Present status and future prospects of Bi-containing semiconductors

M. Yoshimoto and K. Oe
Dept. Electronics, Kyoto Institute Technology, Japan
Acknowledgement

RBS: Prof. K. Takahiro (Kyoto Inst. Tech.), Dr. A. Chayahara (AIST)
Photoreflectance: Prof. T. Kita (Kobe Univ.)
EXAFS: Prof. M. Tabuchi, Prof. Y. Takeda (Nagoya Univ.)
Raman spectroscopy: Prof. Harima, Dr. P. Verma (Kyoto Inst. Tech.)

Post. Doc. Dr. W. Huang, Dr. G. Feng
Graduate students: Mr. S. Murata, Mr. Y. Tanaka,
                   Ms. Y. Tominaga, Mr. K. Yamada, Mr. T. Fuyuki
Outline

- Background

- MOVPE growth of GaAsBi and InAsBi
  - RBS, Raman, EXAFS: substitutional incorporation of Bi
  - Photoluminescence, Photoreflectance: temperature-insensitive $E_{PL}$, $E_g$

- MBE Growth of GaAsBi
  - GaAsBi growth: surfactant-like effect of Bi atom
  - GaNAsBi and InGaAsBi: expansion of luminescence wavelength
  - GaAs/GaAsBi multi-quantum wells: smooth interface w/o segregation

- Device-quality epilayers
  - Laser emission from GaAsBi by photo-pumping
  - Issue of GaAsBi growth

- Summary
Earliest days of epitaxy of Bi-containing semiconductors

MBE growth of InSbBi to obtain III-V alloys with the narrowest possible band gap.


Key to growth

K. Oe, et al: JJAP

low-temperature growth

no growth of InSbBi
Sb/In>1

থmirror-like surface
Sb/In<1

থrough surface (Sb inclusion)
Sb/In<1

InSb sub.

Fig. 5. Dependence of the maximum InBi mole fraction in the alloy film on the growth substrate temperature. InBi mole fraction is calculated from the angular spacing between peaks of the InSb$_{1-x}$Bi$_x$ and InSb in the rocking curve.

Fig. 1. Cu K$_{\alpha_1}$ rocking curves for the (004) reflection of the films grown at 380°C on (001) InSb substrates. The arrival rate ratios are (a) Sb/In > 1, (b) Sb/In ≈ 1, and (c) Sb/In < 1.
Wavelength-Division Multiplexing (WDM)

GaInAsP laser diode (LD): temperature dependence of bandgap and refractive index

⇒ fluctuation of lasing wavelength

LD equipped with Peltier device

⇒ drawback: cost, energy consumption

Materials with low ΔE_g/ΔT

⇒ LD with an emission of temperature-insensitive wavelength: elimination of Peltier device

Proposal of GaInAsBi as a active-layer materials of LD


Semiconductor: GaAs   Semimetal: GaBi   ⇒   Alloy: GaAsBi
MOVPE growth of GaAsBi

Low-pressure MOVPE
- **Sources**: TIPGa, TMBi, TBAs
- **Substrate**: GaAs(100)
- **Growth temperature**: 365°C
- **Growth rate**: 1μm/h

X-ray diffraction pattern

- Successful epitaxial growth
- Lattice constant increases with GaBi molar fraction.
  - GaBi molar fraction: Rutherford backscattering spectroscopy
- Thermally stable after anneal in As pressure at 560°C for 30min

K.Oe, JJAP 41 (2002) 2801
Determination of GaBi molar fraction $x$ for GaAs$_{1-x}$Bi$_x$.

Rutherford backscattering spectroscopy (RBS)

Fitting Function

$x = 6.93 \Delta 2\theta$

M. Yoshimoto, et.al, JJAP 42 (2003) L1235

$\Rightarrow$ determination of GaBi molar fraction by X-ray diffraction
Angular scan in Rutherford backscattering spectroscopy

Angular yield profile for [100] and [110] channel

\[
\text{Yield(Bi)} = \text{Yield(Ga+As)}
\]

\Rightarrow \text{Bi atoms are located exactly on substitutional sites.}

Note

Interstitial site in a zinc-blend lattice

[100]: shadowed, [110]: visible

GaBi-like and InBi-like modes ⇒ substitutional incorporation of Bi atoms

Raman spectroscopy and EXAFS of GaAsBi and InAsBi

The majority of Bi atoms substituted the As site of InAsBi

P. Verma, et.al JAP 89(2001) 1657
H.Ofuchi, et.al JJAP 38 (1999) Suppl. 38-1, 545
Temperature dependence of PL for GaAsBi

\[ \frac{\Delta E_g}{\Delta T} \text{ GaAs}_{0.974} \text{Bi}_{0.026} \approx \frac{1}{3} \cdot \frac{\Delta E_g}{\Delta T} \text{ GaAs} \]

K. Oe, JJAP 41 (2002) 2801
Photoreflectance spectra of GaAsBi

Decrease in bandgap of \( \text{GaAs}_{1-x}\text{Bi}_x \) with increasing GaBi molar fraction

\( \Delta R/R \) (arb. unit)

\( j=1 \)

\( E_g = 1.396 \pm 0.006 \text{eV} \)

\( F_j \)

\( 0 \)

\( 5 \)

\( 10 \)

\( 1.4 \)

\( 1.6 \)

\( 1.8 \)

\( 2.0 \)

\( 1.4 \)

\( 1.6 \)

\( 1.8 \)

\( 2.0 \)

\( 0 \)

\( 0.01 \)

\( 0.02 \)

\( 1.3 \)

\( 1.4 \)

\( 1.5 \)

\( 1.6 \)

\( 12\text{K} \)


\( \text{GaAs}_{0.995}\text{Bi}_{0.005} \)

Franz-Keldysh oscillation due to built-in electric field
Temperature dependence of bandgap of GaAsBi

\[
\frac{\Delta E_g}{\Delta T} \text{ GaAs}_{0.974}\text{Bi}_{0.026} \approx \frac{1}{3} \cdot \frac{\Delta E_g}{\Delta T} \text{ GaAs}
\]

Drawbacks of MOVPE growth of GaAsBi

× MOVPE:
• insufficient decomposition of metalorganic at low $T_{sub}$
  $\Rightarrow$ difficulty in incorporation of In with existence of Ga at low $T_{sub}$
• segregation of Bi on surface

OMBE:
• low-temperature growth without decomposition process
• no Bi segregation: desorption from surface
MBE Growth of GaAsBi

X-ray diffraction

*Bi-flux dependence*

\[
\text{Intensity (arb. units)}
\]

- **GaAs(004) Kα₁**
- **GaAsBi(004) Kα₁**
- **Kα₃**

**Bi flux** (x10⁻⁸ Torr)
- 0
- 2
- 4
- 6
- 8

**INTENSITY** (arb. units)

**2θ (deg)**
- 65.5
- 66
- 66.5

**Lattice constant increases with Bi flux, followed by saturation.**

**RBS: Substitutional incorporation of Bi**

**Thickness**: 0.5 μm
**Substrate temperature**: 380 °C
**Ga flux**: 3 × 10⁻⁷ Torr
**As flux**: 8 × 10⁻⁶ Torr

M. Yoshimoto, et al., JJAP 42 (2003) L1235
GaBi molar fraction vs. Bi flux and substrate temperature

![Graph showing GaBi molar fraction vs. Bi flux and substrate temperature.](image)

M.Yoshimoto, et.al, JJAP 42 (2003) L1235
Effect of As flux on MBE growth of GaAsBi

- Thickness: 0.5 μm
- Substrate temperature: 380 °C
- Ga flux: 3 × 10⁻⁷ Torr
- Bi flux: 2 × 10⁻⁸ Torr

Bi is incorporated with a limited As flux.

Photoluminescence from GaAsBi

Luminescent GaAsBi can be obtained by low-temperature MBE growth (<400°C), probably due to a surfactant-like effect of Bi atoms.

W.Huang, et.al, JAP 98(2005) 053505
Plasma-assisted MBE

GaAs buffer layer (thickness: 100nm, T\textsubscript{sub} 500\degree C)

GaNAsBi

- substrate temperature: 350~400\degree C
- source: Ga (10\textsuperscript{-7}Torr), As (10\textsuperscript{-6}Torr), Bi (10\textsuperscript{-8}Torr)
- plasma activated nitrogen(13.56MHz)

Key to Bi incorporation:
- narrow process window for As flux
- low-temperature growth (<400\degree C)

M. Yoshimoto, et.al, JJAP, 43 (2004) L845
Substitutional incorporation of Bi atoms were also confirmed by channeling RBS.

X-ray diffraction of GaNAsBi

Lattice matched to GaAs

Constant supplies of Ga, As, Bi

W. Huang, et al., JAP 98(2005) 053505
PL emission from lattice-matched GaNAsBi

W. Huang, et al., JAP 98(2005) 053505

- Ga(N_{0.34}Bi_{0.66})_{z}As_{1-z}: Lattice matched to GaAs
- PL emission in the optical fiber communication waveband
Photoluminescence of GaNAsBi

**Low temp. coefficient**

Temperature coefficient of the PL peak energy

★ 0.14 meV/K (150-300k) = 1/3 InGaAsP ★

W.Huang, et.al, JAP 98(2005) 053505
Growth of GaAsBi Multi-quantum wells

Layer-by-layer growth

Y. Tominaga, et.al, APL 93 (2008)131915
GaAs$_{0.948}$Bi$_{0.052}$ layer / GaAs layer = 7nm / 14nm, 14 periods

- Smooth interface
- Laue function: $N' = N - 2$
Cross-sectional TEM image

GaAs$_{0.952}$Bi$_{0.048}$/GaAs MQWs (Growth temperature: 350°C)

Y. Tominaga, et.al, APL 93 (2008)131915
Quantum size effect

Photoluminescence (PL) spectra of GaAs$_{1-x}$Bi$_x$/GaAs MQW

Excitation wavelength: 488nm (Ar$^+$ laser)

GaAs$_{0.948}$Bi$_{0.052}$/GaAs = 3~12nm / 14nm, 10~15 periods

Y. Tominaga et al.: PSS(c) 5, 2719 (2008)
PL at a wavelength of 1.3µm

◆ PL spectra of GaAs$_{1-x}$Bi$_x$ / GaAs MQWs

GaAs$_{1-x}$Bi$_x$ / GaAs = 7nm / 14nm, 5~10 periods

Y. Tominaga, et.al, APL 93 (2008)131915
Thermal stability

◆ Annealing: 10 minutes under N$_2$ flow

GaAs$_{0.984}$Bi$_{0.016}$/GaAs MQW

Y. Tominaga, et.al, APL 93 (2008)131915
Laser emission from GaAs$_{1-x}$Bi$_x$ by photo-pumping

\[ \text{Intensity (arb. units)} \]

\[ \text{Wavelength (nm)} \]

- GaAs
- GaAsBi

- RT

Integrated intensity (arb. units)

Pumping density (mJ/cm$^2$)

Laser emission from GaAs\textsubscript{1-x}Bi\textsubscript{x} by photo-pumping

![Graph showing laser emission spectra and integrated intensity vs. pumping density.](image)

Temperature dependence of lasing wavelength

\( \text{GaAs}_{0.975}\text{Bi}_{0.025} \)

<table>
<thead>
<tr>
<th>GaBi molar fraction</th>
<th>( \Delta E_{PL}/\Delta T ) 150-300K (meV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (GaAs)</td>
<td>-0.42</td>
</tr>
<tr>
<td>0.025(Laser)</td>
<td>-0.18</td>
</tr>
<tr>
<td>0.025(PL)</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

Low-temperature coefficient of lasing wavelength

\( T_0=83\text{K} \)

**Issue of GaAsBi growth**

**Key to InSbBi growth (1981)**

- Low-temperature growth
- Graph showing mole % of InSbBi vs. substrate temperature
- Indium antimonide (InSbBi) sub.
- Sb/In $\leq 1$
- Mirror-like surface
- Rough surface (Sb inclusion)
- $\text{Sb/In} > 1$
- No growth
- Narrow window of Sb/In ratio

**Key to GaAsBi growth (at present)**

- Low-temperature growth
- Graph showing GaBi molar fraction vs. substrate temperature
- Narrow window of As/Ga ratio
- As/Ga $> 1$
- $\text{As/Ga} \approx 1$
- As/Ga $< 1$
The essence of growth conditions for GaAsBi-based alloys is exactly the same as that of InSbBi growth in the early 80s!!

**Conventional essence**
- low temperature growth (<400°C)
- As (or Sb) flux adjustment in a limited range on the brink of As (or Sb) shortage on the growing surface

An innovative growth technique is expected for further improvement in GaAsBi-based alloys.
Summary

MOVPE growth of GaAsBi and InAsBi
✓ Bi atoms occupy substitutional sites (RBS, Raman, EXAFS).
✓ A single-peak PL (10 – 300K).
✓ Temperature dependence of $E_g$ of GaAs$_{0.974}$Bi$_{0.026}$ is 1/3 of the value of GaAs.

MBE growth of GaAsBi
✓ **Key to growth**: (1)Control of As flux within narrow limits, (2)low-temperature growth.
✓ **A surfactant-like effect**: Luminescent GaAsBi grown at low temperature (<400°C).
✓ **Expansion of luminescence wavelength to longer wavelength**
  - GaNAsBi/GaAs: fairly luminescent (1.4 μm emission).
  - InGaAsBi/InP: weak luminescence (extremely low temperature growth <300 °C).
✓ **MQW structure**: abrupt interface w/o segregation, thermally stable (<800 °C), luminescent (1.3 μm@10.9%Bi), quantum-size effect.

Device-quality epilayer
✓ Laser-emission can be obtained, however, very narrow process window.
✓ The essence of growth conditions for GaAsBi-based alloys is exactly the same as that of InSbBi growth in the early 80s!!
✓ An innovative growth technique is expected for further improvement in GaAsBi-based alloys.