The Application of X-ray Scattering in the Studies of Nanomaterials

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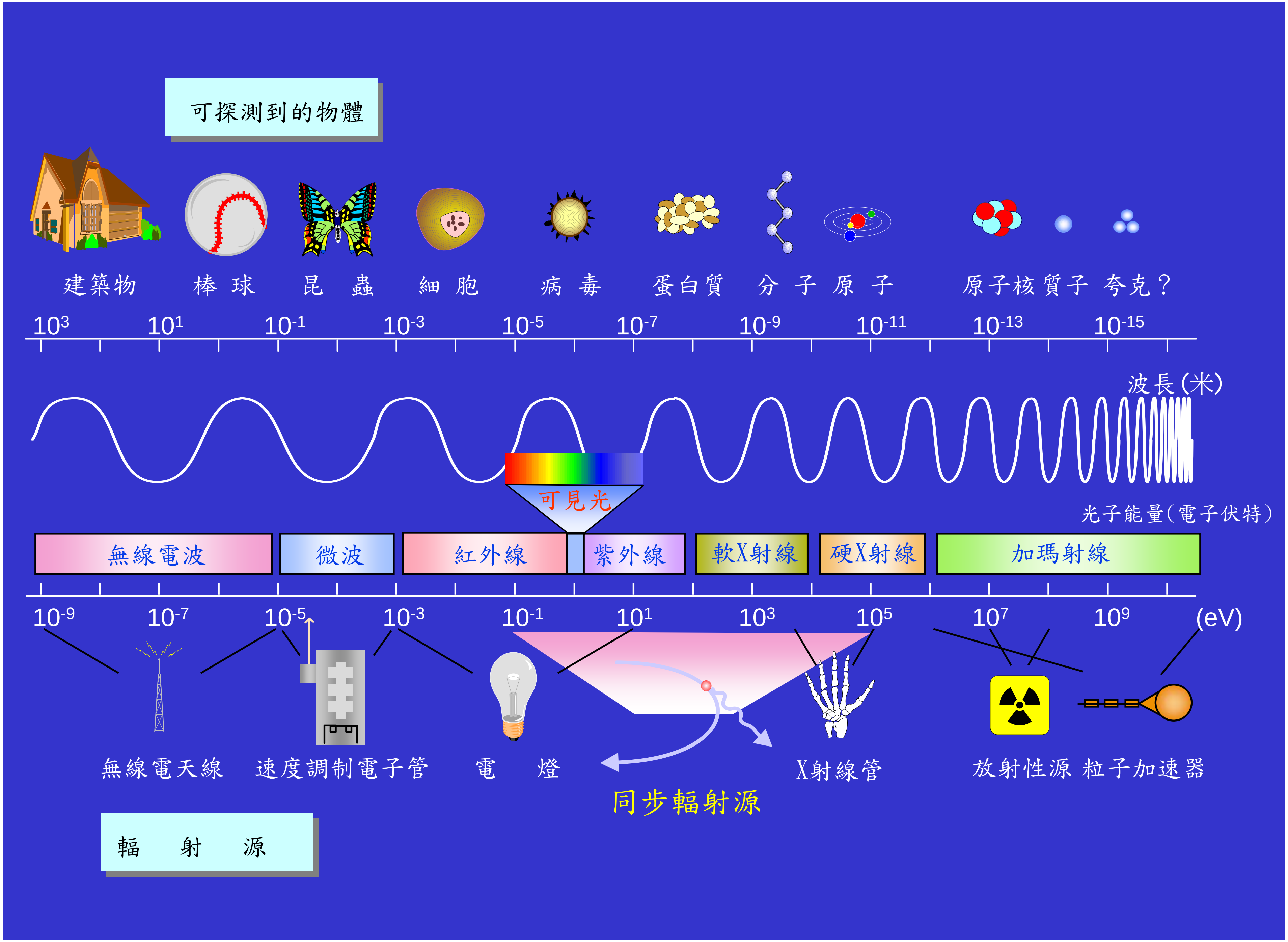
Introduction of X-ray scattering
The growth of ZnO on Si using a Y_2O_3 buffer layer
Domain Matching Epitaxy
Summary


可探測到的物體
建築物
棒 球
昆 蟲
細 胞
病 毒
蛋白質
分 子
原 子
原子核
質子
夸克？
10^3 10^1 10^-1 10^-3 10^-5 10^-7 10^-9 10^-11 10^-13 10^-15
波長(米)
可見光
光子能量(電子伏特)
無線電波
微波
紅外線
紫外線
軟X射線
硬X射線
加瑪射線
10^-9 10^-7 10^-5 10^-3 10^-1 10^1 10^3 10^5 10^7 10^9 (eV)
無線電天線
速度調制電子管
電 燈
X射線管
放射性源
粒子加速器
同步輻射源
輻 射 源

The Properties of Synchrotron Radiation

- High Intensity

  $I_{SR} > 10^6 * I_{tube}$

- Continuous Spectrum

  (NSRRC 35 keV > E > 0.05 eV)

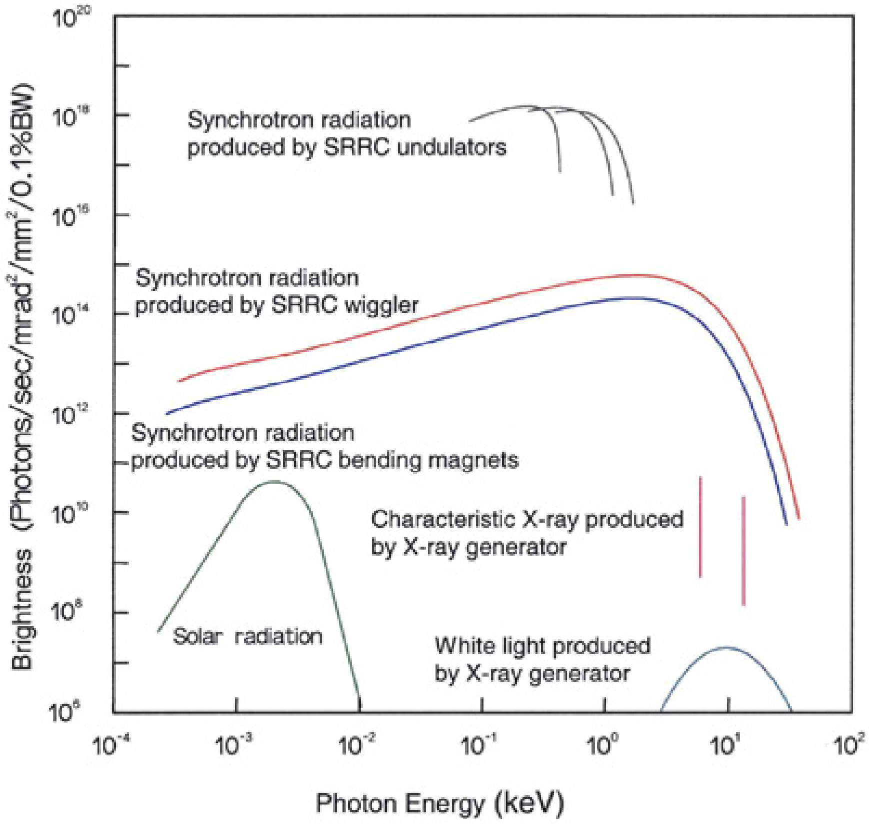
- Excellent Collimation
- Low Emittance
- Pulsed-time Structure (NSRRC)

  bunch length: 25 ps
  pulse separation: 2 ns
  no. of buckets: 200

- Polarization

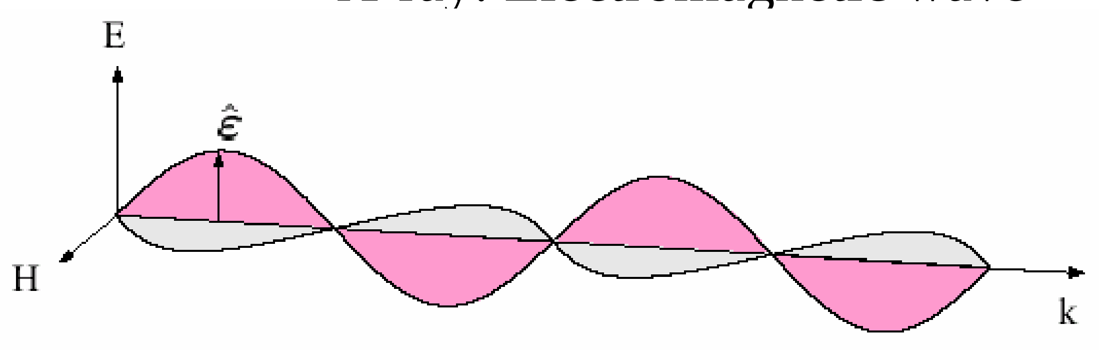
  linear polarization, elliptical pola

- Coherence (laser)



(Elastic) X-ray Scattering

X-ray: Electromagnetic wave $E = hc/\lambda$

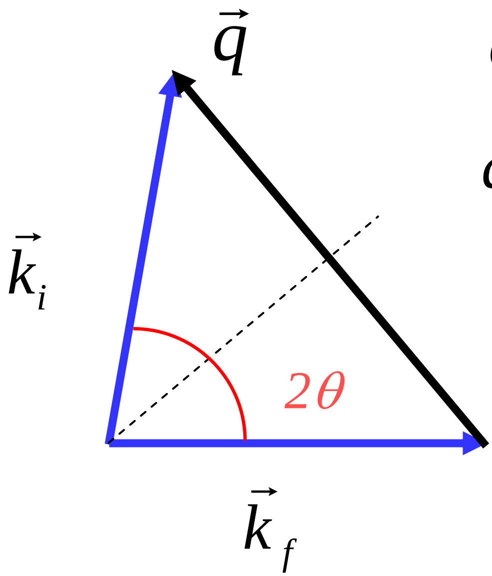


$\vec{q} = \vec{k}_f - \vec{k}_i$

$q = 4\pi \sin(\theta)/\lambda$

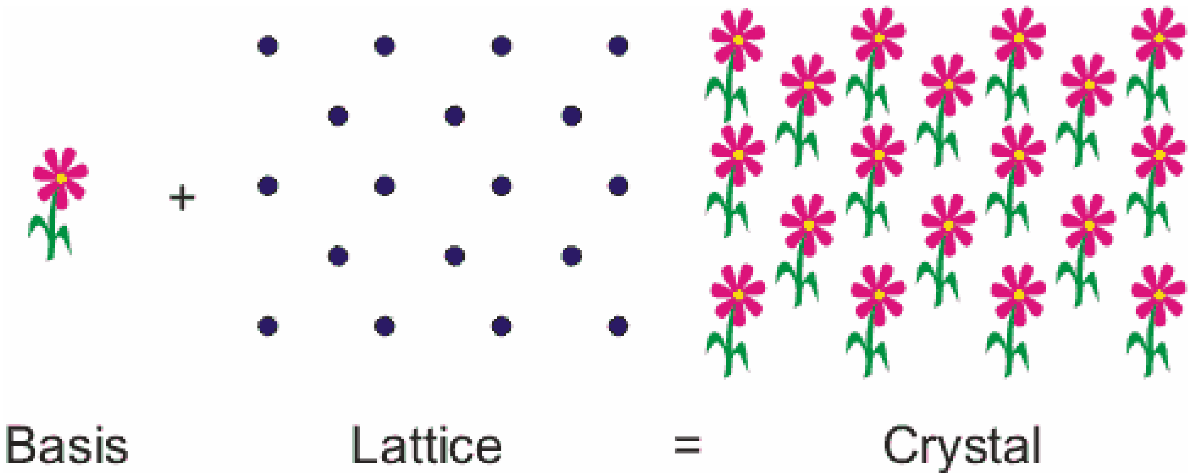
$E_i = E_f$ i.e. $\lambda_i = \lambda_f$ (elastic scattering)

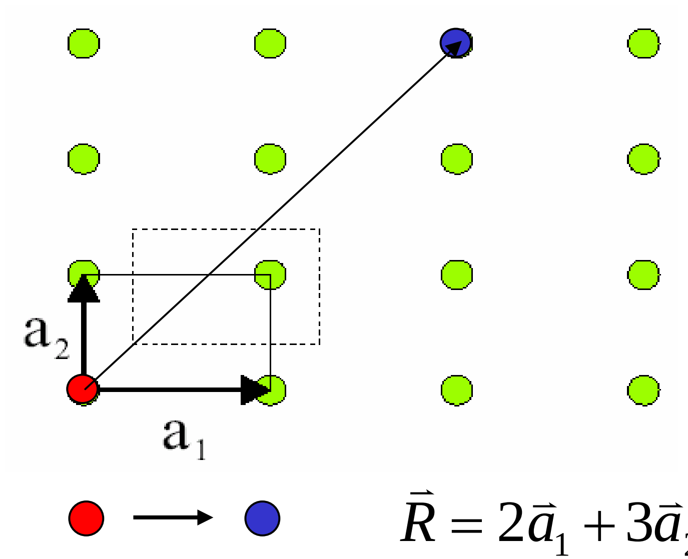
wave vector $k = 2\pi/\lambda$; $|k_i| = |k_f|$



wave vector (energy), amplitude, phase

Crystal Structure





$$\vec{R} = 2\vec{a}_1 + 3\vec{a}_2$$

in 3-D

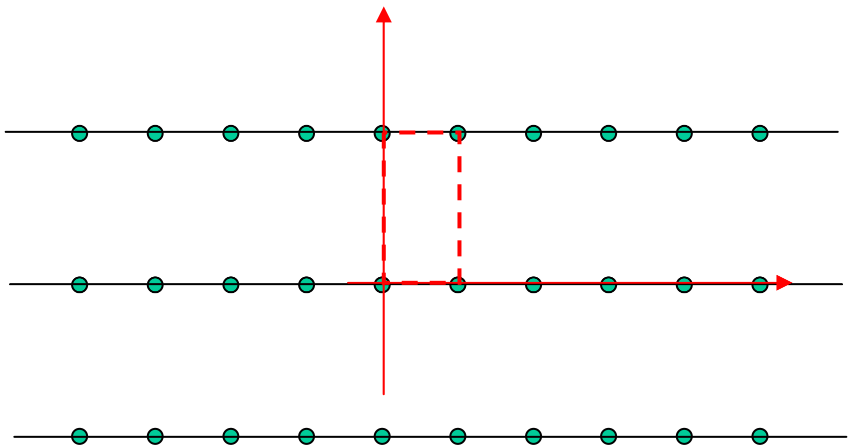
basis vectors: a_1, $a_{2,}$ a_3

Any lattice point $\vec{R}$ can be obtained by translation

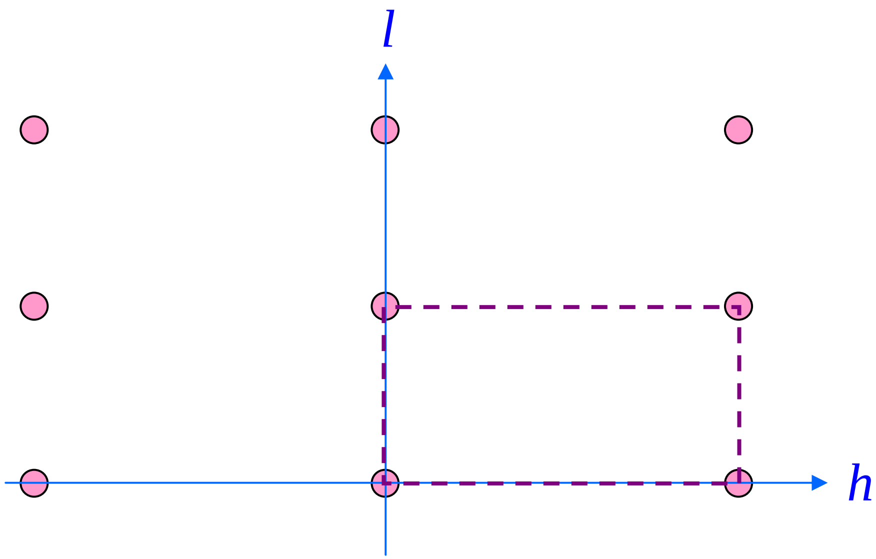
$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

Lattice

Real space lattice



Reciprocal space lattice



Fourier Transfer

Condition for Bragg reflection

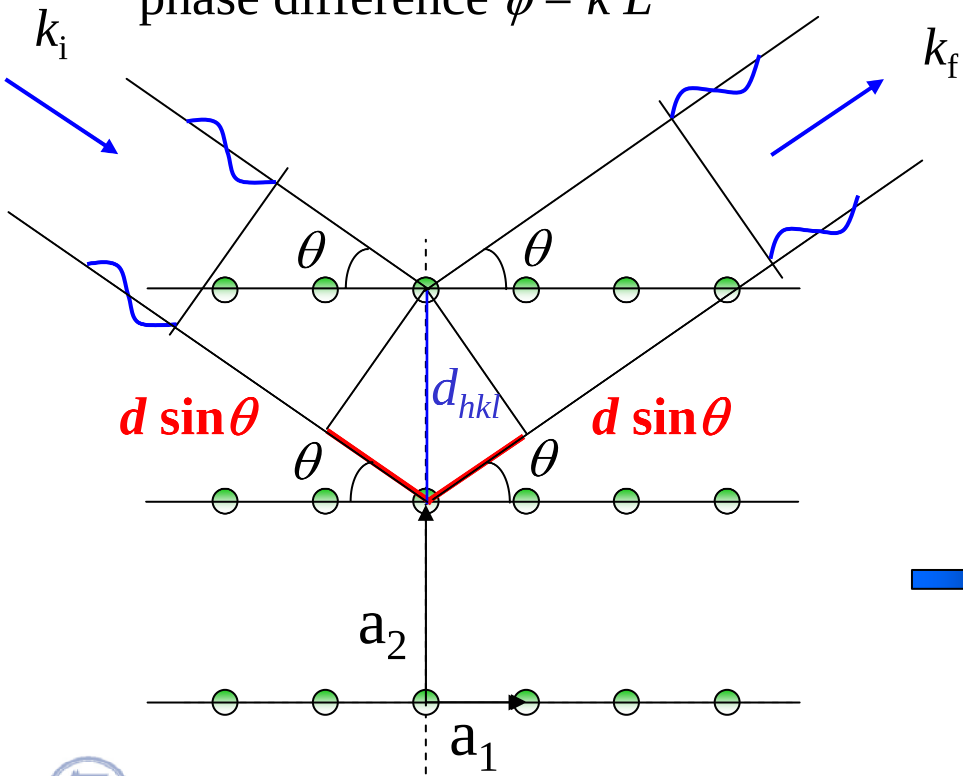
Real space

Bragg Law $2d\sin\theta = \lambda$

Path Difference $L = 2d_{hkl}\sin\theta$

Constructive interference: $L = n\lambda$

phase difference $\phi = k\,L$



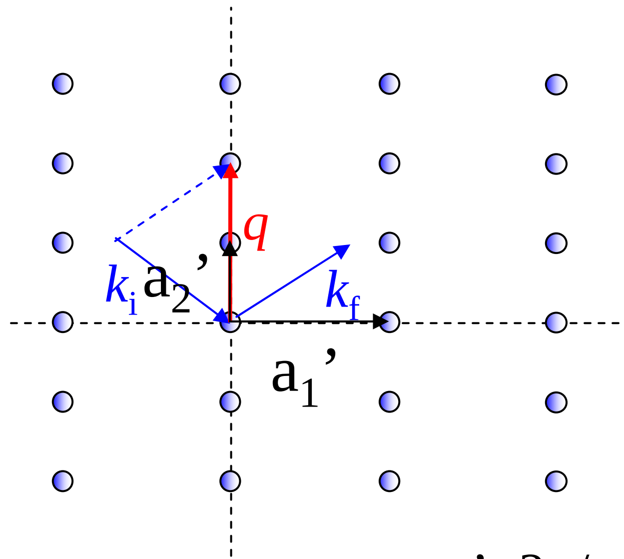
a_1=a

Reciprocal space

$$2\frac{2\pi}{\lambda}\sin\theta = \frac{2\pi}{d_{hkl}}$$

$$\vec{q} = \frac{4\pi}{\lambda}\sin\theta\,\hat{q} = \frac{2\pi}{d_{hkl}}\hat{n} = \vec{G}_{hkl}$$

FT



a_1'=2π/a

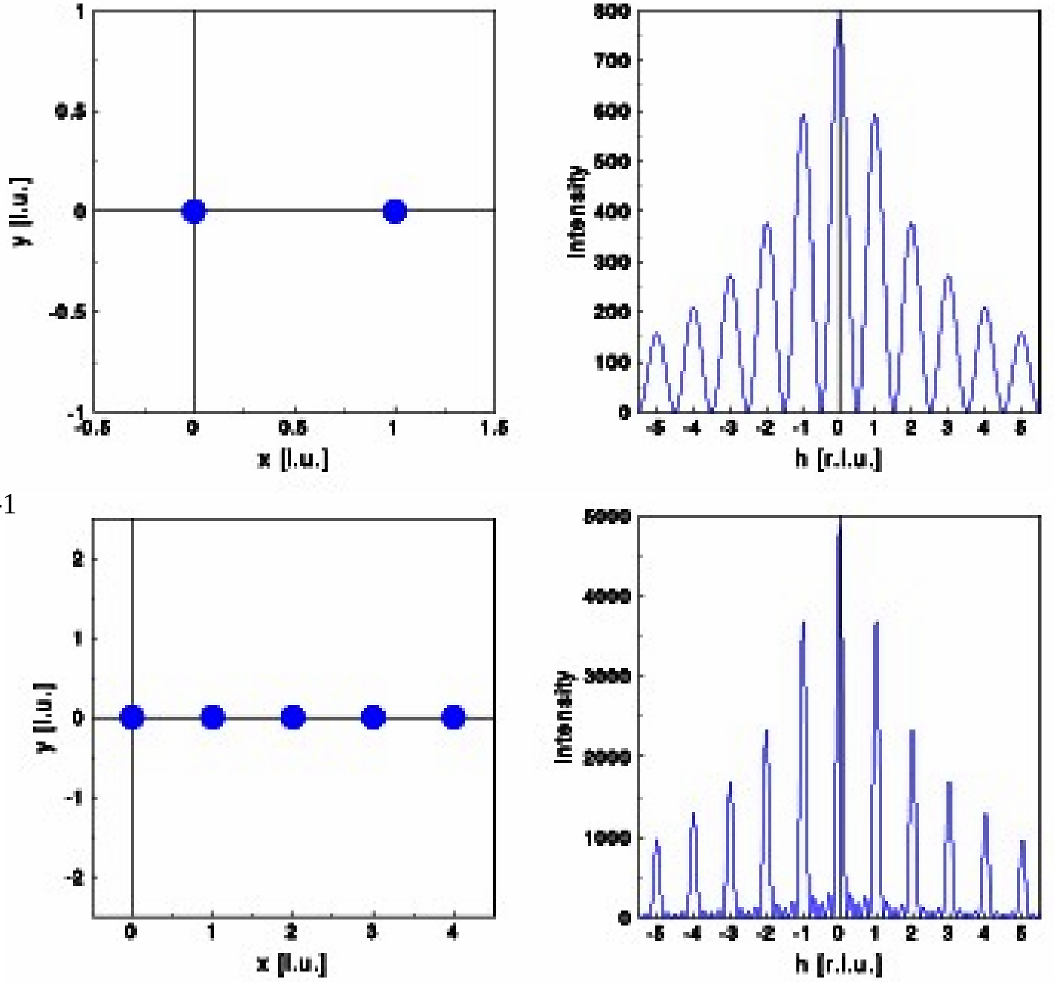
Size Effect - Diffraction Pattern of A Row of Atoms

2 atoms

5 atoms

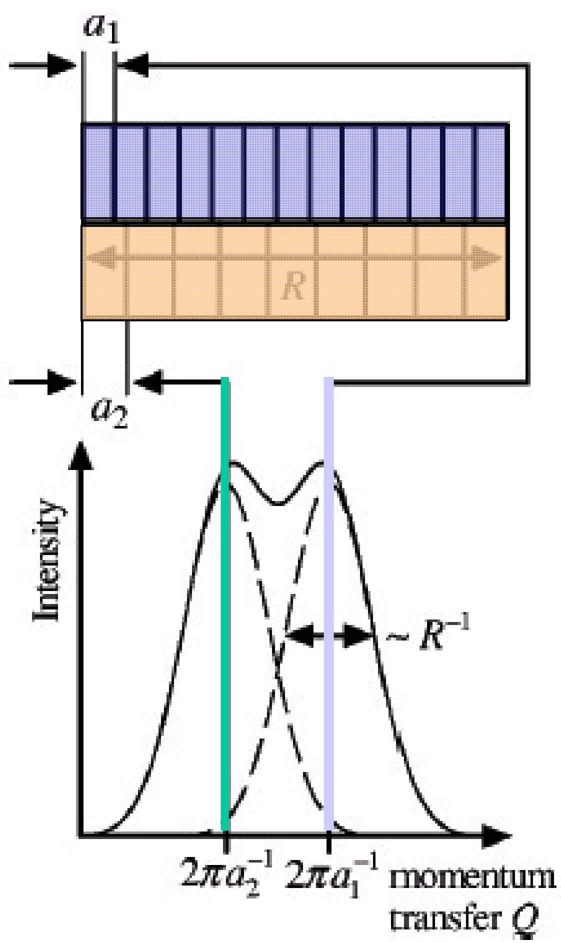
1 l.u.= a Å

1 r.l.u. = $2\pi/a$ Å^{-1}



Scherrer's equation $$L \approx \frac{2\pi}{FWHM(q)}$$ $$L \approx \frac{0.9\lambda}{FWHM(2\theta)\cos\theta_B}$$

Effect due to Lattice Constant Change
(Strain Effect)



$$2\pi(a_2^{-1} - a_1^{-1}) \geq R^{-1}$$

National Synchrotron Radiation Research Center

Structural and Optical Properties of ZnO films Gown on Si with a Y_2O_3 Buffer Layer

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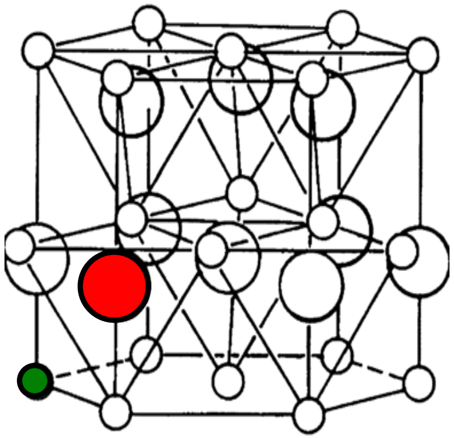
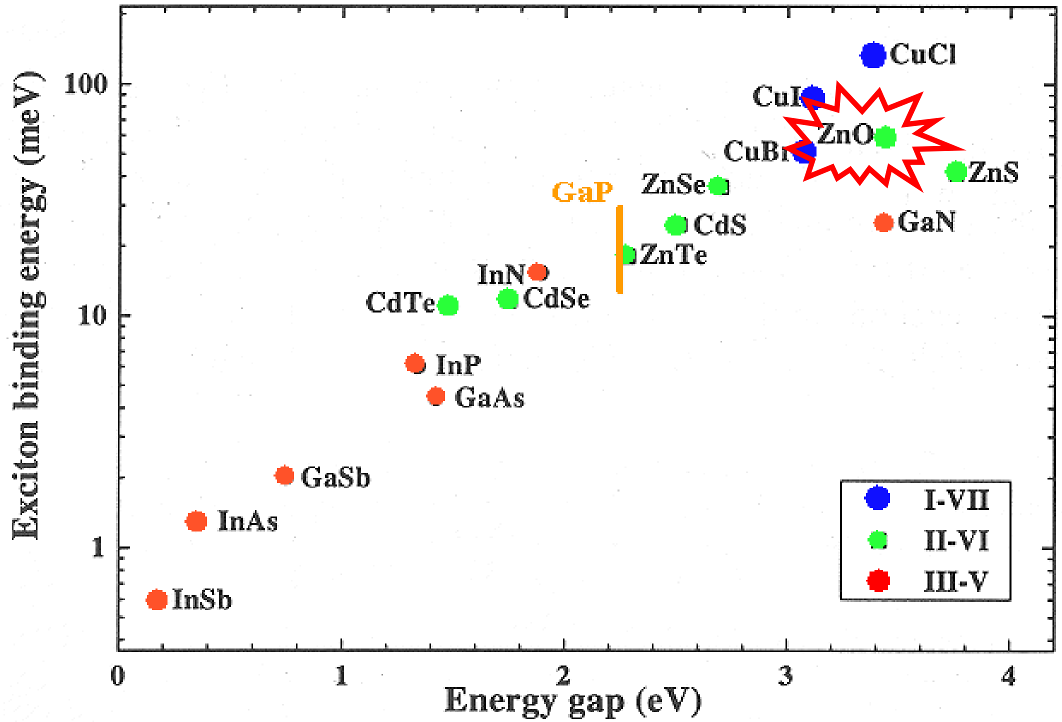
李威縉 李毅君 洪銘輝 清大材料
郭瑞年 清大物理
林碧軒 楊智凱 徐嘉鴻 同步輻射

ZnO

Wurtzite (hexagonal)





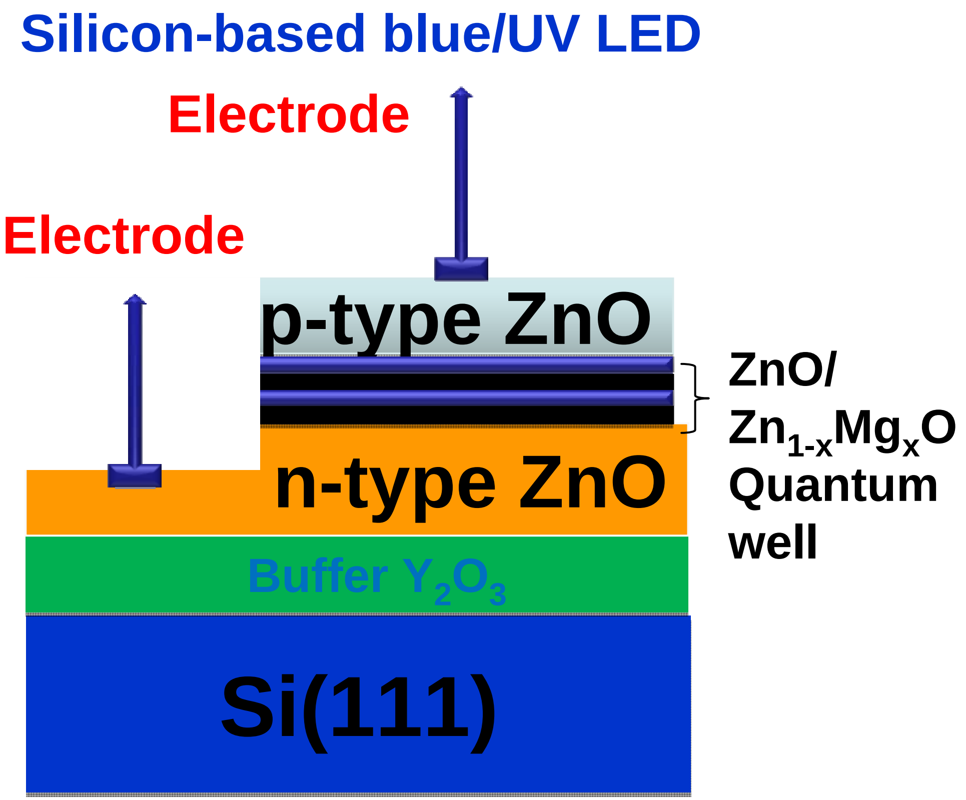
ZnO bulk: a =3.24382Å c =5.20364Å

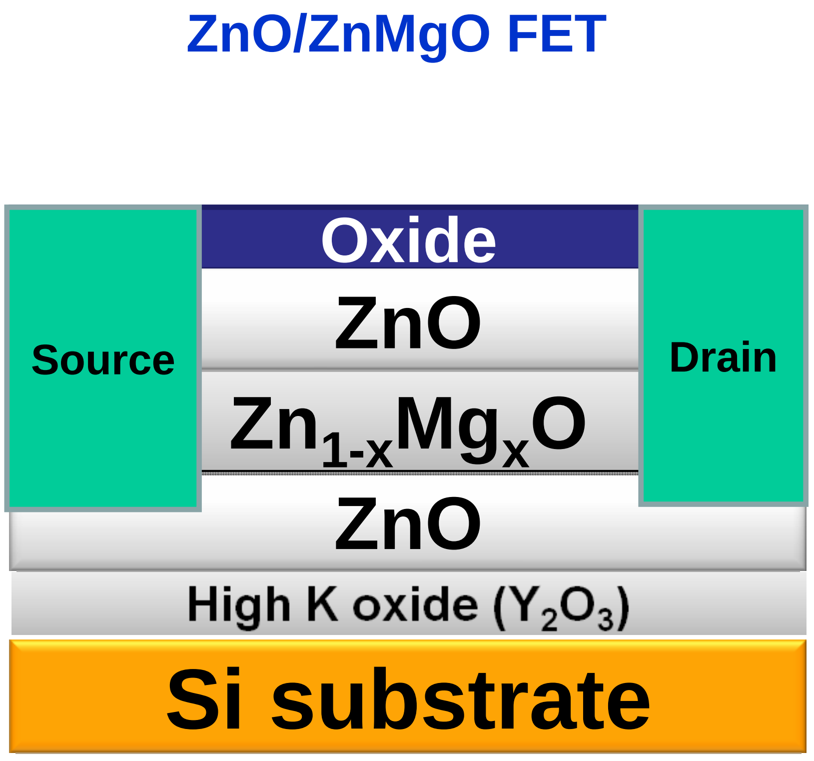
- **II-VI wide direct band gap (3.37eV) wurtzite-type semiconductor**
- **Large binding energy of free exciton (60 meV)**
- **Free exciton emission at room temperature**

GaN (25 meV)
ZnSe (22 meV)

Thermal Energy (26 meV)

Why ZnO on Si





or being an buffer for GaN on Si (small lattice mismatch between GaN and ZnO)

Obstacles for the growth of high quality ZnO on Si

Large lattice mismatch (-15%) between ZnO (a = 3.24 Å) and Si ($a/\sqrt{2}$) = 3.84 Å)

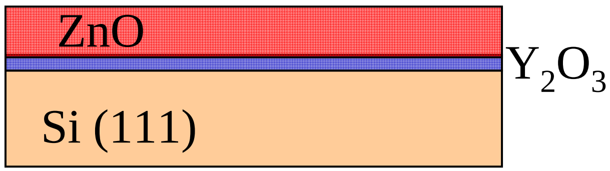
Large thermal mismatch between ZnO ($\alpha = 4.75\times10^{-6}\,K^{-1}$) and Si ($\alpha = 2.56\times10^{-6}\,K^{-1}$)

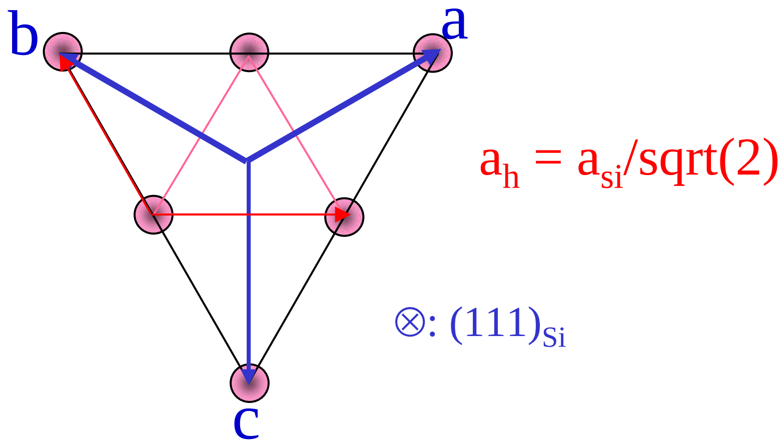
thermal stress → the formation of cracks

Formation of an amorphous SiO_2 layer → polycrystalline or textured ZnO layer

(ΔH_{SiO_2}= -910.7 kJ/mole, ΔH_{ZnO} =-350.5 kJ/mole, $\Delta H_{Y_2O_3}$=-1905.31 kJ/mole)

Possible solution: buffer layer



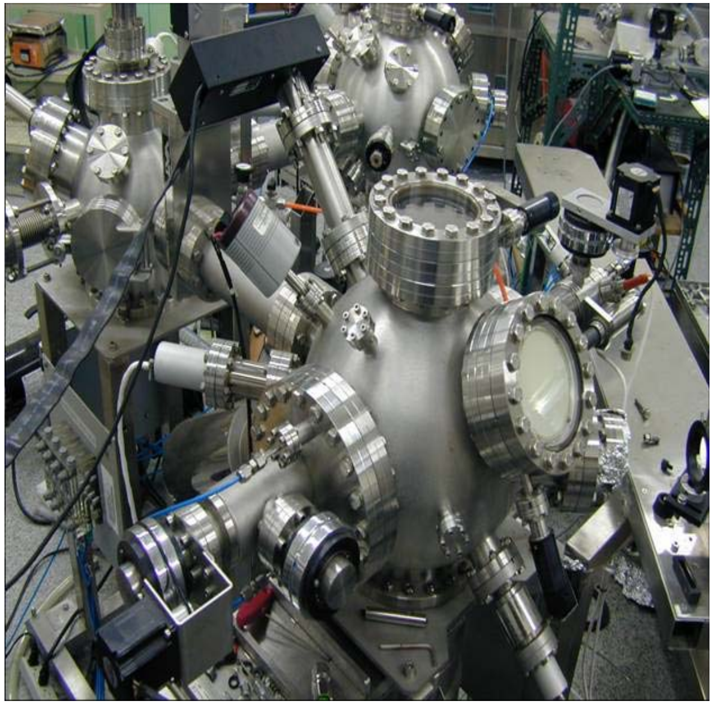


ZnO: a = 3.244 Å, c = 5.204 Å

Y_2O_3: a = 10.606; on (111) a_h= 7.50 Å

Si: a = 5.431 Å; on (111) a_h= 3.84 Å

Sample preparation and characterization



Growth condition

Pulsed laser deposition (PLD) or laser MBE

KrF pulsed excimer laser: 248 nm,10 Hz, 7 J/cm^2

Substrate : Y_2O_3/Si(111) (grown by MBE);

Target : 5N ZnO target

Growth rate and sample thickness: 0.27 Å/s and ~0.21 μm

Chamber basic pressure: 2.4×10^{-8} torr

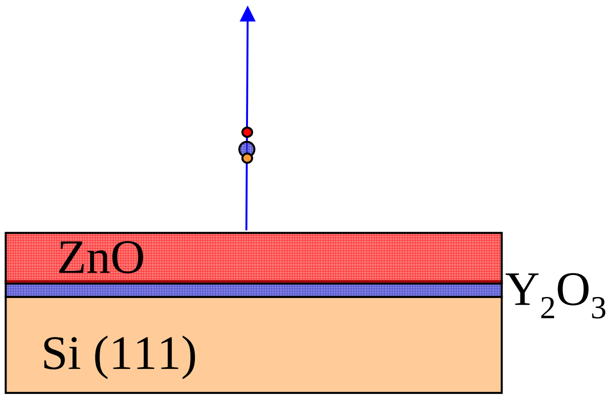
Characterization

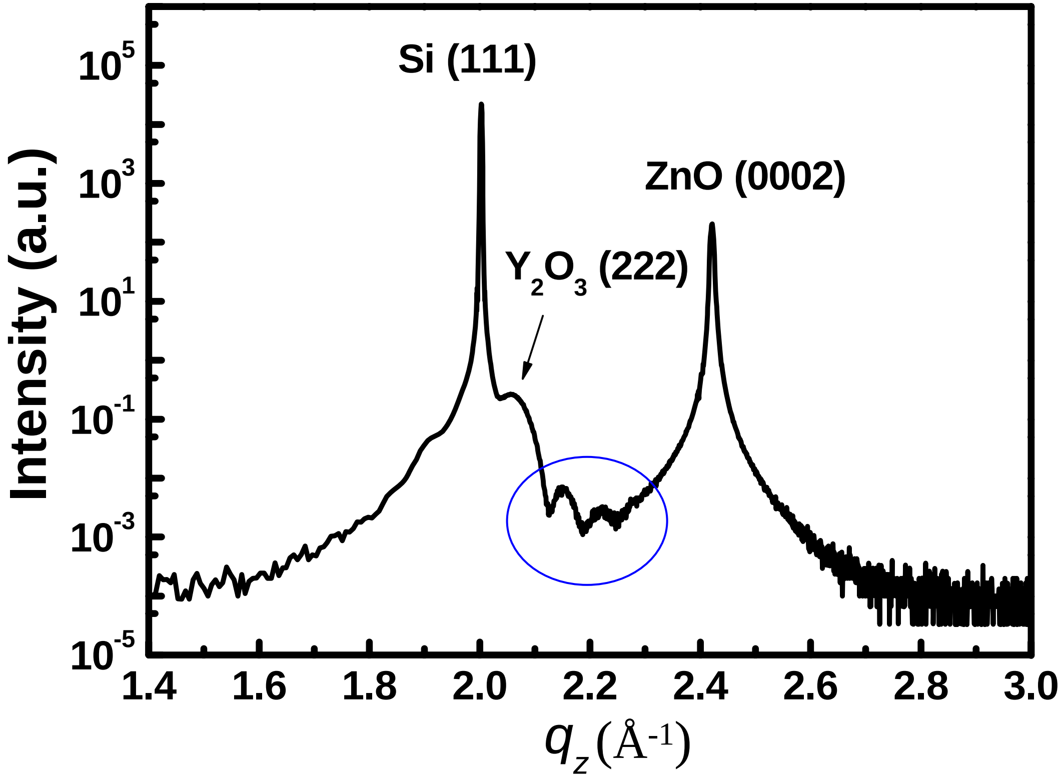
XRD : 4-circle diffractometer at BL17A, NSRRC

TEM : Philips Tecnai F-20.

PL : He–Cd laser (325 nm).

Radial scan along surface normal



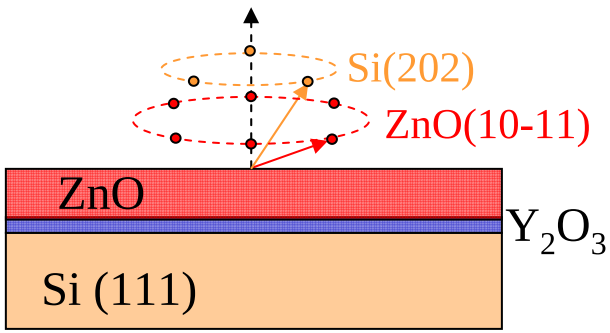


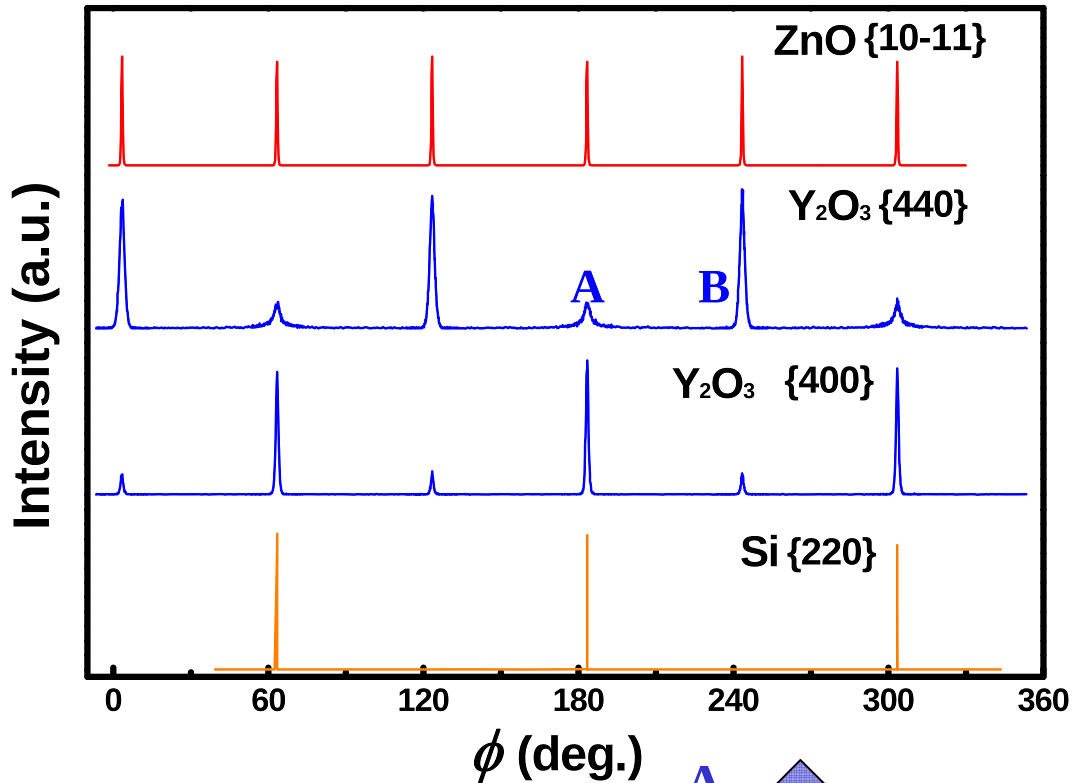
$(0002)_{ZnO} \parallel (222)_{Y_2O_3} \parallel (111)_{Si}$

Thickness fringe: period ➡ Y_2O_3 layer thickness ~ 9.6 nm

Sharp interface and good crystalline quality

Azimuthal scans across off-normal reflections





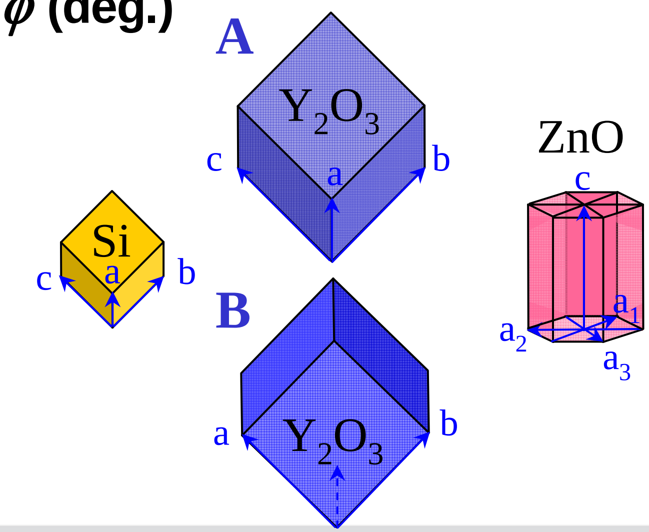
In-plane orientation

A: $(10\bar{1}0)_{ZnO} \parallel (11\bar{2})_{Y_2O_3} \parallel (11\bar{2})_{Si}$

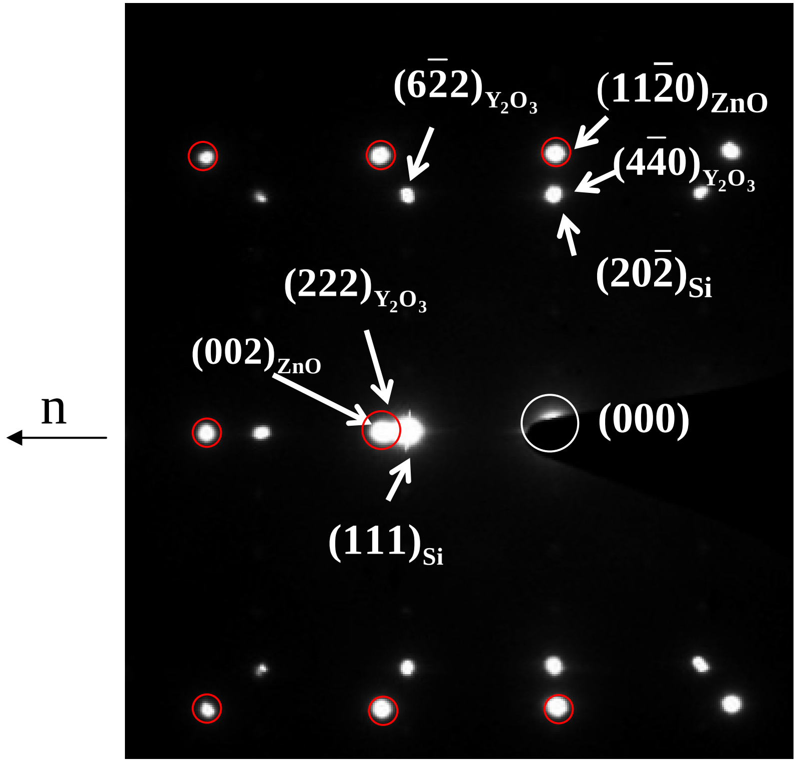
60° off

B: $(10\bar{1}0)_{ZnO} \parallel (2\bar{1}\bar{1})_{Y_2O_3} \parallel (11\bar{2})_{Si}$

dominant



Selected Area Electron Diffraction (SAED) Pattern



$$(0001)_{ZnO} \parallel (111)_{Y_2O_3} \parallel (111)_{Si}$$

$$\{11\bar{2}0\}_{ZnO} \parallel \{4\bar{4}0\}_{Y_2O_3} \parallel \{2\bar{2}0\}_{Si}$$

Lattice mismatch ~ -15.9%

Domain Matching Epitaxy (DME)

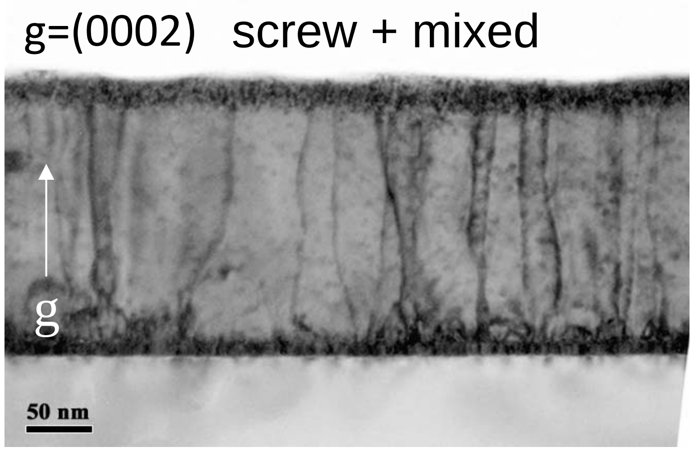
Strain $$\varepsilon = \frac{d_f}{d_s} - 1$$ > ~7%

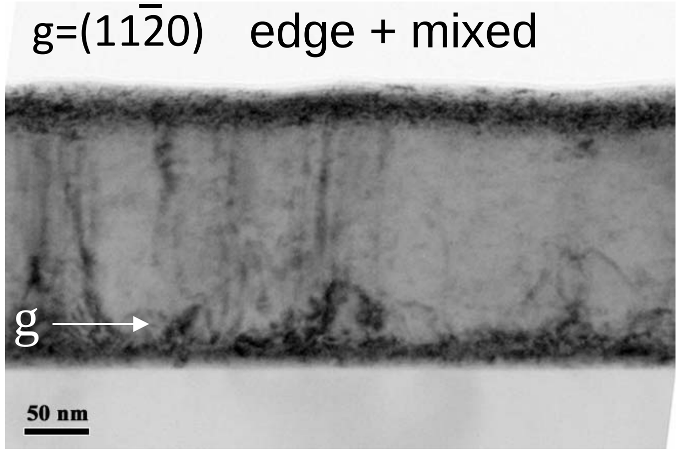
$$(m+\alpha)d_f = (n+\alpha)d_s, \quad m, n : \text{integer} ; \alpha < 1$$

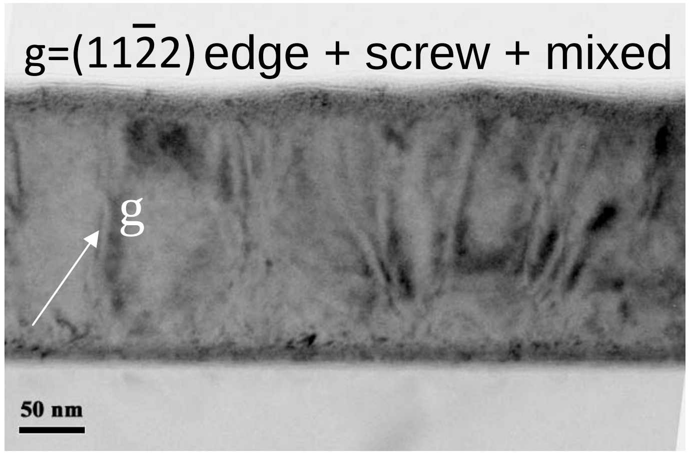
Residual strain $$\varepsilon_r = \frac{md_f}{nd_s} - 1$$

Residual strain of ZnO grown on Y_2O_3 reduces down to ~1%

TEM Contrast Analysis (two-beam condition)







Invisible criterion $\vec{g} \cdot \vec{b} = 0$

g: diffraction vector

b: dislocation Burgers vector

pure edge $\boldsymbol{b}_E$ = 1/3· $<11\bar{2}0>$

pure screw $\boldsymbol{b}_C$ = <0001>

Defect structure is predominantly screw and mixed type TDs. Near the interface, there are high density of misfit dislocations.

Summary

• High quality ZnO epitaxial films have been successfully grown by pulsed-laser deposition on Si (111) substrates with a thin Y2O3 buffer layer.

• Two (111) oriented domains with 60° in-plane rotation coexist in the Y_2O_3 buffer layer. The in-plane epitaxial relationship between the wurtzite ZnO, cubic Y_2O_3 and cubic Si follows .

• The growth of ZnO on Y_2O_3 can be well described by domain matching epitaxy.

• The photoluminescence spectra of ZnO epi-films exhibit superior optical properties at room temperature even for films of thickness as thin as 0.21 μm.