Present status and future prospects of Bi-containing semiconductors

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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

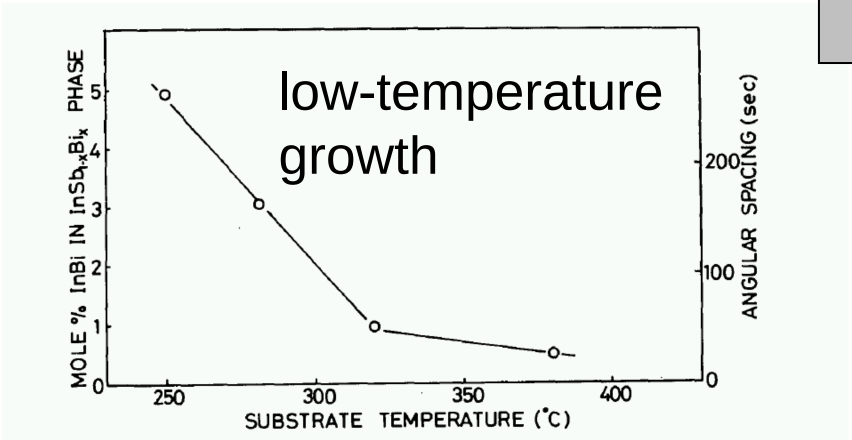
Earliest days of epitaxy of Bi-containing semiconductors

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

① K. Oe, S. Ando, K.Sugiyama: Jpn. J. Appl. Phys. **20** (1981) L303.
② A.J.Noreika, W.J. Takei, H. Francombe and C.E.C Wood: J.Appl.Phys. **53** (1982) 4932

Key to growth

K. Oe, et.al:JJAP



low-temperature growth

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.

no growth of InSbBi Sb/In>1	☺mirror-like surface Sb/In≒1	☠rough surface (Sb inclusion) Sb/In<1

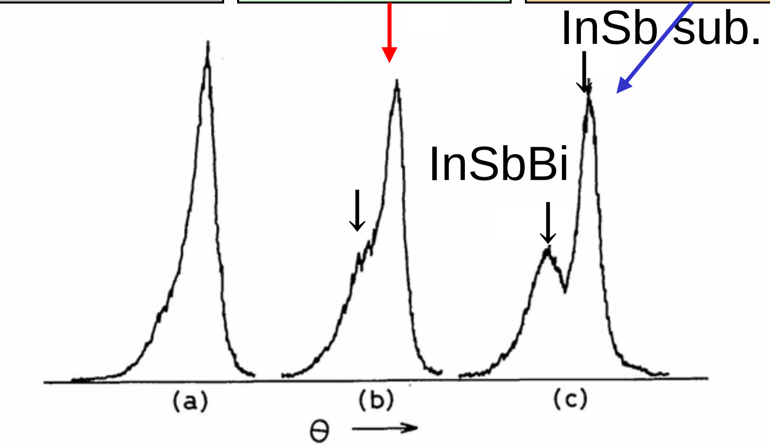


Fig. 1. Cu Kα_1 rocking curves for the (004) reflection of the films grown at 380°C on (001) InSb substrates. The arrival rate ratios are (a) Sb/In>1, (b) Sb/In≈1, and (c) Sb/In<1.

Why low $\Delta Eg/\Delta T$?

★Wavelength-Division Multiplexing (WDM)

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

⇒ *fluctuation of lasing wavelength*

Laser diode $\Delta\lambda/\Delta T$: 0.1 nm/K

↕

Dense WDM *(example)*
λ Division: 0.4 nm/channel

LD equipped with Peltier device

⇒ *drawback: cost, energy consumption*

★Materials with low $\Delta Eg/\Delta T$

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

Proposal of GaInAsBi as a active-layer materials of LD
K. Oe and H. Asai, Proc. Electronic Materials Symp. '95, Izu, Japan p.191

Semiconductor : GaAs Semimetal: GaBi ⇒ Alloy : GaAsBi

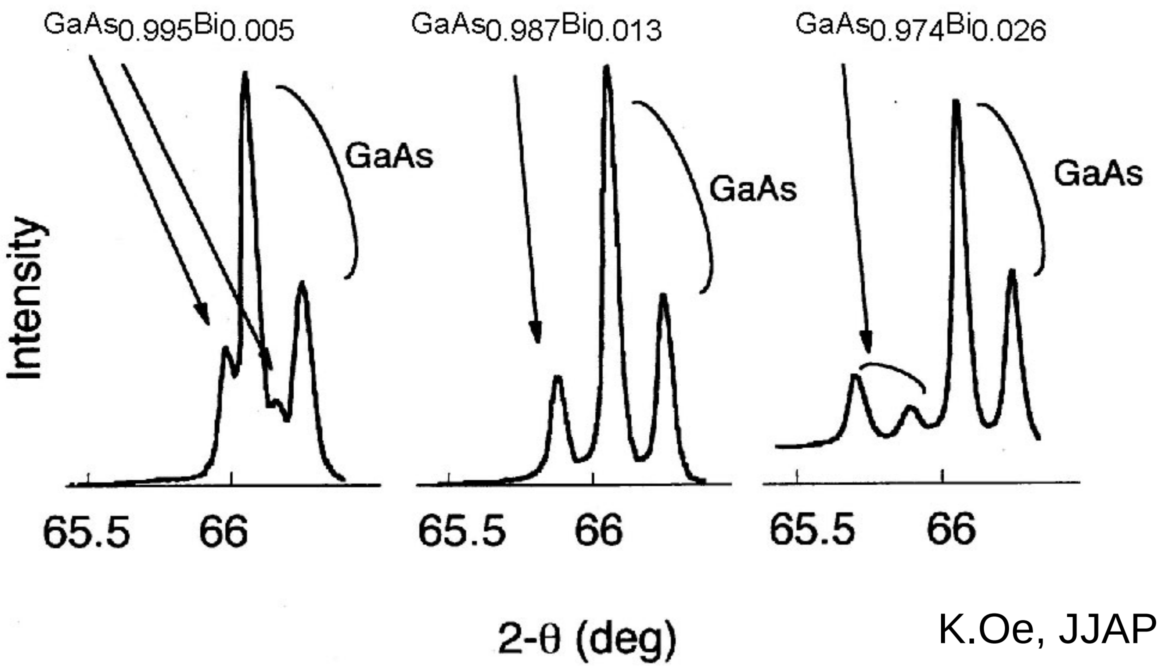
MOVPE growth of GaAsBi

Low-pressure MOVPE

Sources: TIPGa, TMBi, TBAs, *Substrate*: GaAs(100)

Growth temperature: 365°C *Growth rate*: 1μm/h

X-ray diffraction pattern



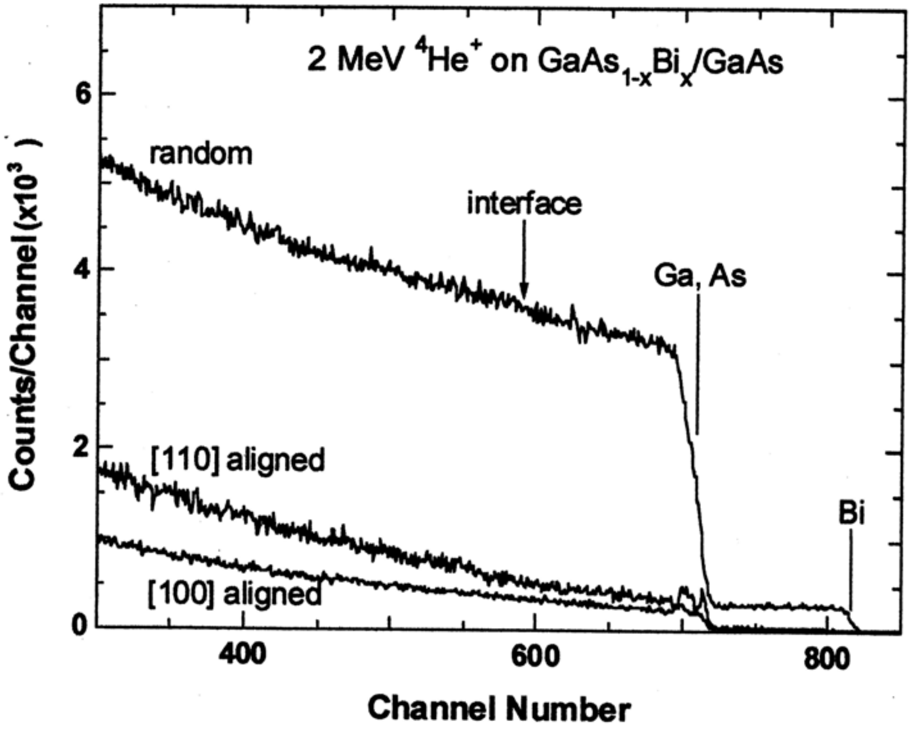
K.Oe, JJAP 41 (2002) 2801

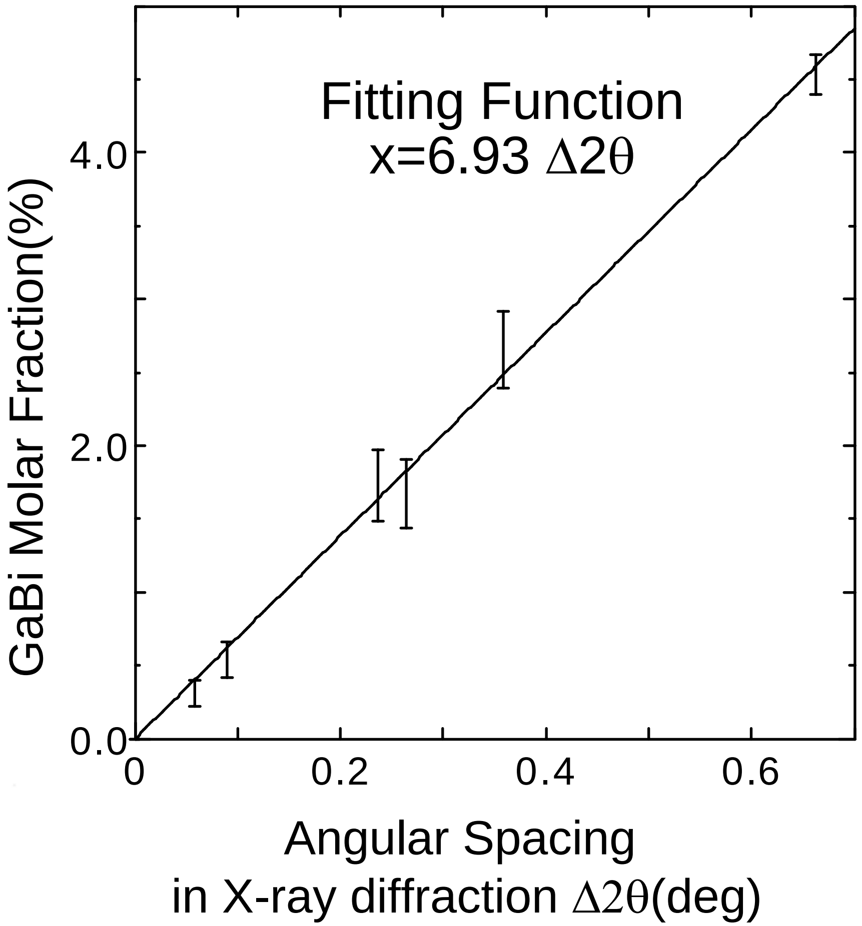
- Successful epitaxial growth
- Lattice constant increases with GaBi molar fraction.

  GaBi molar fraction: Rutherford backscattering spectroscopy
- Thermally stable after anneal in As pressure at 560°C for 30min

Determination of GaBi molar fraction *x* for $GaAs_{1-x}Bi_x$

Rutherford backscattering spectroscopy(RBS)



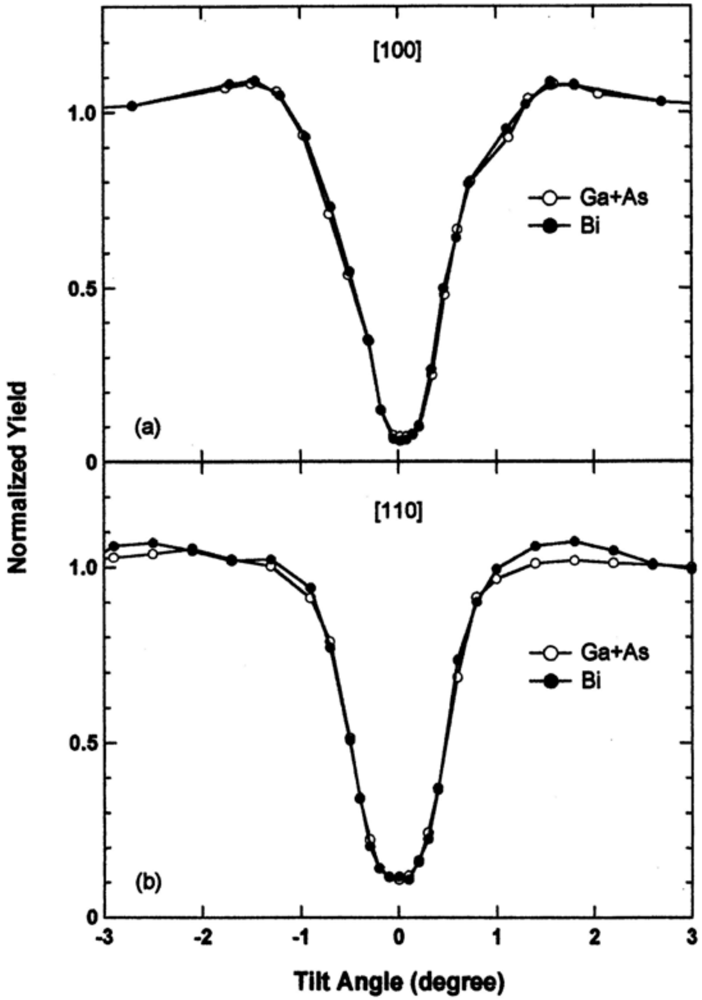


K. Takahiro, et.al, J. Electron. Matter. 32 (2003)34.

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

⇒determination of GaBi molar fraction by X-ray diffraction

Angular scan in Rutherford backscattering spectroscopy



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

Yield(Bi)=Yield(Ga+As)

⇒Bi atoms are located exactly on substitutional sites.

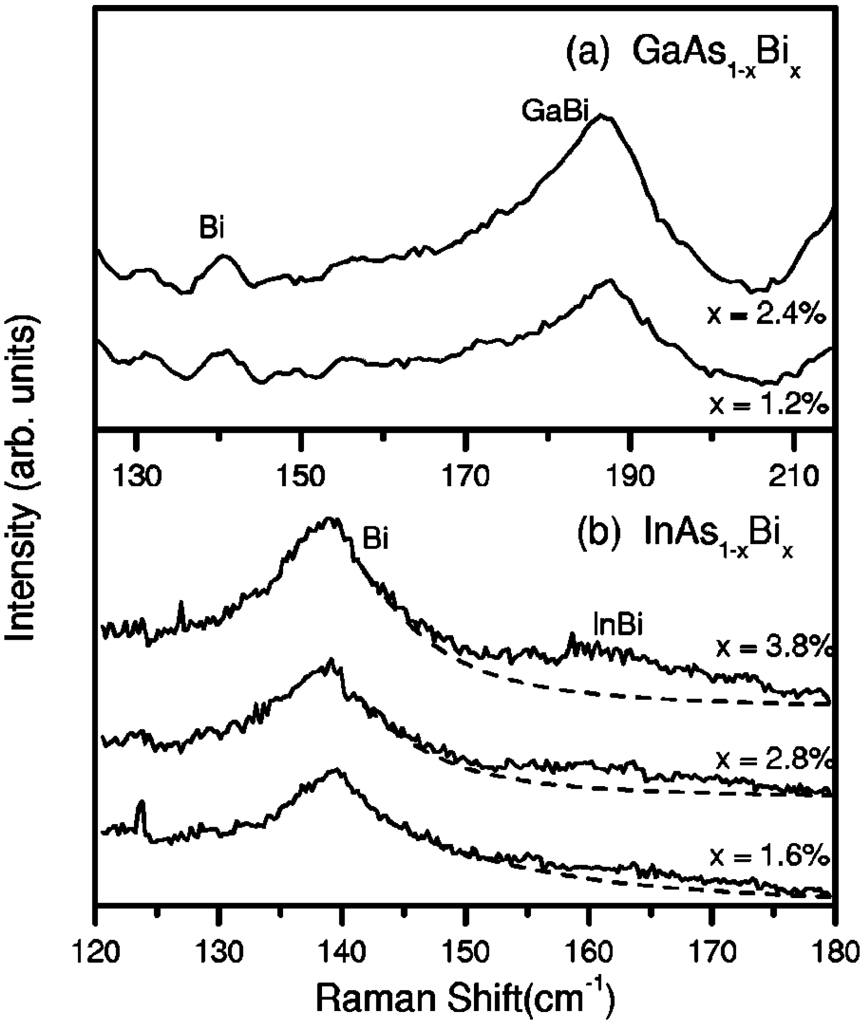
Note

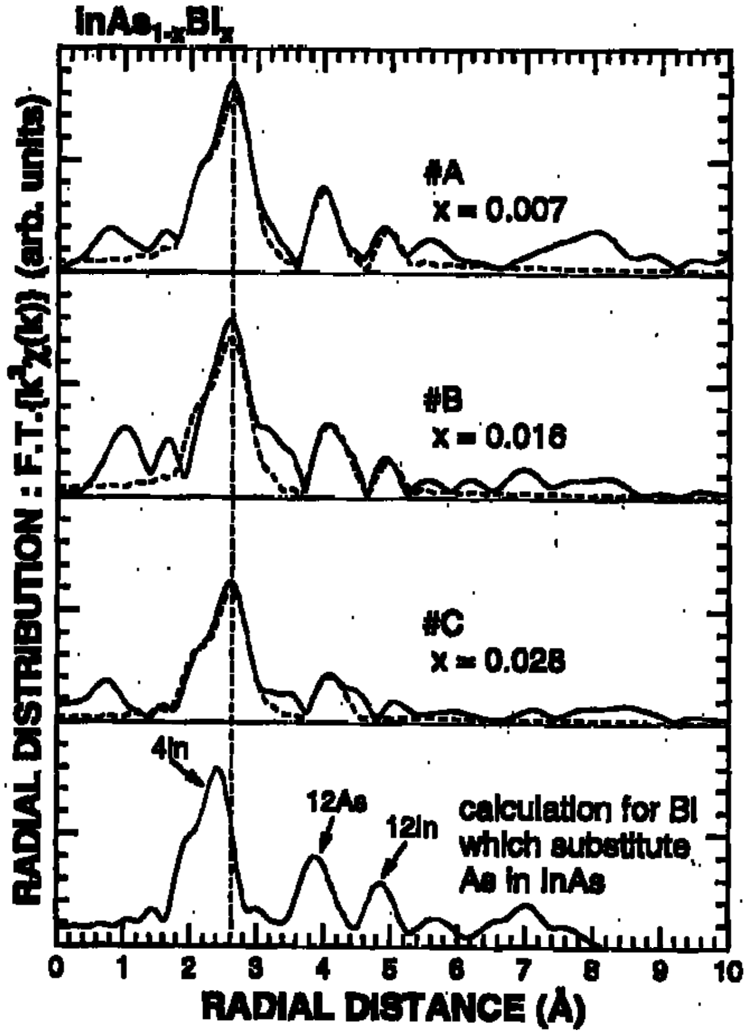
Interstitial site in a zinc-blend lattice

[100]: shadowed, [110]: visible

K. Takahiro, et.al, J. Electron. Matter. 32 (2003)34.

Raman spectroscopy and EXAFS of GaAsBi and InAsBi





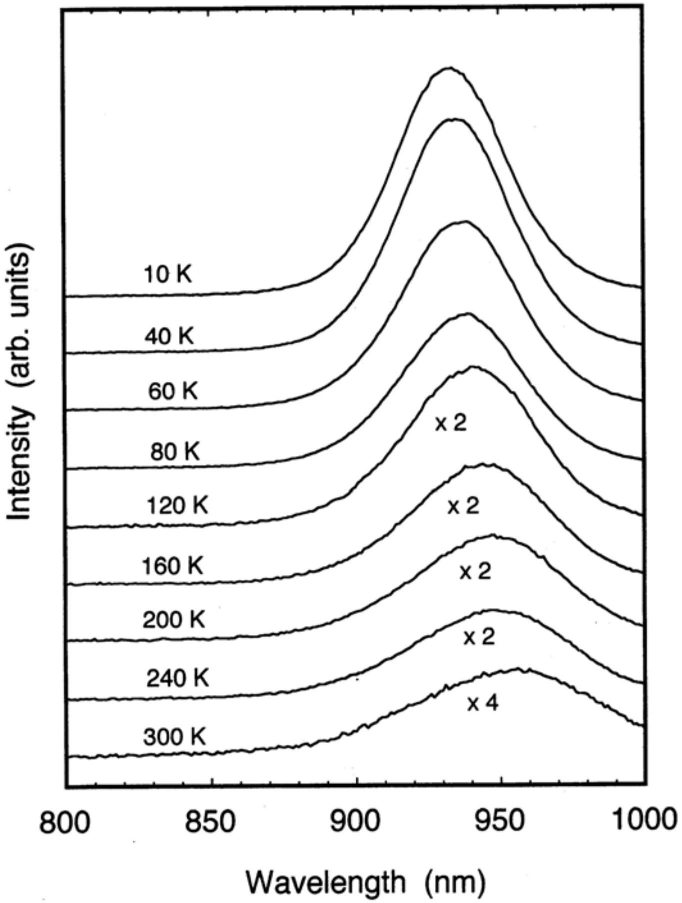
GaBi-like and InBi-like modes
⇒substitutional incorporation of Bi atoms

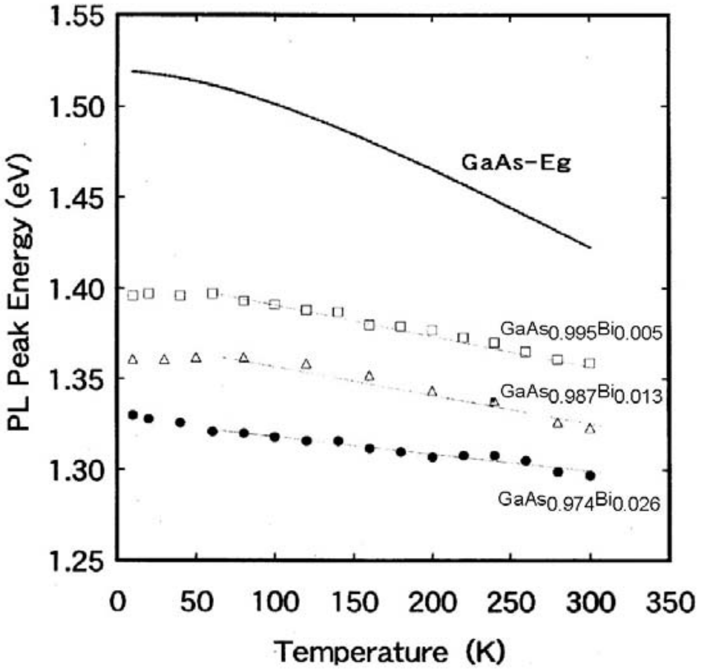
The majority of Bi atoms substituted the As site of InAsBi

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

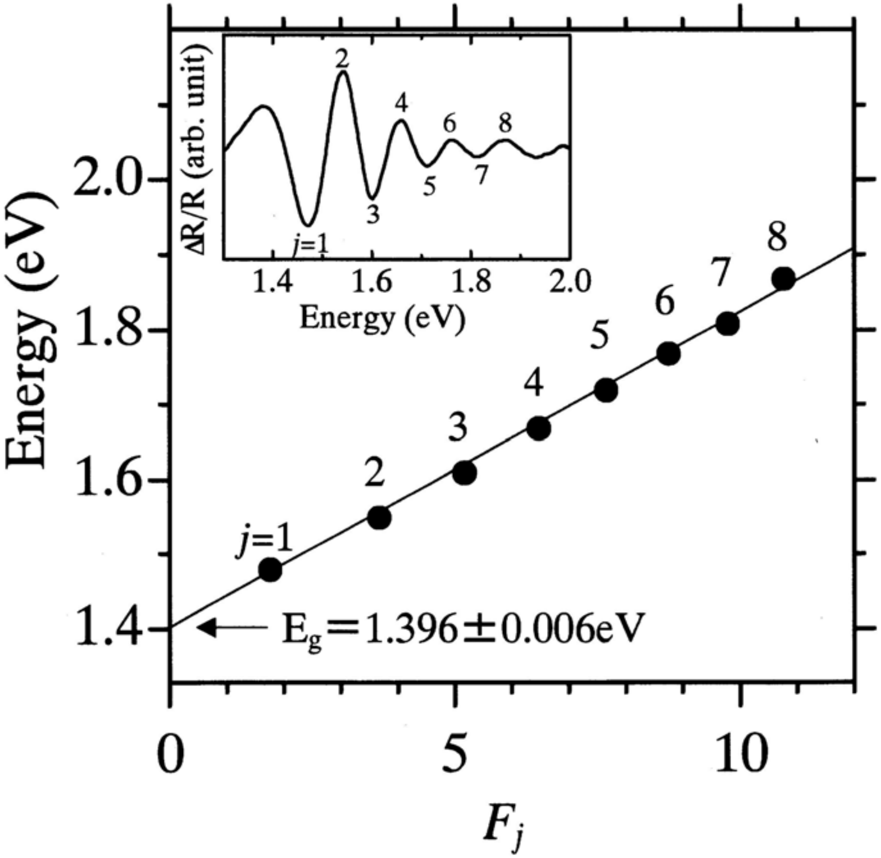




$$\left.\frac{\Delta E_g}{\Delta T}\right|_{\mathrm{GaAs_{0.0974}Bi_{0.026}}} \approx \frac{1}{3}\cdot\left.\frac{\Delta E_g}{\Delta T}\right|_{\mathrm{GaAs}}$$

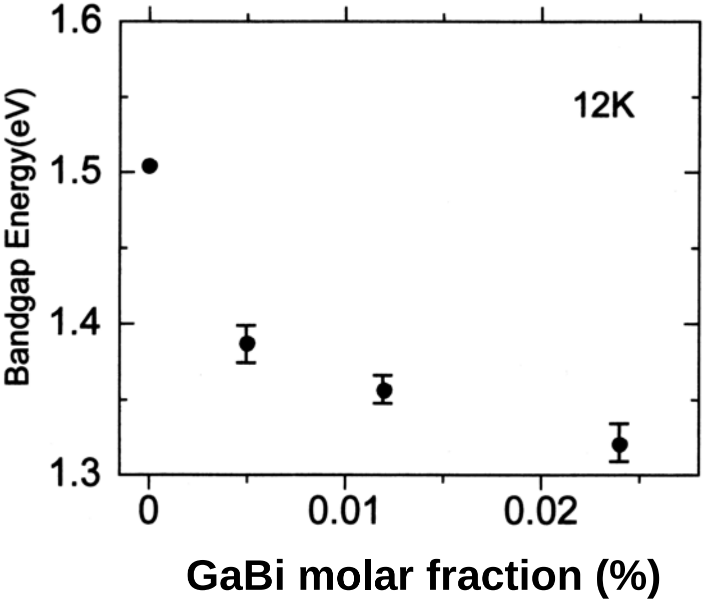
K.Oe, JJAP 41 (2002) 2801

Photoreflectance spectra of GaAsBi



$GaAs_{0.995}Bi_{0.005}$

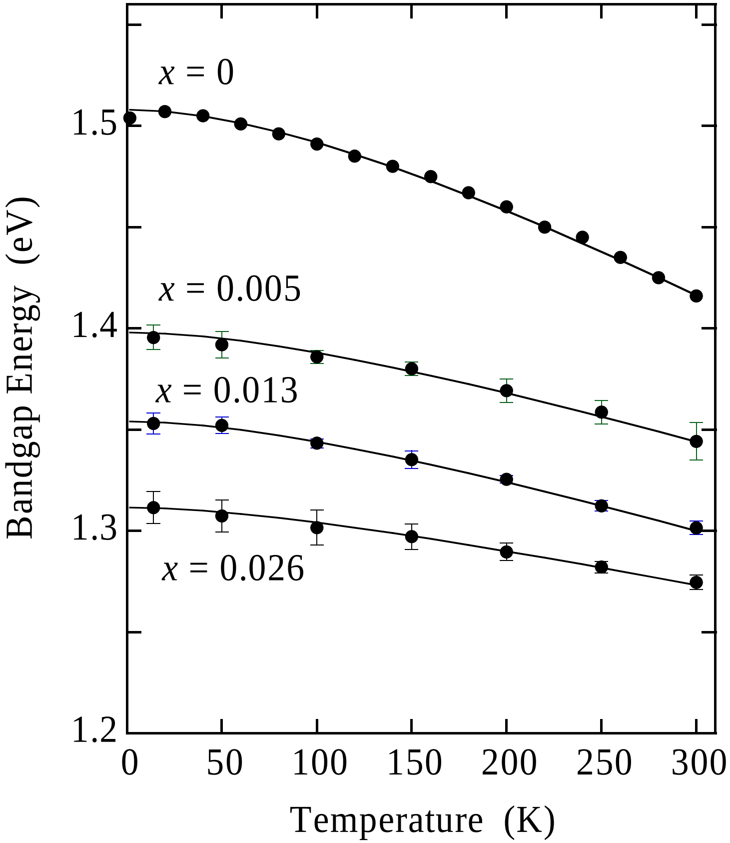
Franz-Keldysh oscillation due to built-in electric field



Decrease in bandgap of $GaAs_{1-x}Bi_x$ with increasing GaBi molar fraction

J.Yoshida, et al., JJAP **42** (2003) 371

Temperature dependence of bandgap of GaAsBi



GaBi molar fraction	$\Delta E_g/\Delta T$ 150-300K (meV)
0 (GaAs)	-0.42
0.005	-0.24
0.013	-0.23
0.026	-0.15

Temperature-insensitive bandgap

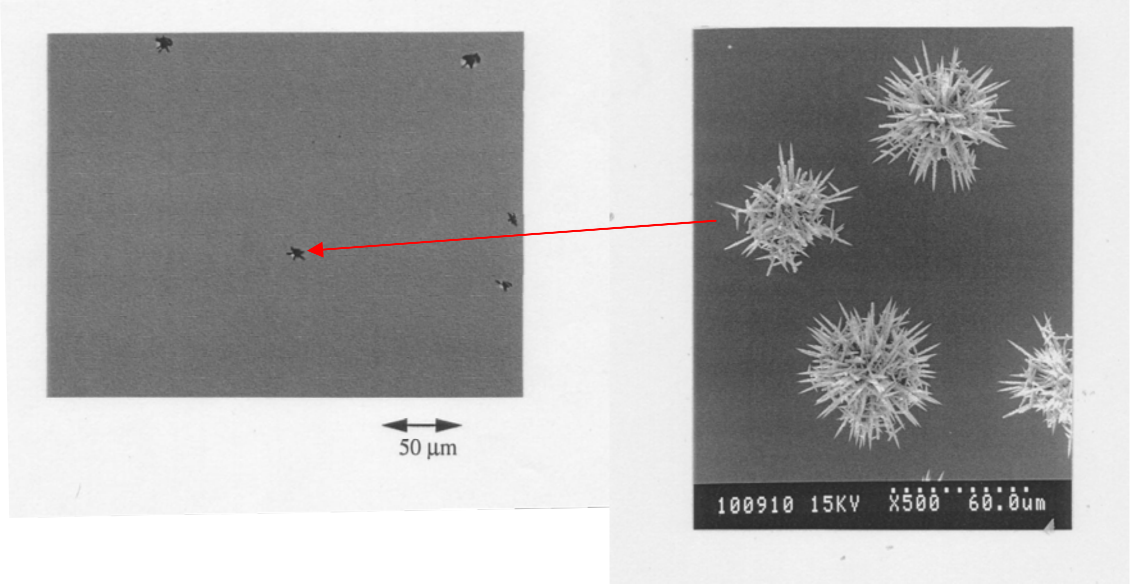
$$\frac{\Delta E_{\mathrm{g}}}{\Delta T}_{\mathrm{GaAs}_{0.0974}\mathrm{Bi}_{0.026}} \approx \frac{1}{3}\cdot\frac{\Delta E_{\mathrm{g}}}{\Delta T}_{\mathrm{GaAs}}$$

J.Yoshida, et al., JJAP **42** (2003) 371

Drawbacks of MOVPE growth of GaAsBi

× MOVPE:

- insufficient decomposition of metalorganic at low T_{sub}
  ⇒difficulty in incorporation of In with existence of Ga at low T_{sub}
- segregation of Bi on surface



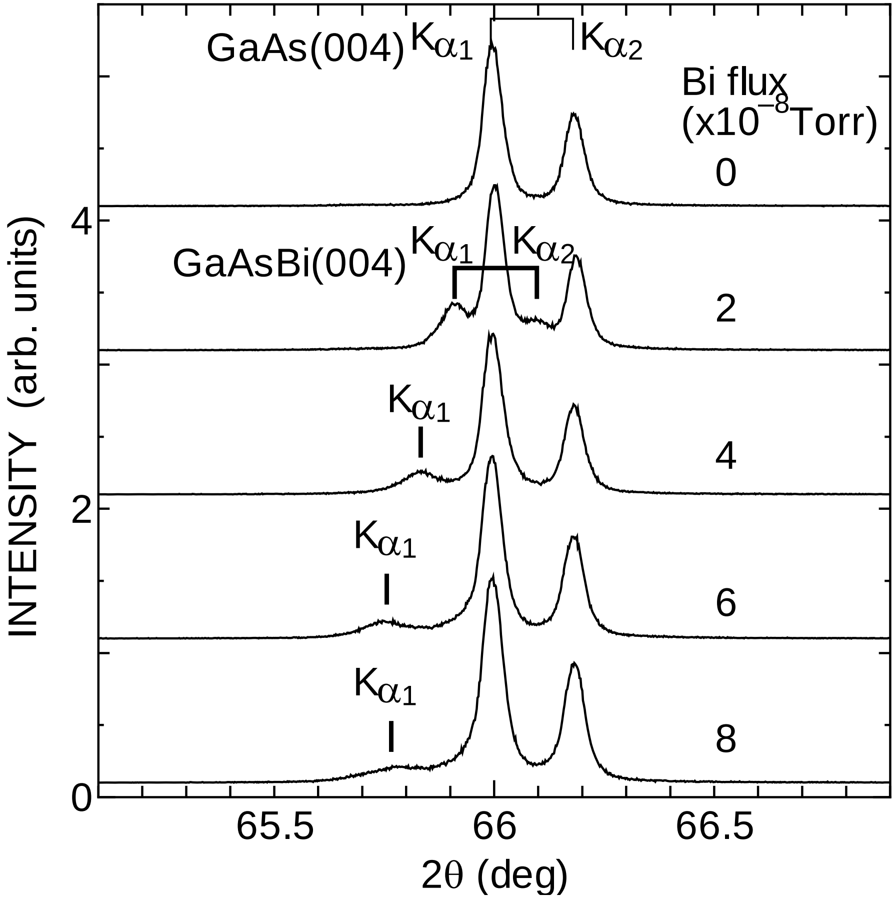
○MBE:

- low-temperature growth without decomposition process
- no Bi segregation: desorption from surface

MBE Growth of GaAsBi

X-ray diffraction

Bi-flux dependence



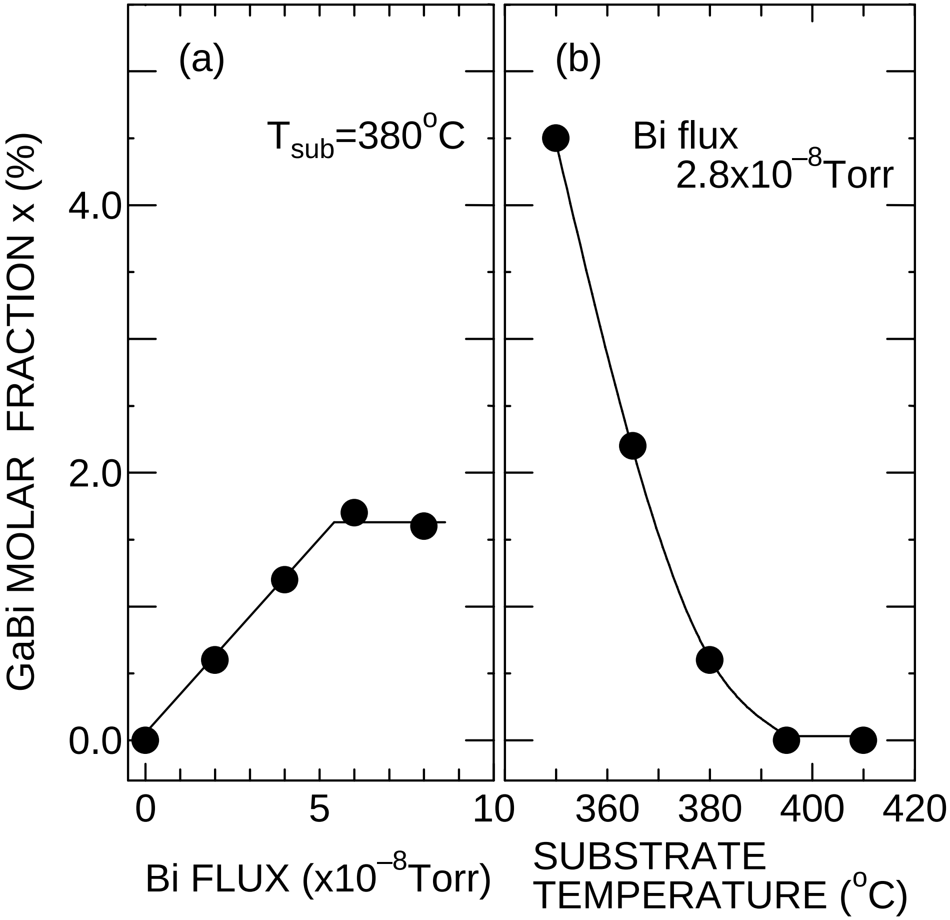
Thickness: 0.5 μm
Substrate temperature: 380 °C
Ga flux: 3×10^{-7} Torr
As flux: 8×10^{-6} Torr

Lattice constant increases with Bi flux, followed by saturation.

RBS: Substitutional incorporation of Bi

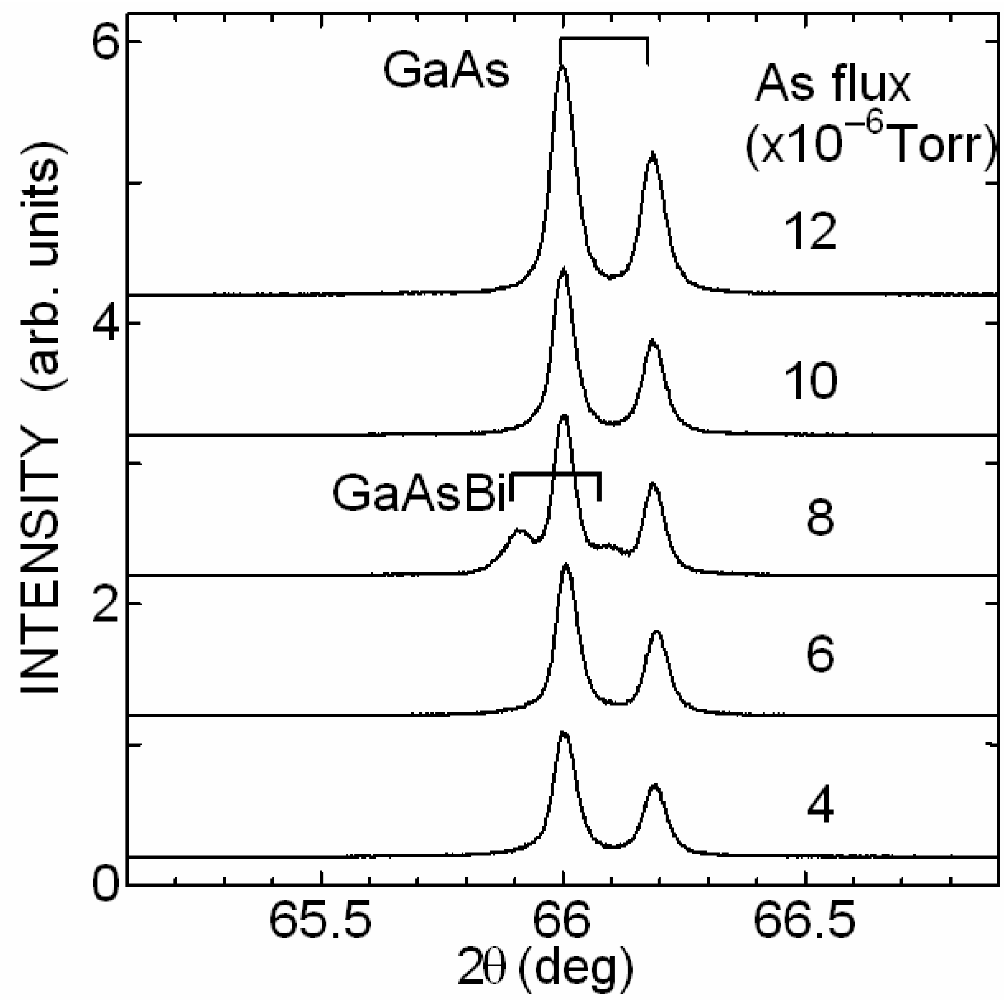
M.Yoshimoto, et.al, JJAP 42 (2003) L1235

GaBi molar fraction vs. Bi flux and substrate temperature



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

☠As/Ga>1

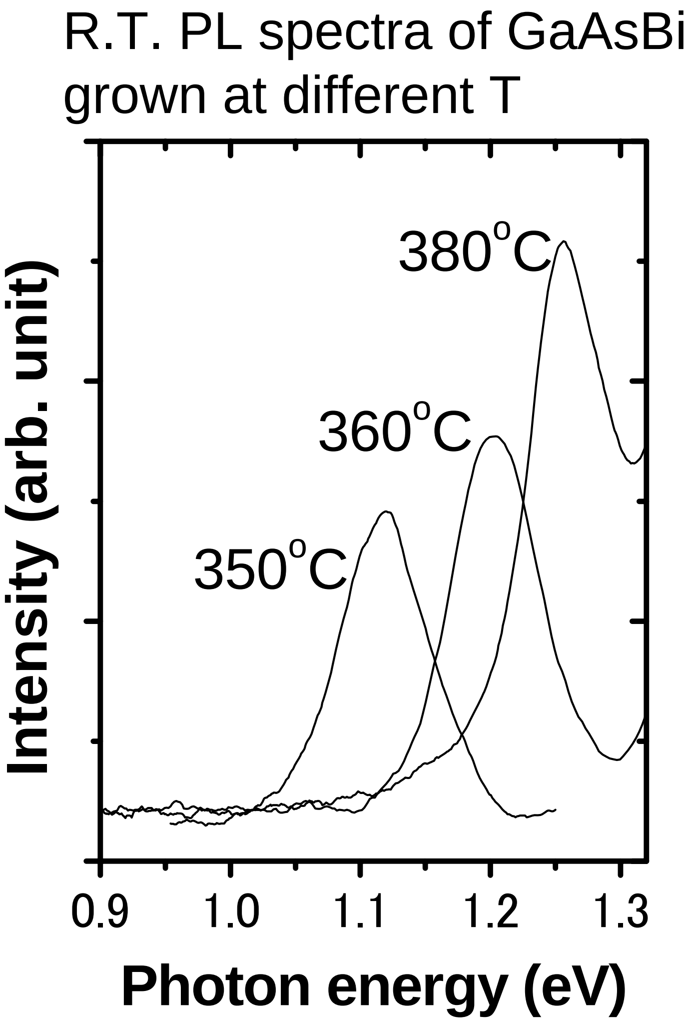
←☺As/Ga≒1

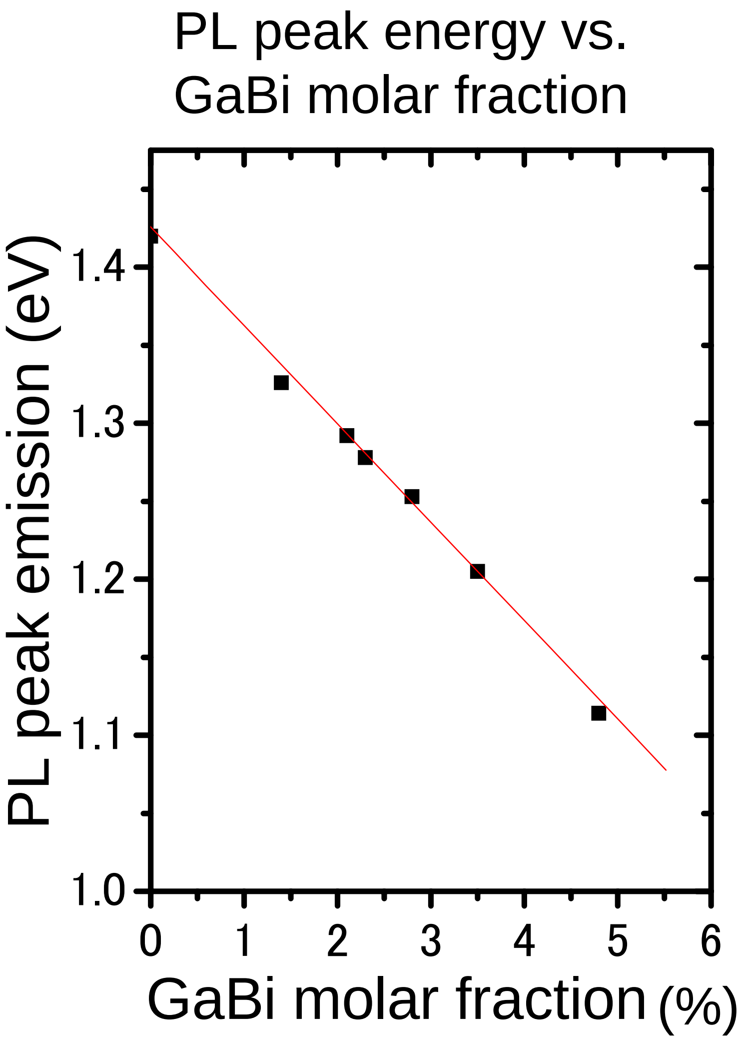
☠As/Ga<1

Bi is incorporated with a limited As flux.

M. Yoshimoto, et.al, Mater. Res. Soc. Symp. Proc. 891 (2006) 0891-EE11-06

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

Expansion of luminescence wavelength to longer wavelength － GaNAsBi

Plasma-assisted MBE

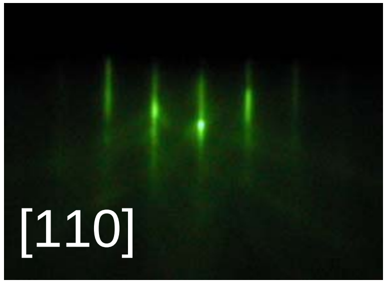
GaAs buffer layer (thickness: 100nm, T_{sub} 500°C)

GaNAsBi

substrate temperature: 350~400°C

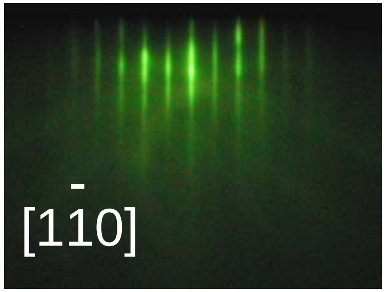
source: Ga (10^{-7}Torr), As (10^{-6}Torr), Bi (10^{-8}Torr)

plasma activated nitrogen(13.56MHz)



Key to Bi incorporation:

- narrow process window for As flux
- low-temperature growth (<400℃）

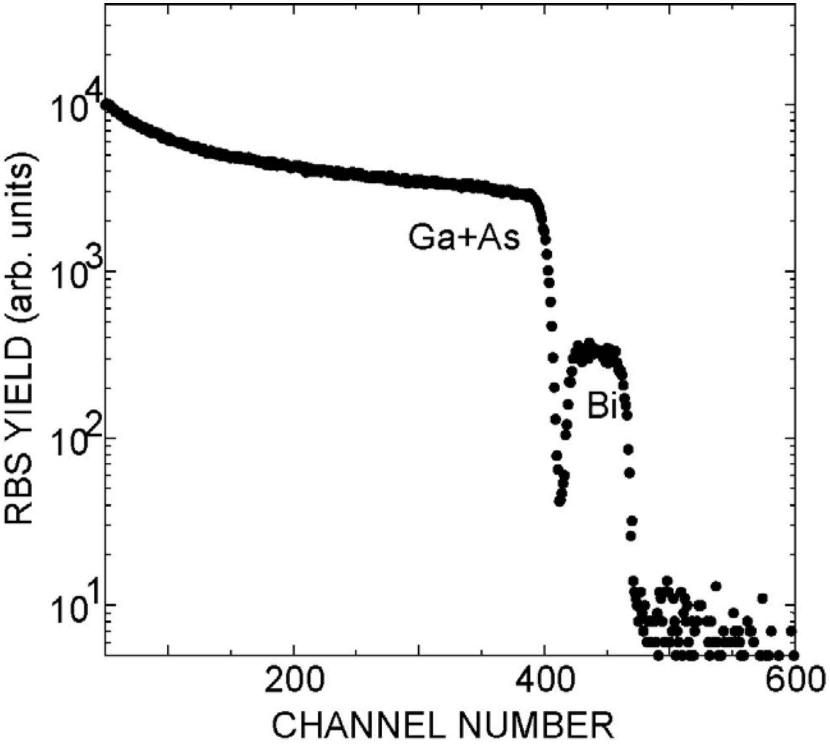


GaNAsBi RHEED

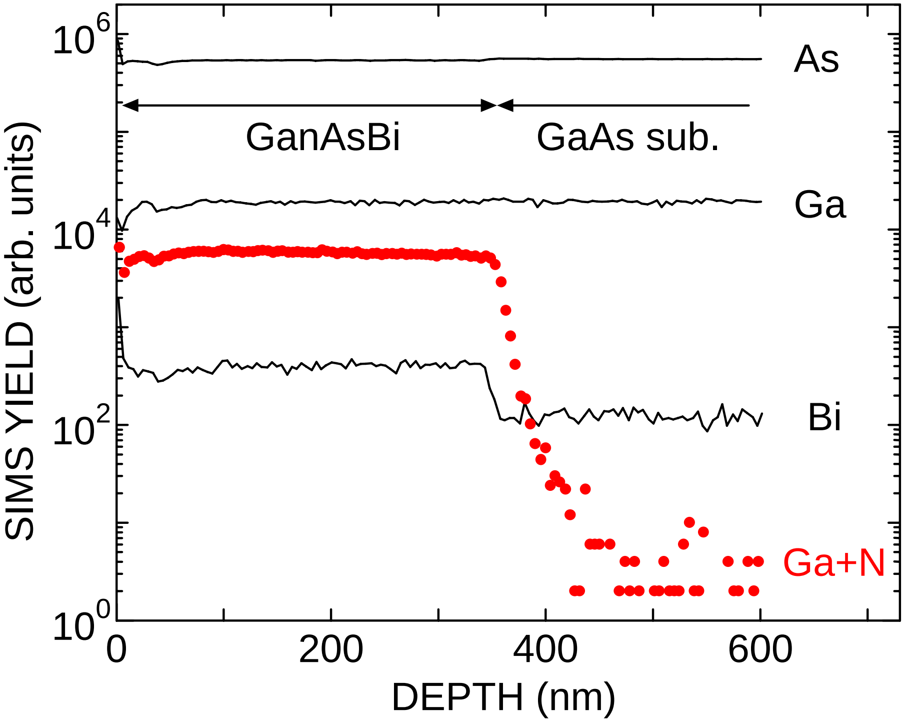
M. Yoshimoto, et.al, JJAP, 43 (2004) L845

GaNAsBi: composition determination

GaBi molar fraction by RBS



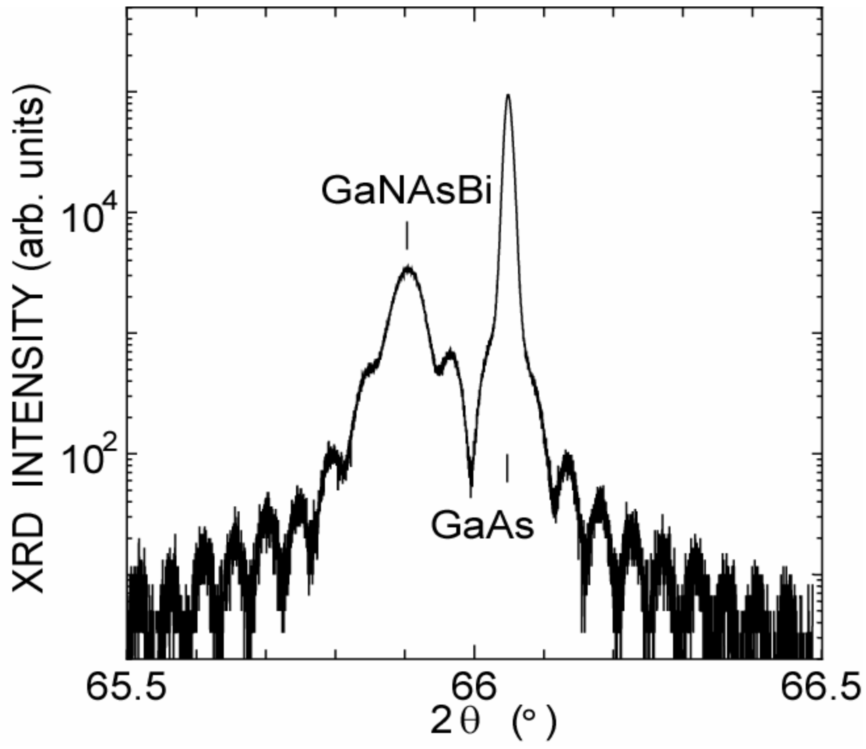
GaN molar fraction by SIMS

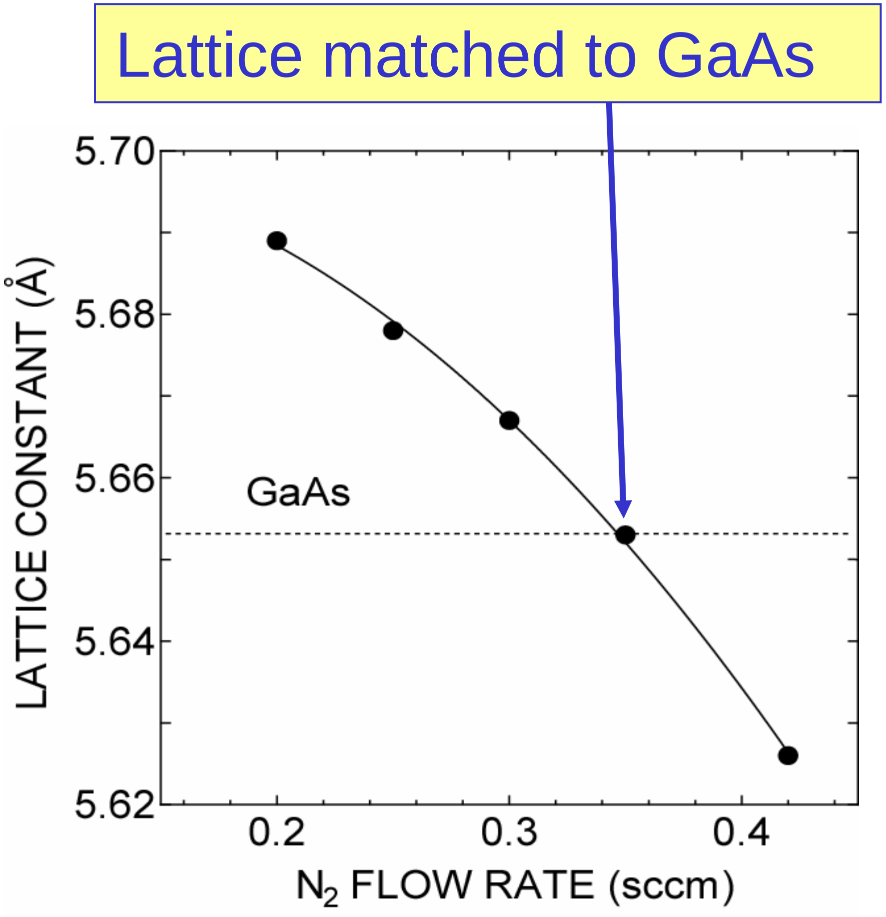


Substitutional incorporation of Bi atoms were also confirmed by channeling RBS.

M. Yoshimoto, et.al, MRS Symp. Proc. 891 (2006) 0891-EE11-06

X-ray diffraction of GaNAsBi



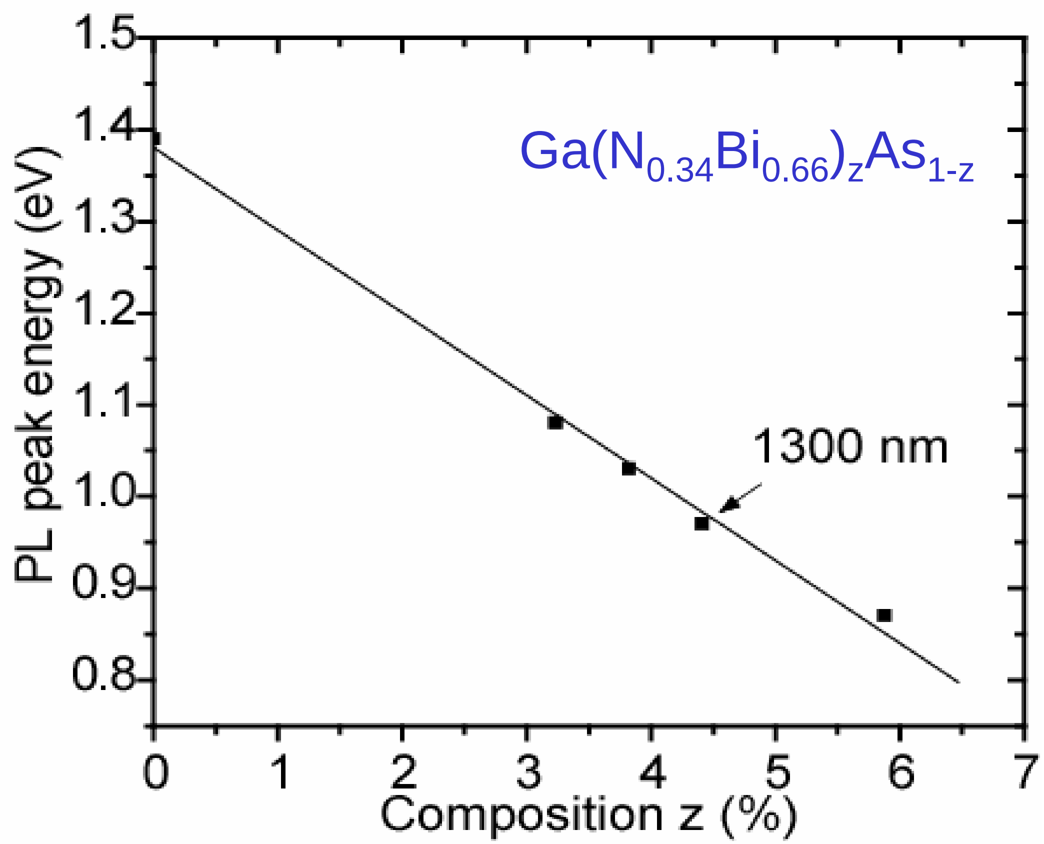


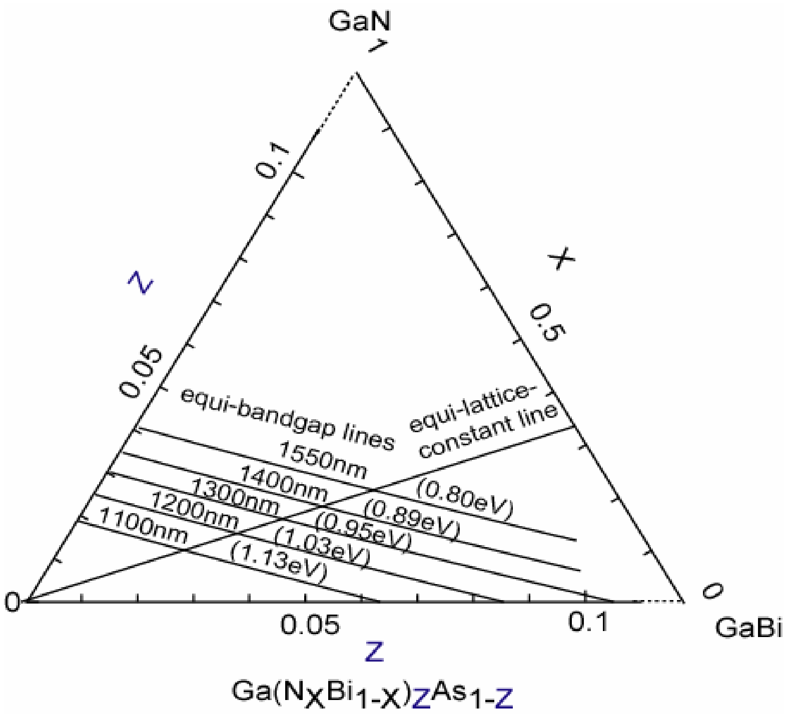
Lattice matched to GaAs

Constant supplies of Ga, As, Bi

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

PL emission from lattice-matched GaNAsBi





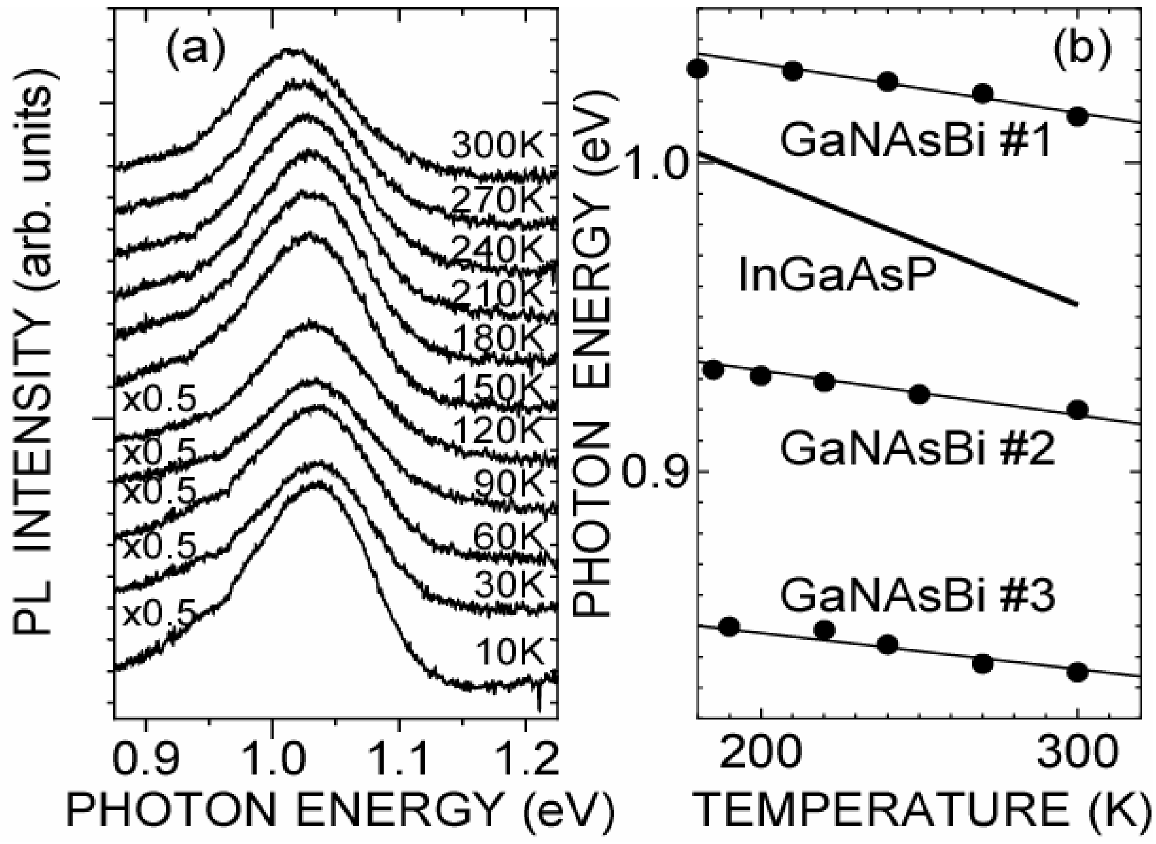
W.Huang, et.al, JAP 98(2005) 053505

M. Yoshimoto, et.al, 16th IPRM, Kagoshima, Japan, 2004, IEEE #04CH37589, p.501.

- $Ga(N_{0.34}Bi_{0.66})_zAs_{1-z}$: Lattice matched to GaAs
- PL emission in the optical fiber communication waveband

Photoluminescence of GaNAsBi

Low temp. coefficient

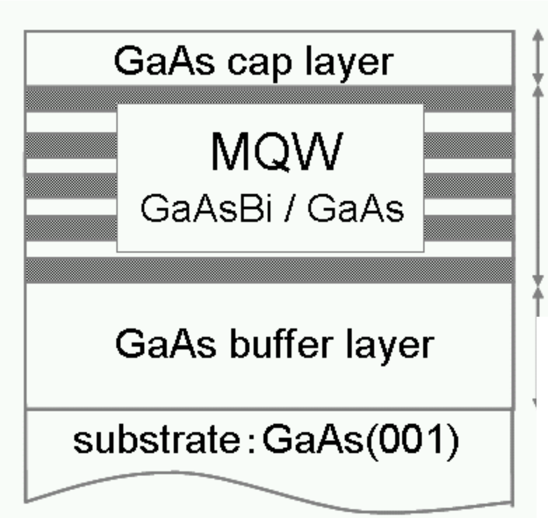


Temperature coefficient of the PL peak energy

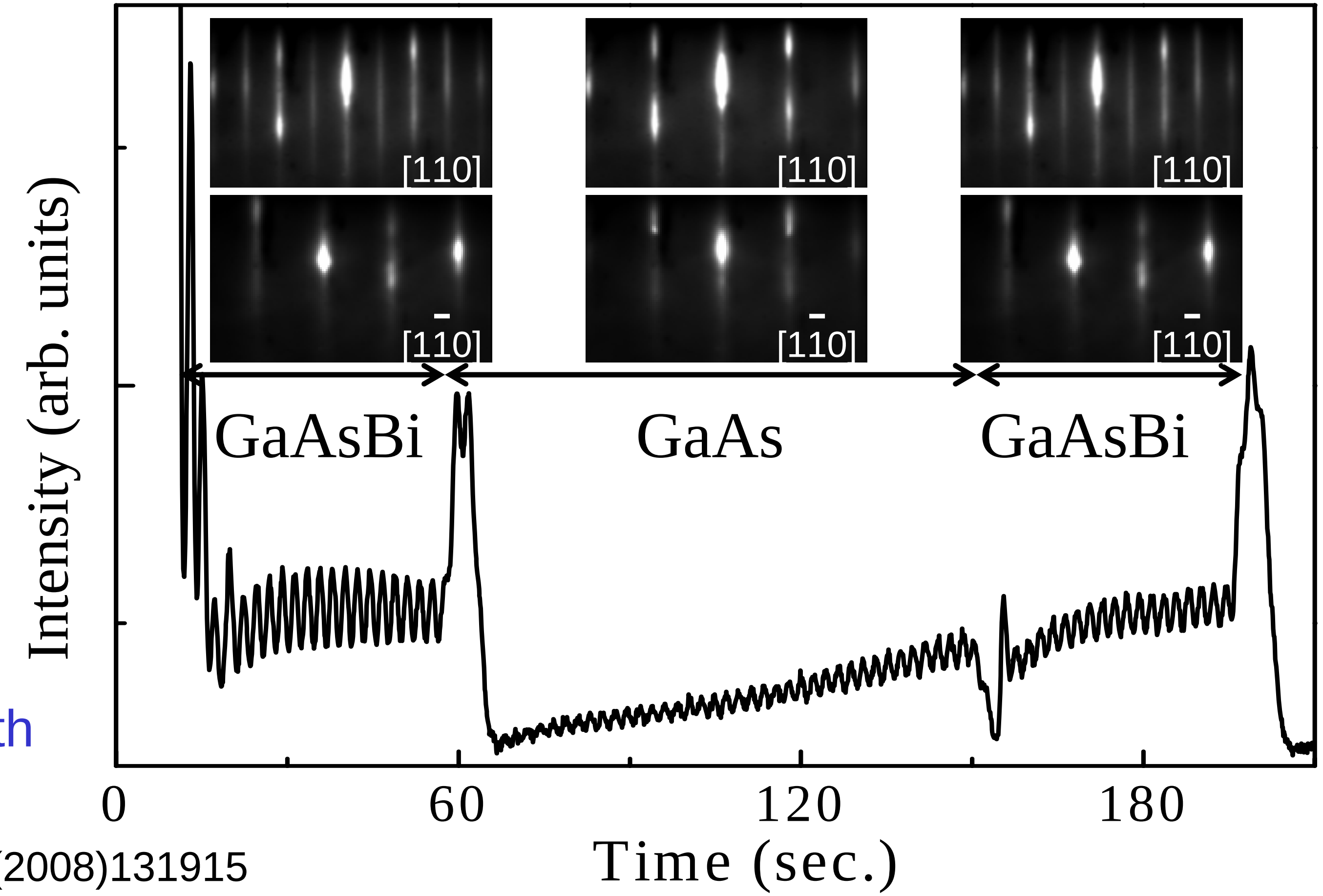
★ 0.14 meV/K (150-300k) = 1/3 InGaAsP ★

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

Growth of GaAsBi Multi-quantum wells



20nm
$GaAs_{1-x}Bi_x$: 6~7nm
GaAs : 13~16nm
5～24 periods
300nm

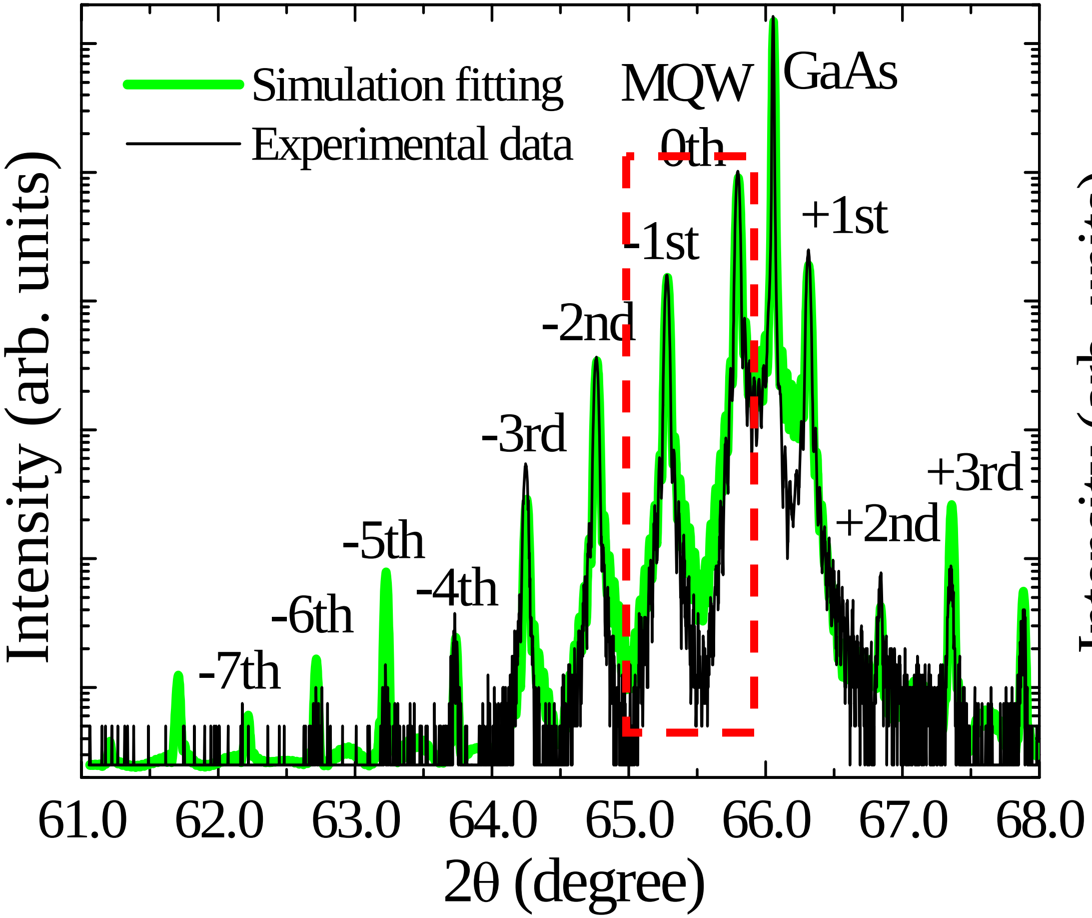


Layer-by-layer growth

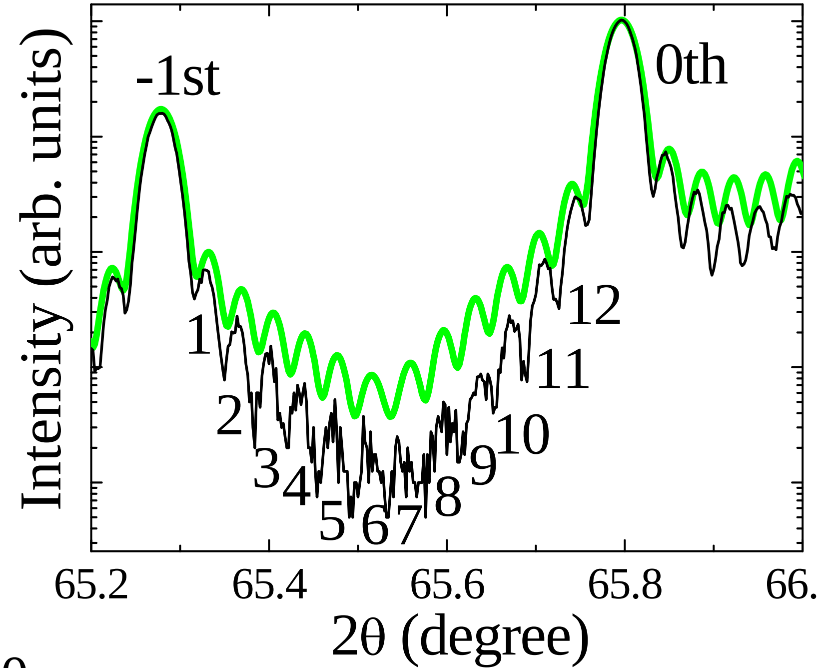
Y. Tominaga, et.al, APL 93 (2008)131915

(400) X-ray diffraction pattern

$GaAs_{0.948}Bi_{0.052}$ layer / GaAs layer = 7nm / 14nm, 14periods



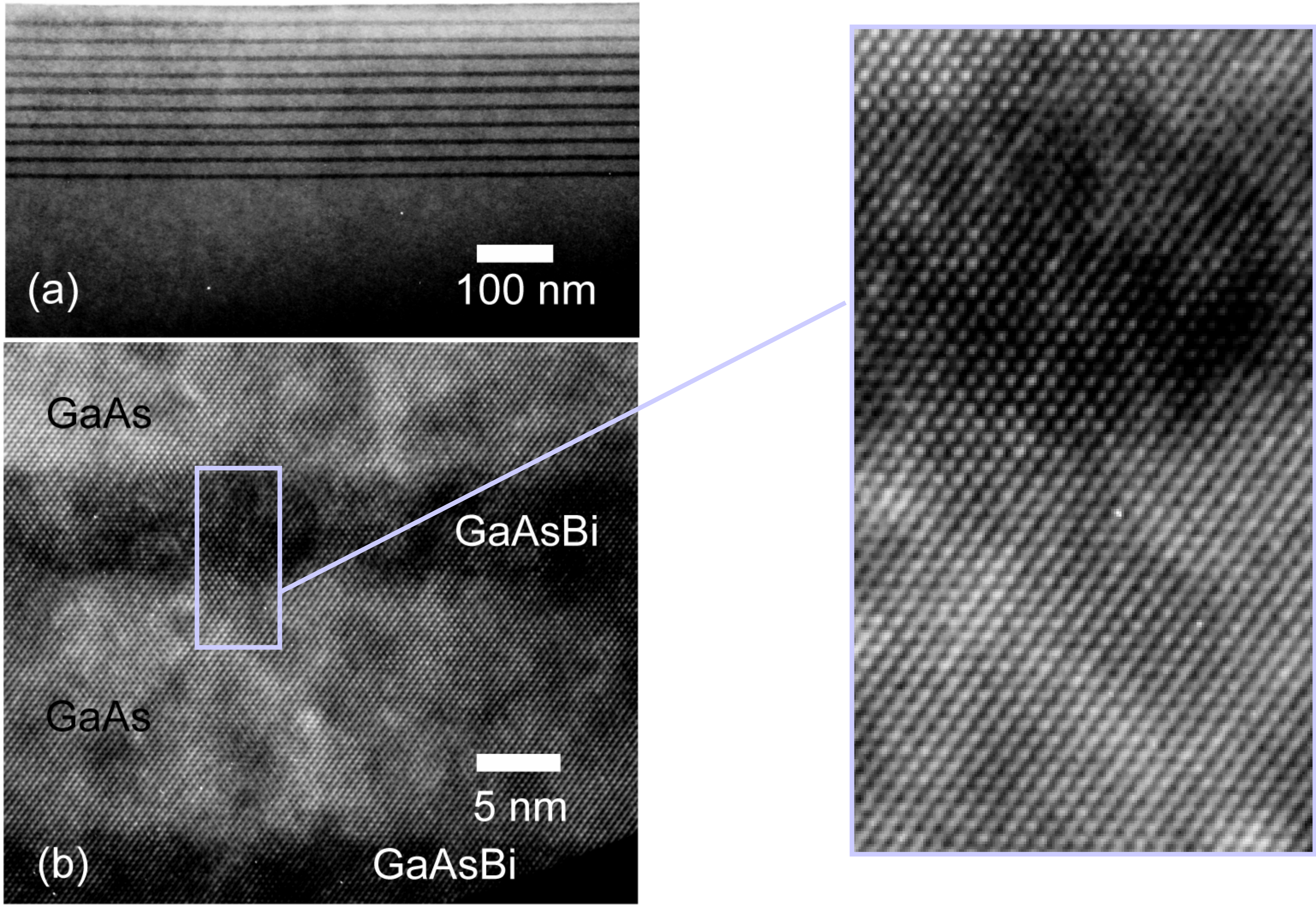
- Laue function: N'=N-2



Smooth interface

Cross-sectional TEM image

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



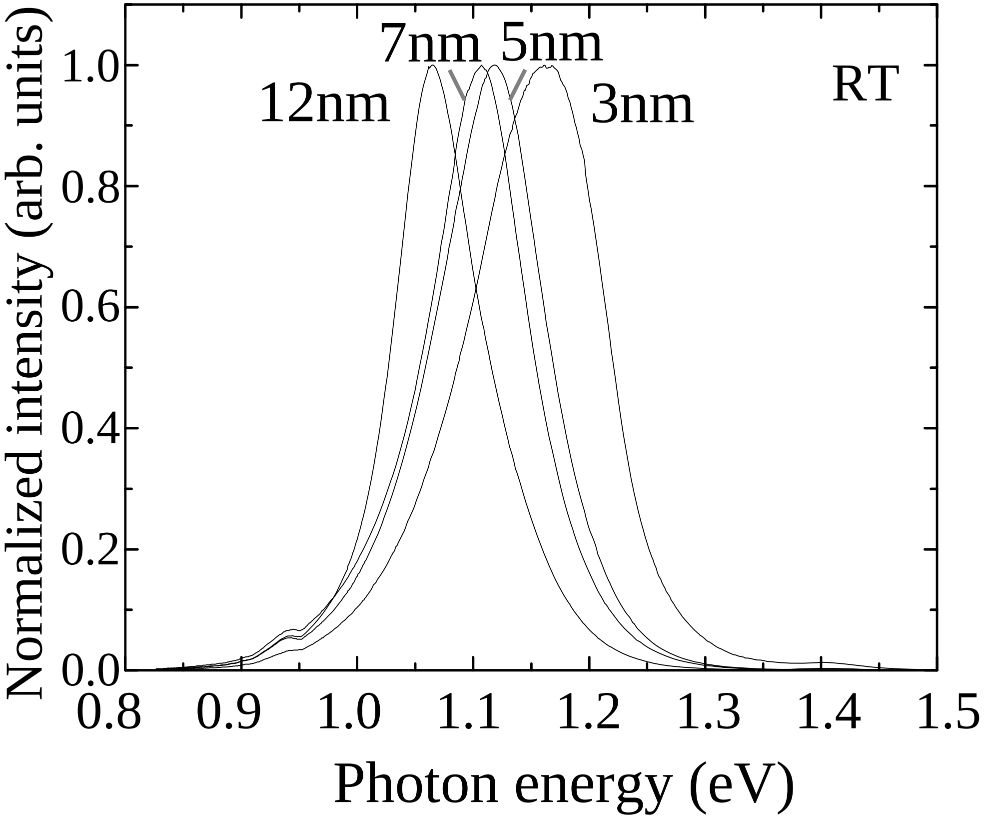
Y. Tominaga, et.al, APL 93 (2008)131915

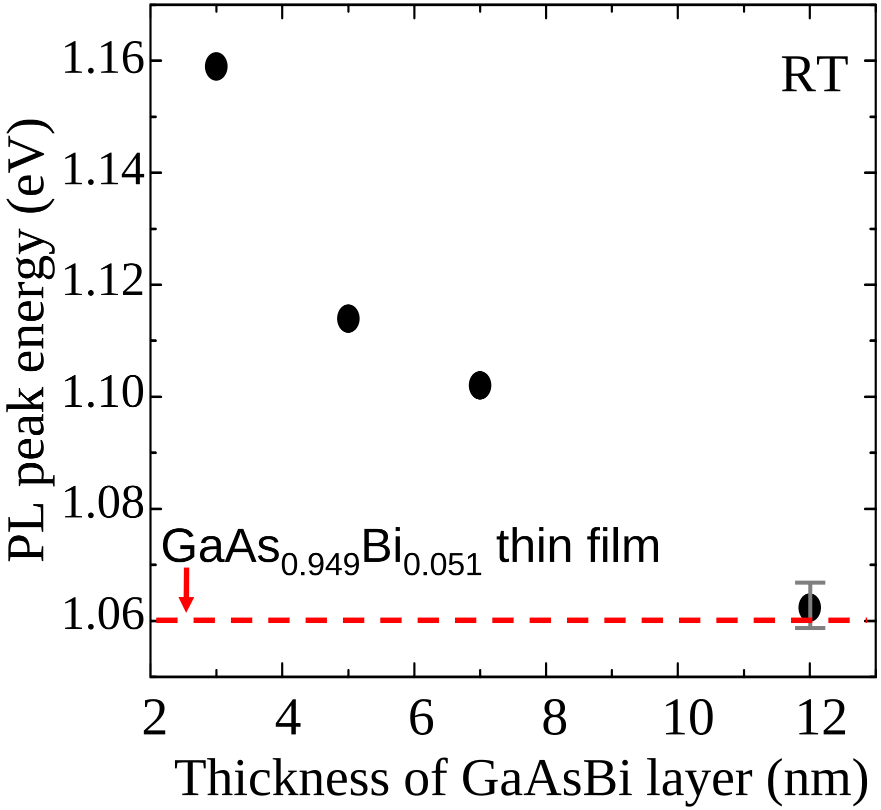
Quantum size effect

◆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



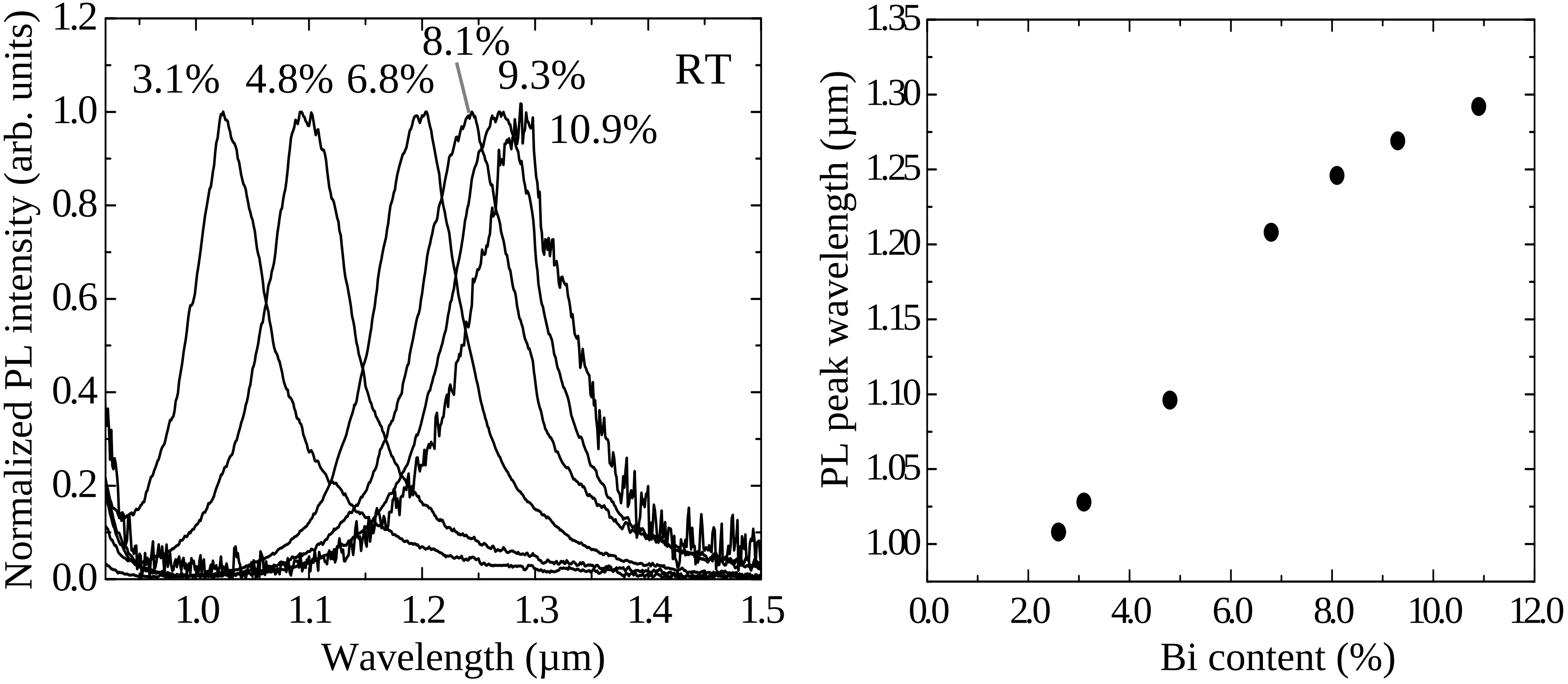


Y. Tominaga et al.:PSS(c) **5**, 2719 (2008)

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

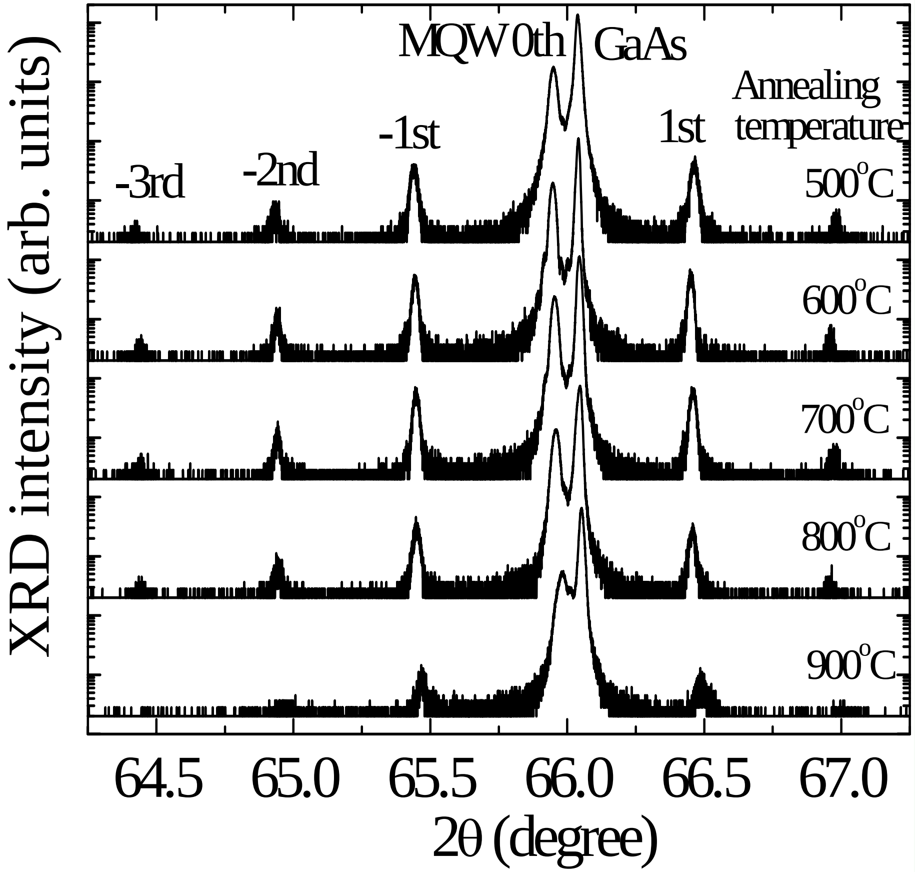


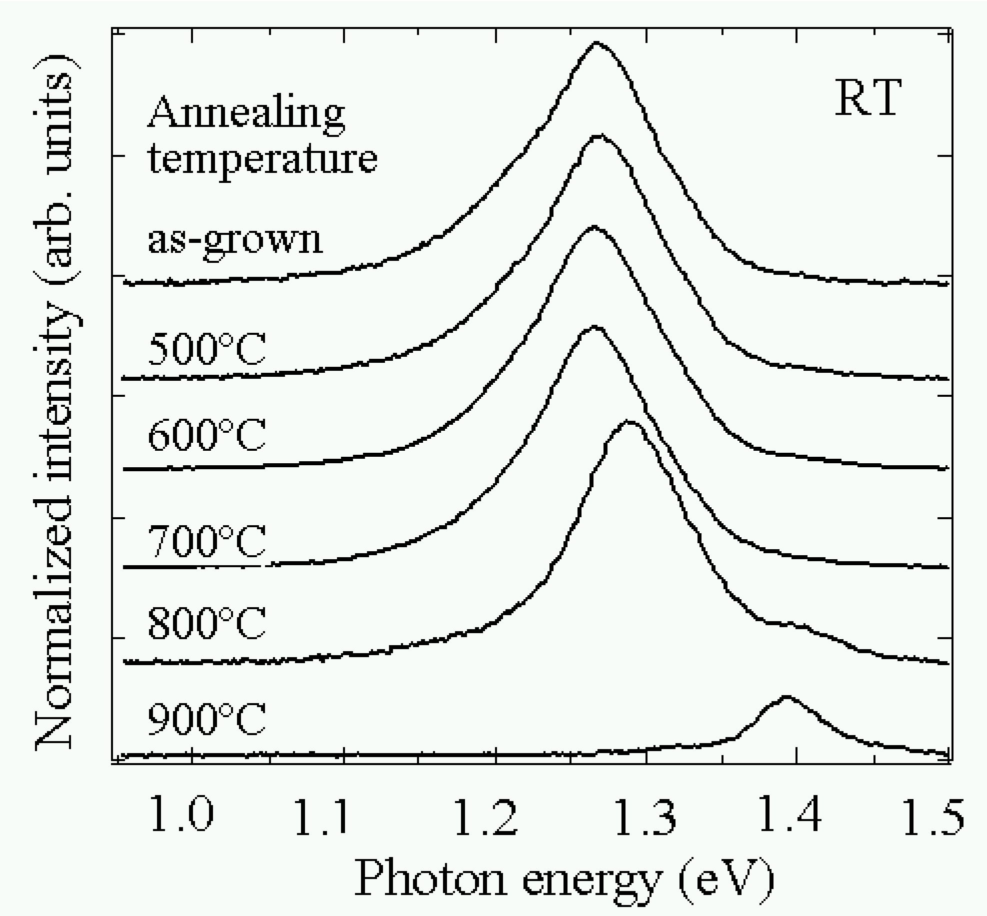
Y. Tominaga, et.al, APL 93 (2008)131915

Thermal stability

◆Annealing:10 minutes under N_2 flow

$GaAs_{0.984}Bi_{0.016}/GaAs$ MQW

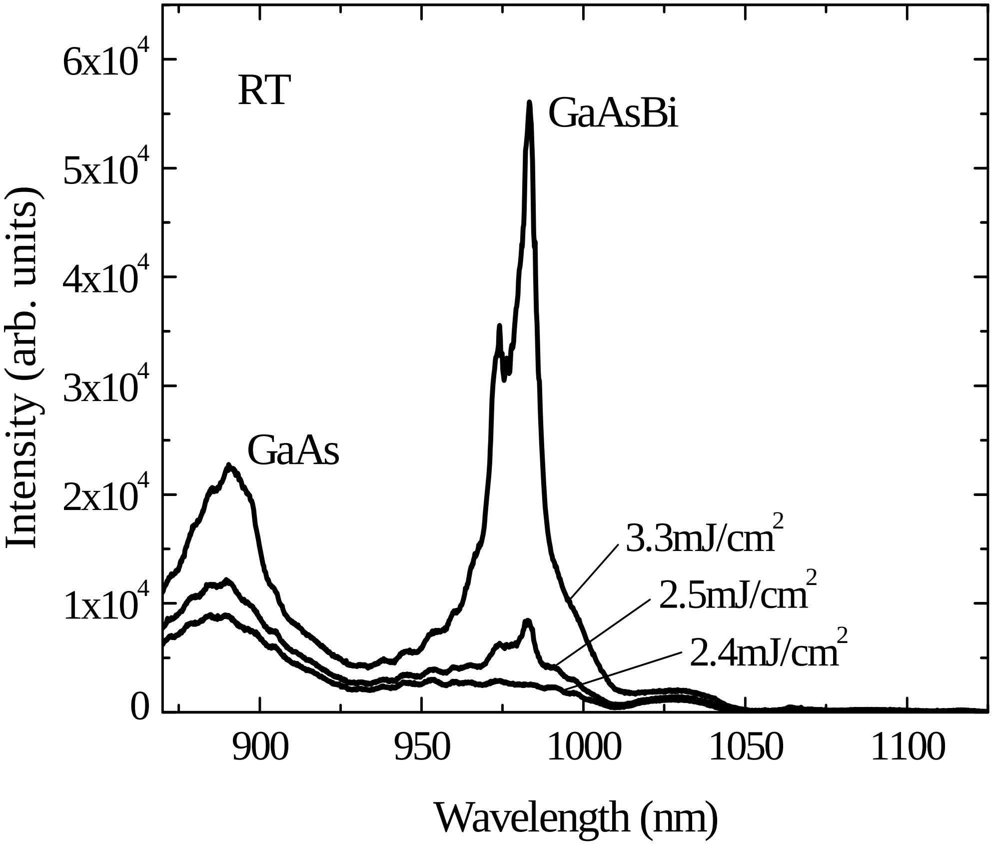


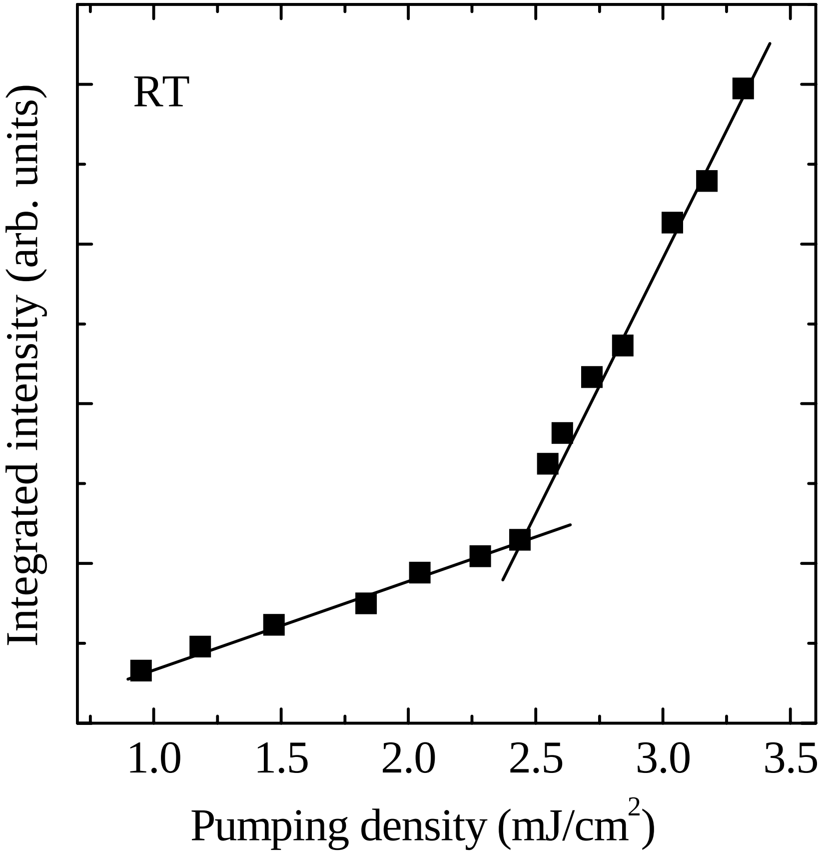


Y. Tominaga, et.al, APL 93 (2008)131915

Laser emission from $GaAs_{1-x}Bi_x$ by photo-pumping

- $GaAs_{0.975}Bi_{0.025}$

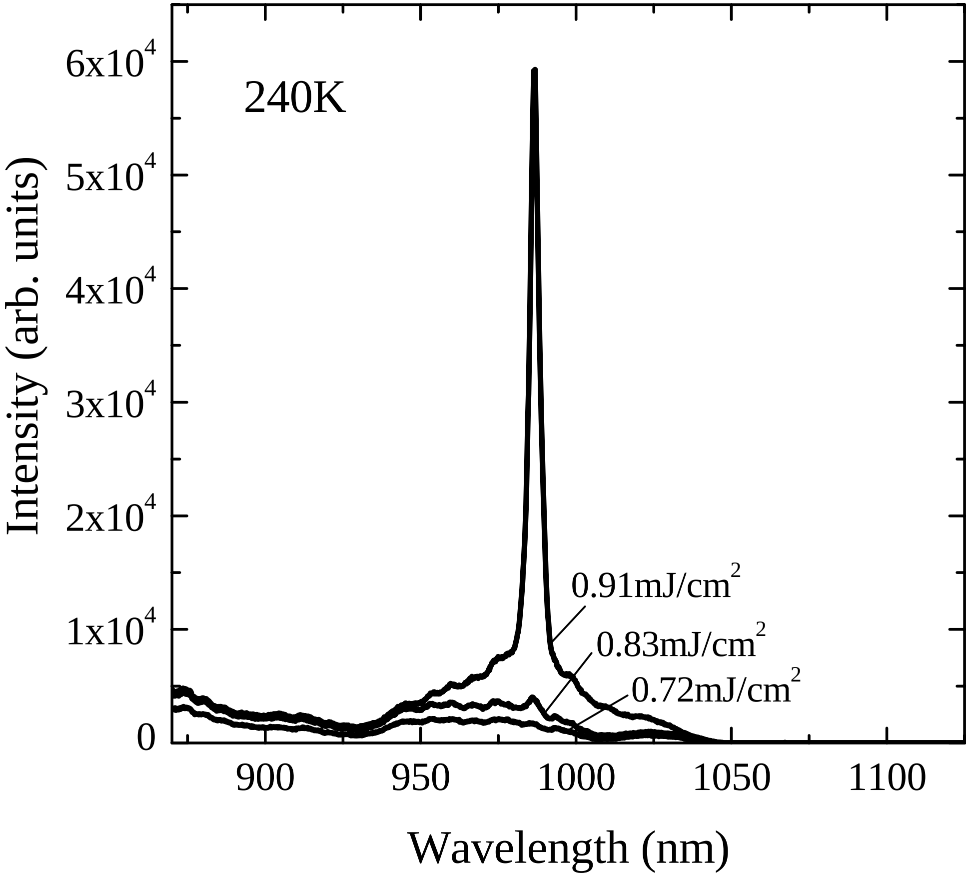


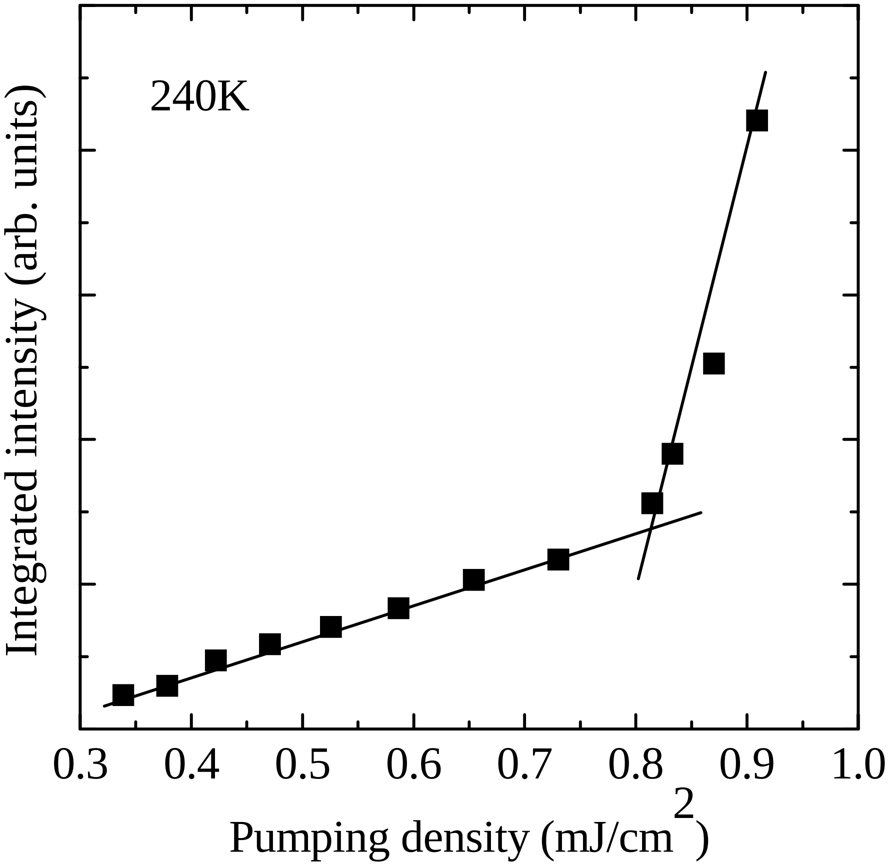


Y. Tominaga, et.al, Appl. Phys. Express 3 (2010) 062201

Laser emission from $GaAs_{1-x}Bi_x$ by photo-pumping

- $GaAs_{0.975}Bi_{0.025}$





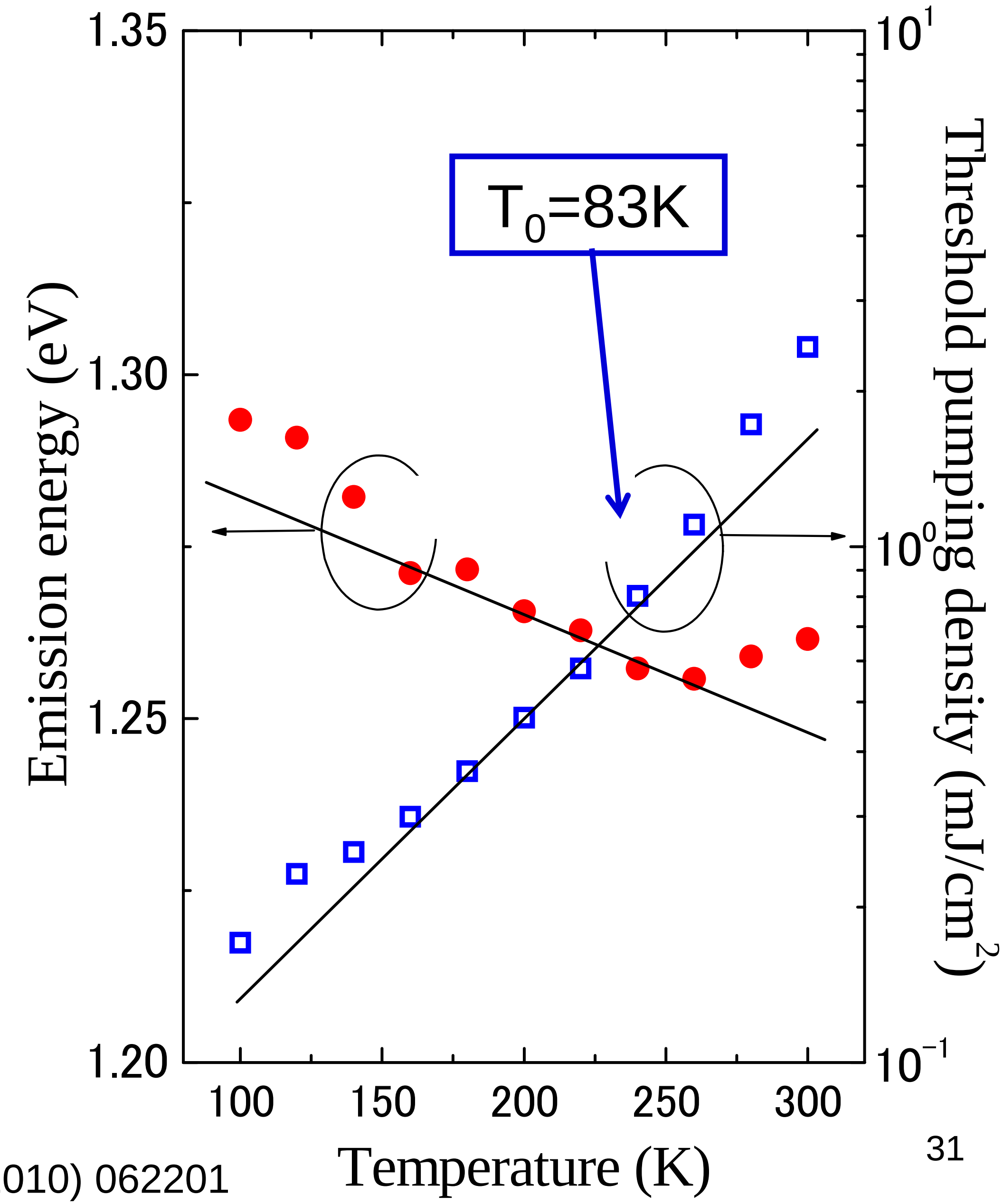
Y. Tominaga, et.al, Appl. Phys. Express 3 (2010) 062201

Temperature dependence of lasing wavelength

◆ $GaAs_{0.975}Bi_{0.025}$

GaBi molar fraction	$\Delta E_{PL}/\Delta T$ 150-300K (meV/K)
0 (GaAs)	-0.42
0.025(Laser)	-0.18
0.025(PL)	-0.15

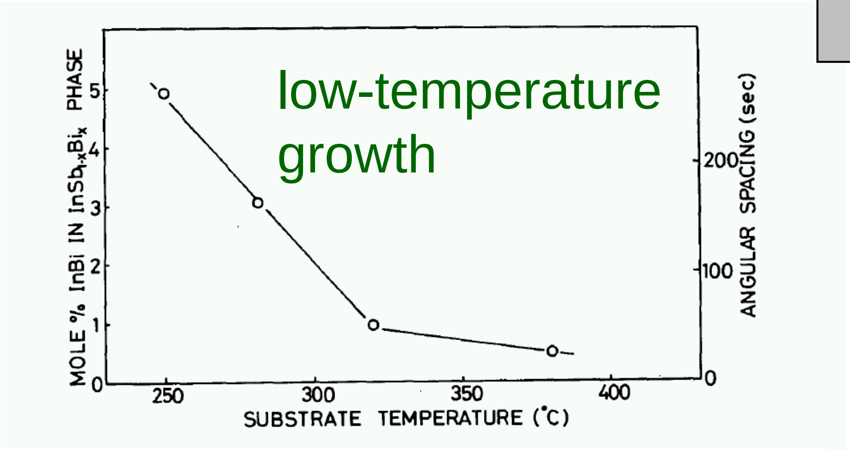
Low-temperature coefficient of lasing wavelength



Y. Tominaga, et.al, Appl. Phys. Express 3 (2010) 062201

Issue of GaAsBi growth

Key to InSbBi growth (1981)

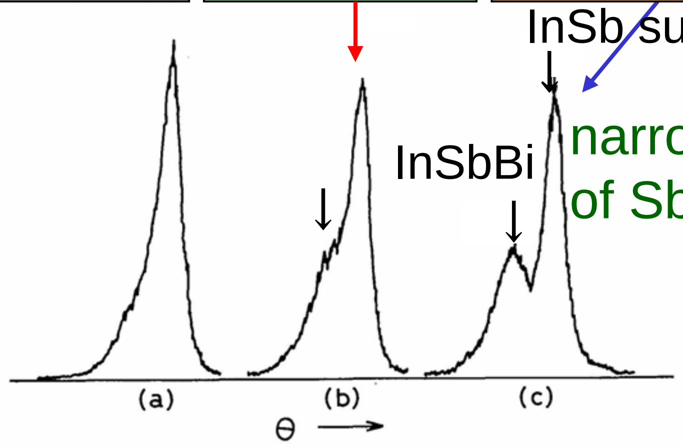


low-temperature growth

☠no growth of InSbBi Sb/In>1

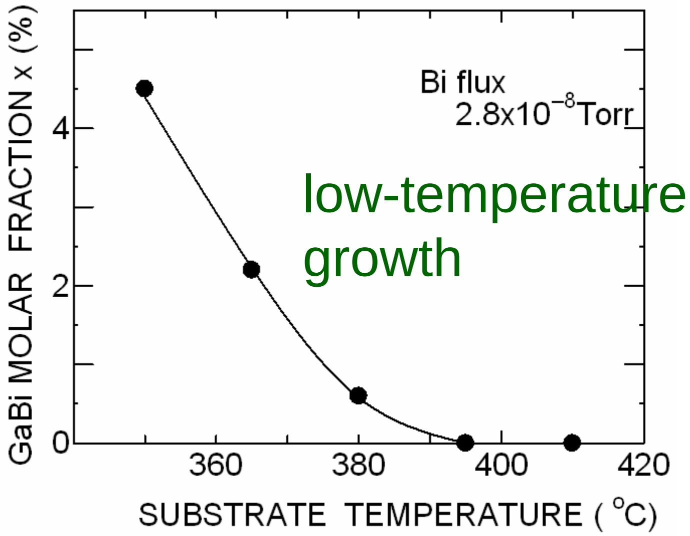
☺mirror-like surface Sb/In≒1

☠rough surface (Sb inclusion) Sb/In<1

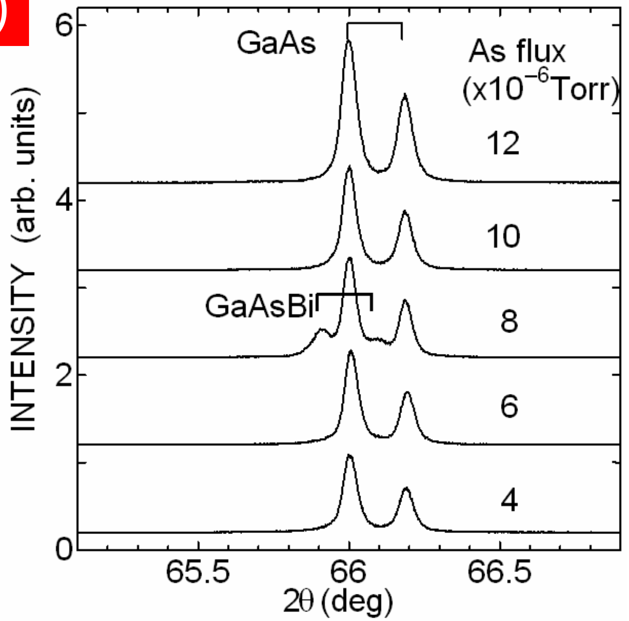


narrow window of Sb/In ratio

Key to GaAsBi growth (at present)



low-temperature growth



narrow window of As/Ga ratio

☠As/Ga>1

☺As/Ga≒1

☠As/Ga<1

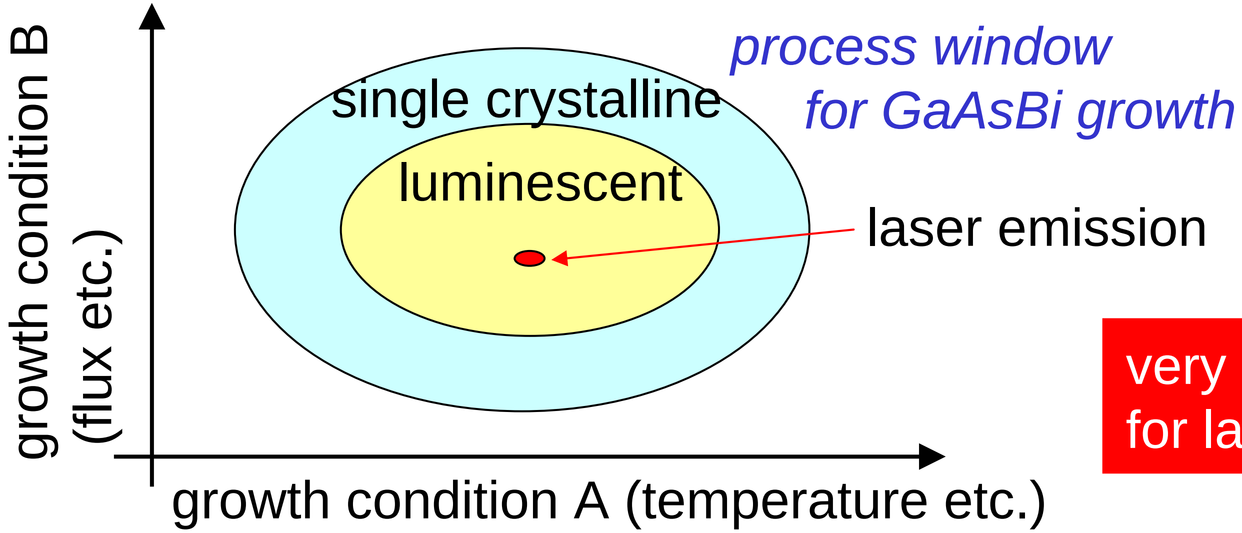
Issue of GaAsBi growth

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^{o}C)

✓As (or Sb) flux adjustment in a limited range on the brink of As (or Sb) shortage on the growing surface



very narrow process window for laser emission

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^{o}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 ^{o}C).

✓***MQW structure***: abrupt interface w/o segregation, thermally stable (<800 ^{o}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.