Molecular Beam Epitaxy Growth of GaAs$_{1-x}$Bi$_x$

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Topics

- Surfactant effects
- Bismuth incorporation
- Metal droplets
- Transport and optical properties
- Bismide LED’s
**Periodic Table**

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
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<tbody>
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<td>Al</td>
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<td>P</td>
<td>S</td>
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<td>Zn</td>
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<td>Ge</td>
<td>As</td>
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<td>Sb</td>
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<tr>
<td>Hg</td>
<td>Th</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
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</tbody>
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Semiconductors outside the box

Where else can we go?
Concentration dependence of $E_g$ as $x \to 0$:

- 11 meV / % In
- 20 meV / % Sb
- 88 meV / % Bi
- 190 meV / % N

Shane Johnson, ASU
States of Impurity Elements Resonant with Band Edges

N 2s orbital resonant with the bottom of the conduction band
Bi 6p resonant with the top of the valence band
Schematic Band Alignment with GaAs

- Drawn to scale for 3% Bi, N
- Favourable band alignment for heterojunction bipolar transistor
Schematic of molecular beam epitaxy growth chamber

Plasma source (N$_2$)

Effusion cell (eg Ga, Bi)

Heated substrate holder (250-600°C)

RHEED Gun

RHEED screen

Not shown:
• As$_2$ cracker cell
• CBr$_4$ dopant source

Effusion cell (eg Ga, Bi)
Bismuth acts as a surfactant on GaAs

- Good surfactant should be a metal, non-directional bonding
- Lowers surface energy of semiconductor, enhances surface mobility
- Does not incorporate
- May block contaminants

Zhang and Lagally, 1996
Bi surfactant smoothing

Growth temperature 460°C, 0.4% GaNAs

No Bi flux
1.2 nm rms

Bi flux $10^{-7}$ Torr
0.4 nm rms

Huge flux!

Bi flux $1.4 \times 10^{-5}$ Torr
0.1 nm rms

Tixier, Adamcyk et al JCG 2003
Bi enhances surface mobility enabling RHEED oscillations at low temperature

RHEED oscillations during growth of GaAs with Bismuth

(not normally observed below ~ 500°C in GaAs)

Substrate temperature 290°C
Bi flux $2 \times 10^{-9}$ Torr (450°C)
Growth rate 0.128 µm/hr
Surface reconstruction 1x3
Bi Surfactant Increases Photoluminescence Intensity

Dilute GaNAs

AlGaAs

Bi surfactant improves PL intensity in dilute nitrides and in AlGaAs
Bi surfactant enhances nitrogen incorporation in dilute nitride growth

- Increasing Bi flux
- Increasing [N]
How does one get Bi to incorporate in MBE?

Answer:

• Low growth temperature
• Low As overpressure

Sebastien Tixier et al APL (2003)
Bi content determined by x-ray diffraction

![Graph showing the 004 reflection of GaAs$_{0.95}$Bi$_{0.5}$ and GaAs with different Bi contents](image)

- 004 reflection
- GaAs$_{0.95}$Bi$_{0.5}$
- GaAs
- 1.4%
- 5%
- 10%

Diffracted intensity (a.u.) vs. Theta (arcsec)
Arsenic flux controls Bi incorporation

300°C growth temp, all conditions identical except As₂ flux
Dependence of Bi concentration on growth conditions

Vary temperature, As flux, Ga flux, Bi flux

How do we explain this?
Bi droplets easier to avoid at low growth rates

• Flux of Bi in excess of the amount incorporated must be less than the evaporation rate

\[ 0 < F_{Bi} - xF_{Ga} < Bi \text{ Evap. Rate} \]

“excess Bi”

• Less precise control of Bi flux required to satisfy this condition at low growth rates - wider process latitude.
Bismide growth model

- Bi surface layer in equilibrium with the vapour
- Bi incorporation takes place from the surface layer
- As displaces Bi through thermally activated insertion into Ga-Bi bonds
- Incoming Ga bonds to surface As atoms does not attach to surface Bi

Xianfeng Lu et al, APL 2008
Two part Bi incorporation model

Thermodynamic equilibrium part

• Bi surface coverage described by Langmuir isotherm modified to take into account Bi incorporation

\[
\theta_{Bi} = \frac{b \left( F_{Bi} - xF_{Ga} \right) e^{U_0/kT}}{1 + b \left( F_{Bi} - xF_{Ga} \right) e^{U_0/kT}}
\]

\( U_0 \) - binding energy of Bi to the surface

Kinetic part

• Bi content determined by competing rates of Bi and As incorporation

\[
\chi = \frac{F_{Ga} \theta_{Bi}}{aF_{As} e^{-U_1/kT} + F_{Ga} \theta_{Bi}}
\]

\( U_1 \) - activation barrier to Ga-Bi displacement by As
Two part model gives good description of Bi incorporation

16 samples, different growth conditions

Parameters: $U_0 = 1.3 \text{ eV}$, $U_1 = 0.8 \text{ eV}$
Bismuth droplets can be a problem

$\text{[Bi]} = 1\%$

Optical image
Same sample AFM image: ball and socket type Bi droplets

AFM
60 nm z-scale

$[\text{Bi}] = 1\%$
Can also get Gallium droplets: SEM image
Droplets show composite structure at high magnification
Composition map: composite droplets include both Ga and Bi

800 nm diameter droplet

Gallium

Bismuth
Gallium droplets leave tracks, must be moving
Composition map of a droplet track

Gallium droplet, gallium arsenide track
AFM images of droplet-free samples

[Bi] = 2%

[Bi] = 5%
Room temp. photoluminescence as function of Bi content

PL shows shift in bandgap to IR with [Bi]

“White” IR emission spectra, broader than $kT$
Composition dependence of $\text{GaAs}_{1-x}\text{Bi}_x$ bandgap

Xianfeng Lu APL (2009)

Achieve pseudomorphic 1.5 μm bandgap layer without N strain compensator due to large critical thickness for lattice relaxation at low growth temperature.
“Giant” increase in spin-orbit splitting

Photoluminescence measurements of bandgap and SO splitting

Increase in spin-orbit splitting in parallel with reduction in bandgap

Almost all of the bandgap decrease goes into increasing S-O splitting

Fluegel, Mascarenhas et al. PRL 97, 067205 (2006)
PL intensity increases with Bi at low concentration

Interpretation: Bi clusters trap holes, enhance PL, similar to GaInN?

Xianfeng Lu et al APL, 2009
Photoluminescence Intensity Comparison

GaAs capped 50 nm GaAs$_{0.955}$Bi$_{0.045}$ layer shows comparable PL intensity to p$^+$ GaAs wafer.
Frequency Dependent Conductivity
(Cooke, Hegmann U. Alberta)

Terahz experiment measured 10 ps after optical injection of $\sim 10^{18}$ cm$^{-3}$ e-h pairs

- Optically induced conductivity dominated by electrons
- Bismide, nitride behave differently, N affects conduction band, Bi val. band
Terahertz Measurements of Electron Mobility

1% N has drastic effect on electron mobility, 1% Bi has comparatively little effect

Hall mobility of holes in GaAs$_{1-x}$Bi$_x$ at room temperature

(Dan Beaton talk on Friday)

Hole mobility decreases with increasing Bi content, but not as fast as electron mobility in the dilute nitride.

D. A. Beaton et al, (in preparation 2010)
Light emitting diode structure

Light collected from the top around the periphery of the metal dots - not an efficient device design!
Light emitting diode emission spectrum

![Graph showing GaAsBi and GaAs emission spectra with different current densities.](image)

R. B. Lewis, MSc Thesis, UBC, 2008 and JCG 2009
LED emission temperature dependence #1

![Photoluminescence spectra for GaAs$_{1-x}$Bi$_x$LED structure over a temperature range of 8 K to 300 K. The inset shows the peak emission energies as a function of temperature for both the GaAs and GaAs$_{1-x}$Bi$_x$ peaks. A fit to the data using the Varshni equation is also shown.](image)

Temperature dependence tracks GaAs bandgap
LED emission - temperature dependence #2

- Bismide emission wavelength independent of temperature
- Tradeoff between bandgap shift and thermal distribution of excitons in localized states  (see Imhof et al APL 96, 131115 (2010))
Summary

• Bi acts as a surfactant, smoothes the surface, improves crystal quality

• Best bismide films grown with (2x1) surface reconstruction

• Strong PL in bismides even though growth temperature is low

• Charge carrier mobility less sensitive to Bi alloying than N alloying

• Electronic structure of bismides analogous to amorphous semiconductors, localized states, kinetically limited relaxation

• Large bandgap reduction with Bi alloying (4x bigger than Sb)
Future

- Alloys with higher Bi concentrations
- Other Bi alloys in addition to Ga-As-Bi
- Larger lattice constant substrates, GaSb, InP
- Optical devices - emitters and detectors
- Physics of charge transport and energy relaxation
- Spin transport and relaxation
- Strain relaxation, critical thickness

Will bismides take their place as full contributing members of the III-V semiconductor family?