Nanostructures for energy device applications

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Goals and Rationale of CEN

Develop the scientific understanding required to improve the performance and cost of solar cells and LEDs to make them the technologies of choice for clean energy generation and lighting.

- Strong, complementary team of leaders in semiconductor nanostructures and organic materials.
- **Sophisticated characterization tools** to probe the materials properties and physical mechanisms.
- **Atomistic simulations** to address the fundamental issues that limit acceptance of these technologies.
- Solar cells and LEDs have synergistic requirements and limiting issues that can be addressed by fundamental research on these emerging materials.
Multijunction Solar Cells

- Solar cell efficiency is a pacing factor in the adoption of solar energy because the energy source is dilute and neither land nor installation costs are free.
- To date only multijunction solar cells have produced solar cells with efficiencies greater than the maximum theoretical value for a single junction cell.
- 44.0% Recently achieved using triple junction of InGaAsNSb/GaAs/InGaP on GaAs substrate
- How can we translate this expensive technology into a lower cost platform?
Tandem Design Elements

Monolithic Solar Cells

Tunnel Diodes
Maximum Theoretical Efficiencies of Multijunction Solar Cells

<table>
<thead>
<tr>
<th>No. of Cells</th>
<th>Optimal Bandgaps (eV)</th>
<th>Max. Eff. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_{g1} )</td>
<td>( E_{g2} )</td>
</tr>
<tr>
<td>1</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.97</td>
<td>1.70</td>
</tr>
<tr>
<td>3</td>
<td>0.82</td>
<td>1.30</td>
</tr>
<tr>
<td>4</td>
<td>0.72</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>0.66</td>
<td>0.97</td>
</tr>
<tr>
<td>6</td>
<td>0.61</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Series Connected Cell at AM 1.5

Traditional multijunction solar cell: III-V film-based tandem solar cells are fabricated on Ge due to lattice-match constraints -- **Very Expensive**

**Why Nanowires?**

Natural Strain relief in the radial direction
- Relax lattice-match requirement between materials
- Enable growth of III-V (GaAs, GaAsP, InGaP) nanowires on Si (not possible to grow as films due to lattice and thermal mismatch)
- Eliminate expensive Ge substrates used in film-based multi-junction solar cells
- Leverage silicon solar cell infrastructure

Reduce dislocations by spatial filtering and elimination

Adjustable bandgap and absorption threshold of each cell

Optical Concentration of light

“Natural” Antireflection Properties
Device Design Issues

Vertically Stacked MJ NW cells

Core-Shell MJ NW cells

- how does **current matching** constrain geometry?
- are **optimal band gap combinations** the same as for bulk?
- how much can **material volume be reduced** without sacrificing efficiency?

“Limiting efficiencies of tandem solar cells consisting of III-V nanowire arrays on silicon,”
Huang et. al., J. Appl. Phys. 112, p 064321 (2012)
Methods

- **Ultimate Efficiency**: quantifies broadband absorption
  [Hu and Chen, Nano Lett. 7, 3249–3252 (2007)]
  upper bound on efficiency, assuming one electron-hole pair per photon and perfect carrier collection

- **Highly-accurate numerical calculations**
  - parallelized codes
    - transfer matrix method
    - finite-difference time domain method

\[ \eta = \int_{\lambda_g}^{\lambda_{310nm}} \frac{I(\lambda) A(\lambda)}{310nm - 4000nm} d\lambda \]
### Conclusions: optical simulations

<table>
<thead>
<tr>
<th></th>
<th>Limit efficiency</th>
<th>Designed efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>40.88%</td>
<td>33.2% with GaAs(1.43eV) 30.74% with InP (1.2eV) 35.72% with AlGaAs (1.7eV) 36.03% with InGaP (1.8eV)</td>
</tr>
<tr>
<td>GaAs</td>
<td>44.65%</td>
<td>38.22% with AlGaAs (2.0eV) Optimization ongoing</td>
</tr>
<tr>
<td>Silicon</td>
<td>44.65%</td>
<td>27.03% with InGaP (1.8eV) Optimization ongoing</td>
</tr>
</tbody>
</table>
Selective Area Nanostructure Growth

- Localized growth rate controlled by vapor phase diffusion and surface migration to growth surface.
- Unidirectional growth controlled by growth kinetics of facets.
- Process conducted without intermediate metals.
- Sharp transitions between layers in nanostructure.
## Nanowire SAG Growth Habits

<table>
<thead>
<tr>
<th>Material</th>
<th>Substrate Growth Plane</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>GaAs (111)B</td>
<td>Zincblende</td>
</tr>
<tr>
<td>InAs</td>
<td>GaAs or InP (111)B</td>
<td>Zincblende</td>
</tr>
<tr>
<td>InGaAs</td>
<td>GaAs (111)B</td>
<td>Zincblende</td>
</tr>
<tr>
<td>GaP</td>
<td>GaAs (111)B</td>
<td>Zincblende</td>
</tr>
<tr>
<td>InP</td>
<td>InP or GaAs (111)A</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>InAsP or InGaP</td>
<td>No NW Growth</td>
<td>------</td>
</tr>
<tr>
<td>GaN</td>
<td>(0001) Ga or N</td>
<td>Wurtzite</td>
</tr>
</tbody>
</table>
Growth on Reconstructed (111)B Surface

- **Surface reconstruction of (111)B**
  - Electron counting model
    - All group III dangling bonds must be empty
    - All group V dangling bonds must be filled
  - In group V precursor over pressure,
    - Group V adatoms form trimers to stabilize dangling bonds
    - GaAs shows 2×2 reconstruction

- **Bond Dissociation Energy (BDE)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>BDE(kJ/mol)</th>
<th>Bond</th>
<th>BDE(KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-P</td>
<td>201</td>
<td>As-As</td>
<td>146</td>
</tr>
<tr>
<td>In-P</td>
<td>197.9 ± 8.4</td>
<td>Ga-As</td>
<td>202.5</td>
</tr>
<tr>
<td>Ga-P</td>
<td>227.9 ± 12.6</td>
<td>In-As</td>
<td>201±10</td>
</tr>
</tbody>
</table>

→ As trimers can be broken without breaking Ga-As bonds, but
→ Dissociation of P trimers affects In-P bonds.

Window of crystal growth in group V partial pressure (GaAs and InAs NS-SAG)

Growth suppression by trimers (InP NS-SAG)
• Mixed alloys of InP will not grow vertically on (111B) orientation like all other III-V’s. e.g. InAsP, InGaP, InAlP?
• InP mixed alloys may grow radially on existing (111B) wires allowing InAlGaP to be used as a passivation layer on material with $E_g$ up to ~2.5 eV.
GaAs Nanowire Arrays Grown by NS-SAG

(111)A

(111)B

• Growth conditions
  – Temperature: 650 °C ~ 750 °C
  – TMG partial pressure: 1.9~7.6×10^{-7} atm
  – AsH₃ partial pressure: 0.6~2.4×10^{-4} atm

• GaAs nanowire arrays on (111)A
  – Nonuniform
  – Tilted toward nearest <111>B or <112>B

• GaAs nanowire arrays on (111)B
  – Uniform and vertical
  – Zincblende phase down to 25 nm in diameter
  – Low growth temperature and high precursor partial pressure promote cluster formation and burying of nanowires in dense arrays
  – High growth temperature and low precursor partial pressure suppress growth in vertical direction and degrade uniformity of sparse arrays.
NW growth via in-situ formed metal droplet

- Relatively fast growth rate
- Relatively low growth temperature (600 °C)
- Growth from liquid metal droplet may reduce defects in NW.

In-situ deposition of Ga droplets  Self-catalyzed growth  Longer nanowires
Dense GaAs NW Arrays on Si

- Oxide Removal
- Si Surface Reconstruction
- As treatment of surface
- Nucleation of GaAs “Seed”
- Nanowire Growth
GaAs nanowire arrays on Si as photoanodes and tandem solar cells – A CEN / JCAP Collaboration

Scientific Achievement
- GaAs-nanowire/Silicon-substrate multijunction structure developed at USC / CEN
- Demonstrated optical absorption, carrier generation and electron transfer properties suitable for high-efficiency solar water splitting at Caltech / JCAP.

Significance and Impact
A promising III-V / Si photoanode and tandem solar cell
- High absorption and minimal reflection at both normal and off-normal incidence
- Radial junction: ~100% carrier collection
- $V_{oc}$ and $J_{sc}$ at maximum values already

Research Details
- Angle-dependent experimental and theory study for enhanced absorption and in-coupling
- GaAs nanowire-arrays on Si demonstrated
- Near unity carrier-collection efficiencies
- Open-circuit potential: 590±15mV
- Short-circuit current density: 24.6±2.0mA cm$^{-2}$
- Energy-conversion efficiency: ~ 8.1%

Axial Junction GaAs NR Solar Cells

Low $J_{sc}$ and $V_{oc}$ limit efficiency
Excess Leakage Current
Short Diffusion Length
Field Assisted Carrier Collection
NW Surface Area Can Dominate Properties

- Surface Fermi level pinning can lead to carrier depletion.

AlGaAs / GaAs Core Shell NWs

Surface states can lead to short carrier lifetimes and diffusion lengths.

AlGaAs and GaP surface cladding layers cause ~ 30X to 100X increase in PL efficiency.
Crystal Phase Amiguity

- Nanowires exhibit a high density of stacking faults and/or twin defects.
- Stacking defects are a result of minimization of facet surface energy on the NW.
What is twin?

- Twin plane: (111) plane
- Carrier scattering or confinement effect
- High resistivity
- Shorter carrier life-time

Motivation

- Improved crystal quality
- Better electrical and optical properties
- Grating Solar Cell

- Twin planes at equal plane
- Carrier scattering and optical properties effect
- Highings Solar Cell
- Shorter carrier life-time
Effects of Twins on Electronic Transport

- Twin-scattering contribution to electron mobility estimated by density functional theory

\[ \mu = \sqrt{\frac{\pi}{8k_B T}} \frac{e}{m^*} \left[ \int dx \ln \left( 1 + \frac{m^*(v_0 \delta)^2}{2\hbar^2 k_B T x^2} \right) e^{-x^2} \right]^{-1} l_{\text{twin}} \]
Intrinsic Core/Shell Structures in Nanowires

- Core/shell structure in adatom energy → nucleation of the next layer at a corner of the nanowire top surface

Z. Yuan et al., Appl. Phys. Lett. 100, 153116 ('12); ibid. 100, 163103 ('12)
Two kinds of GaAs nucleations:
Both are tetrahedral in shape but one is 180 degree rotated with respect to the other.

Twins are caused by alternation of the two forms of tetrahedron growth. The alternation of the two orientations forms 6-fold symmetric hexagonal nanowires on 3-fold symmetric GaAs (111)B substrate.

GaAs nano-sheets are grown on GaAs (111)B along <11-2>.

Nano-sheets share the same {-1-10} facets as <11-2> tetrahedron nuclei; but keep two (1-10) and (111)B facets as nanowires.

Growth rates on 3 inclined (110) planes and two (1-10) planes are greatly reduced; growth only occurs on the exposed (111)B surface.

Nanosheet can be seen as part of (11-2) tetrahedron nucleation.
Twin density in nanosheet and nanowire

- No twins are observed within nano-sheet by TEM; however high density of twins are observed within most nano-wire structures.
- Sail-like nanosheet
Twin-free nanosheet growth condition

Arsine = 17 sccm; V/III = 434

TMGa = 2.4 sccm; V/III = 2

TMGa = 0.8 sccm; V/III = 6
Morphology change due to twins

1. Growth of (11-2) nanosheet terminated with 3 (110) planes
2. Single twin forms at the tip of nanosheet
3. 180 degree rotated nanosheet initializes on top of bottom nanosheet
4. Inclined planes of bottom nanosheet start to grow
5. (111)A planes are formed
Stacking of two triangle growths which are 180 degree rotated to each other.

Boundary line between two triangle growths which correspond to twin plane.

FFT images show rotational twin near the tip of nanosheet.
Summary

- Twin-Free GaAs nanosheets were grown on $<11-2>$ nano-stripe by SAG
- Low Arsine, high TMGa partial pressure can reduce driving force for twin formation
- Twinned nanosheet supports Ikejiri’s twinning model for NW formation
- Twinning can result in surface energy reduction
- Two vertical $<1-10>$ planes of nanosheet mitigate surface energy reduction brought by twinning
Challenges for lighting applications

Strong piezoelectric field from strain

The spatial separation between the electron and hole wavefunctions reduces the radiative recombination efficiency.

Efficiency droop

Efficiency drops with increasing injection current

High cost of nonpolar GaN bulk

Fair light extraction efficiency

Fresnel loss

Critical angle loss
GaN nanorod arrays on c-plane substrates

- Nonpolar sidewall facets are exposed.
- Surface area of nonpolar planes is proportional to the height of the GaN nanorods to potentially increase junction area.
- Core-shell InGaN/GaN quantum wells will be grown on the nonpolar facets by altering the growth mode.
- Light extraction can be enhanced from the nanostructures.

http://dx.doi.org/10.1021/nl301307a
GaN nanosheet arrays on c-plane substrates

- Long parallel nonpolar sidewall facets are exposed.
- GaN nanosheet structure facilitates electrical conduction path for device fabrication.
- 3D junction morphology reduces current density.
• 3-D morphology is the result of growth competition between planes
• Planes with slower growth rate will dominate the shape
• Typical plane of GaN nano-structure:
  – Polar plane (0001), (c-plane)
  – Non-plane {1-100}, (m-plane)
  – Semi-polar plane {1-101}
GaN nanorods arrays grown with different pitches

- Uniform GaN nanorod arrays have been demonstrated in different spacings.
- All the sidewalls are non-polar planes serving as growth templates for InGaN/GaN MQWs.
- Growth rates of > 5 μm/hr achievable http://dx.doi.org/10.1021/nl301307a
GaN nanosheet arrays

- The growth mask is patterned along \(<11-20>\) direction.
- Vertical sidewalls are non-polar planes, \(m\)-planes.
- Large connected non-polar sidewalls can be used as MOW growth templates.

*Appl. Phys. Lett.* **100** 033119 (2012)
InGaN/GaN core-shell MQWs on GaN nanorods
TEM X-Sections of InGaN/GaN MQW on GaN Nanorods
Cathodoluminescence analysis

- Dominant light emission from non-polar planes is verified by CL mapping.
- No light emission is observed from the MQW grown on c-plane due to the termination of c-plane growth surface.
Both the height of nanrods and the pattern spacing of growth masks must be carefully designed to grow uniform MQWs on the m-planes.
Tuning the peak emission with patterns

• Samples were grown on the same substrate with different mask opening diameters.

• The peak positions shifted to shorter wavelengths with increasing opening diameter.

• Emission wavelength may be controllable by careful mask design and control of the nonpolar plane surface area.
GaN NanoLED structures

• Piezoelectric fields in MQWs grown on the nonpolar planes eliminated.
• Thicker quantum wells can be grown on the nonpolar planes to enhance radiative recombination.
• Efficiency droop mitigated in the thick quantum wells.

• Linked thin p-GaN

• Coalescent thick p-GaN

• 300 μm × 300 μm NanoLED
Electroluminescence of NanoLED

Emission area: $4.5 \times 10^{-4}$ cm$^2$, Current injection:

Spectral Broadening and Emission Peak Tuning affected by:
- Nanorod size variation
- Current crowding effects along nanorod
- Current spreading in p-GaN layer.
- Composition variation and band filling.
- Built-in electric field due to p-n junction.
L-I Characteristics

- The maximum efficiency occurs at 60 A/cm$^2$.
- No heat sinking employed.
- Device structure and process requires optimization.
Wide Spectral Emission Range

Normalized EL intensity (a.u.) vs. Wavelength (nm)

- 601 nm
- 589 nm
- 509 nm
- 494 nm
- 472 nm
Summary

• Ordered GaN nanorod and nanosheet arrays are successfully grown by selective area growth. The exposed vertical sidewalls are nonpolar planes.

• The growth of MQWs on the m-planes is confirmed by cross-sectional TEM images of both nanorods and nanosheets.

• Light emission from regions of a InGaN / GaN nanorod investigated by cathodoluminescence confirm the light emission is predominantly from the MQWs grown on m-planes.

• NanoLEDs fabricated from nanorod arrays by p-layer overgrowth have been demonstrated.

• GaN nanorod and nanosheet arrays are candidates for enhancing LED efficiency.
Contributors

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