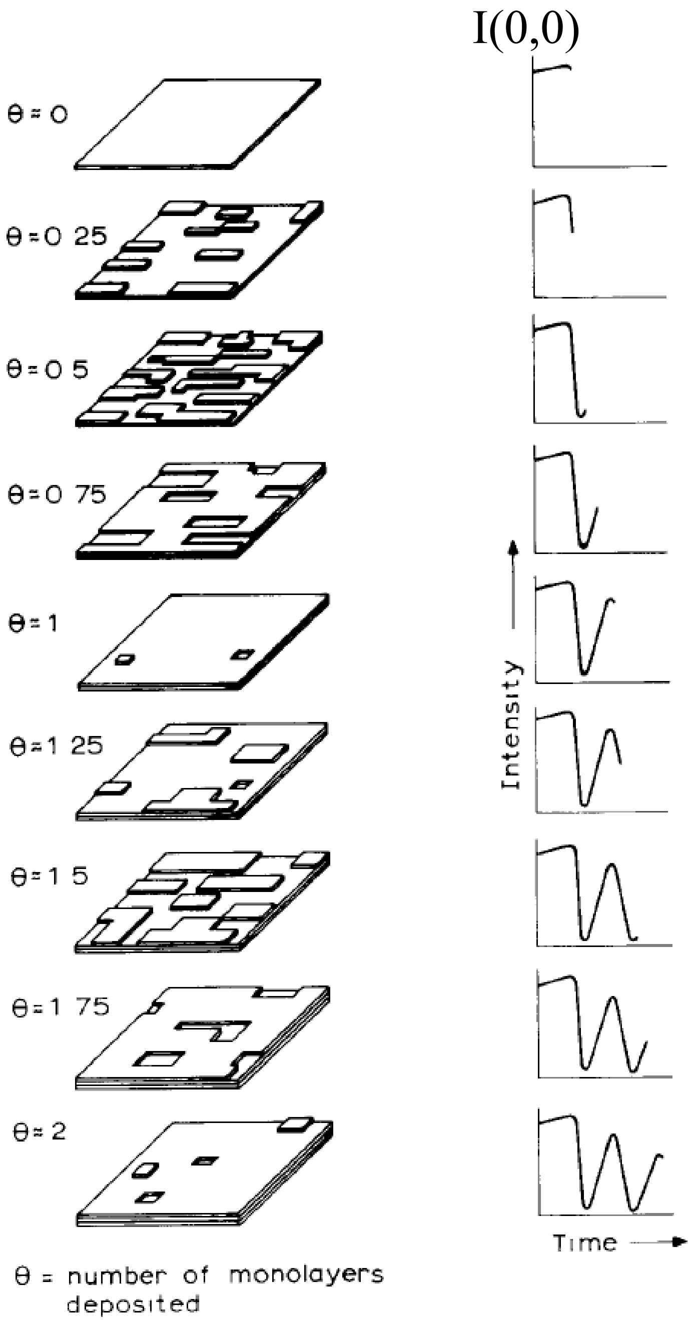


Evolution of the diffraction spots / strikes intensities are used to check the evolution of the crystal structure

RHEED for growth control

Intensity of the
specular signal vs time

It depends on the
surface roughness
(step edge density)



During layer-by-layer growth:
maximum roughness at 0.5 ML

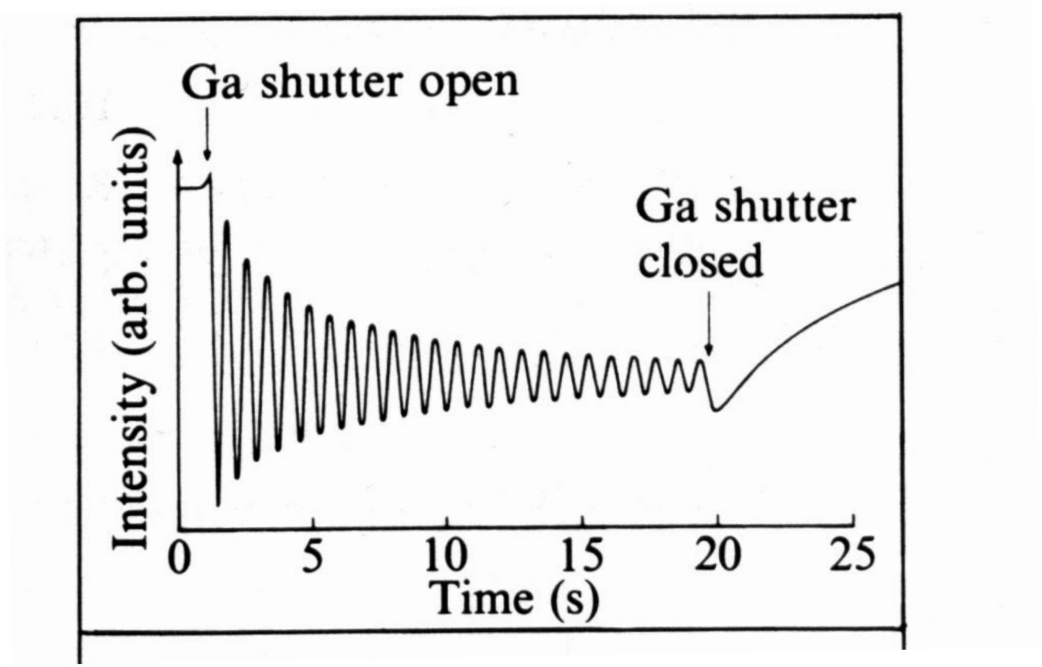
Oscillation period of I(0,0): 1 atomic layer

Surface Science **168,** 423-438 (1986)

Example: growth of GaAs

Exercise 7.6

Growth of GaAs(100) by
Molecular Beam Epitaxy (MBE)



Oscillation periodicity: 1 atomic layer
Intensity: decreasing with number of layers

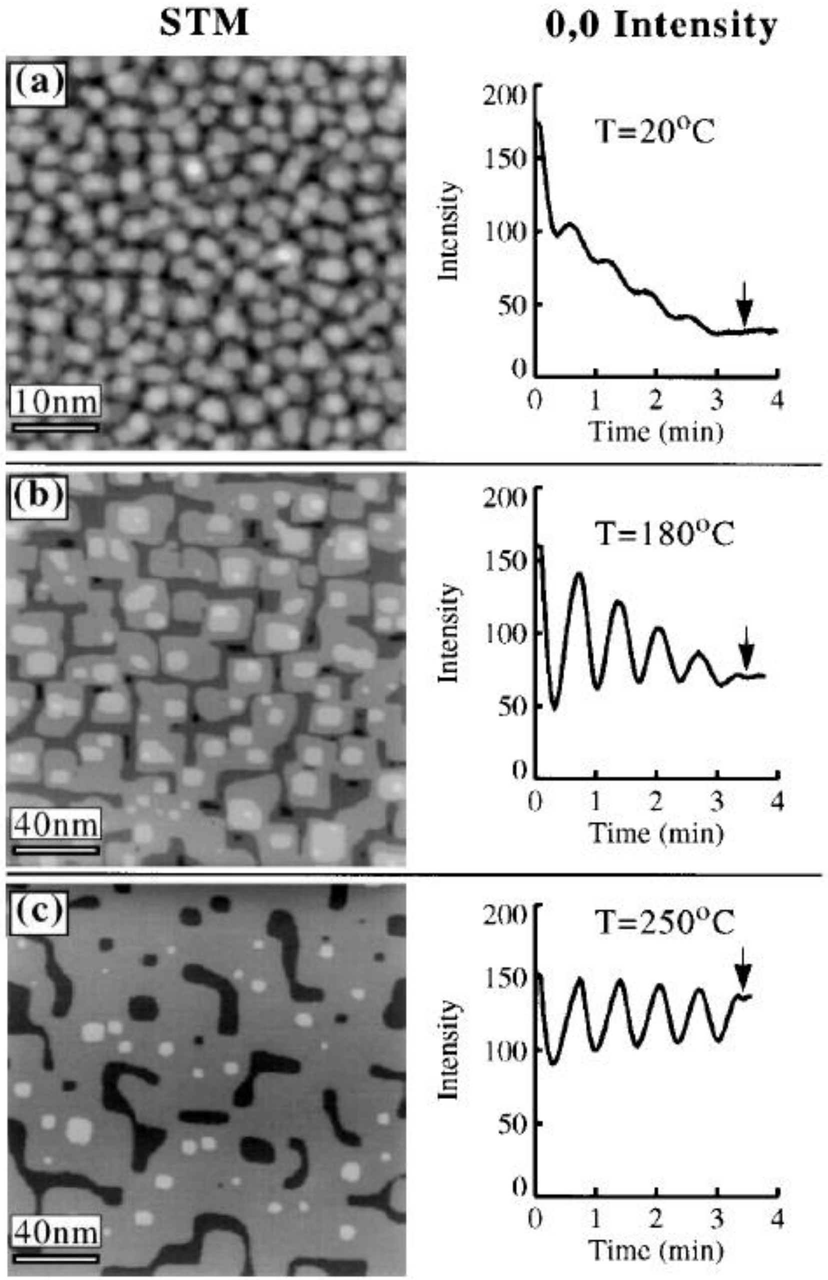
Imperfect layer-by-layer growth

Interpretation of the evolution of the intensity minimum is more subtle

The intensity oscillations of the specular spot (0,0) can be used to measure the number of deposited layers and surface roughness

Neave *et al.* Appl. Phys. **A 31**, 1 (1983)

Example: growth of Fe / Fe(100)



Growth of Fe on Fe(100) as seen by STM and RHEED:

change of growth mode from

three-dimensional island growth at room temperature

to

layer-by-layer growth at higher temperature

Advances in Physics **47**, 511 (1998)

Transmission Electron Microscope (TEM)

Due to the limited penetration depth of electrons in solids, the samples should be very thin: the acceptable thickness is 10-100 nm for conventional microscopes with accelerating voltages of 50-200 keV.

The electron beam loses part of its intensity due to scattering.
The loss is greater for thicker regions and regions with species of higher atomic number →
thicker regions and regions of higher atomic number appear dark.

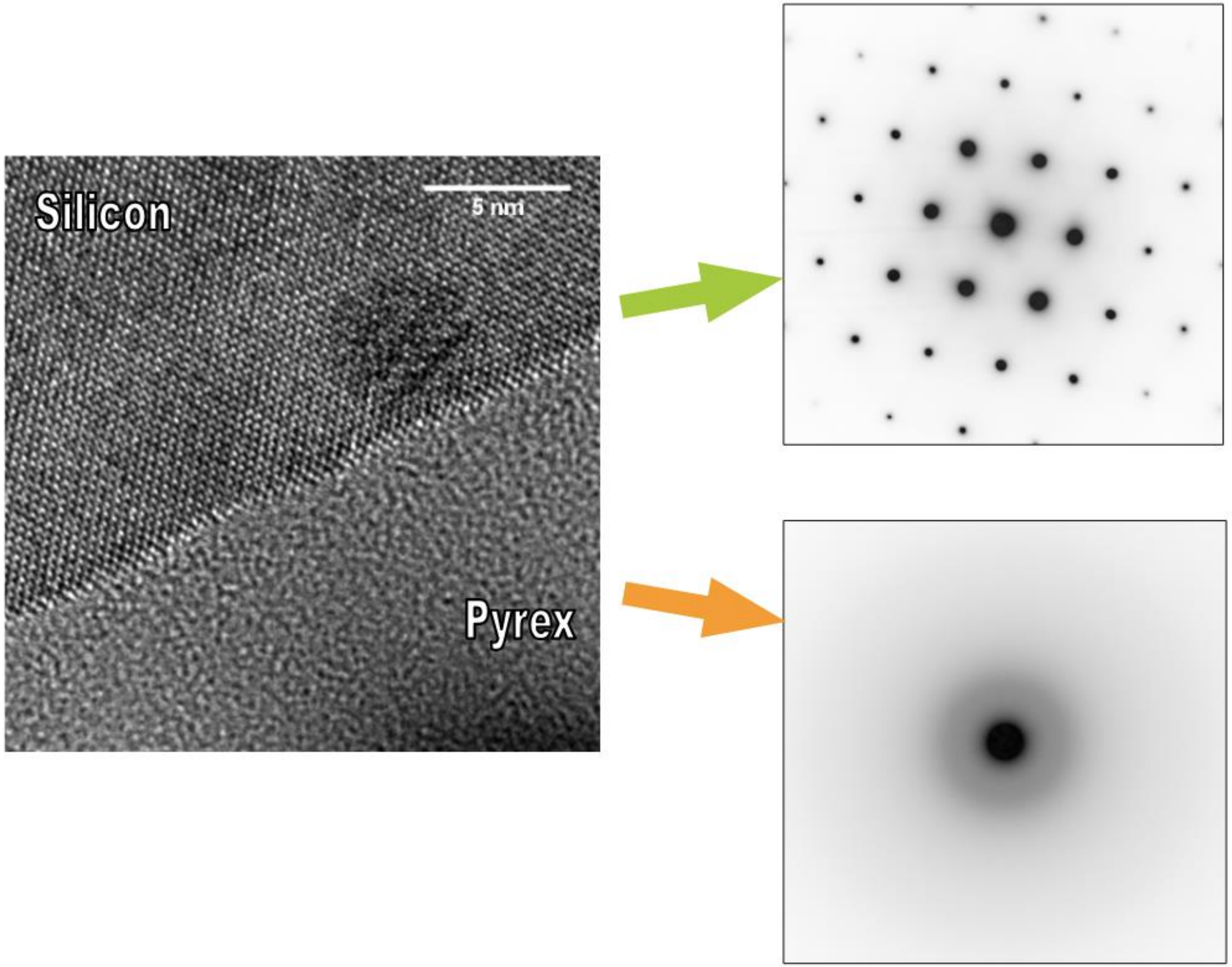
With high-resolution TEM, images showing the atomic structure can be obtained.
For complex systems, numerical image simulations are required for a reliable interpretation of the image features in terms of atomic structure.

Very sophisticated optics are required

A diffraction mode is also possible

TEM images and diffraction patterns

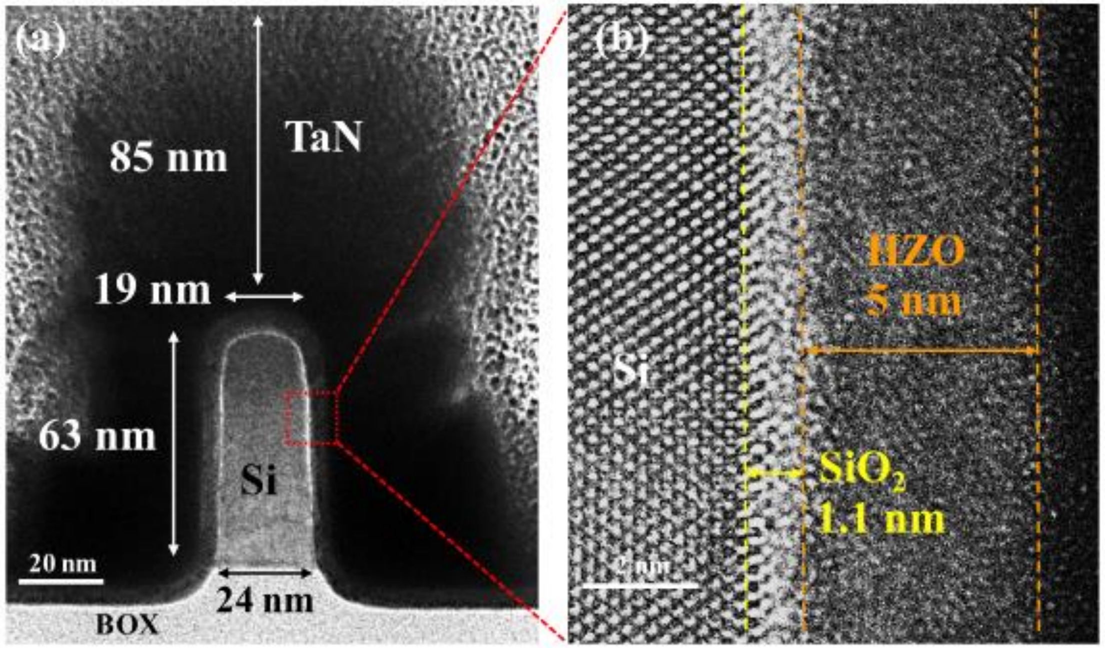
Silicon – Pyrex (glass) interface



Diffraction pattern of a crystallized material

Diffuse rings typical of amorphous material

Gate oxide layer in a FinFET

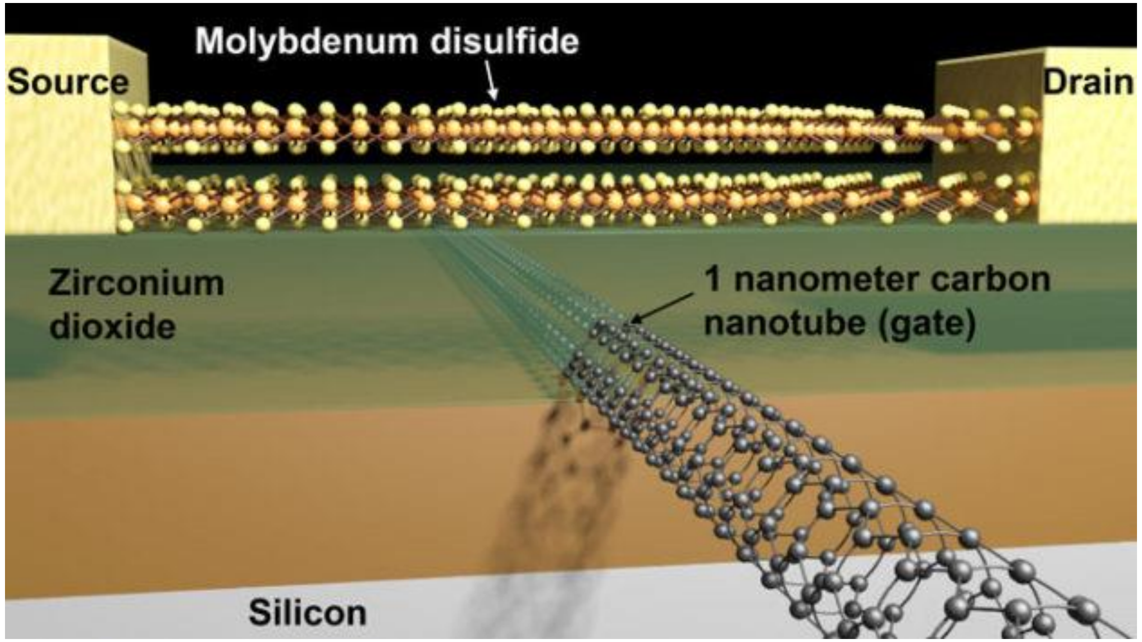


$Hf_{0.5}Zr_{0.5}O_2$ (HZO) $\kappa \approx 20 - 40$

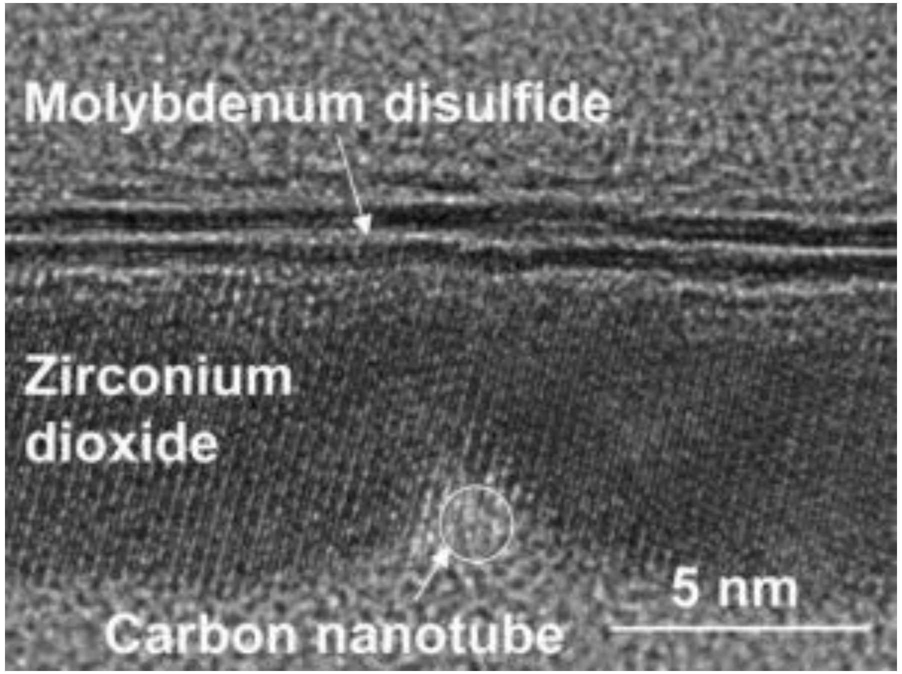
(a) TEM image of a FinFET
(b) Gate oxide stacks of SiO_2 and HZO layers

DOI:10.1109/JEDS.2019.2942381

FET with carbon nanotube gate



Schematic of a transistor with a molybdenum disulfide channel and 1-nanometer carbon nanotube gate



TEM image of a cross section of the transistor

DOI: 10.1126/science.aah4698

Atomic Electron Tomography

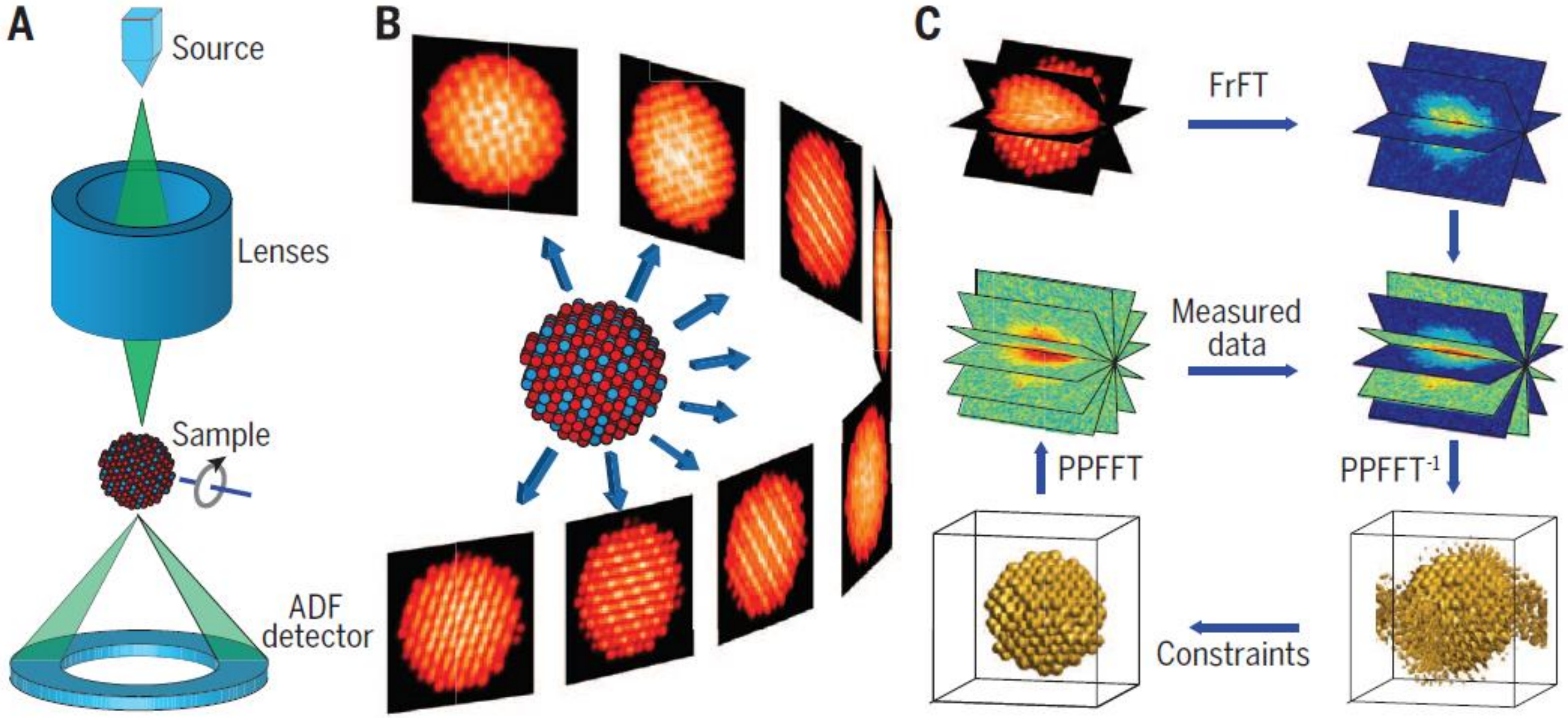


Fig. 1. Schematic layout of AET. (**A**) An electron beam is focused on a small spot and scanned over a sample to form a 2D image. The integrated signal at each scanning position is recorded by an ADF detector. (**B**) By rotating the sample around a tilt axis, a series of 2D images is measured at different tilt angles. (**C**) After preprocessing and alignment, the tilt series is inverted to Fourier slices by the fractional Fourier transform (FrFT). A 3D reconstruction is computed by using a Fourier-based iterative algorithm. From the 3D reconstruction, the coordinates of individual atoms are traced and refined to produce the 3D atomic model of the sample.

10.1126/science.aaf2157