Growth and Properties of the Dilute Bismide Semiconductor $GaAs_{1-x}Bi_x$

T. Tiedje
University of British Columbia

Outline of Presentation

- Introduction
- Bismuth as a surfactant in semiconductor epitaxy
- Electronic structure of bismide alloys
- Transport properties
- Unsolved problems

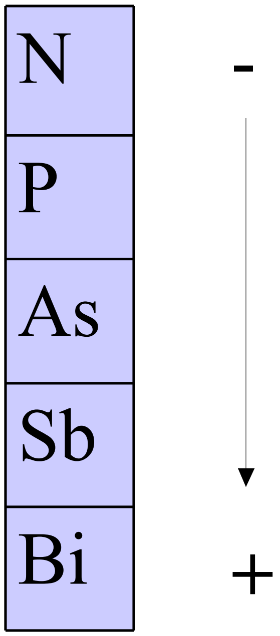
Introduction

- Bi is heaviest non-Radioactive element
- Non-toxic
- Strong tendency to surface segregate in MBE
- Large spin-orbit coupling

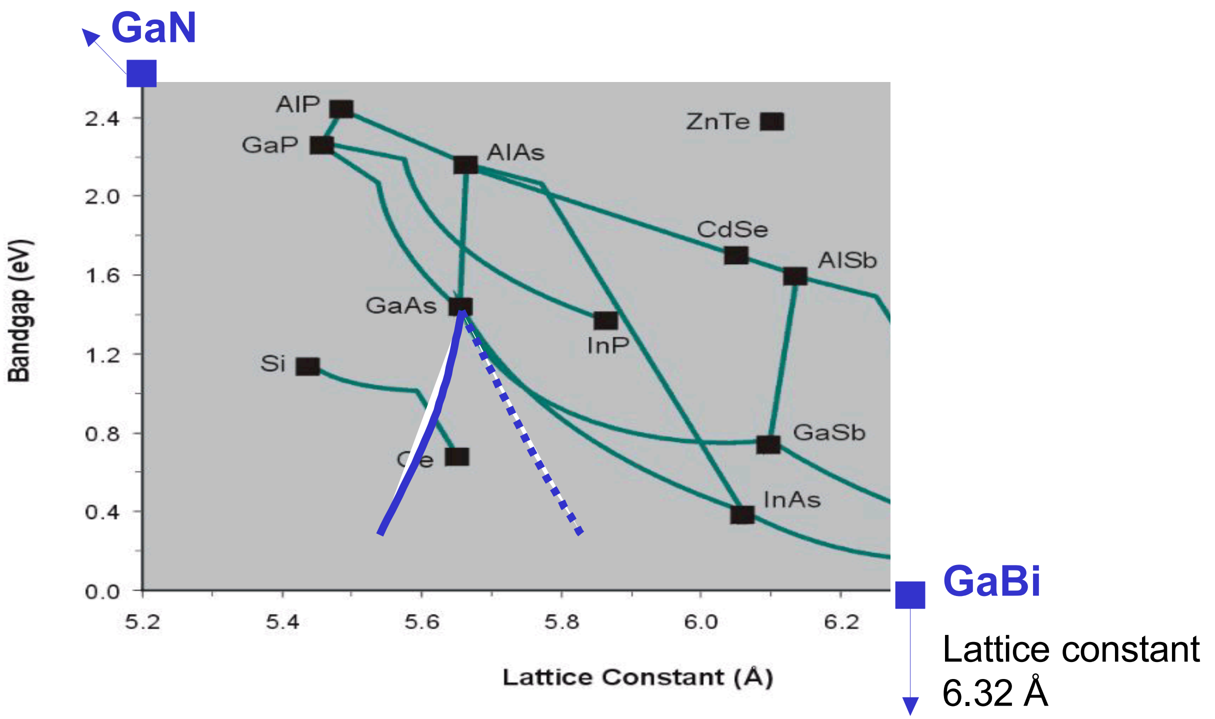
Devices

- Semiconductor alloys with temperature insensitive bandgap (Oe, Kyoto)
- Low threshold, low power HBT (Hase, Sony US6936871, 2006)
- Local strain compensator for nitrogen, solar cells (Mascarenhas, NREL)

Group V



Giant Bandgap Bowing in Both Nitrides and Bismides

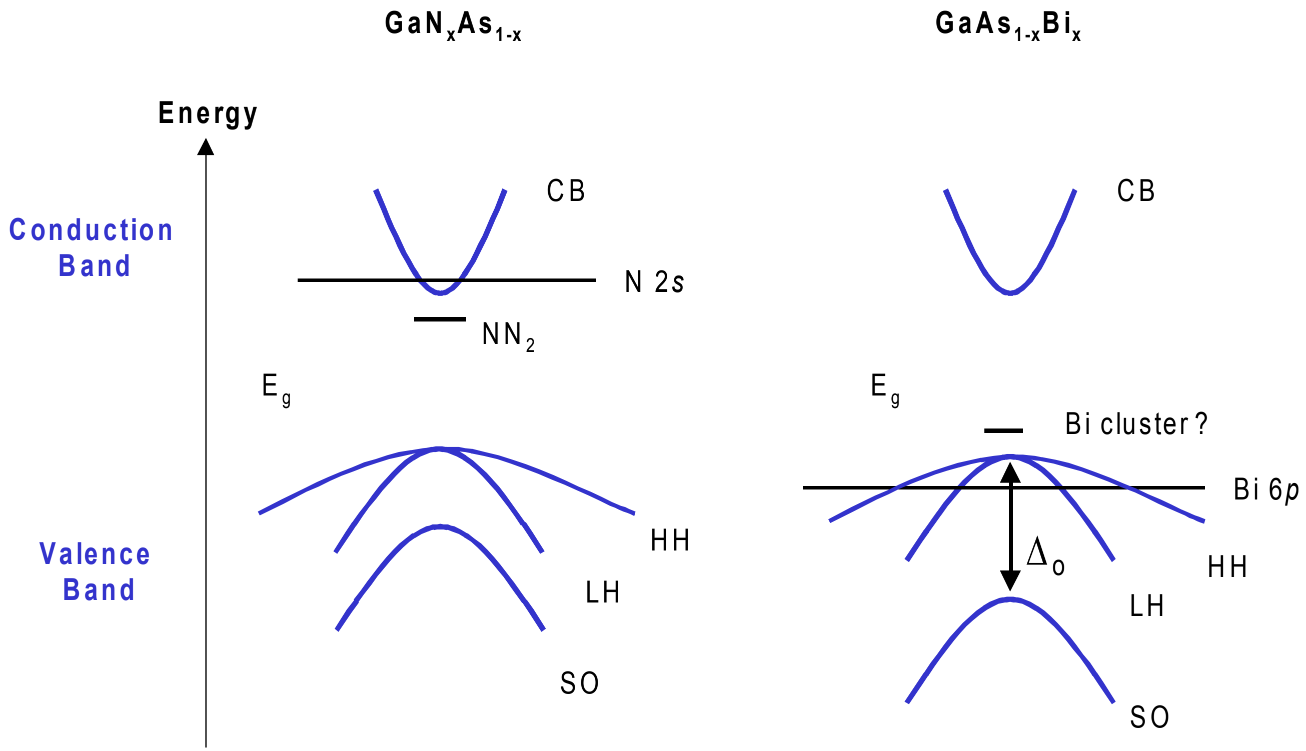


Bandgap bowing with Bi:
88 meV/%Bi

Francoeur et al, APL **82** (2003)

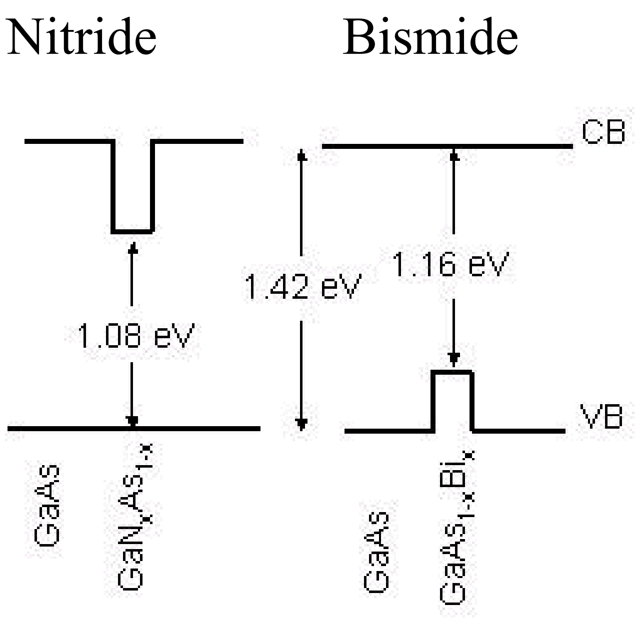
Tixier et al. APL 82, 2245 (2003)

States of Impurity Elements Resonant with Band Edges



N 2s orbital resonant with the bottom of the conduction band and Bi 6p resonant with the top of the valence band

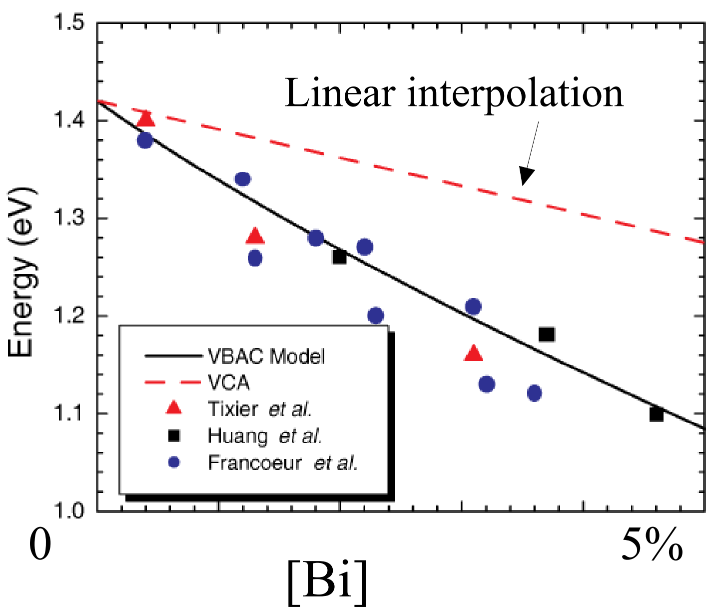
Band Alignment



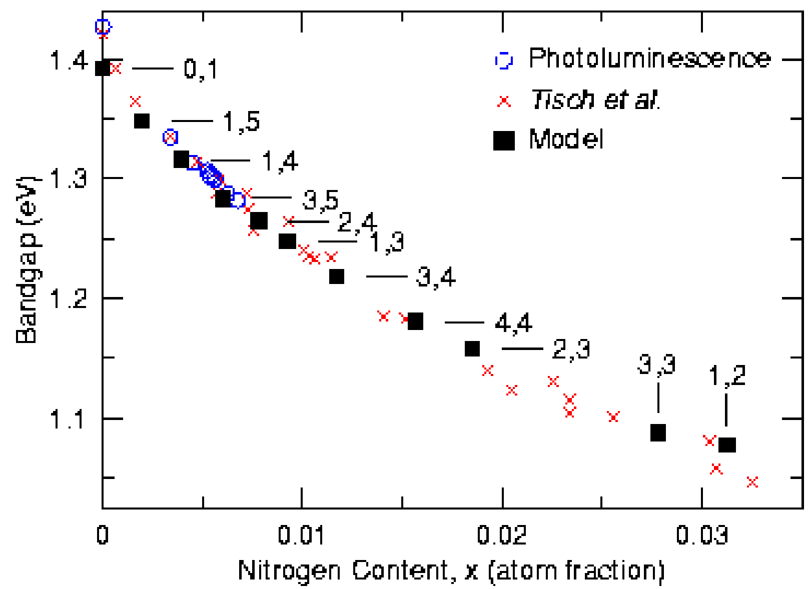
- Drawn to scale for 3% Bi, N
- Favourable band alignment for GaAs/GaAsBi HBT

Giant Bandgap Bowing Effect

Bismide



Nitride

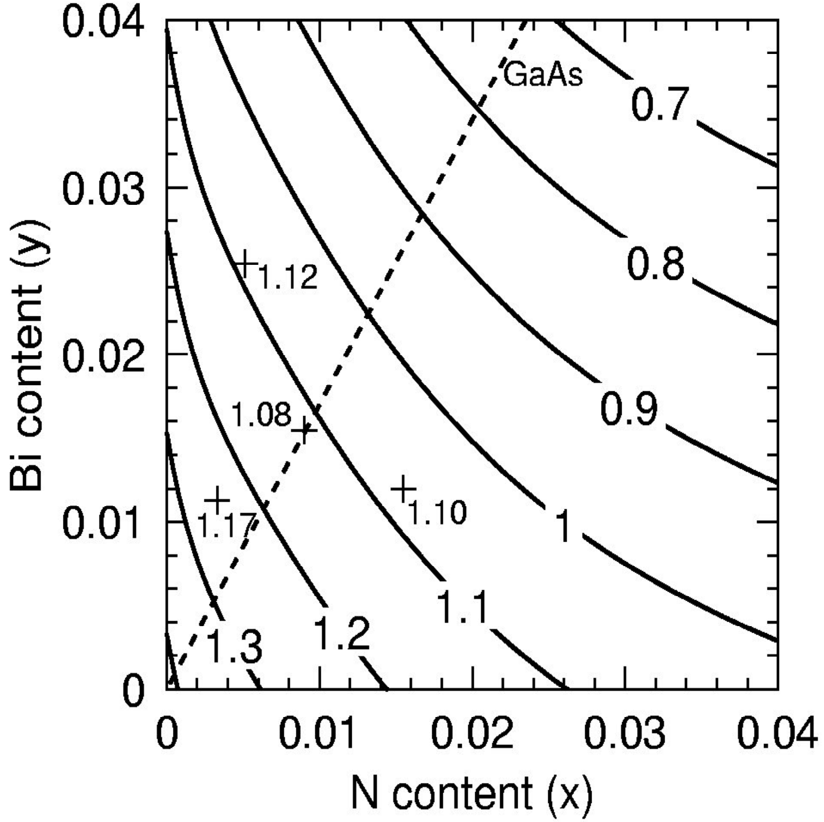


•In bismides, 85 meV/% bandgap change much bigger than in InGaAs which is 11 meV/%

•>100 meV/% in dilute nitride, opposite sign!

E. Nodwell et al Phys Rev. B 155210 (2004)

Bismide-Nitride Bandgap Map



Example, 3.5% Bi + 2% N gives 1.55 μm bandgap, lattice matched to GaAs

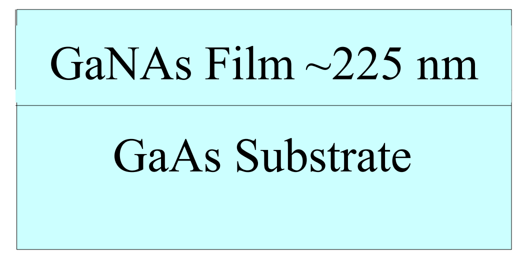
Tixier et al. APL, 86, 112113 (2005)

Bandgap control with low N content

Surfactant MBE Growth of Dilute Nitrides

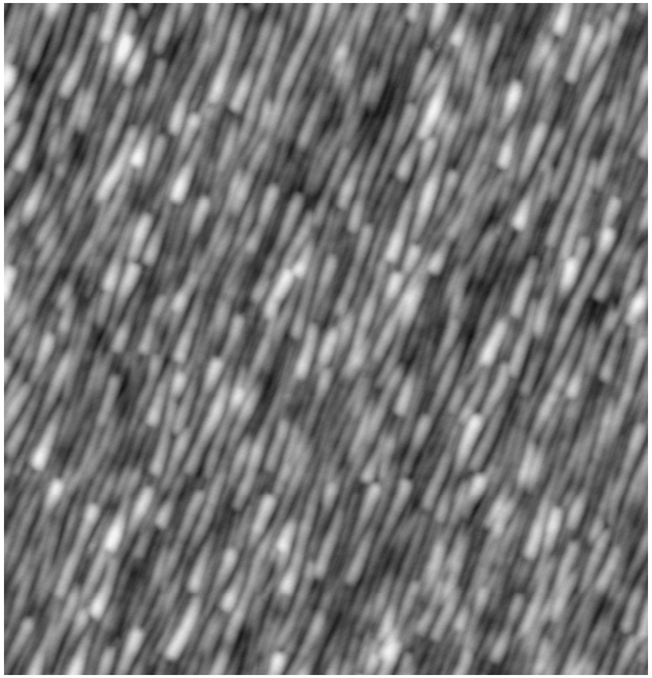
- VG-V80H solid source MBE deposition system
- Helical RF plasma source for nitrogen
- Conventional Knudsen effusion cell for Bi
- Bi BEP up to 10^{-5} Torr, 450-750^{o}C

  incorporation < 2 x 10^{17} cm^{-3}
- Substrate temperatures 400^{o}C - 600^{o}C
- V/III flux ratio between 1 and 8

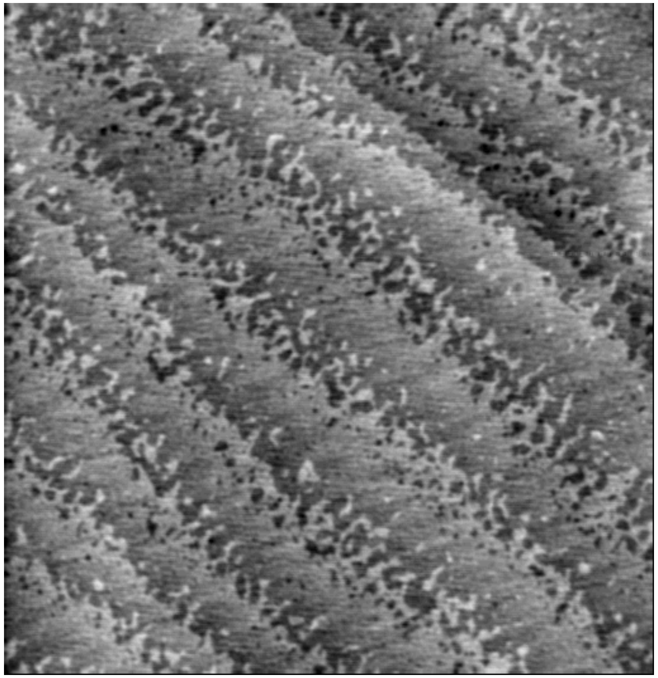


Surfactant Effect on Surface Morphology

2 x 2 μm AFM images $GaN_{0.004}As_{0.996}$



Vertical scale: 10 nm



Vertical scale: 0.8 nm

No Bi Flux
V/III ratio =1, rms ~ 1.2 nm

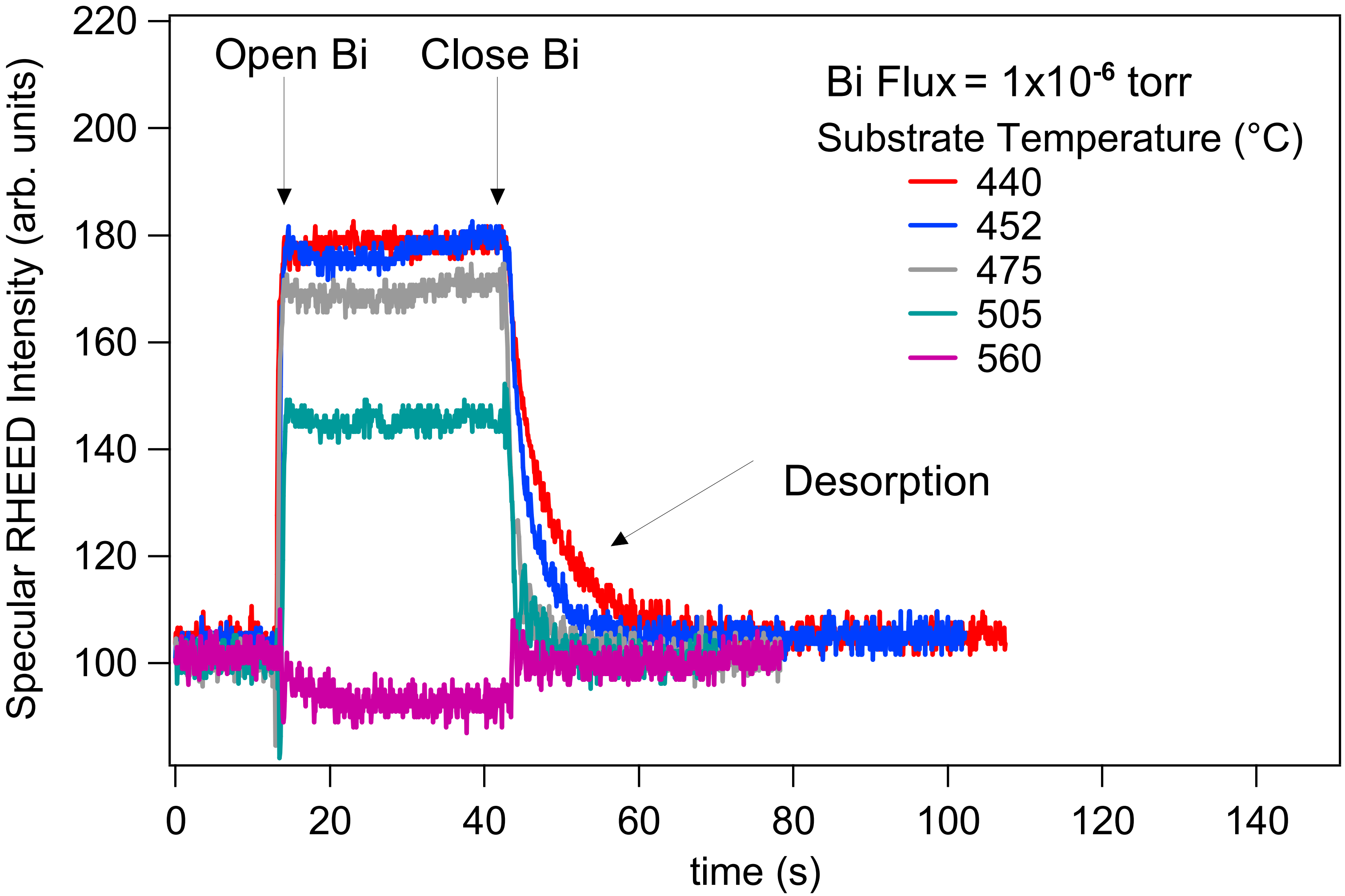
High Bi Flux (~10^{-5} torr)
V/III ratio =1, rms ~ 0.1 nm

- Step flow growth at 460C, no Bi incorporation in SIMS
- Ideal surfactant?

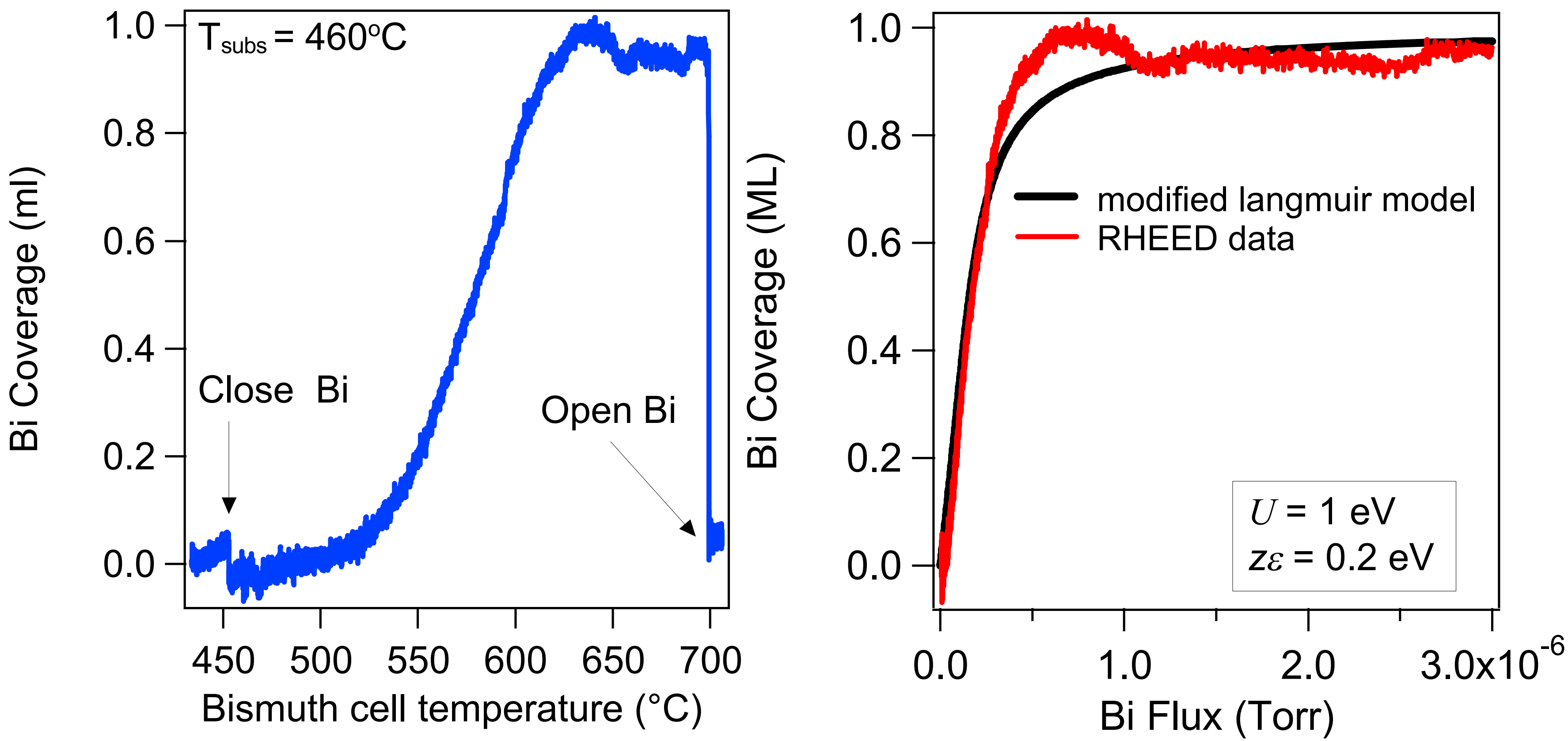
Tixier et al., J. Cryst. Growth 251 (2003), 449

Measurement of Bi Coverage with RHEED

- Change to 3x1 reconstruction with Bi flux
- Specular intensity increases with Bi coverage



Pressure Dependence of Bi Coverage



Langmuir Model for Bi Surface Coverage

- Langmuir isotherm modified to include attractive Bi-Bi interactions on surface

$$\theta = \frac{bP}{1+bP} \qquad b = b_o \exp\left(\frac{U + z\varepsilon\theta}{kT}\right)$$

θ - Bi surface coverage

P - Bi pressure

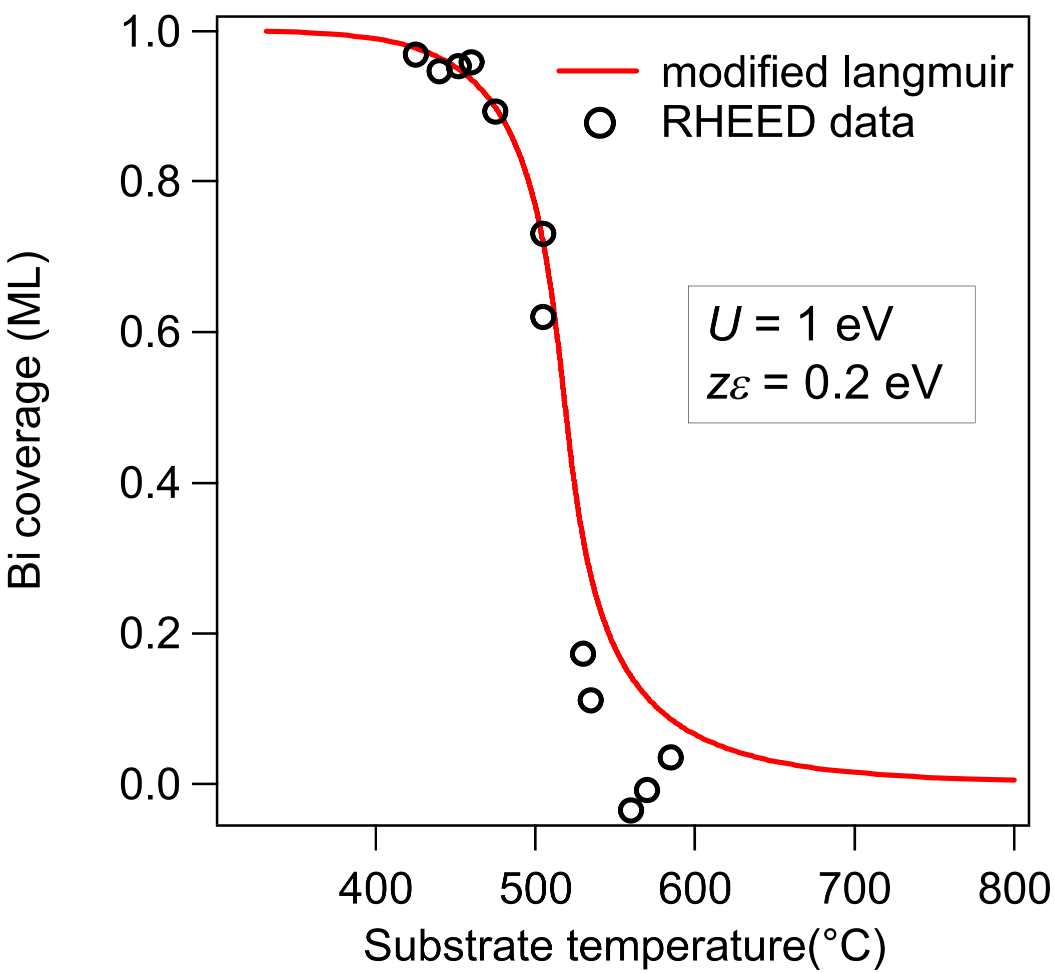
U - binding energy of Bi to the surface

ε - lateral Bi-Bi interaction energy

z - coordination number of Bi

Temperature Dependence of Bi Coverage

- Langmuir isotherm modified for lateral interactions



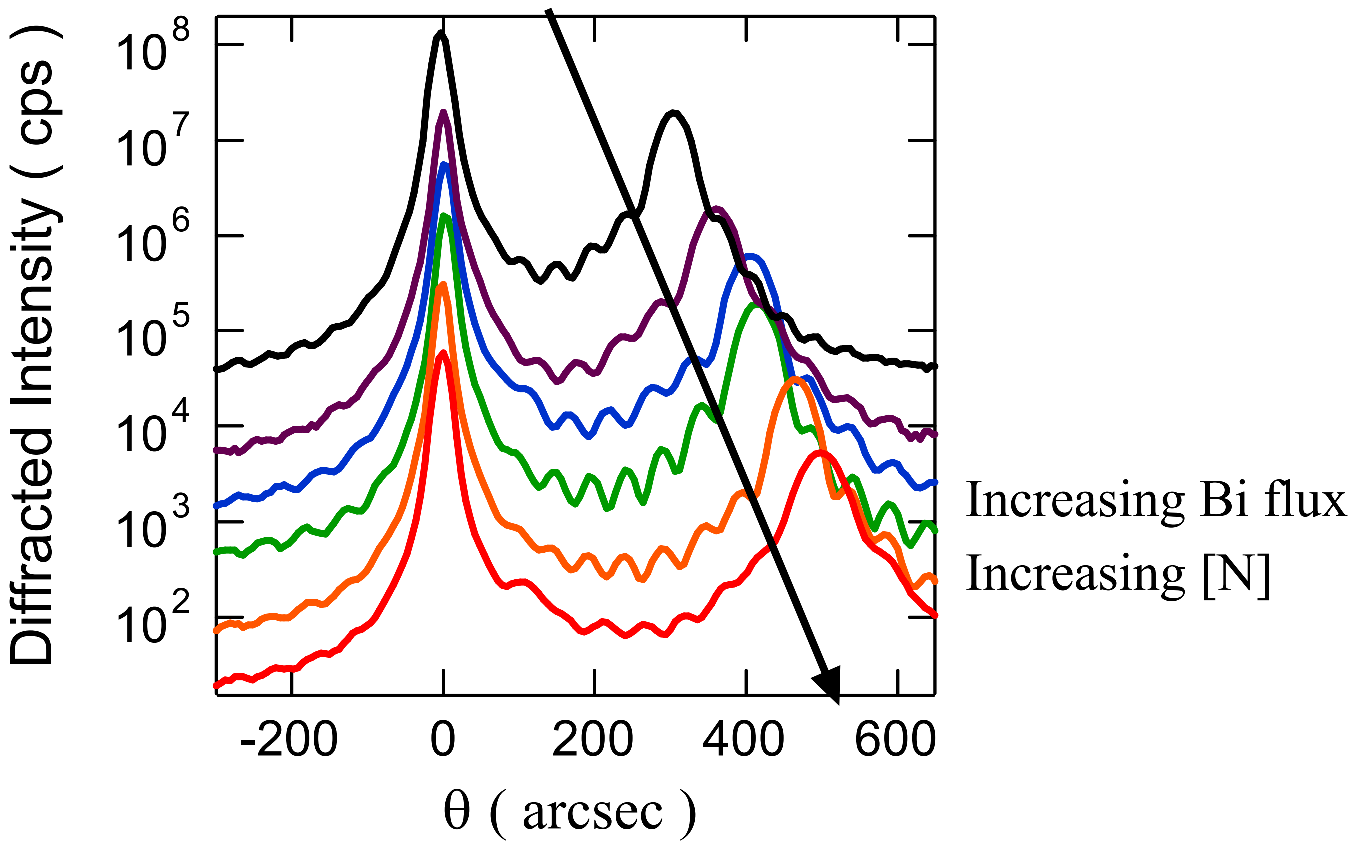
Surface binding energy, vapour pressure, close to liquid Bi

Surfactant layer similar to liquid Bi

E. C. Young et al. J. Cryst. Growth 279, 316 (2005)

Effect of Bi on Nitrogen Incorporation

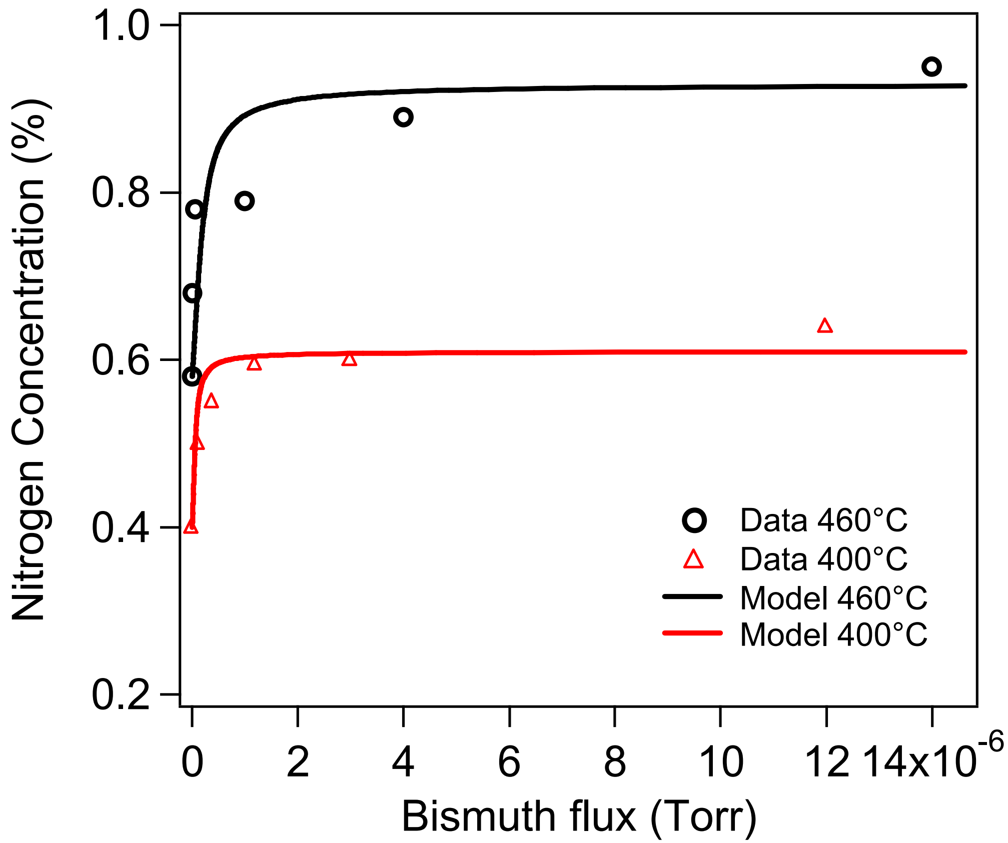
(004) x-ray diffraction peaks



Unexpected behaviour as both N, Bi are group V, competing for lattice sites

Effect of Bi on Nitrogen Incorporation

- N content determined by x-ray diffraction



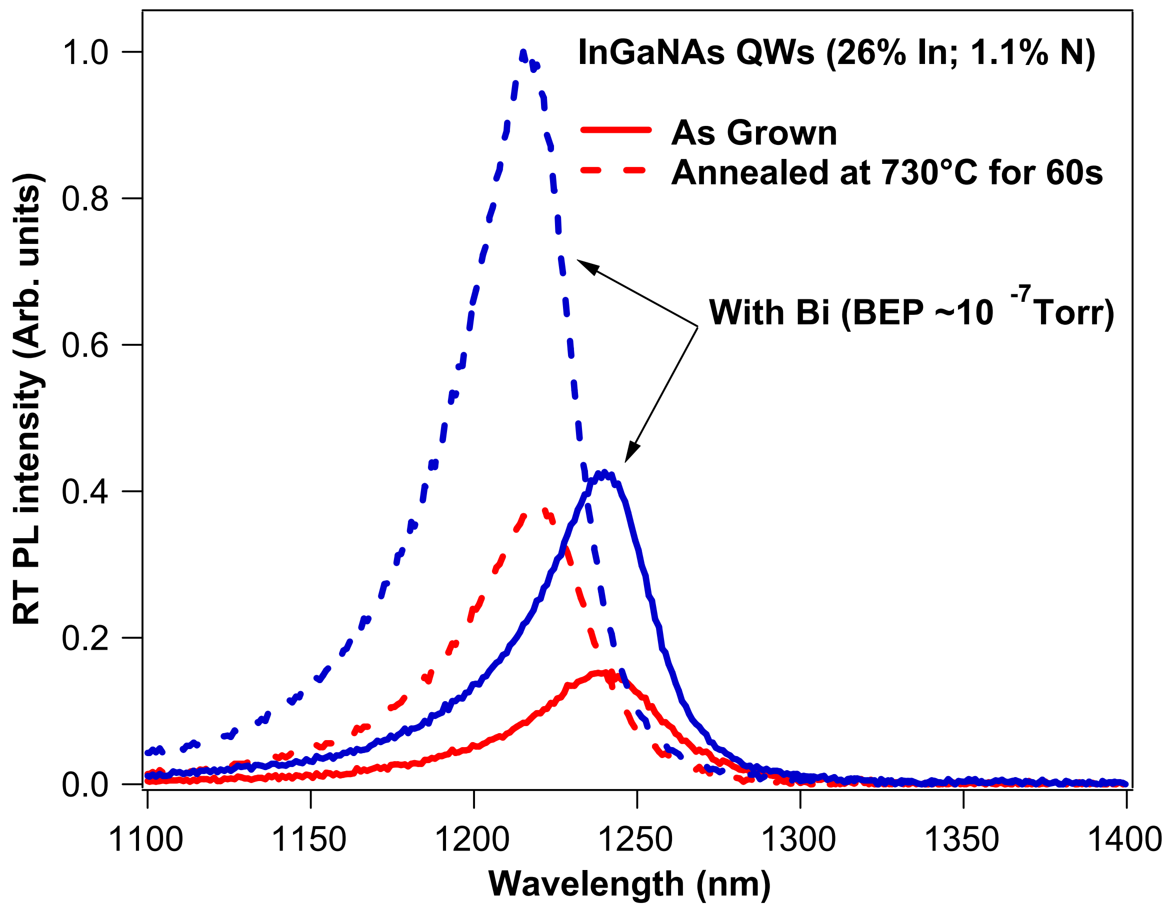
$$[N] \propto \theta_{Bi} + 0.58\%$$

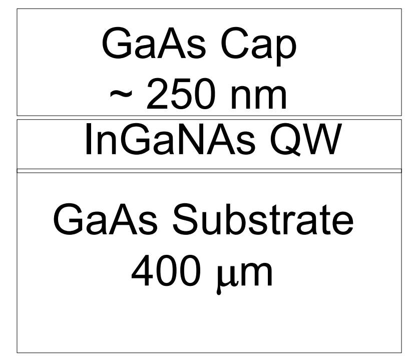
$$[N] \propto \theta_{Bi} + 0.40\%$$

- Possible mechanism: N content increases with Bi coverage due to suppression of AsN re-evaporation (?)

Room Temperature Photoluminescence of InGaNAs:Bi QWs

- low Bi flux ~ 10^{-7} torr

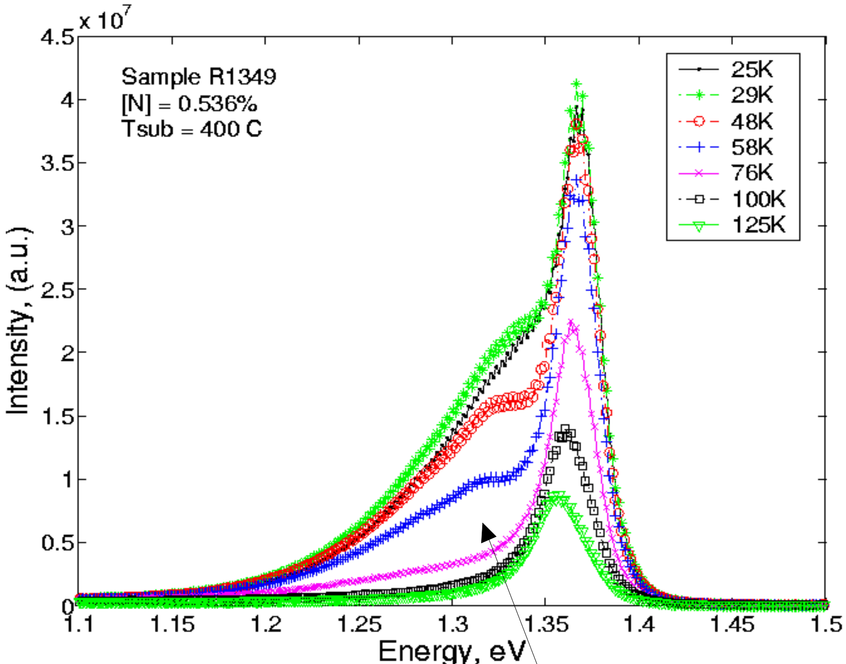




Effect of Bi on PL Spectrum

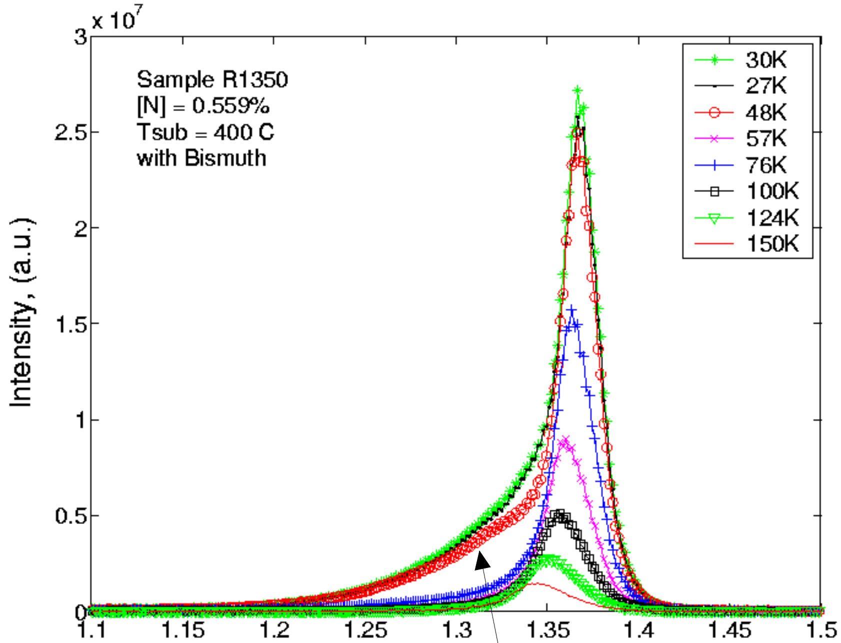
• Temperature dependence of PL spectrum with and without Bi surfactant

0.54% N, no Bi



Emission from N_x cluster states

0.56% N, with Bi



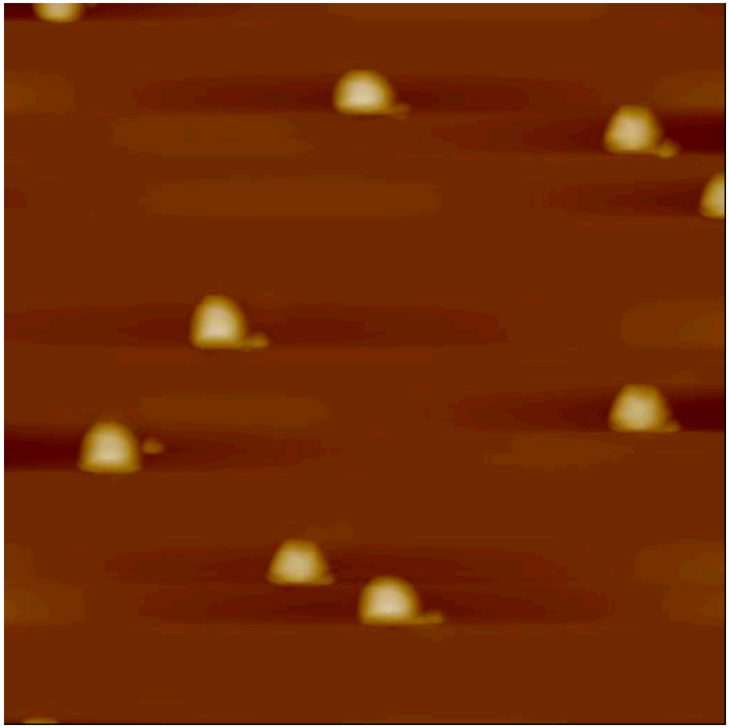
Low energy tail in PL reduced with Bi

Surfactant reduces density of localized N cluster states

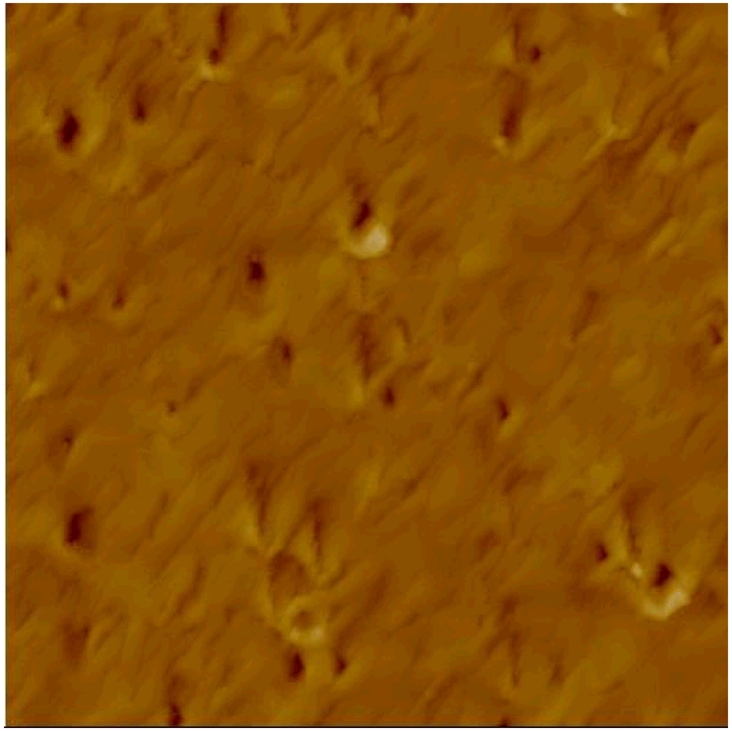
D. Beaton, MSc Thesis UBC

Challenge of GaAsBi growth:

→ avoid Bi and Ga droplet formation

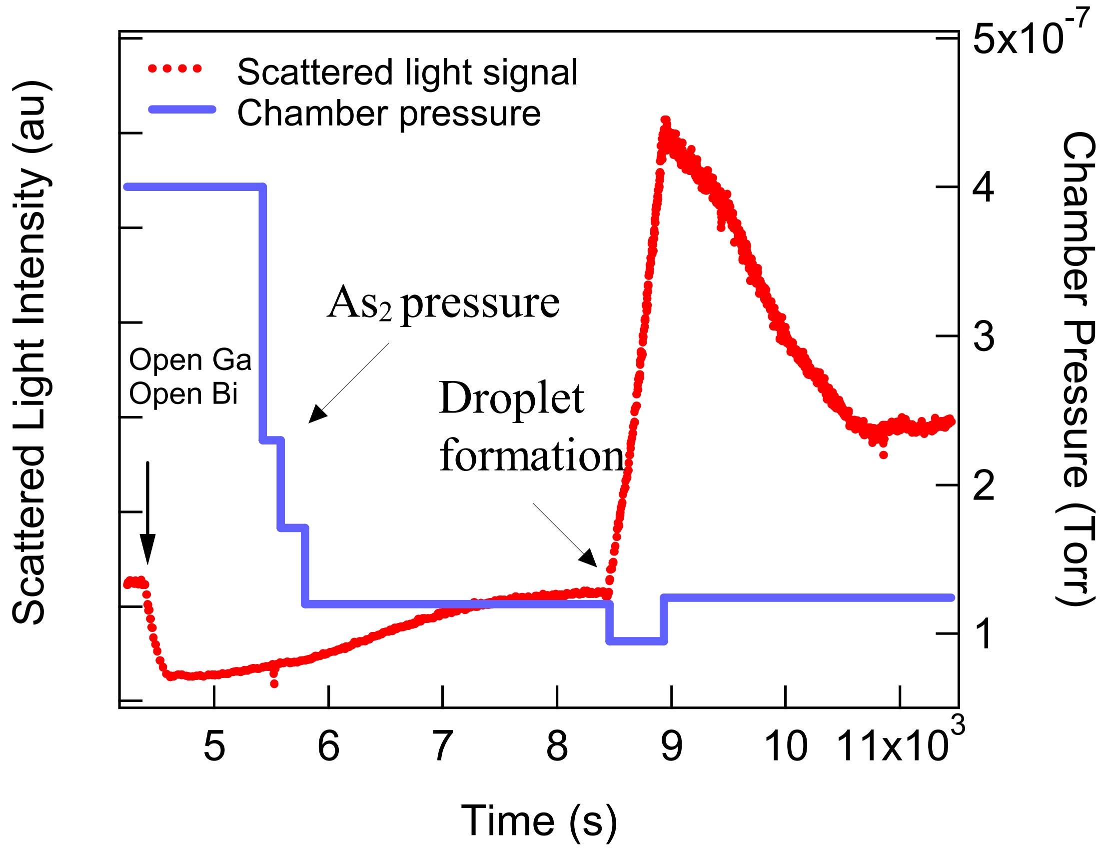


5 x 5 μm scan
Vertical scale 350 nm



10 x 10 μm scan
Vertical scale 250 nm

In-situ Light Scattering Guides MBE Growth

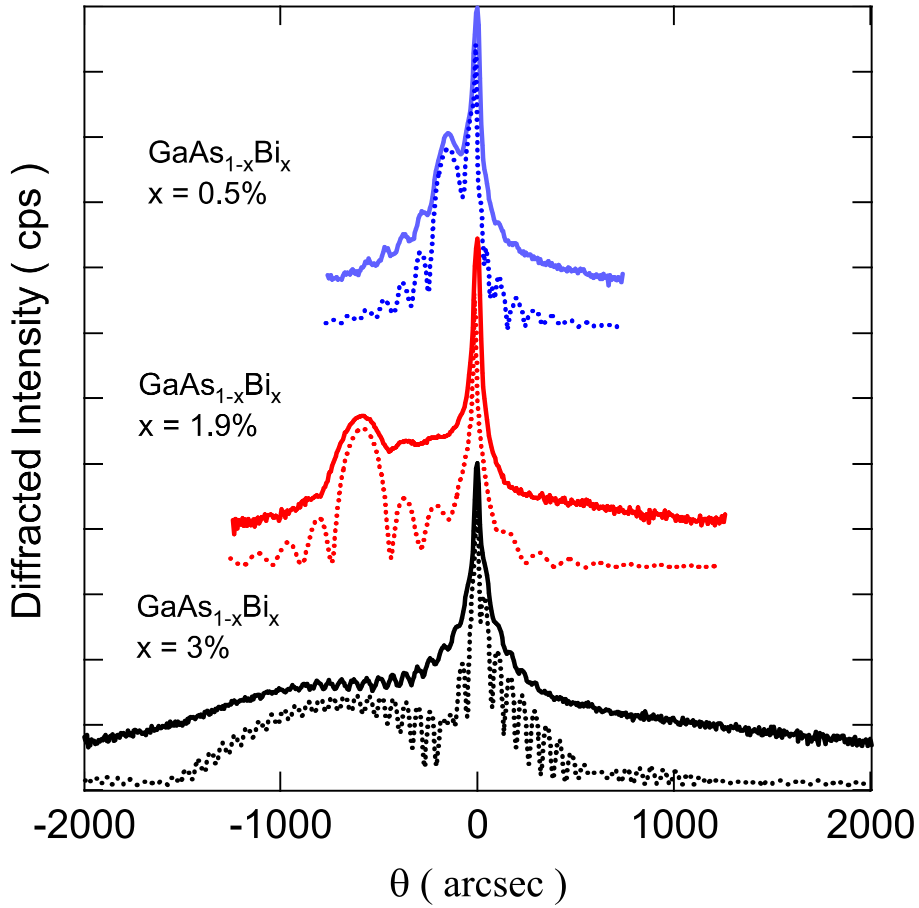


•UV light scattering highly sensitive to metal (Ga, Bi) droplet formation

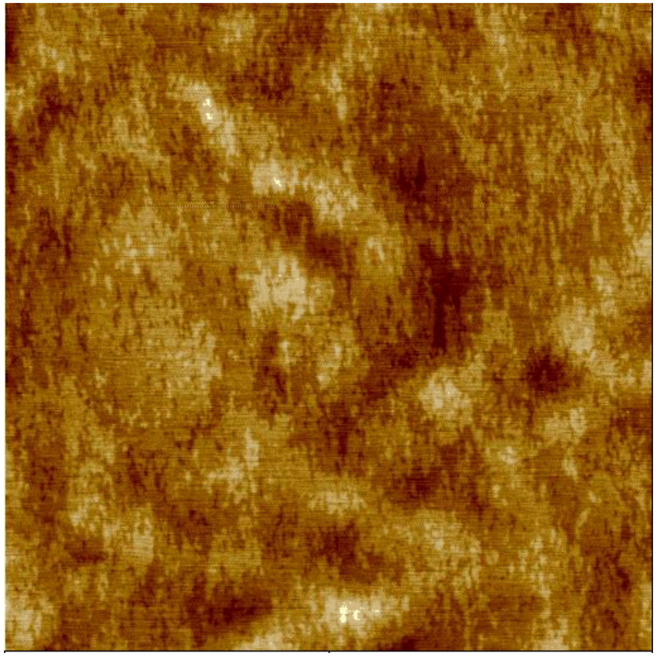
•Narrow process window

E. C. Young et al., Phys. Stat. Sol. (2007)

Good Structural Quality



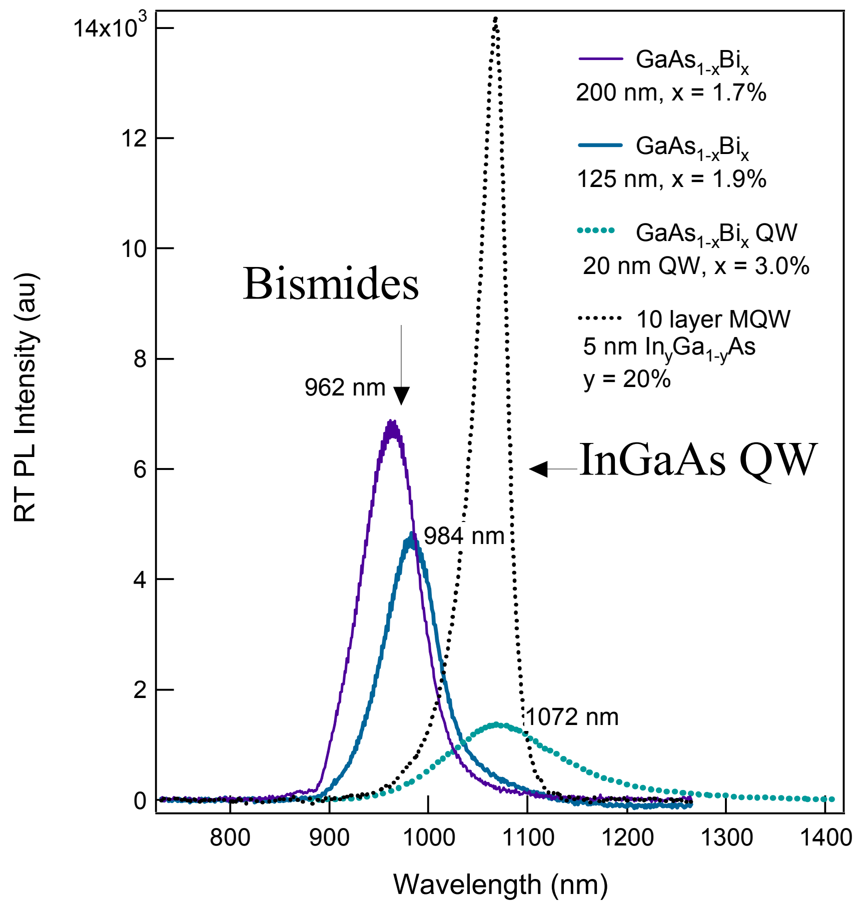
2 x 2 μm AFM



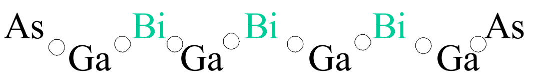
Vertical scale 3 nm
rms roughness 0.205 nm
Growth temp. 390 C !!

E. C. Young et al., PSS (2007)

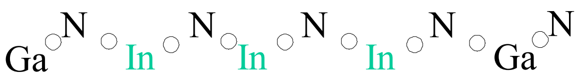
Bismides: Strong Room Temperature Photoluminescence



•Light emitting center a Bi cluster?



•Indium cluster, light emitting center in Ga(In)N

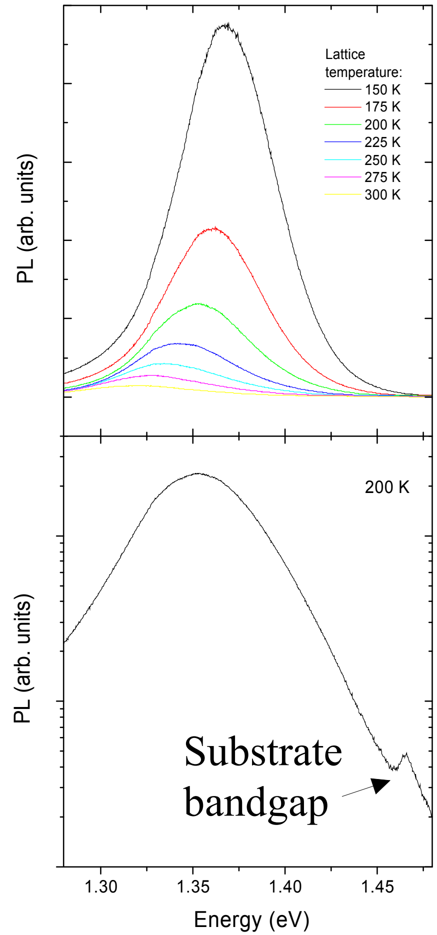


E. C. Young, PhD Thesis, UBC (2007)

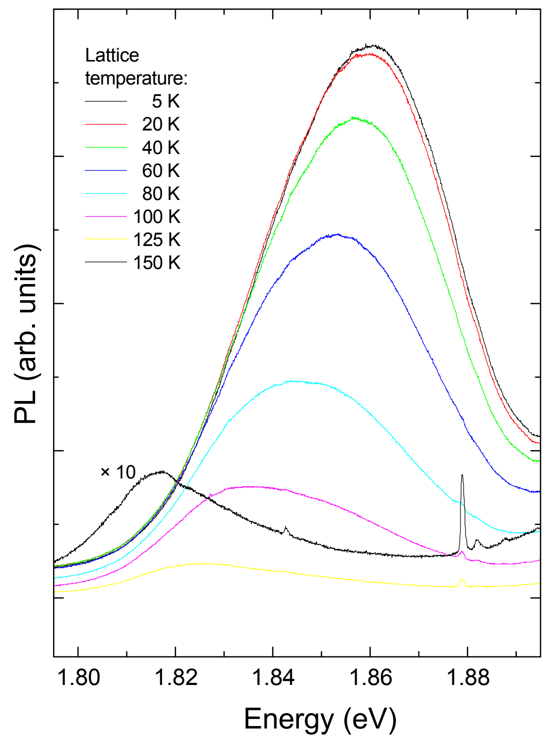
Efficient PL in low temperature grown material (T=360C), that is normally full of As antisites and poor electronic quality

Small Spot Photoluminescence in Bismides

Conduction band to Heavy Hole

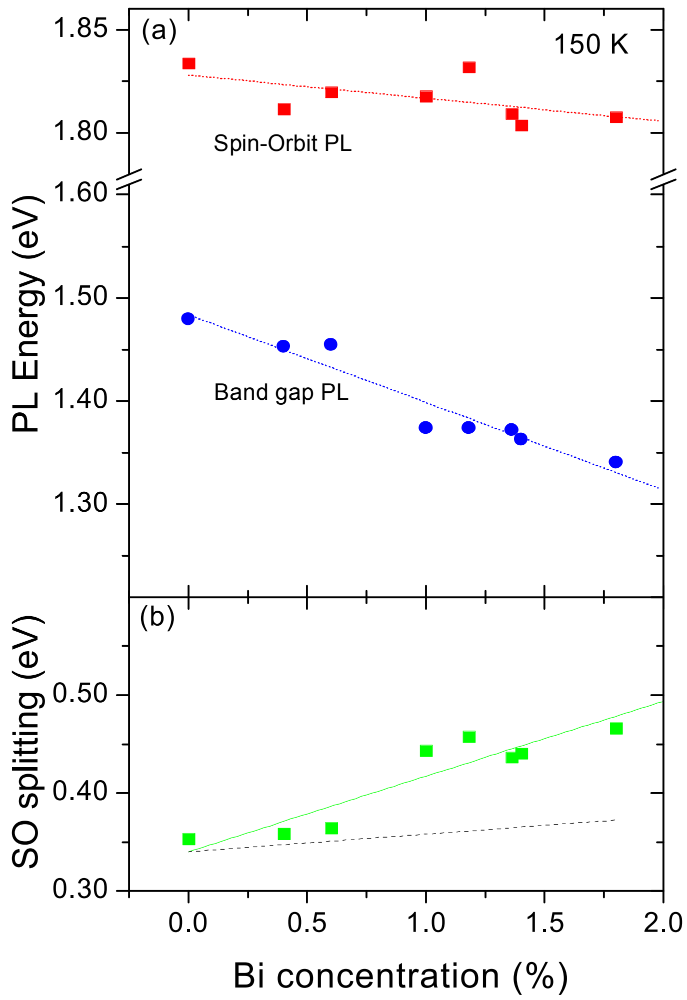


Split-off hole band



S-O hole band measure of spin-orbit splitting   Fluegel, Mascarenhas, NREL

“Giant” Increase in Spin-Orbit Splitting



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

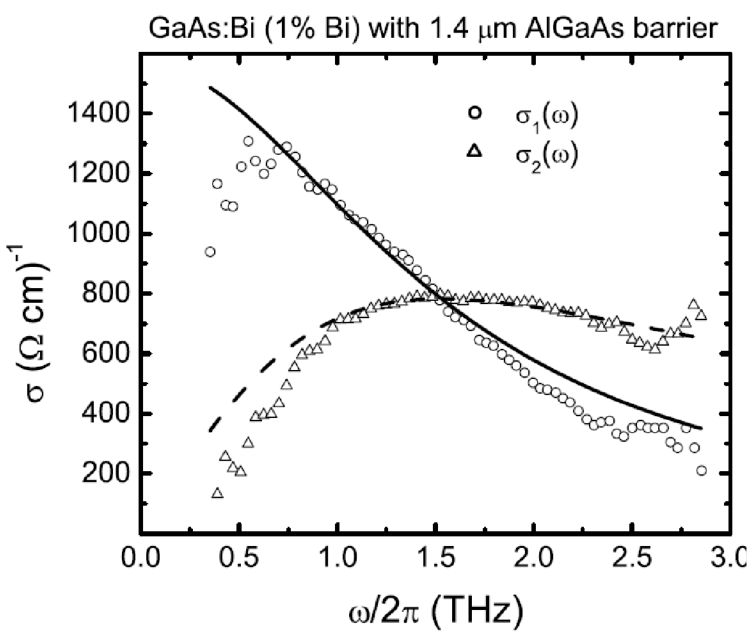
Fluegel, Mascarenhas et al. PRL 97, 067205 (2006)

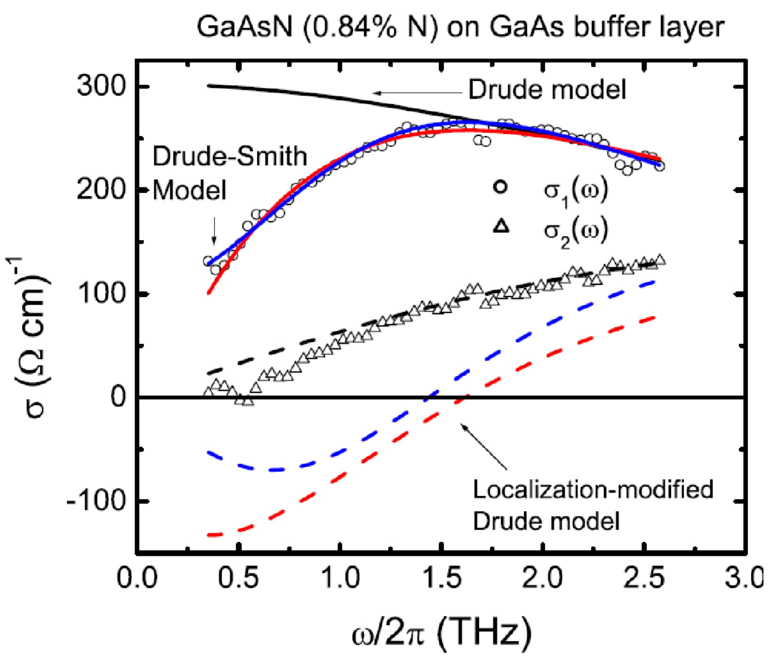
Frequency Dependent Conductivity

Measured 10 ps after optical injection of ~10^{18} cm^{-3} e-h pairs

Bismide: Drude-like

Nitride: non-Drude

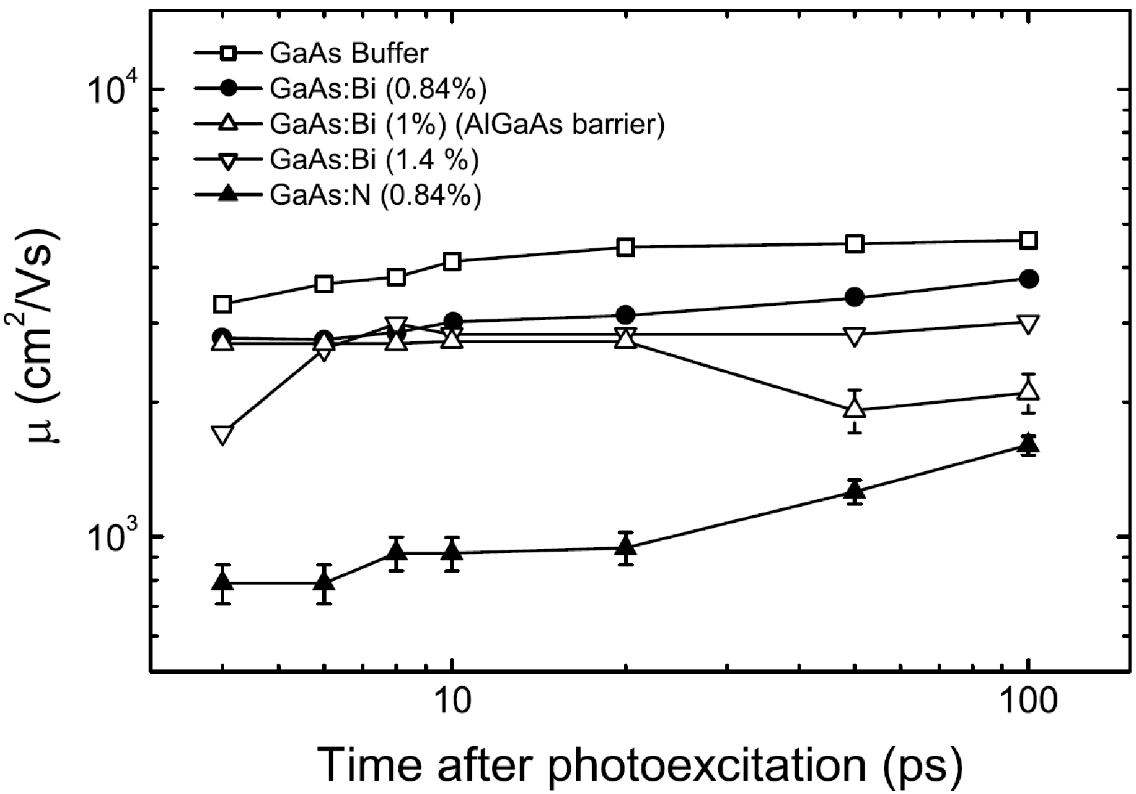




•Conductivity is dominated by electrons

•Bismide result similar to host GaAs, nitride rather different, consequent of N affect on the conduction band. Explanation?

Terahertz Measurements of Electron Mobility



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

D. Cooke, F. Hegmann et al APL 89, 122103 (2006)

Conclusions

- Dilute bismide semiconductors belong to a class of semiconductor alloys with a dilute, impurity-like component, analogous to dilute nitrides (GaAsN) etc.
- Bi is an ideal surfactant (no incorporation) under certain conditions, improves structure and electronic properties, enables low temperature growth
- Need for calculations of spin-orbit splitting in bismides, conduction band and valence band
- Promising device applications

www.phas.ubc.ca/mbelab