Compound Semiconductor Nanowires for Next Generation Optoelectronics

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Overview

- **Motivation**

- **Growth of Nanowires (NWs) by Metal Organic Chemical Vapour Deposition (MOCVD)**
  - GaAs NWs
  - GaAs/AlGaAs NWs
  - InP NWs (ZB, WZ, WZ-ZB)
  - GaSb/GaAs NWs

- **Optical Properties of NWs**

- **Conclusions**
Semiconductor Optoelectronics and Nanotechnology Group
Nanowires as Building Blocks for Electronics and Photonics

overcome fundamental limitation of lattice mismatch
axial heterostructure nanowires
radial heterostructure nanowires (core/shell nanowires)
branch nanowires

LEDs, Lasers
Single Electron Transistors
Photodetectors
Bio-sensors
Solar Cells

Future nanowire OEIC

International Technology Roadmap for Semiconductors
Historical Vapour-Liquid-Solid (VLS) Growth Mechanism

- VLS growth of silicon whiskers was discovered by Wagner and Ellis in 1964.
- At growth temperature, a eutectic liquid droplet of Au/Si formed.
- The droplet was supersaturated with Si from the surrounding vapour.
- Precipitation of Si from the droplet.
- Nucleation occurred at the solid/liquid interface and growth continued in this direction.

Highly anisotropic whisker growth.
- Vapour-Liquid-Solid growth mechanism.
Vapor-Liquid-Solid Growth of GaAs (111)B nanowires

[111] Axial growth

Source Molecules (vapor)

Molten Au:Ga Eutectic (liquid)

Reaction species diffusion

Radial growth

Triangular/hexagonal base

45° tilt FE-SEM image (The inset is top view)

- Supersaturation of molten droplet with Ga species
- High incorporation efficiency of Ga vapor into the molten droplet
- [111] is energetically preferred direction

Surface free energy $E$
$E(111)B < E(110) < E(100)$

K. Hiruma, 1990s, III-Vs
Nanowire Growth: MOCVD Conditions

- Horizontal-flow low-pressure metalorganic chemical vapor deposition system
- Growth time = 10 min ~ 40 min
- Growth temp = 390 ~ 510 °C
- Growth temp >100 °C lower than usual
- Source flows ~10 times smaller than usual
- TMGa, TMIn, TMAI, AsH₃, PH₃

Au-Ga or Au-In or Au-Al Eutectic

(111) Growth Direction
GaAs nanowires growth by gold colloidal solution

1. **Poly-L-lysine deposition**
   - Poly-L-lysine (PLL, one of polymer electrolytes) treatment
   - attracts negatively charged Au nanoparticles
   - prevents the agglomeration of Au nanoparticles

2. **30 nm Au colloidal solution deposition (30 ±3 nm)**

3. **MOCVD growth**

See the difference!

- without PLL treatment
- with PLL treatment
GaAs Nanowires

510 °C

450 °C

390 °C

↑ \( T \)

Lateral growth enhanced, tapering

↓ \( T \)

Kinking more frequent
Two-temperature process

1. Brief nucleation step, $T_n$:
   - 1 minute at a high temperature
   - $T_n = 450 \, ^\circ C$
   - Promotes nucleation and growth of straight, epitaxial, vertical [111]B-oriented nanowires

2. Prolonged growth step, $T_g$:
   - Temperature rapidly ramped down
   - $350 \, ^\circ C \leq T_g \leq 390 \, ^\circ C$
   - Growth continues at $T_g$
   - Low growth temperature minimises radial growth

SEM comparison

Original procedure (single-temperature)

Two-temperature procedure

$T_n = 450 \ ^\circ\mathrm{C}$

$T_g = 390 \ ^\circ\mathrm{C}$

$T_g = 350 \ ^\circ\mathrm{C}$
TEM comparison
(in collaboration with University of Queensland)

Original procedure

450 °C

Twin defects
Facetted sidewalls

Two-temperature procedure

\( T_n = 450 \, ^\circ \text{C}, \ T_g = 390 \, ^\circ \text{C} \)

No planar defects
Smooth sidewalls
Photoluminescence comparison

Original procedure
450 °C

AlGaAs shell 650 °C

Two-temperature procedure
\( T_n = 450 \, ^\circ C \)
\( T_g = 390 \, ^\circ C \)

10 K
Excitonic emission 1.515 eV

PL intensity (arb. units)

Energy (eV)

Room temperature \( \mu \)-PL

1 μm
III-V nanowires

- GaAs (111) nanowires
- AlGaAs (111) nanowires (Zinc Blende- Cubic)
- InAs and InP nanowires (Wurtzite-Hexagonal)
Carrier Dynamics in Nanowires

Large surface to volume ratio ...

Small structures (nanowires) → More surface interactions → Shorter lifetimes

Surface recombination velocity \((S)\) → characterizes effects of nonradiative surface states

Nonradiative recombination reduces quantum efficiency. Occurs at surfaces \((t_{NR} = d/2S)\) and defects within wire.
Time resolved Photoluminescence (TRPL) InP Nanowires

- Surface recombination velocity \( S = 5 \times 10^3 \text{ cm/s} \)

- Non-radiative lifetime \( \tau = \frac{d}{2S} = 2 \text{ ns} \)

- Experiments InP \( \rightarrow 1.5\text{ns} \)

- Intrinsic (non surface dominated) properties visible

InP Epilayer 1.67 ns

1500 ps

InP Wires

InP PL time decays at peak energies

L. Titova et al.
Nano Letters 7, 3383 (2007)
GaAs (core) nanowire comparison

GaAs comparison
• $S = 10^6$ cm/s!
• $\tau_{nr} = d/2S = 1.5$ ps!
• Experiments on bare GaAs nanowires $\rightarrow$ 1ps

GaAs nanowires: low quantum efficiency due to non-radiative surface recombination

GaAs/AlGaAs core-shell nanowires

- Core-shell GaAs-AlGaAs nanowires have much higher quantum efficiency (20-100x larger PL intensity)

Two-temperature growth

1. **Twin Free Core growth**
   - High nucleation temperature,
     \[ T_n = 450 \, ^\circ\text{C} \text{ for } 1 \text{ minute} \]
   - Low growth temperature,
     \[ T_g = 375 \, ^\circ\text{C} \text{ for } 30 \text{ minutes} \]

2. **AlGaAs/GaAs shell/cap growth**
   - Temperature increased to 650°C
   - 20nm AlGaAs shell; add 5nm GaAs cap
Lifetime Comparison - GaAs NWs

Excitation: 780nm, 200fs pulsed laser, low power

Emission: decay times measured at 1.51 eV exciton peak

Radial heterostructure nanowires

- Low temperature → axial nanowire growth (GaAs core at 450 °C)
- High temperature → radial shell growth (AlGaAs shell at 650 °C)
- GaAs core passivated by AlGaAs shell
  - enhanced PL (excitonic emission 1.515 eV)

• Blue-shifted PL peak from GaAs/AlGaAs core-multishell structures
  - Quantum well shells? Or AlGaAs related emission more likely!!!!

Radial NW Heterostructures

AlGaAs shell

GaAs shell quantum well ??

GaAs core

substrate

Photoluminescence (arbitrary units)

Energy (eV)
Rethinking InP nanowires …

• InP – long lifetimes
  ➢ InP – nanowire with
    ➢ Zincblende (ZB) structure only – 420°C
    ➢ Wurtzite (WZ) structure only – 480°C
    ➢ Implications?

➢ InP nanowire with both ZB and WZ!
Temperature dependent PL

(PLs normalized for clarity)

PL of both structures persist up to room temperature:
Low non-radiative recombination rate

Fit modified Varshni:

\[ E = E_0 - \alpha T^4 / (T^3 + \beta) \]

Estimated band gap for WZ
\(~80\,\text{meV}\) higher than ZB
PL selection rules

Zincblende

- \( \Gamma_6 \rightarrow \Gamma_8 \): unpolarized
- Dielectric contrast responsible for polarization

Wurtzite

- \( \Gamma_7 \rightarrow \Gamma_9 \): dipole allowed only if E-field is perpendicular to the c-axis
Polarization dependent PL

**Zincblende (NW A):** Strongly polarized along the wire axis

**Wurtzite (NW 1):** Strongly polarized perpendicular to the wire axis

- Laser is circularly polarized
- PL analyzed at angle $\theta$ relative to the wire’s axis

InP with both WZ and ZB – within the same nanowire

TEM

Energy level diagram:

TRPL at different energies

~6400 ps at 1.44 eV

~900 ps at 1.49 eV

~200 ps at 1.55 eV

Axial heterostructure nanowires

- Axial heterostructure segments grown by switching gas flows, e.g. switching on TMG and switching on/off TMI
- Growth interrupt of between 1 and 5 minutes, to deplete the Au particle of the previous group III species
- Thin axial segments $\rightarrow$ *axial quantum wells*
- Diffusion of adatoms from the substrate is a confounding factor and difficult to predict QW In Composition
- Indium incorporation towards the base when TMI is introduced
- Kinking occurs with Smaller Au particles & Higher TMI flow
Ordered Nanowires
(Single Photon Sources, Photonic Crystals, NW Solar Cells)

Dual Beam Focused Ion Beam and Nanoimprint Lithography
Conclusions

• Understanding Nanowire growth is important to control the size, shape and composition and in turn electronic and optical properties

• Developing Nanowire heterostructures (axial and radial) and understanding their properties will be important for device applications
Acknowledgements

- Australian National University, Canberra
  Hannah Joyce, Su Paiman, Jordan Kang, Tim Burgess, Vidya Ramesh, Shriniwas Deshpande, Michael Gao, Fu Lan, Jenny Wong-Leung, Michael Aggett, Hoe Tan
- University of Queensland, Australia
  Mohan Paladugu, Yanan Guo, Xin Zhang, Graeme Auchterlonie, Jin Zou
- University of New South Wales, Australia - Peter Reece, Mike Gal
- Dong-A University, Pusan, Korea - Yong Kim
- Univ of Cincinnati, USA
  S. Perera, A. Mishra, M. Fickenscher, L.V. Titova, T. Hoang, Leigh Smith, Howard Jackson, Jan Harrison-Rice (Miami University)
- Oxford University, UK - P. Parkinson, Laura Herz, Michael Johnston
- Fudan University, Shanghai S.C. Shen, Z. Chen
- Shanghai Institute of Technical Physics, CAS, China- Wei Lu

Australian Research Council –Funding
DIISR-NCRIS - EIF Programs – Australian National Fabrication Facility
DIISR – International Science Linkages Program – China Grant
DIISR – Australia-India Strategic Research Fund - India Grant

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