III-V and Group IV Epitaxy for Low Energy Optoelectronics

Christopher Heidelberger$^1$, Seth Fortuna$^2$, Ming Wu$^2$, Eugene A. Fitzgerald$^1$

$^1$Department of Materials Science and Engineering, Massachusetts Institute of Technology

$^2$Department of Electrical Engineering and Computer Sciences, University of California, Berkeley

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Novel III-V epitaxy: enabling a path towards low-energy optoelectronics

Antenna-enhanced LED

Photodetector

Si Photonic Waveguide

(1)
- InGaAs/InGaAsP MQW structure
- Heavy p-type doping in active device region

(2)
- III-V monolithic integration with Si could enable photodetector or high-transimpedance transistor for amplification of signal

Top figure from M. Wu, E3S Retreat, August 2015
Electrically-injected III-V antenna-enhanced nanoLED

Advantages:
• high speed
• no threshold current
• directional light emission
• thermal heat-sink
• electrical contact

From Fortuna, et al., E3S Seminar, December 8, 2016
Active region p-doping analysis from UC Berkeley

Assumptions:
(1) Surface recombination velocity = 3e4 cm/s
(2) Auger recombination coefficient = 2e-29 cm^-6s^-1
(3) Sp. Em. Enhancement = 640, Antenna Efficiency = 45%
Q-factor = 37
(4) Bulk SRH ignored
(5) Injection carrier density = 1.5e18cm^-3
InGaAs/InGaAsP LED epitaxial structure

- p+ active layer modeled to increase device speed while maintaining efficiency
- InGaAs/InGaAsP MQW structure grown via MOCVD
  - composition calibrated via XRD
  - doping measured via Hall effect
  - InGaAsP $E_g$ measured via PL

LED structure schematic:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Control (Experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs top contact</td>
<td>n++ (1 x 10^{19} cm^{-3})</td>
</tr>
<tr>
<td>InP top contact</td>
<td>n++ (1 x 10^{19} cm^{-3})</td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td>undoped</td>
</tr>
<tr>
<td>InGaAs QW</td>
<td>p+ active region:</td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td></td>
</tr>
<tr>
<td>InGaAs QW</td>
<td></td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td></td>
</tr>
<tr>
<td>InGaAs QW</td>
<td></td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td></td>
</tr>
<tr>
<td>InP bottom contact</td>
<td></td>
</tr>
<tr>
<td>InP (substrate)</td>
<td></td>
</tr>
</tbody>
</table>
Metalorganic chemical vapor deposition (MOCVD)

- Thomas Swan/Aixtron close-coupled showerhead reactor (c. 2005)
- hydride precursors for group IV and V
- unique group IV growth capability
  - removable quartz chamber liner
  - third mixing rail for group IV precursors
**Growth of undoped LED structure**

LED structure schematic:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP top contact</td>
<td>30 nm</td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td>40 nm</td>
</tr>
<tr>
<td>InGaAs QW</td>
<td>6 nm</td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td>10 nm</td>
</tr>
<tr>
<td>InGaAs QW</td>
<td>6 nm</td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td>10 nm</td>
</tr>
<tr>
<td>InGaAs QW</td>
<td>6 nm</td>
</tr>
<tr>
<td>InGaAsP barrier</td>
<td>60 nm</td>
</tr>
<tr>
<td>InP bottom contact</td>
<td>300 nm</td>
</tr>
<tr>
<td>InP (substrate)</td>
<td></td>
</tr>
</tbody>
</table>

**XTEM**

HT = 200 kV, (110) on pole
Luminescence of undoped LED structure

PL of blanket film

Quantum efficiency (large-area LEDs, UC Berkeley)

- >10X increase in quantum efficiency
- 1550 nm target

Normalized quantum efficiency vs. current density (A/cm²)
Options for p-doping of active region

C:
- high max incorporation
- low diffusivity
- specific growth conditions required
- complex calibration

Zn:
- incorporates at standard growth temperatures
- simple calibration
- limited max incorporation
- high diffusivity
LED structure with Zn p-type doping

undoped active region: (Zn doping ~ 5 x 10^{18}):  

- InGaAs contact
- InP contact
- InGaAs/InGaAsP MQW
- InP contact

p+ active region:  

- InGaAs/InGaAsP MQW

poor EL and IV characteristics for fabricated LED

PL of Blanket Films

DIC Image

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Diffusivity of Zn in III-As semiconductors

Zn diffused in from surface: complete intermixing of SL structure

J-V degradation of sequentially-grown GaAs PV cells attributed to Zn diffusion


C doping of InGaAs via MOCVD

- C precursor, CBrCl$_3$, interacts strongly with both group III and group V species

- Mechanism governing incorporation
  - C and As fight for group V sites
  - AsH$_3$ overpressure necessary to prevent formation of Ga droplets

- Parasitic reactions
  - $2\text{CBrCl}_3 \rightarrow 2\text{C} + \text{Br}_2 + 3\text{Cl}_2$
  - $3\text{Br}_2 + 3\text{H}_2 + 2\text{Ga(CH}_3)_3 \rightarrow 2\text{GaBr}_3 + 6\text{CH}_4$
  - $3\text{Cl}_2 + 3\text{H}_2 + 2\text{Ga(CH}_3)_3 \rightarrow 2\text{GaCl}_3 + 6\text{CH}_4$

example of parasitic reaction in C-doped GaAsP:

Active C doping in InGaAs

Strain plays effect in C incorporation

Post-growth anneal in N2 ambient reduce H passivation of C dopants


# Growth of heavy C-doped InGaAs structures

<table>
<thead>
<tr>
<th>Challenges</th>
<th>Possible Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>• obtain C concentration in target range</td>
<td>• grow at low growth temperature, V/III ratio</td>
</tr>
<tr>
<td>• ensure high dopant activation</td>
<td>• post growth anneal in N(_2) to activate dopants (removal of H)</td>
</tr>
<tr>
<td>• maintain In/Ga compositional control and growth rate control</td>
<td>• use XRD data to feed back into precursor flow rates for next run</td>
</tr>
<tr>
<td></td>
<td>• use in-situ reflectometry to measure growth rate and ensure adequate layer thickness for characterization</td>
</tr>
</tbody>
</table>
Initial C-doped InGaAs calibration

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
<th>Description</th>
<th>Growth Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP cladding, UID</td>
<td>10 nm</td>
<td></td>
<td>550 C</td>
</tr>
<tr>
<td>InGaAs, C-doped</td>
<td>100 nm</td>
<td></td>
<td>500 C V/III ratio = 3 CBrCl(_3) ratio = 19%</td>
</tr>
<tr>
<td>InP regrowth, UID</td>
<td>20 nm</td>
<td></td>
<td>600 C</td>
</tr>
<tr>
<td>InP substrate (S-I)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Growth temperature

\[
p = 4.5 \times 10^{18} \text{ cm}^3
\]

\[(224)\] XRD Reciprocal Space Map

InP substrate

InGaAs

fully strained

fully relaxed

In fraction = 38%
PL of initial mismatched C-doped InGaAs

In$_{0.38}$GaAs, $4.5 \times 10^{18}$ cm$^{-3}$

Time-resolved (UC Berkeley)

In$_{0.53}$GaAs UID

$\tau \sim 10$ns

Laser power = 500uW
Wavelength = 1000nm
20X objective

In$_{0.38}$GaAs; $4.5 \times 10^{18}$ cm$^{-3}$

$\tau \sim 30$ps

(224) XRD Reciprocal Space Map

InGaAs

InP substrate

Fully strained

Fully relaxed
Lattice matched growth

InP substrate (S-I)

InP cladding, UID
10 nm

InGaAs, C-doped
200 nm

InP regrowth, UID
20 nm

InP substrate (S-I)

Growth temperature
- 550 C
- 500 C
- 600 C

V/III ratio = 4
CBrCl₃ ratio = 9%

\[ \text{In fraction} = 52.2\% \]

\[ p = 3.2 \times 10^{18} \text{ cm}^3 \]
Effect of post-growth $N_2$ anneal on active C doping

RTA anneal:
• 500 C
• time varying from 5 to 15 minutes
• $N_2$ ambient, 1 atm

\[ p = p_0 \{1 - A \exp(-\kappa t)\} \]

Post-growth N$_2$ anneal: effect on PL intensity and lifetime

Decrease in intensity/lifetime after post-growth anneal $\rightarrow$ increased Auger recombination due to higher hole concentration.

Time-resolved (UC Berkeley)

Laser power = 500uW
Wavelength = 1000nm
20X objective

without anneal $\tau \approx 700$ps
with anneal $\tau \approx 140$ps

without anneal, $3.2 \times 10^{18}$ cm$^{-2}$
with anneal, $1 \times 10^{19}$ cm$^{-3}$
InGaAs LED structures: conclusions

- Demonstrated undoped InGaAs/InGaAsP LED structure with good morphology and high quantum efficiency
- Grew C-doped InGaAs with $p > 1 \times 10^{19}$ cm$^{-3}$ and recombination limited by Auger recombination
- Future work
  - Grow InGaAsP cladding layers at similar growth conditions as C-doped InGaAs
  - Grow and characterize InGaAs/InGaAsP LED structure with high p-type doping
  - Fabricate and test antenna-enhanced LED structure with heavily-doped active region (UC Berkeley)
III-V on Si epitaxy: challenges

1. lattice mismatch
2. crystal symmetry

- diamond cubic
- zinc blende
III-V active materials

- GaAs/AlGaAs or GaAs/InGaP
- GaAs\(_x\)P\(_{1-x}\)/In\(_y\)Ga\(_{1-y}\)P
  - higher \(E_g\) than GaAs
  - closer lattice constant to Si
  - reduced CTE mismatch with Si
Device test-bed: GaAsP/InGaP HBT

heterojunction bipolar transistor (HBT):

- high frequency
- high power efficiency
Goals:

- Measure GaAsP/InGaP HBT behavior
  - DC current gain
  - transconductance
  - breakdown voltage

- Understand behavior as function of
  - composition/lattice constant
  - defect type and density
    - threading dislocations vs misfit dislocations vs other...
    - effect of substrate and strain relaxation scheme
GaAsP/InGaP HBTs on GaAs substrates
HBT fabrication

1. structure growth (MOCVD) + characterization
Heavy p-type doping of GaAsP

- C is preferred dopant for heavy p-type GaAs
  - lower diffusivity than Zn
- C precursor: CBrCl₃
  - reduces growth rate due to reaction with Ga or precursors
  - alters GaAsP composition

\[
\frac{1 - x}{x} = C \frac{P_{PH_3}}{P_{AsH_3}}
\]
EBIC Measurements of GaAsP Diodes and HBTs
EBIC images of HBTs on GaAs substrates

GaAs/InGaP

GaAs$_{0.825}$P/InGaP

TDD < 1 x $10^4$ cm$^{-2}$

TDD = 1.5 x $10^5$ cm$^{-2}$
### HBT fabrication

1. **structure growth (MOCVD) + characterization**
2. **emitter mesa etch**
3. **base/collector mesa etch**
4. **sidewall passivation ($\text{Al}_2\text{O}_3$)**
5. **contact metal deposition**

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<table>
<thead>
<tr>
<th>GaAsP subcollector (n+)</th>
<th>GaAsP collector (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAsP collector (n)</td>
<td>GaAsP contact (n++)</td>
</tr>
<tr>
<td>InGaP emitter (n+)</td>
<td>InGaP emitter (n+)</td>
</tr>
<tr>
<td>GaAsP base (p+)</td>
<td>GaAsP base (p+)</td>
</tr>
<tr>
<td>Collector contact</td>
<td>Collector contact</td>
</tr>
<tr>
<td>GaAsP collector (n)</td>
<td>GaAsP collector (n)</td>
</tr>
<tr>
<td>GaAsP contact (n++)</td>
<td>GaAsP contact (n++)</td>
</tr>
<tr>
<td>GaAsP subcollector (n+)</td>
<td></td>
</tr>
<tr>
<td>ΔGaAsP graded buffer (n+)</td>
<td></td>
</tr>
<tr>
<td>GaAs substrate (n+)</td>
<td></td>
</tr>
</tbody>
</table>

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GaAsP/InGaP HBTs IV characteristics

- sidewall passivation reduced \( I_B \) at low voltages
- \( \beta > 100 \) for all devices
- \( \beta \) not largely dependent on composition

Gummel Plots, 60 µm dia.

\[
\begin{align*}
I_C &: \text{GaAs} \\
I_B &: \text{GaAs} \\
I_C &: \text{GaAs}_{0.94}^P \\
I_B &: \text{GaAs}_{0.94}^P \\
I_C &: \text{GaAs}_{0.88}^P \\
I_B &: \text{GaAs}_{0.88}^P \\
I_C &: \text{GaAs}_{0.82}^P \\
I_B &: \text{GaAs}_{0.82}^P
\end{align*}
\]
Modeling collector current as thermionic emission

Collector Currents, 60 µm dia.

\[ I_C = A_E A^* T^2 \exp \left(-\frac{E_A}{kT}\right) \]

- significant underestimation of \( I_C \) for all GaAsP compositions
- \( \Delta E_C \) is much smaller than we thought
Modeling collector current as diffusion across base

Collector Currents, 60 µm dia.

\[ I_C = A_E \frac{qD_{n,B}}{X_B} \frac{n_{i,B}^2}{N_B} \exp \left( \frac{qV_{BE}}{kT} \right) \]
Modeling collector current as diffusion across base

- GaAs device predicted within error
- GaAsP devices all have ~10x higher current than expected \(\rightarrow\) better transconductance
- under further investigation

Collector Current at \(V_{BE} = 0.9\) V

![Graph showing collector current at \(V_{BE} = 0.9\) V for different GaAs\(_x\)P\(_{1-x}\) compositions]
GaAsP/InGaP HBTs on Si substrates
SiGe graded buffer growth

GaAsP device layers

ΔSiGe graded buffer (n+)

Si substrate (n+)

MOCVD

CMP

batch process UHVCVD

\[ \text{GaAs}_{0.82}\text{P}_{0.18} \rightarrow \text{Si}_{0.18}\text{Ge}_{0.82} - \text{End of grading} \]

\[ \text{Si}_{0.5}\text{Ge}_{0.5} \text{ Regrowth} \]

\[ \text{Si}_{0.5}\text{Ge}_{0.5} \text{ CMP} \]

Si Homoepitaxy
GaAsP on Si threading dislocation density

PV-TEM of GaAsP/Si structure

• process control is critical!

• final TDD = (3.7 ± 0.7) x 10^6 cm^-2

• TDD shouldn’t affect HBT performance until ~2 x 10^7 cm^2


200 kV, g = (220)
GaAsP/InGaP HBT on Si: DC characteristics

- low $\beta \sim 10$
- $n = 2$ for $I_B \rightarrow$ SCR recombination at E-B interface
Misfit dislocations at E-B interface

EBIC: GaAsP HBT on Si

XTEM: GaAsP HBT Structure

TDD = $2.7 \times 10^6$ cm$^{-2}$
Misfit Density = $8.3 \times 10^2$ cm$^{-1}$

$200 \, kV$, $g = (220)$

InGaP emitter
GaAsP base
GaAsP collector
misfit dislocation

50 μm
200 nm
Effect of misfit dislocations on $\beta$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>TDD (cm$^{-2}$)</th>
<th>Misfit Density (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs (slow grade)</td>
<td>$1.5 \times 10^5$</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>GaAs (fast grade)</td>
<td>$2.6 \times 10^6$</td>
<td>$1.2 \times 10^2$</td>
</tr>
<tr>
<td>Si</td>
<td>$2.7 \times 10^6$</td>
<td>$8.3 \times 10^2$</td>
</tr>
</tbody>
</table>

GaAs$_{0.82}$P HBT Current Gain

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GaAsP/InGaP HBTs on Si substrates: conclusions

- GaAsP/InGaP HBTs demonstrate high $\beta$
- similar $I_B$ mechanisms as in GaAs/InGaP HBTs
- demonstrated high quality GaAsP growth on Si substrates
- misfit dislocations in active layers diminish device performance on Si substrates
Future work (in progress)

1. Quantify effect of defects on GaAs(P) HBT performance
   - various substrates and strain relief schemes

2. Demonstrate GaAsP HBT on Si with high current gain
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