Self-catalyzed III-V nanowires and heterostructures for photovoltaic applications

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Where are we?
Motivation

- Urgent need for renewable energy harvesting.
- Nanowires in third generation solar cells:

3rd generation PV:
- Reduce cost
- Increase efficiency

Nanoscale materials such as nanowires will pave the route

* Including organic thin film solar cells
How to increase efficiency

- Problem:
  - Energy loss in Carnot cycle
  - Entropy loss in absorption or emission
  - Entropy loss due to non-reciprocity
  - Energy loss due to thermalization or lack of absorption
  - Entropy loss due to lack of angle restriction
  - Entropy loss to incomplete light trapping and reduced QE
  - Conventional single-junction solar cell

- Solution:
  - Intrinsic loss
  - Multi-junction solar cell
  - Surface light directors
  - Light-trapping structures, density of states engineering

- Nanowires
  - Lattice mismatch does not play a role: any material combination allowed
  - Intrinsic light management


How to reduce costs?

1. High quality III-V nanowires and nanowire arrays can be obtained on cheap substrates such as silicon.
3. A coaxial pn junction geometry is advantageous for charge carrier collection.
4. Atomically precise high quality functional layers on the facets of the nanowires are possible: MODEL SYSTEM
1. Fabrication of devices on silicon

Growth mechanisms: diffusion, desorption, doping, passivation.

Outline

2. Design of the nanowire configuration

Catalyst-free (gallium assisted) growth

Nanowire growth mechanisms

Motivation

Nanowire growth mechanisms

Nucleation at SiO₂ pinholes

As-limited growth

Growth on Si: the polarity question

Assuming that growth occurs in the (111)B direction, it is often assumed that:

1. If the first layer nucleates with B polarity, then we have growth perpendicular to the substrate
2. Otherwise, growth proceeds in a 19°
Sequential seed formation and 3D twinning at the initial stages of growth.

Nano Lett. 11, 3827 (2011)

Importance of initial stages

1. Ga
2. Multiple seed + 3D twinning: Non-vertical growth

1ML 3ML

100% yield of vertical wires

Vertical growth

Nanoscale 4 1486 (2012)

Nano Lett. 11, 3827 (2011)
**Motivation**

Nanowire growth mechanisms

**2D growth on the facets**

Growth on the facets is equivalent to high quality 2D MBE growth.

**Vapor-Liquid-Solid (VLS) mechanism**

Growth precursors gathered and preferentially decomposed at the metal catalyst droplet.

Saturation at the metal droplet leads to precipitation → formation of the nanowire underneath

**Radial heterostructures**

**Quantum wells**

**Quantum dots**

Small 4 899-903 (2008)

Optical properties

Small 4 899-903 (2008)

Reduction of the surface recombination

**Reduction of the surface recombination**

Unpassivated wires:
- Existence of depletion region
- Trap density: $10^{12} \text{cm}^{-2}$

Capped wires:
- No depletion region
- Recombination at the interface
- Velocity: $< 2.9 \times 10^3 \text{ cm/s}$


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**Doping mechanisms**

2D growth on the facets
- Doped shells, n or p type, can be achieved.

Incorporation through the Ga droplet
- Si is soluble in Ga
- The doping concentration is governed by the Si flux and the nw growth rate.
- Si incorporates as a p-type dopant.

*Appl. Phys. Lett. 94, 173108 (2009)*

*Nano Lett. 10, 1734 (2010)*

(Si substituting Ga: n-type, Si substituting As: p-type)
Radial heterostructures and doping

**Nw core**
- Ga rich conditions
- Si incorporated in As site
- p-doped core

**Intrinsic middle shell**
- As rich conditions
- Si cell OFF
- Intrinsic shell

**Doped external shell**
- As rich conditions
- Si incorporated in Ga site
- n-doped shell

Nano Lett. 10, 1734 (2010)

Solar cell results

Open circuit voltage = 0.6V
Short circuit current = 10mA/cm²
Fill factor = 65%
Efficiency = 4.5%

C. Colombo et al.
Motivation

Spatially resolved measurements

Photocurrent comes only from p-i-n junction

Photocurrent homogeneous along nanowire

Towards nanowire based photovoltaics

1) Contacting scheme on arrays


2) III-V arrays on silicon

What is the ideal inter-wire distance?

25 mm² Si arrays

η~10%

FF~0.8
Motivation

Light absorption in standing nanowires

Interaction between a planar wave and a standing nanowire:

(Olivier Demichel, Martin Heiss, in preparation)
Absorption cross-section vs optimal pitch

150 nm diameter

AM1.5G

Carrier generation rate m^2/s

Nanowire axis z position (nm)

P = 1800 nm
P = 1400 nm
P = 1200 nm
P = 1000 nm
P = 840 nm
P = 680 nm
P = 520 nm
P = 440 nm
P = 360 nm
P = 280 nm
P = 200 nm

Absorption cross-section vs optimal pitch

150 nm diameter

AM1.5G

Si

P

90 90 120 150 180 210 240 270 300 390 450 510 600 750 900 1050
Optimal pitch

150 nm diameter

Absorption Efficiency (total)

Nanowire pitch (nm)

Absorption

Cover fraction

Single standing nanowire device?

n-type

undoped

p-type

(in cooperation with Sunflake and Niels Bohr Institute, Copenhagen)
Motivation

1. Versatility of Ga-catalyzed GaAs nanowires obtained by MBE.

2. High quality radial heterostructures can be obtained.

3. Control on the type of doping enables the fabrication of pin junctions for solar cell applications.

4. Nanowire arrays act as metamaterials: the optical properties depend on the nw arrangement. This will be used for further optimization of the efficiency-to-cost ratio.

Conclusions
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