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

Introduction of X-ray scattering
The growth of ZnO on Si using a $\text{Y}_2\text{O}_3$ buffer layer
Domain Matching Epitaxy
Summary
The Properties of Synchrotron Radiation

- High Intensity
  \[ I_{SR} > 10^6 \times I_{tube} \]
- 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 \( E = \frac{hc}{\lambda} \)

\[ E_i = E_f \text{ i.e. } \lambda_i = \lambda_f \text{ (elastic scattering)} \]

wave vector \( k = \frac{2\pi}{\lambda} \); \( |k_i| = |k_f| \)

wave vector (energy), amplitude, phase

\[ \vec{q} = \vec{k}_f - \vec{k}_i \]

\[ q = 4\pi \sin(\theta)/\lambda \]
Crystal Structure

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

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

in 3-D

basis vectors: $a_1, a_2, a_3$
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 \( \phi = kL \)

Reciprocal space

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

\[
\bar{q} = \frac{4\pi}{\lambda} \sin \theta \quad \hat{q} = \frac{2\pi}{d_{hkl}} \hat{n} = \vec{G}_{hkl}
\]

\( \bar{q} = 2\pi/a \)

\( a_1 = a \)

\( a_1' = 2\pi/a \)
Size Effect - Diffraction Pattern of A Row of Atoms

2 atoms

1 l.u. = $a$ Å
1 r.l.u. = $2\pi/a$ Å$^{-1}$

5 atoms

Scherrer’s equation

$L \approx \frac{2\pi}{\text{FWHM}(q)}$

$L \approx \frac{0.9\lambda}{\text{FWHM}(2\theta)\cos\theta_B}$
Effect due to Lattice Constant Change
(Strain Effect)

\[ 2\pi \left( a_2^{-1} - a_1^{-1} \right) \geq R^{-1} \]
Structural and Optical Properties of ZnO films Gown on Si with a Y$_2$O$_3$ Buffer Layer
ZnO

Wurtzite (hexagonal)

ZnO bulk:  
\[ a = 3.24382\text{Å} \]
\[ c = 5.20364\text{Å} \]

- 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 \times 10^{-6} \text{K}^{-1}) and Si (\alpha = 2.56 \times 10^{-6} \text{K}^{-1})

thermal stress \rightarrow the formation of cracks

Formation of an amorphous SiO\textsubscript{2} layer \rightarrow polycrystalline or textured ZnO layer

( \Delta H_{\text{SiO}_2} = -910.7 \text{kJ/mole}, \Delta H_{\text{ZnO}} = -350.5 \text{kJ/mole}, \Delta H_{\text{Y}_2\text{O}_3} = -1905.31 \text{kJ/mole} )

Possible solution: buffer layer

\[ a_h = \frac{a_{\text{Si}}}{\sqrt{2}} \]

\( \otimes: (111)_{\text{Si}} \)

ZnO: a = 3.244 Å, c = 5.204 Å

Y\textsubscript{2}O\textsubscript{3}: a = 10.606; on (111) a\textsubscript{h} = 7.50 Å

Si: a = 5.431 Å; on (111) a\textsubscript{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/cm²
Substrate: Y₂O₃/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: 2.4x10⁻⁸ 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 \rightarrow Y_2O_3 layer thickness \sim 9.6 \text{ nm}
Sharp interface and good crystalline quality
Azimuthal scans across off-normal reflections

In-plane orientation

A: \[(10\overline{1}0)_{ZnO} \parallel (11\overline{2})_{Y_2O_3} \parallel (11\overline{2})_{Si}\]

B: \[(10\overline{1}0)_{ZnO} \parallel (2\overline{1}\overline{1})_{Y_2O_3} \parallel (11\overline{2})_{Si}\]

60° off

dominant
Selected Area Electron Diffraction (SAED) Pattern

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

\[ \{1\overline{1}20\}_{ZnO} \parallel \{4\overline{4}0\}_{Y_2O_3} \parallel \{2\overline{2}0\}_{Si} \]

Lattice mismatch \( \sim -15.9\% \)
Domain Matching Epitaxy (DME)

\[
\varepsilon = \frac{d_f}{d_s} - 1 \quad > \sim 7\%
\]

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

Residual strain

\[
\varepsilon_r = \frac{md_f}{nd_s} - 1
\]

Residual strain of ZnO grown on Y\textsubscript{2}O\textsubscript{3} reduces down to \(~1\%)
Defect structure is predominantly screw and mixed type TDs. Near the interface, there are high density of misfit dislocations.

**TEM Contrast Analysis (two-beam condition)**

- $g=(0002)$ screw + mixed
- $g=(1\overline{2}0)$ edge + mixed
- $g=(1\overline{1}2\overline{2})$ edge + screw + mixed

**Invisible criterion**

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

- $g$: diffraction vector
- $b$: dislocation Burgers vector

Pure edge $b_E = 1/3 \cdot <1\overline{1}20>$

Pure screw $b_C = <0001>$
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 Y2O3 buffer layer. The in-plane epitaxial relationship between the wurtzite ZnO, cubic Y2O3 and cubic Si follows.
• The growth of ZnO on Y2O3 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.