Molecular Beam Epitaxy Growth of $GaAs_{1-x}Bi_x$

Dan Beaton, Ryan Lewis, Xianfeng Lu, Mostafa Masnadi-Shirazi, Sebastien Tixier, Erin Young, Martin Adamcyk, UBC, Vancouver, BC

B. Fluegel, A. Mascarenhas, NREL, Golden, CO

D. Cooke, F. A. Hegmann, U. of Alberta, Edmonton, AB

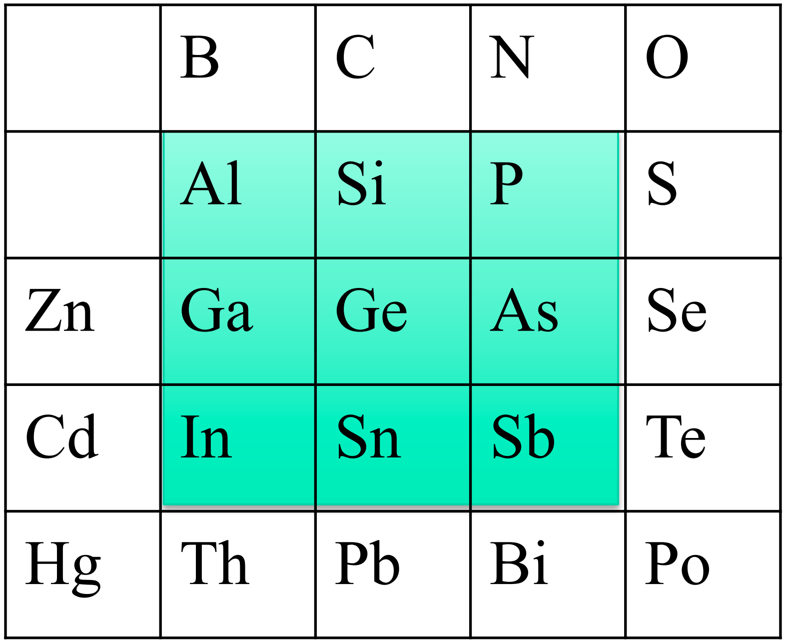
M. J. Fryer, R. A. Herring, T. Tiedje, U. of Victoria, Victoria, BC

Topics

- Surfactant effects
- Bismuth incorporation
- Metal droplets
- Transport and optical properties
- Bismide LED's

University of Victoria
Engineering

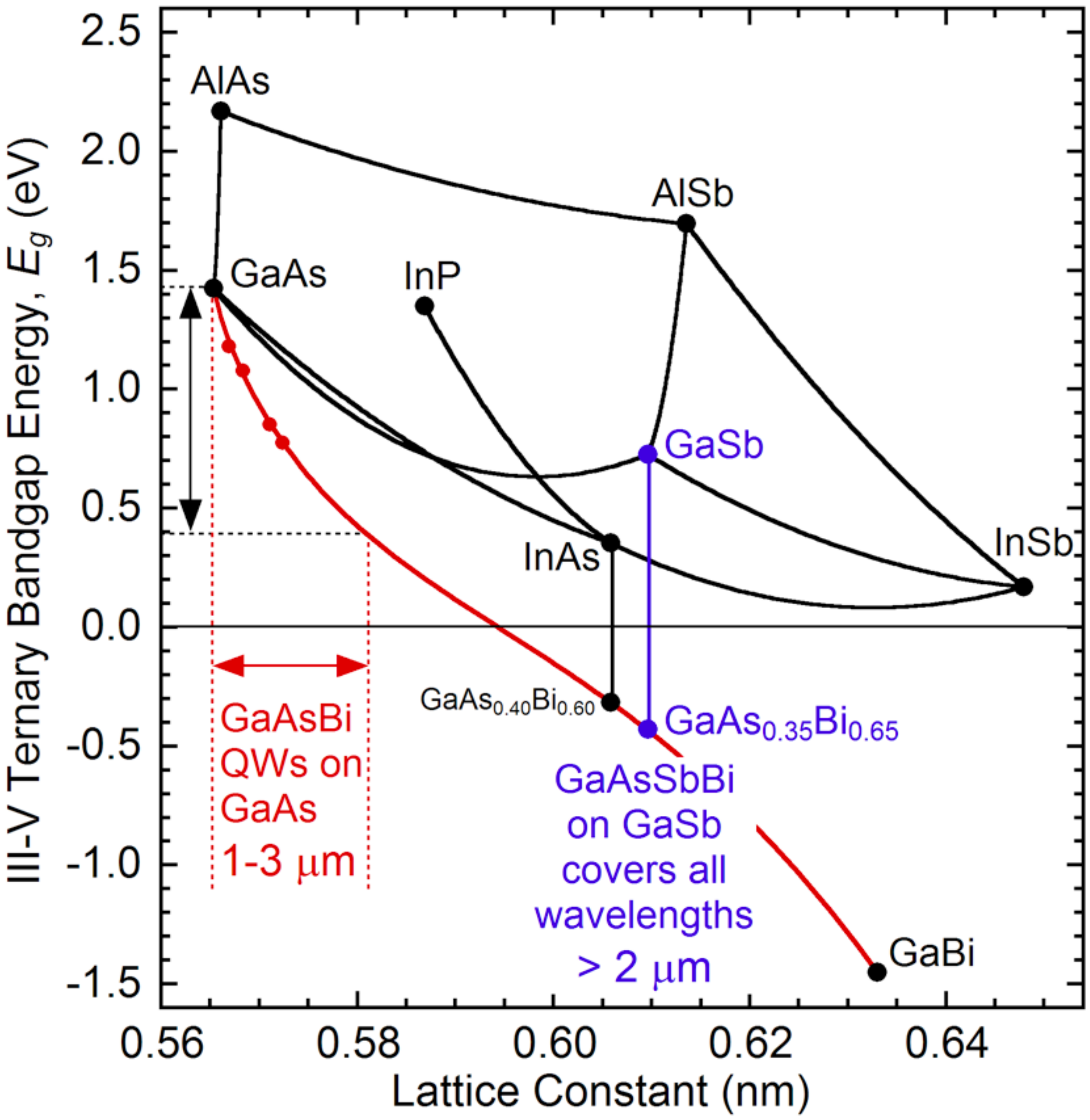
Periodic Table



	B	C	N	O
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te
Hg	Th	Pb	Bi	Po

Semiconductors outside the box

Where else can we go?

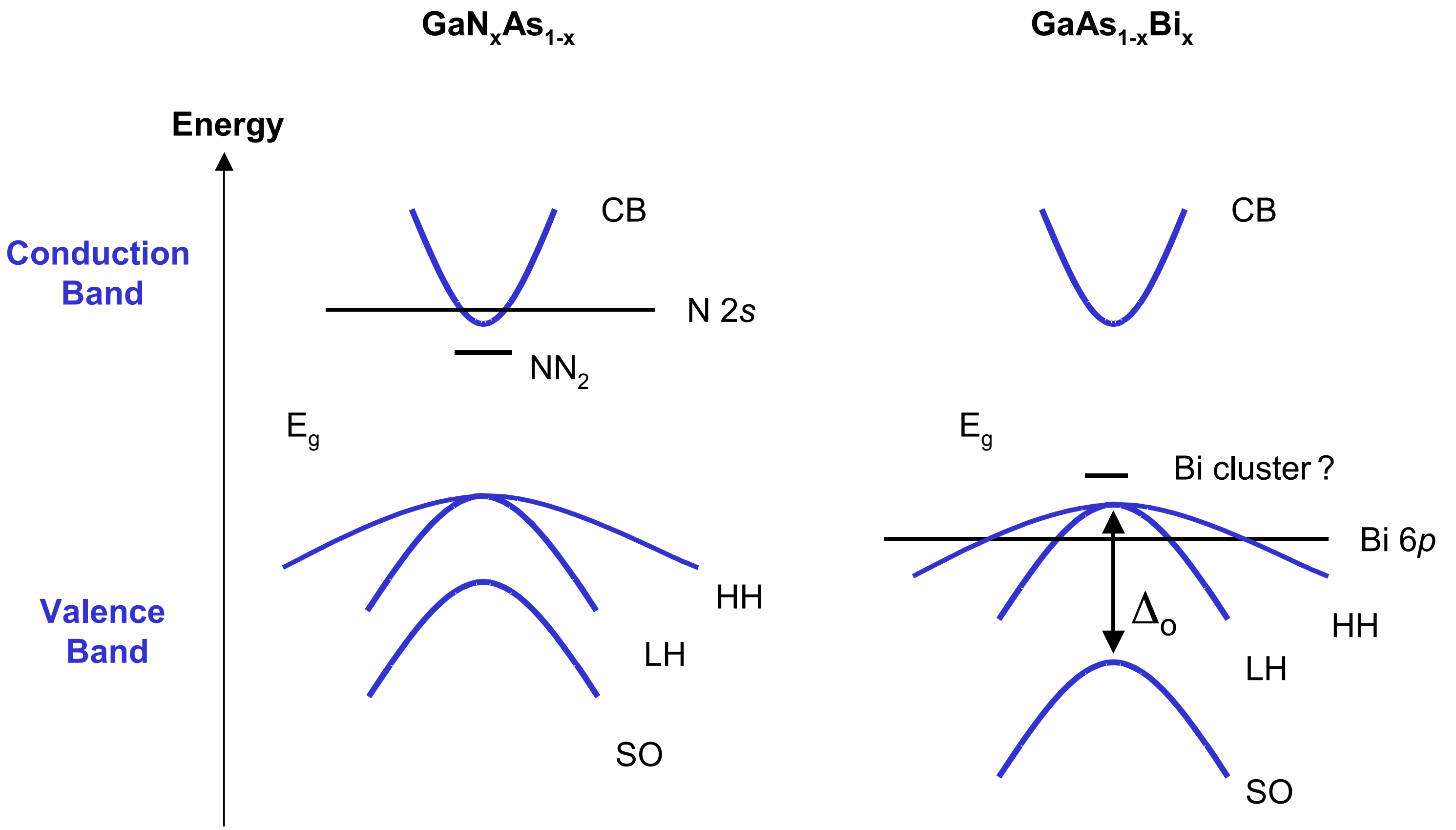


Concentration dependence of E_g as $x \rightarrow 0$:

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

Shane Johnson, ASU

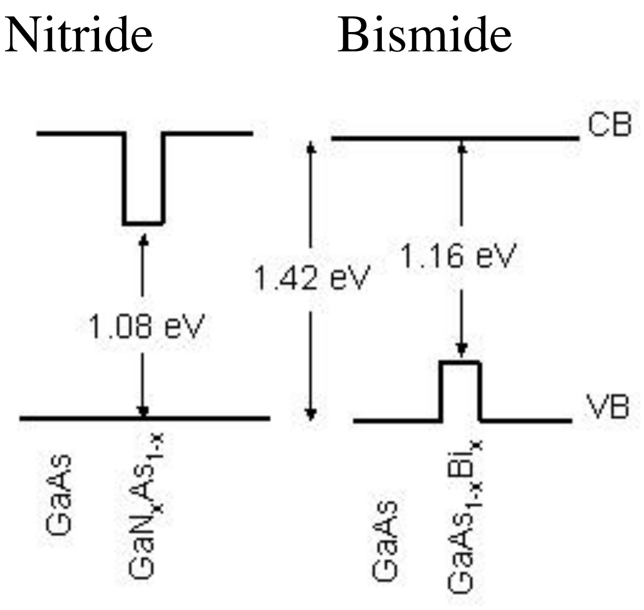
States of Impurity Elements Resonant with Band Edges



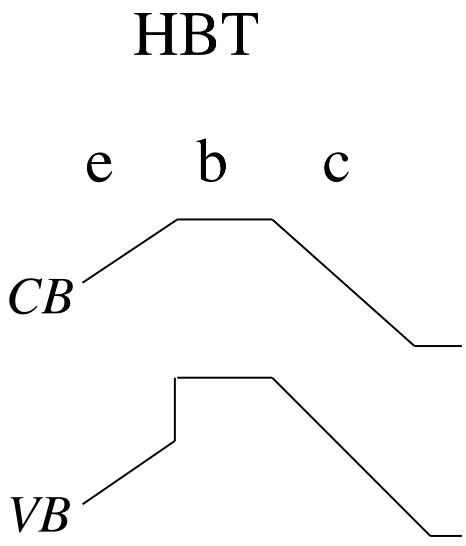
N 2s orbital resonant with the bottom of the conduction band

Bi 6p resonant with the top of the valence band

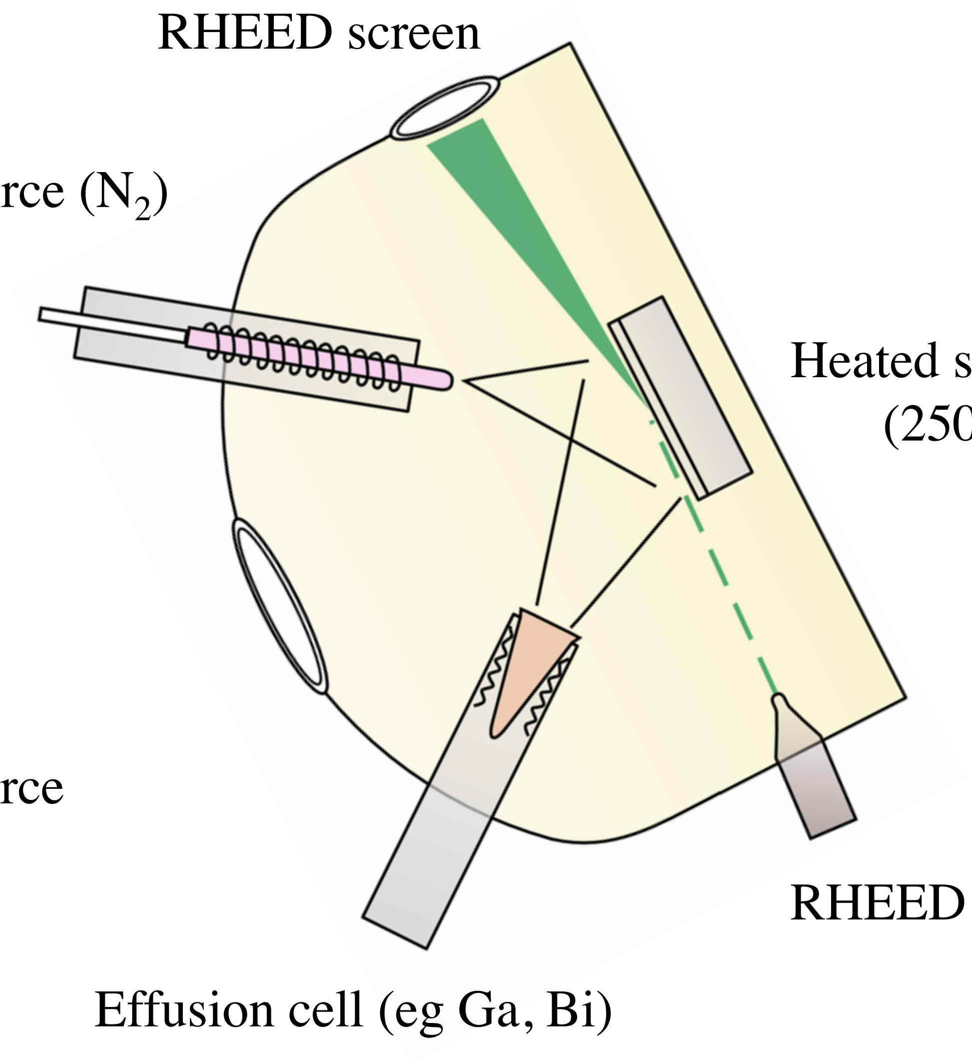
Schematic Band Alignment with GaAs



- Drawn to scale for 3% Bi, N
- Favourable band alignment for heterojunction bipolar transistor



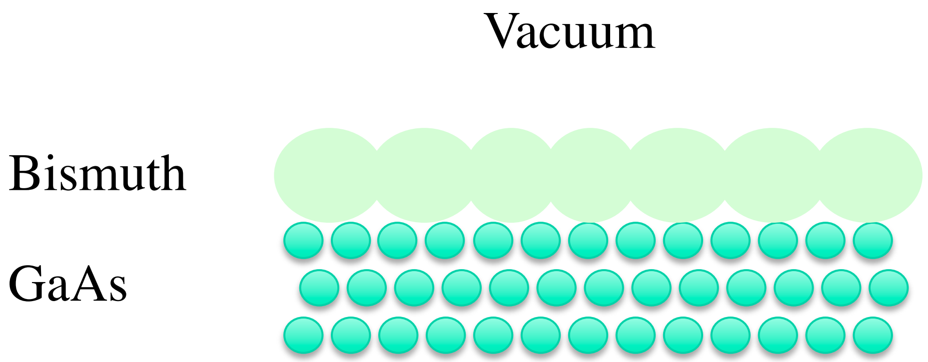
Schematic of molecular beam epitaxy growth chamber



Not shown:

- As_2 cracker cell
- CBr_4 dopant source

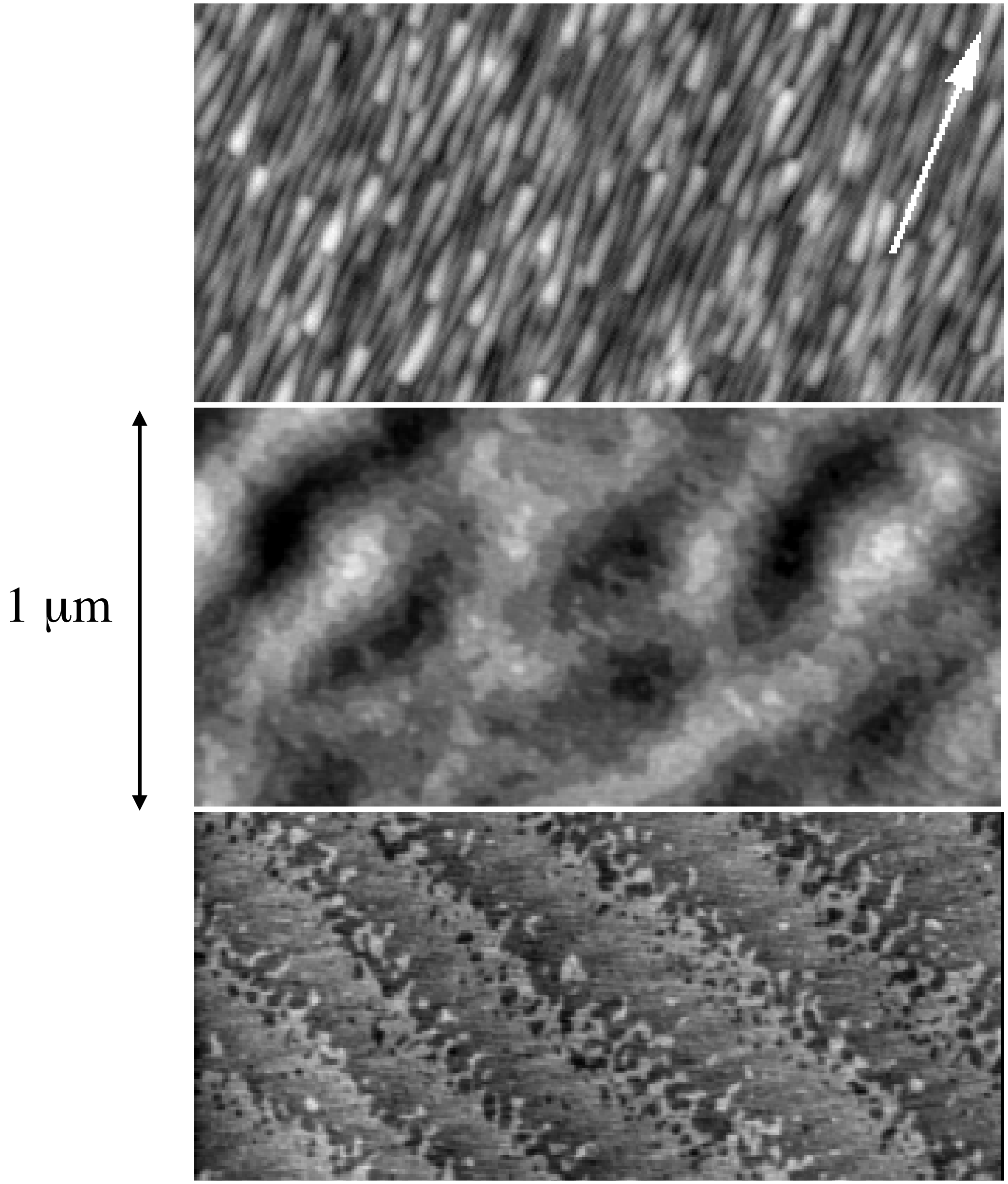
Bismuth acts as a surfactant on GaAs



- 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

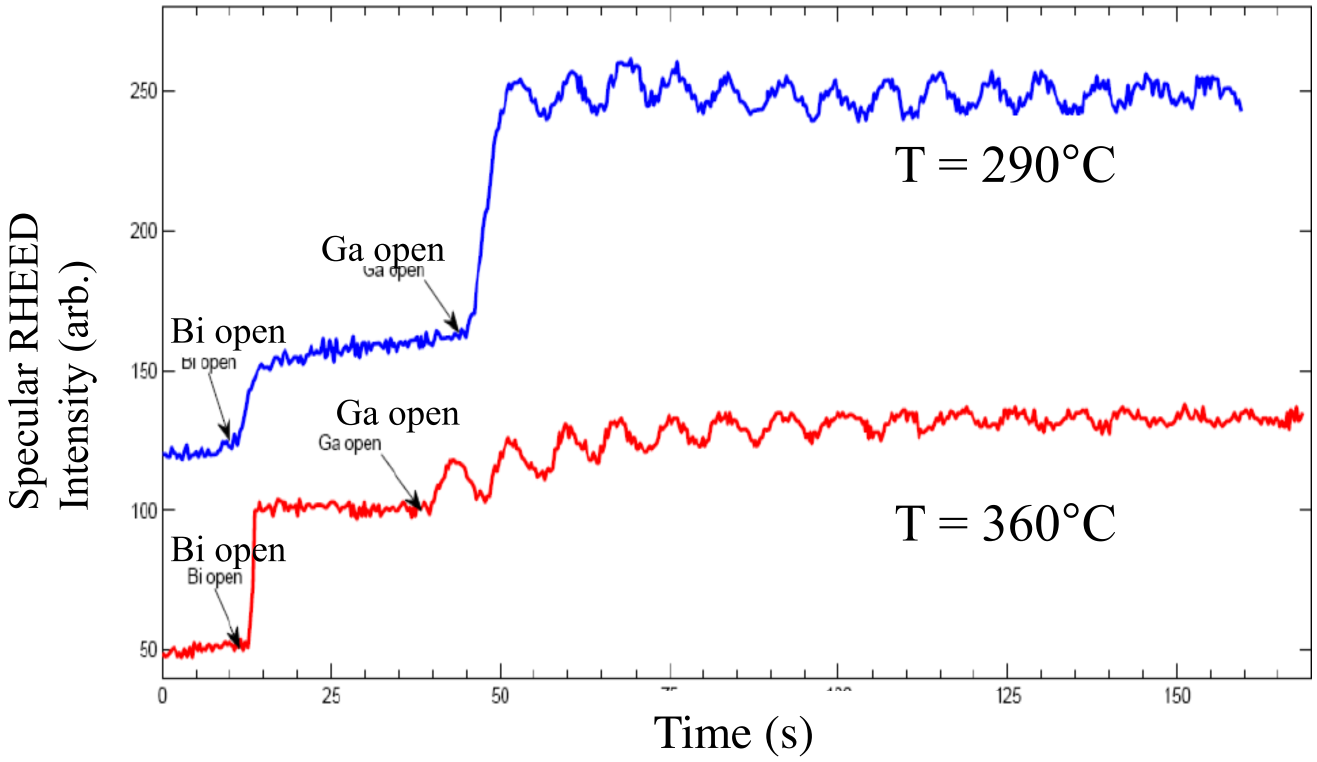
Huge flux!

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

Tixier, Adamcyk et al JCG
2003

RHEED oscillations during growth of GaAs with Bismuth

(not normally observed below ~ 500C in GaAs)



Bi enhances surface mobility enabling RHEED oscillations at low temperature

Substrate temperature 290 C

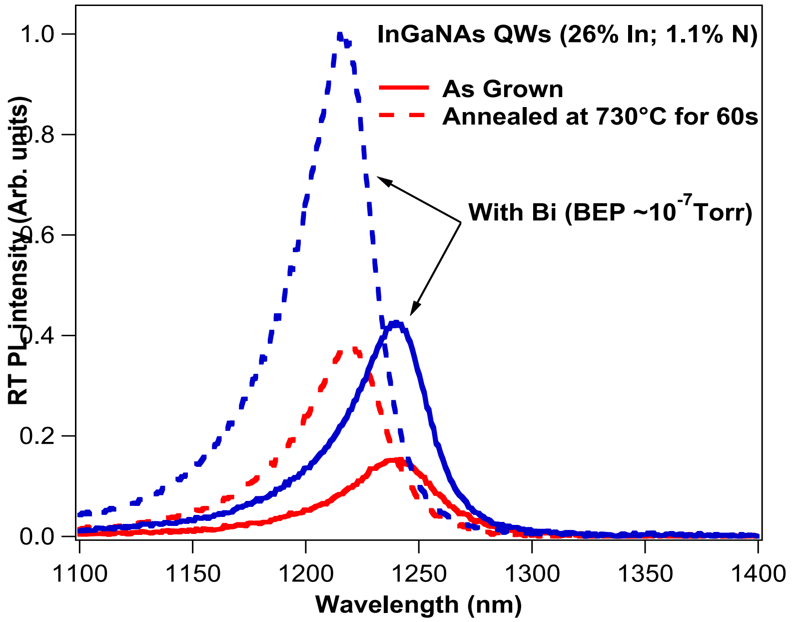
Bi flux 2×10^{-9} Torr (450 C)

Growth rate 0.128 μm/hr

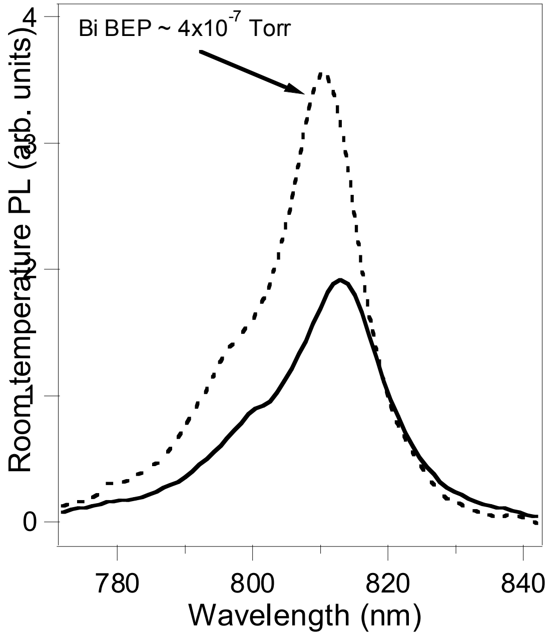
Surface reconstruction 1x3

Bi Surfactant Increases Photoluminescence Intensity

Dilute GaNAs

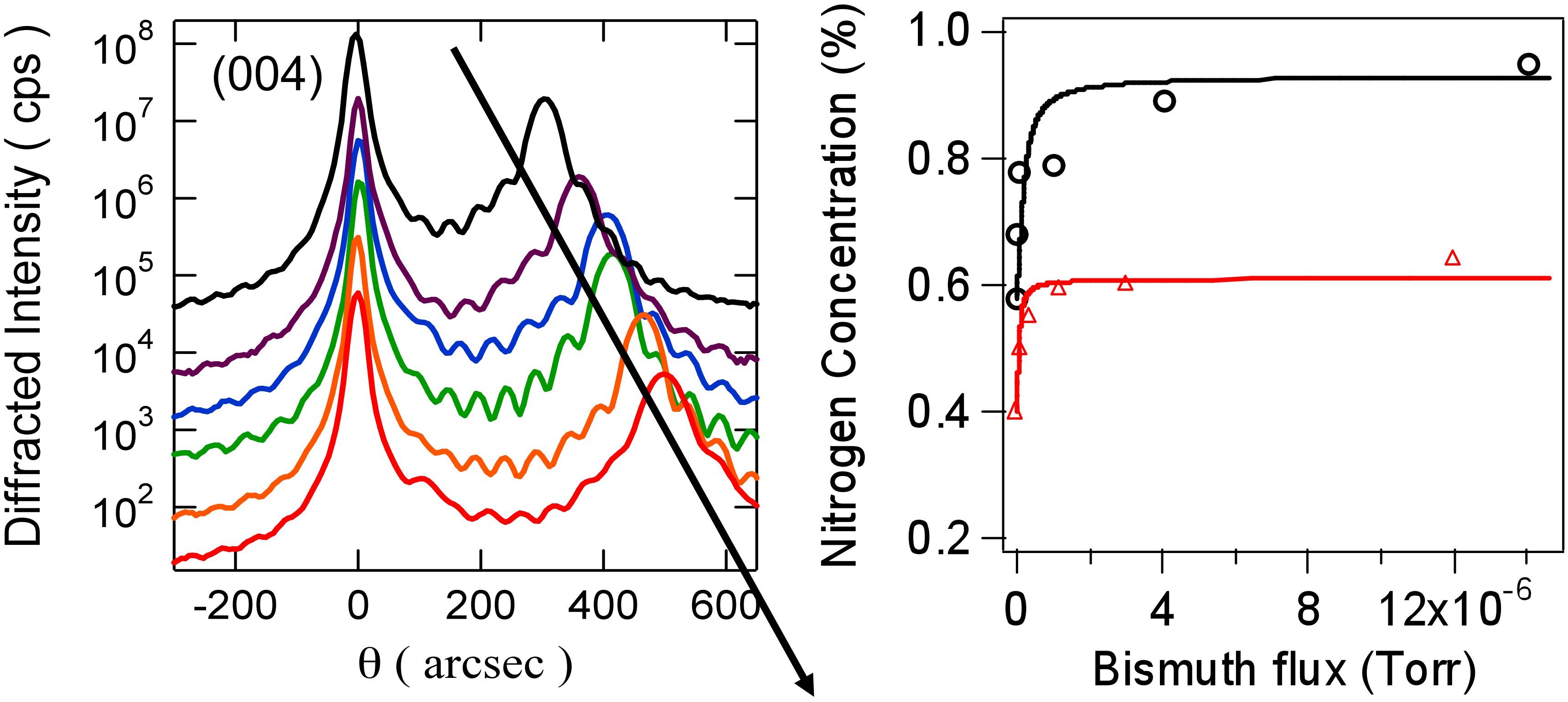


AlGaAs



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]

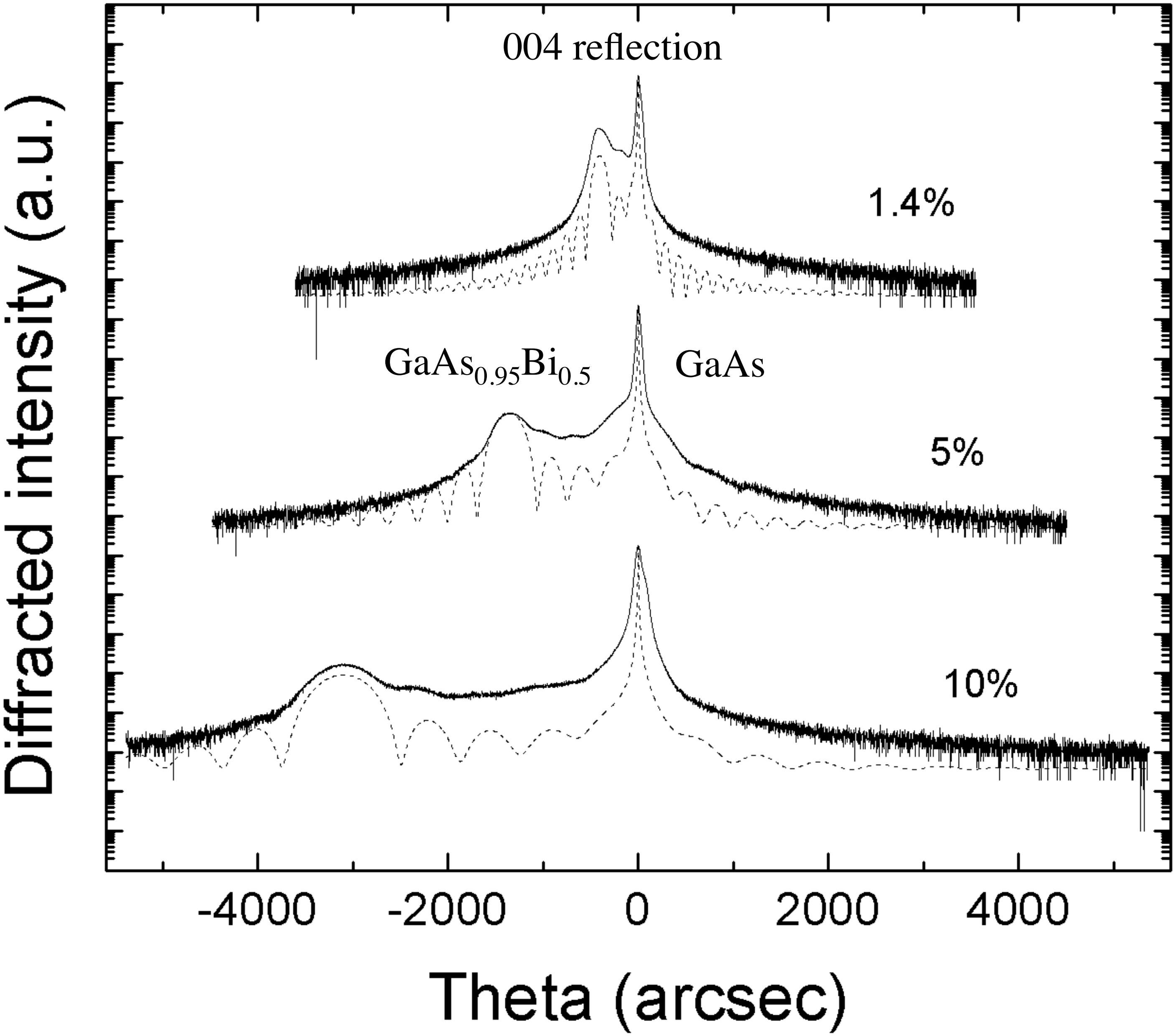
How does one get Bi to incorporate in MBE?

Answer:

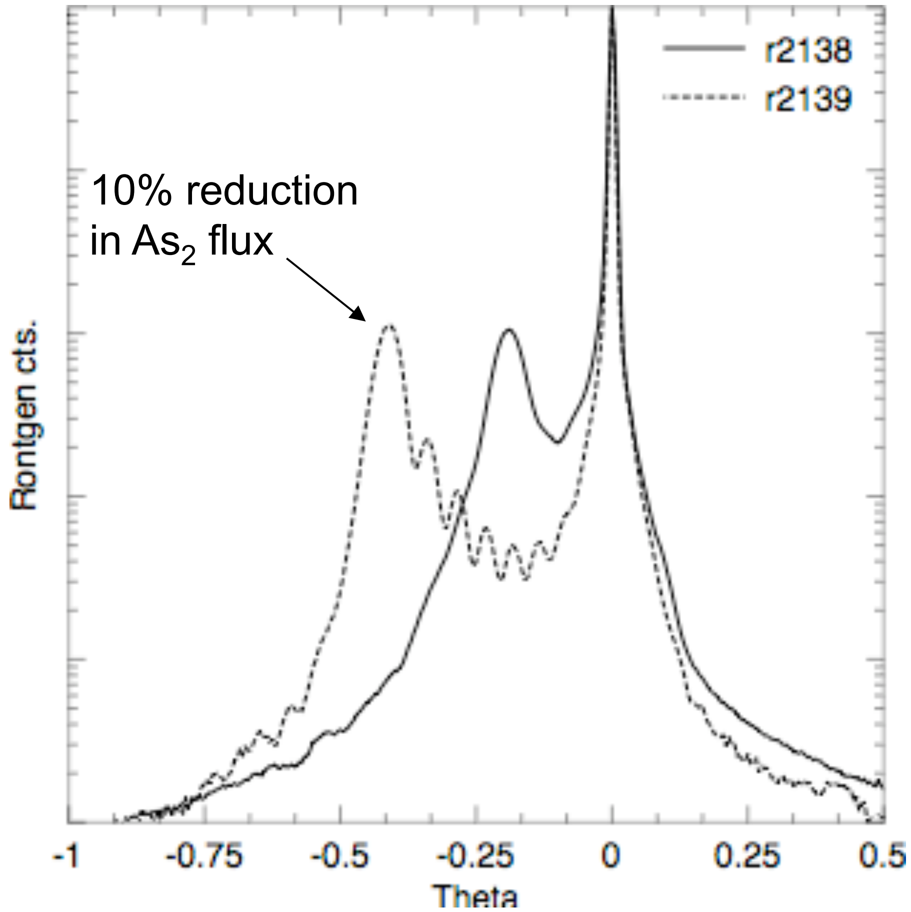
- Low growth temperature
- Low As overpressure

Sebastien Tixier et al APL (2003)

Bi content determined by x-ray diffraction



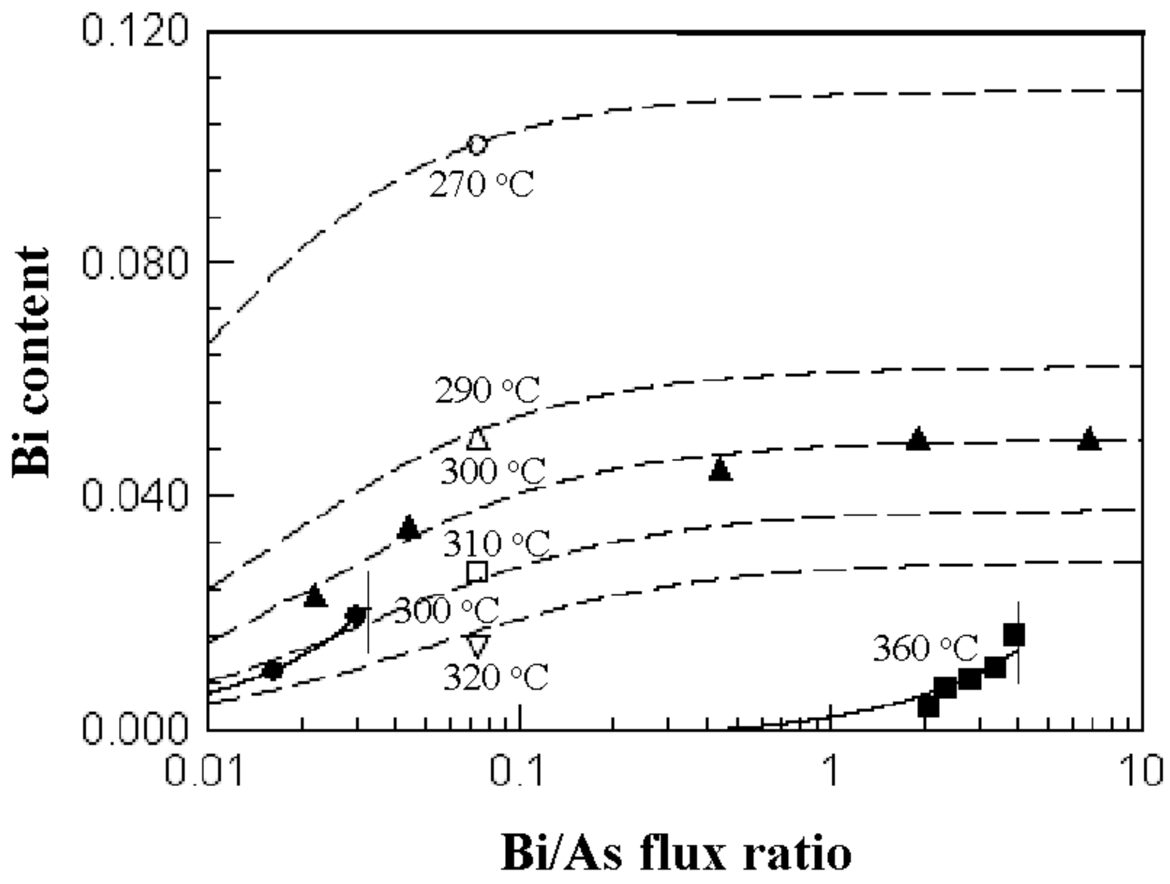
Arsenic flux controls Bi incorporation


10% reduction in As_2 flux

300°C growth temp, all conditions identical except As_2 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

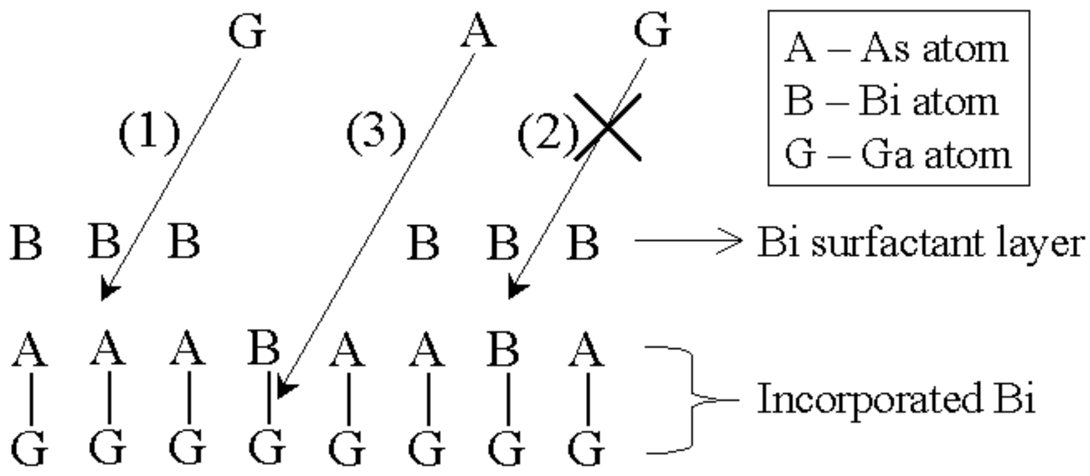
- Flux of Bi in excess of the amount incorporated must be less than the evaporation rate

$$0 < \underbrace{F_{Bi} - xF_{Ga}}_{\text{“excess Bi”}} < Bi\ Evap.\ Rate$$

- 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

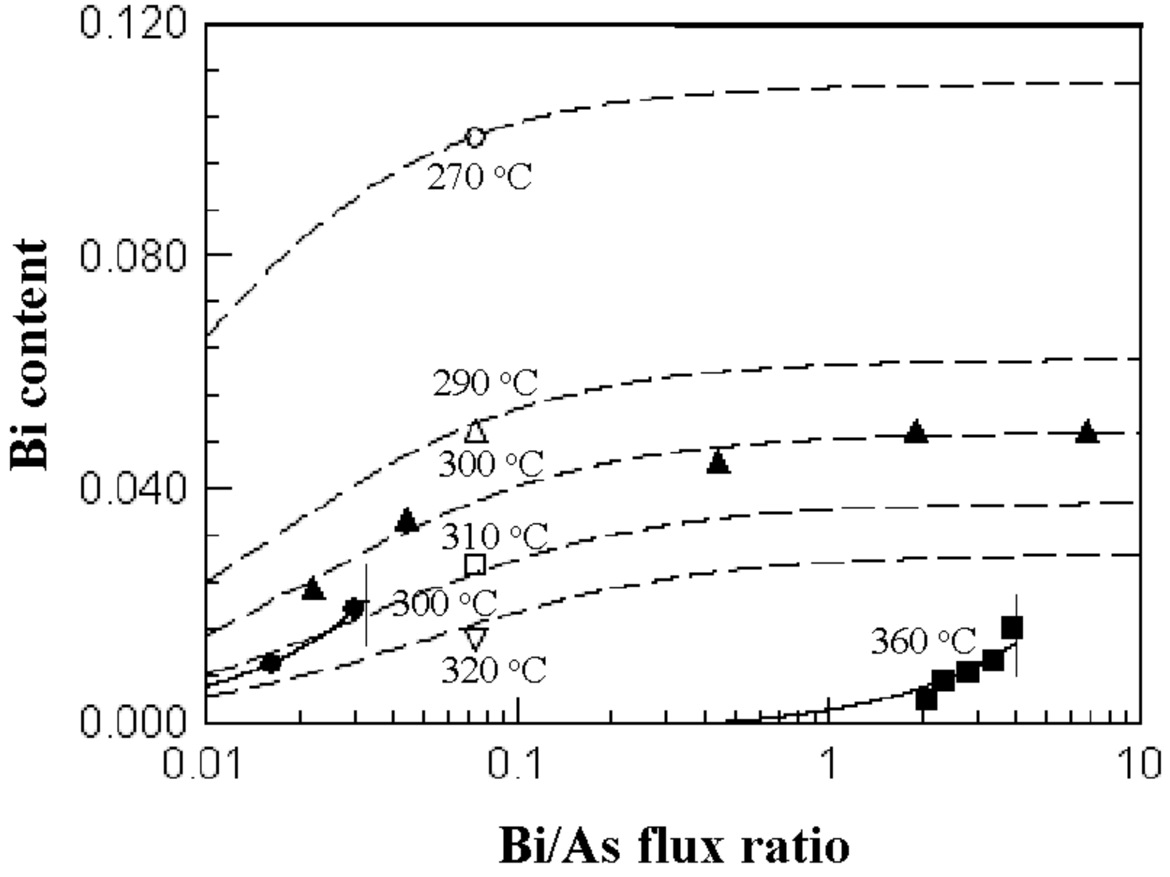
- Bi content determined by competing rates of Bi and As incorporation

$$x = \frac{F_{Ga}\theta_{Bi}}{aF_{As}e^{-U_1/kT} + F_{Ga}\theta_{Bi}}$$

U_1 - activation barrier to *Ga-Bi* displacement by *As*

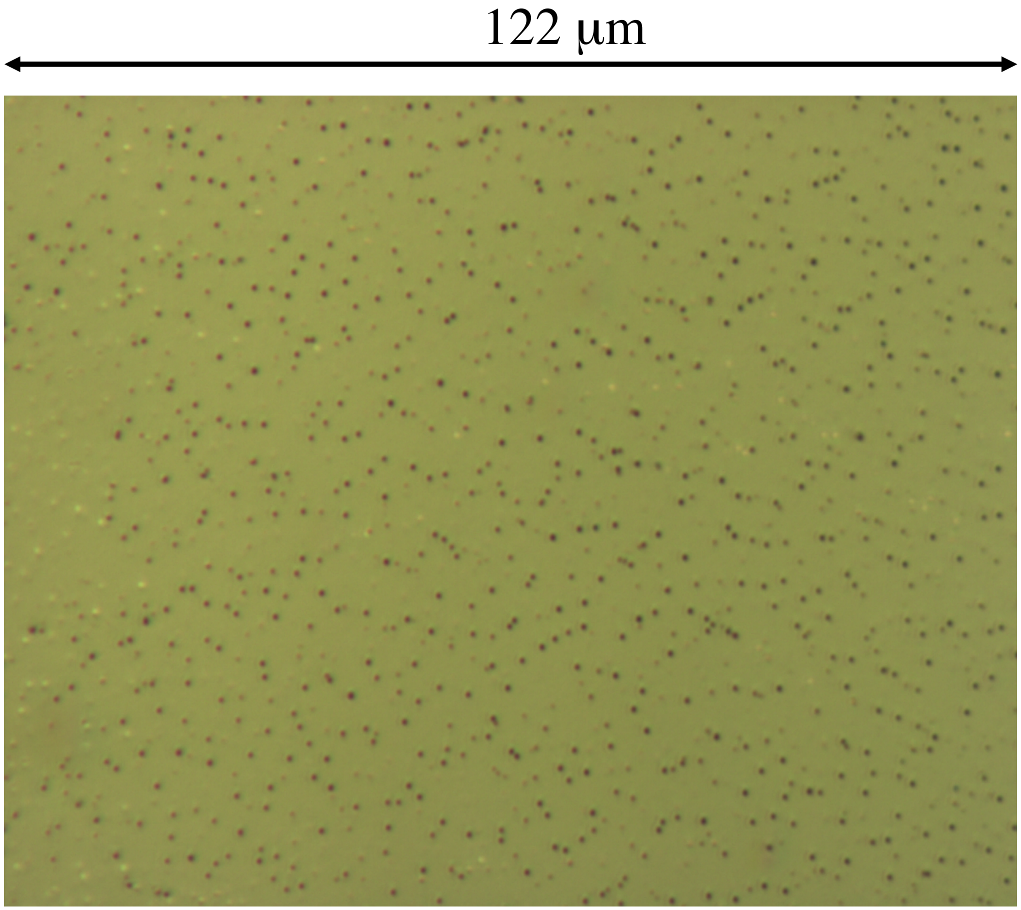
Two part model gives good description of Bi incorporation

16 samples, different growth conditions



Parameters: $U_0 = 1.3$ eV, $U_1 = 0.8$ eV

Bismuth droplets can be a problem



Optical image

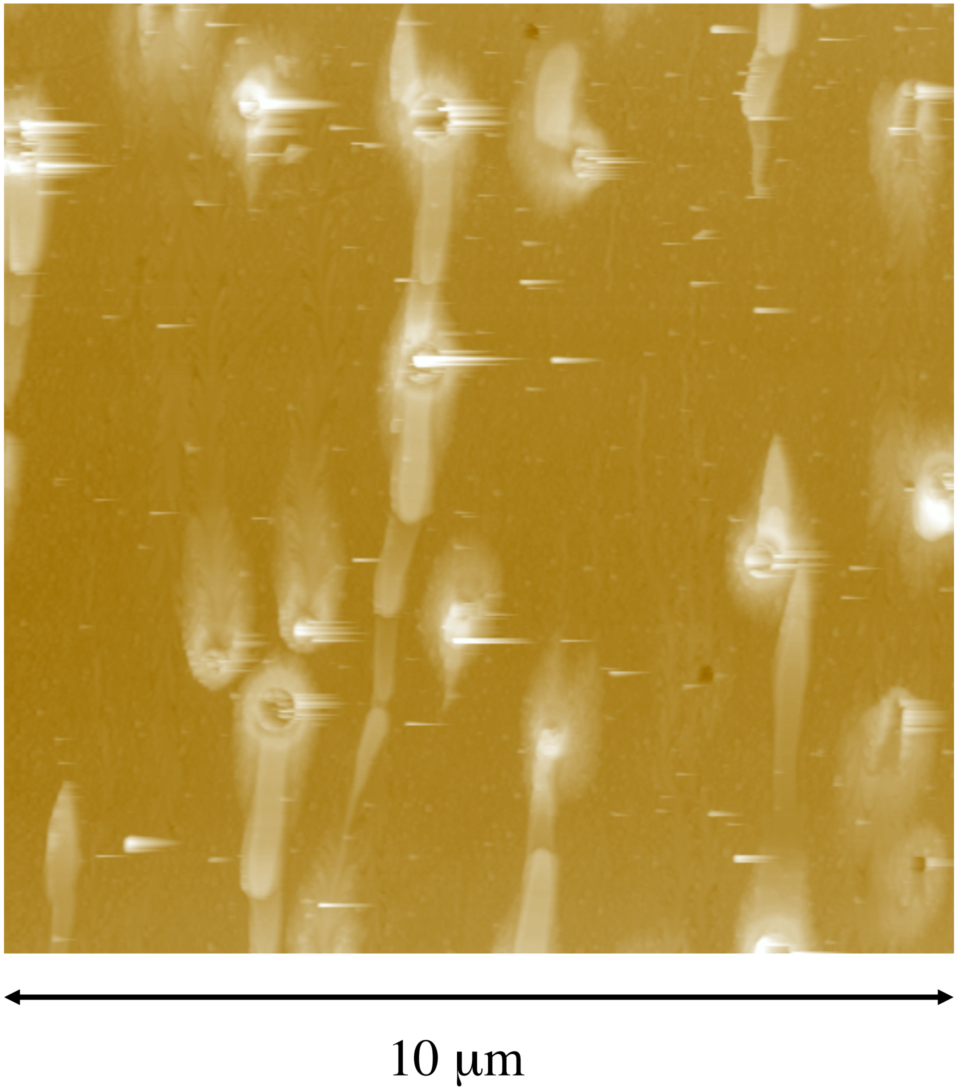
[Bi]=1%

Same sample AFM image: ball and socket type Bi droplets

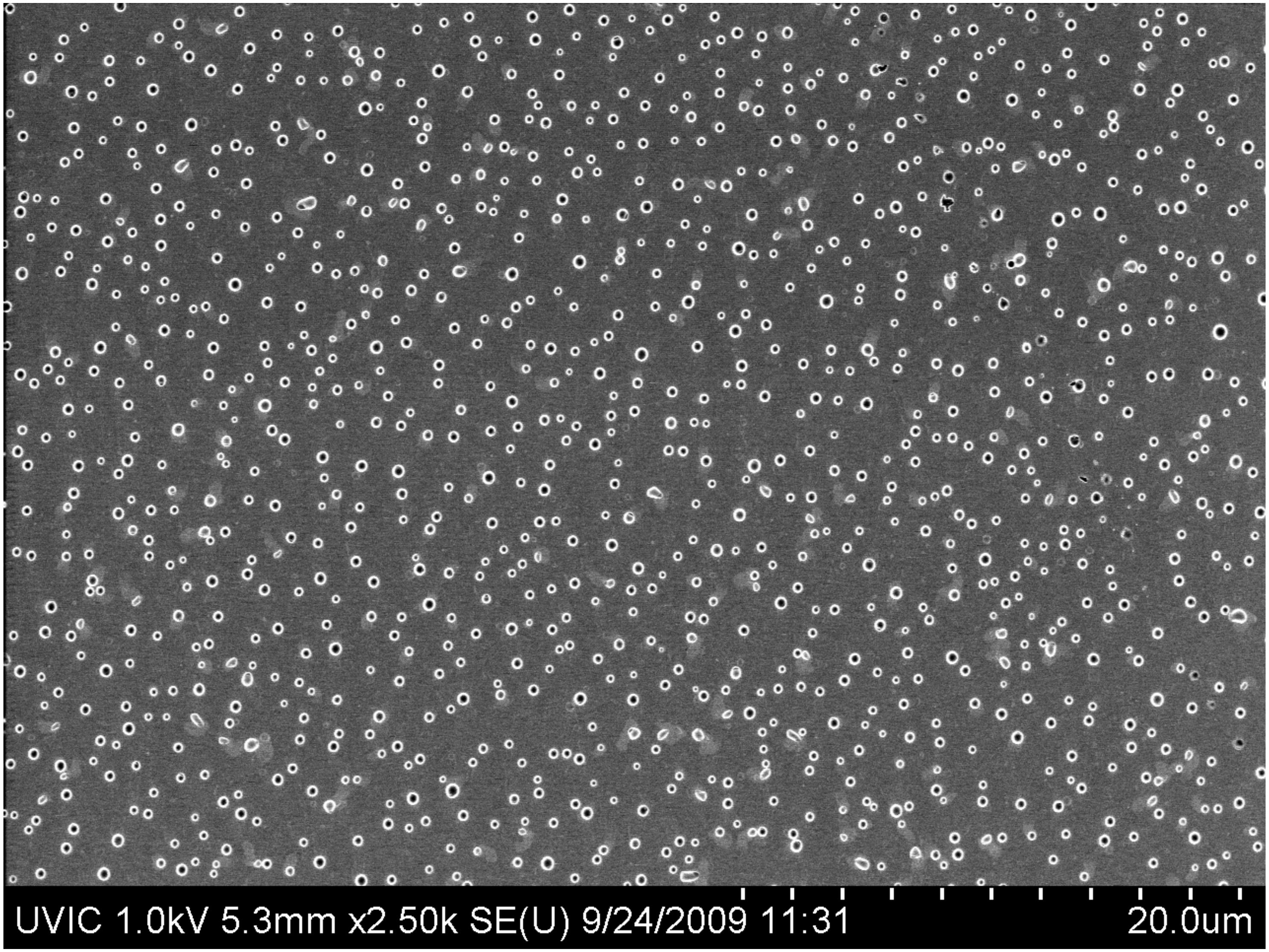
AFM

60 nm z-scale

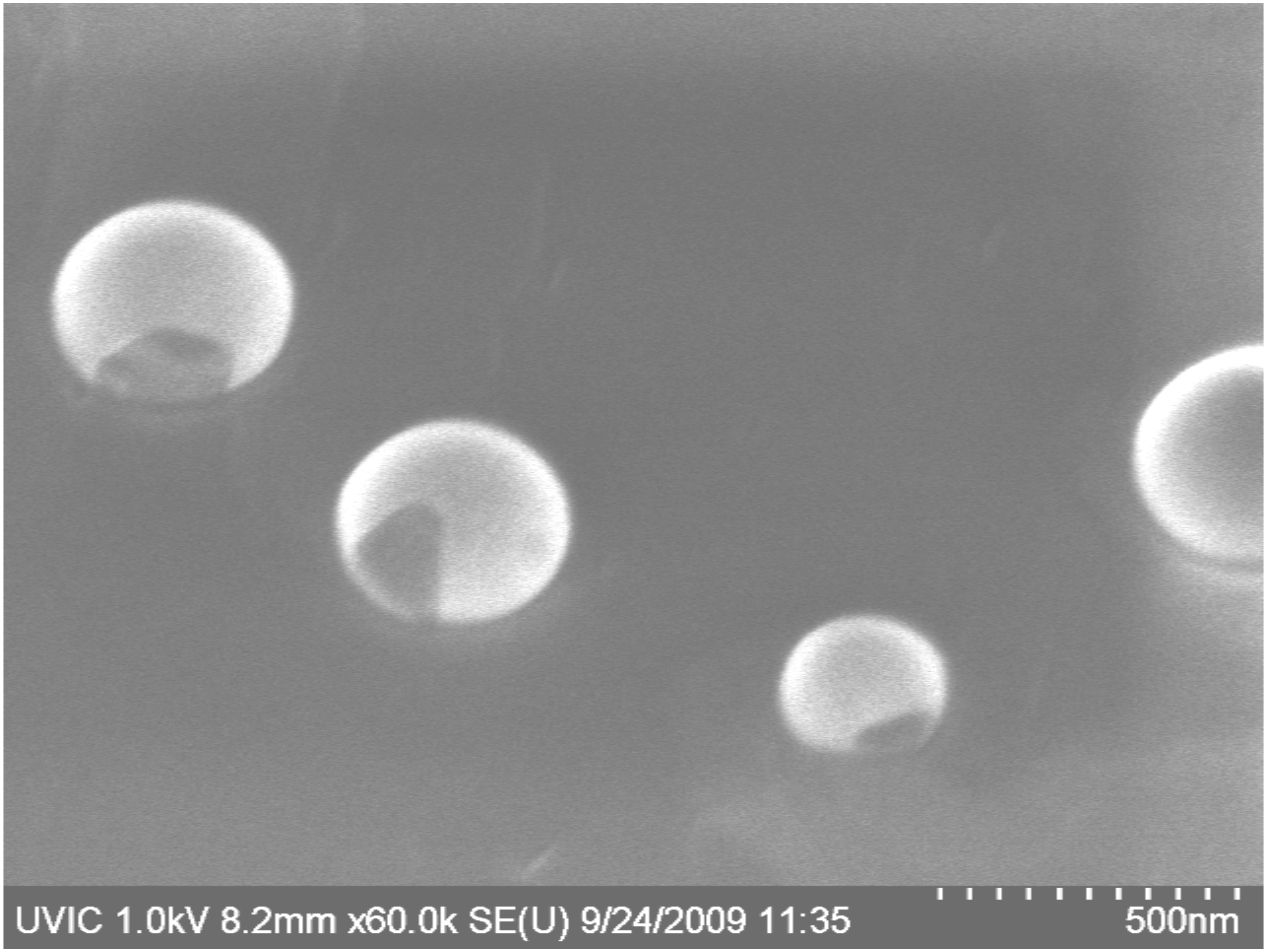
[Bi]=1%



Can also get Gallium droplets: SEM image

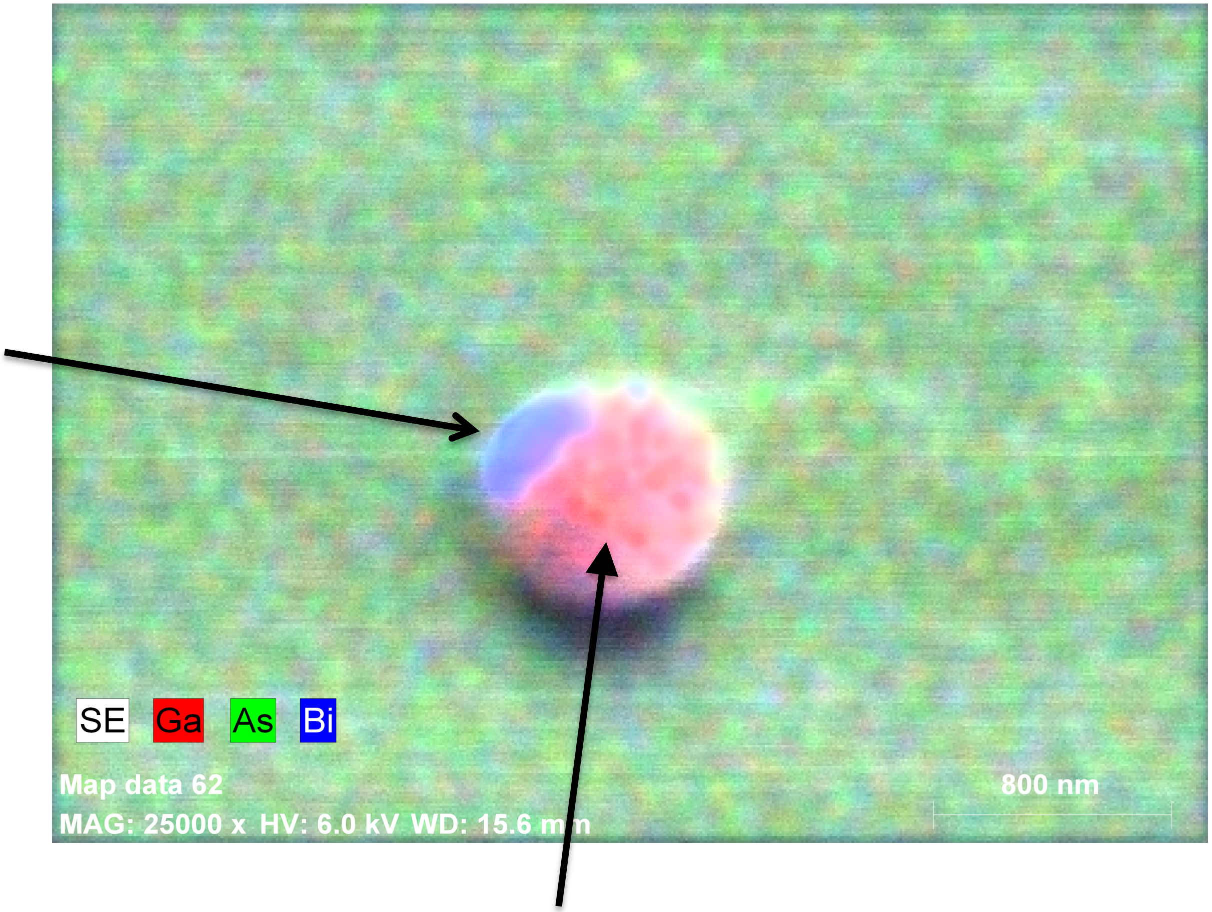


Droplets show composite structure at high magnification



Composition map: composite droplets include both Ga and Bi

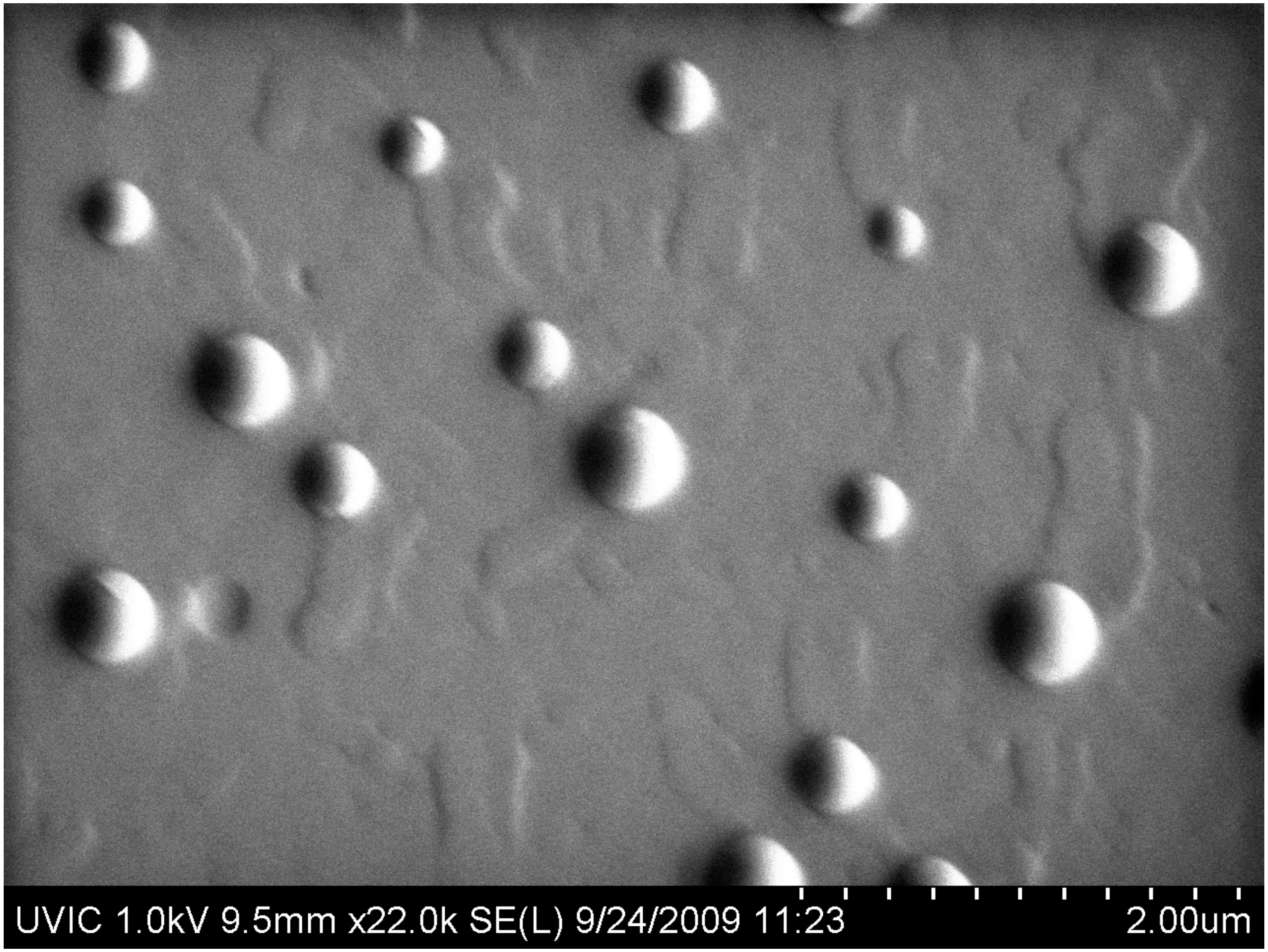
800 nm diameter droplet



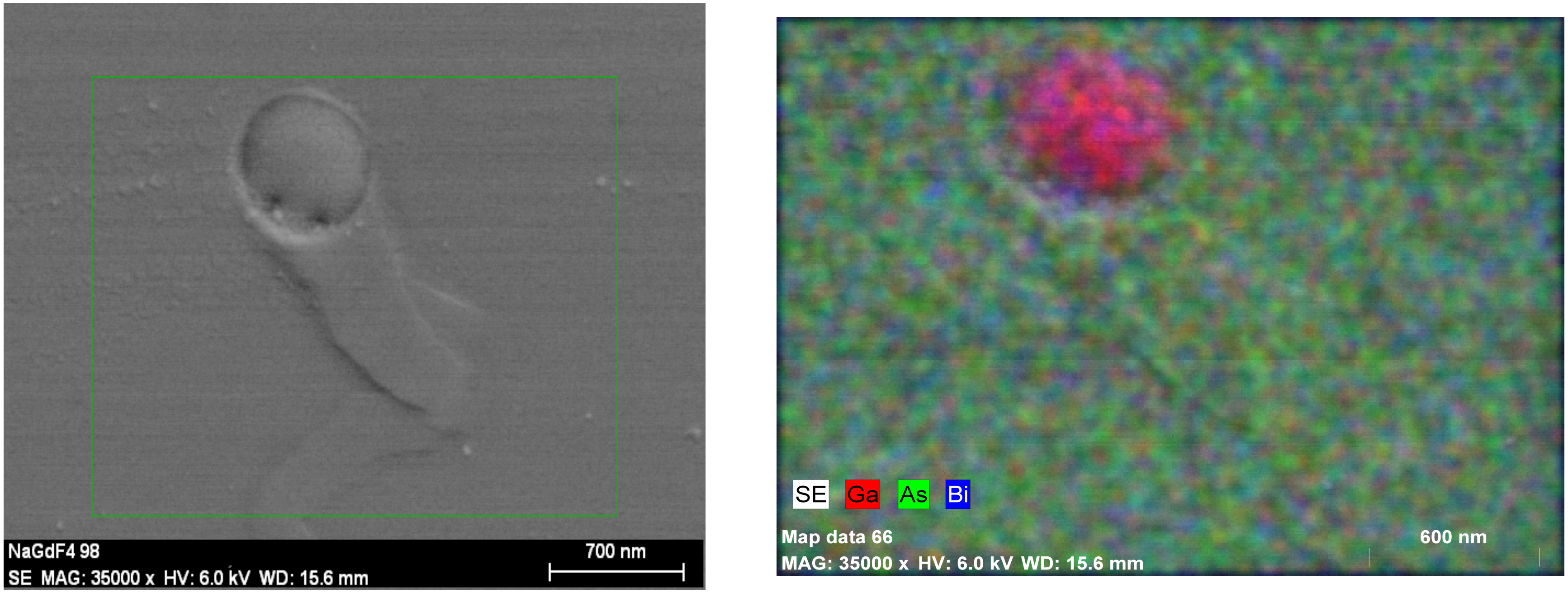
Bismuth

Gallium

Gallium droplets leave tracks, must be moving

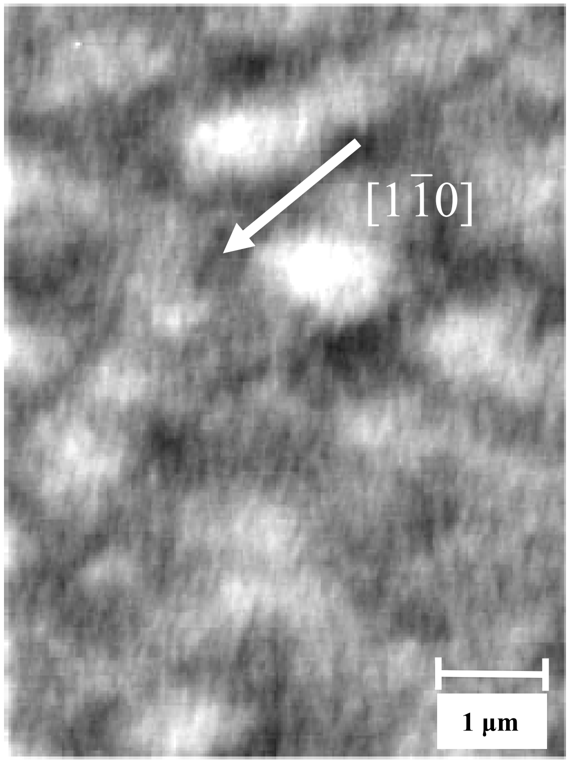


Composition map of a droplet track

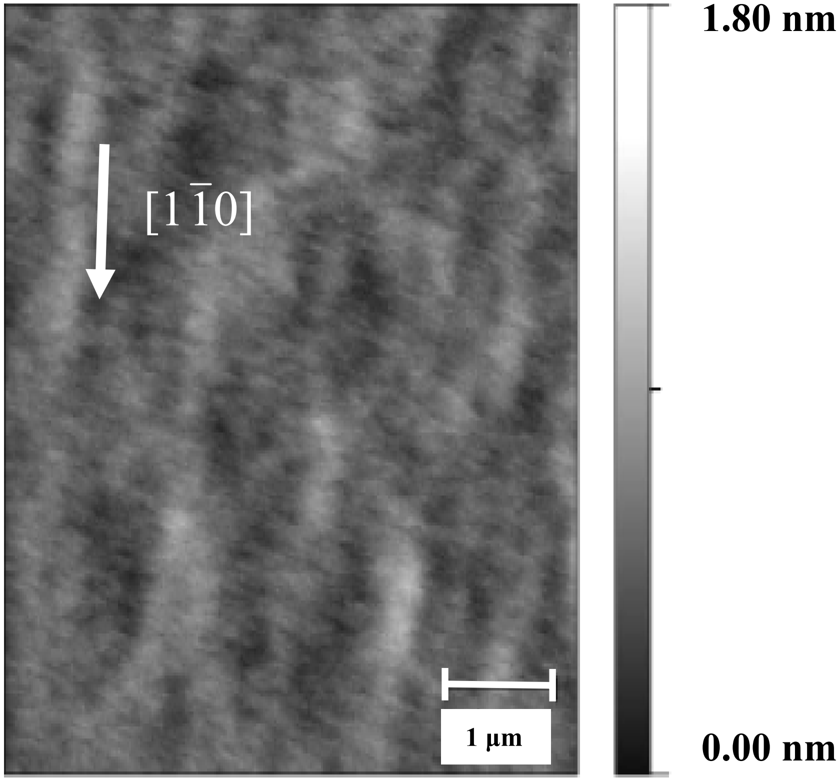


Gallium droplet, gallium arsenide track

AFM images of droplet-free samples

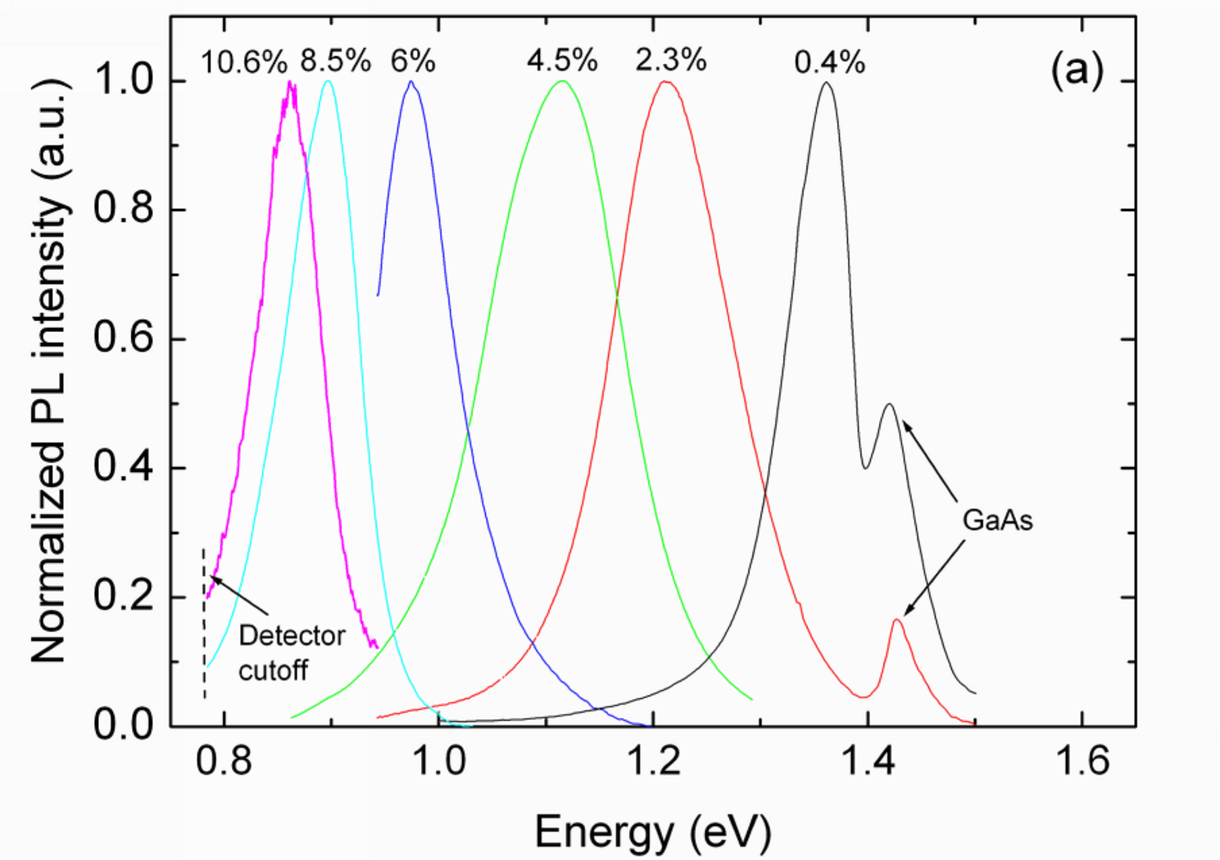


[Bi] = 2%



[Bi] = 5%

Room temp. photoluminescence as function of Bi content

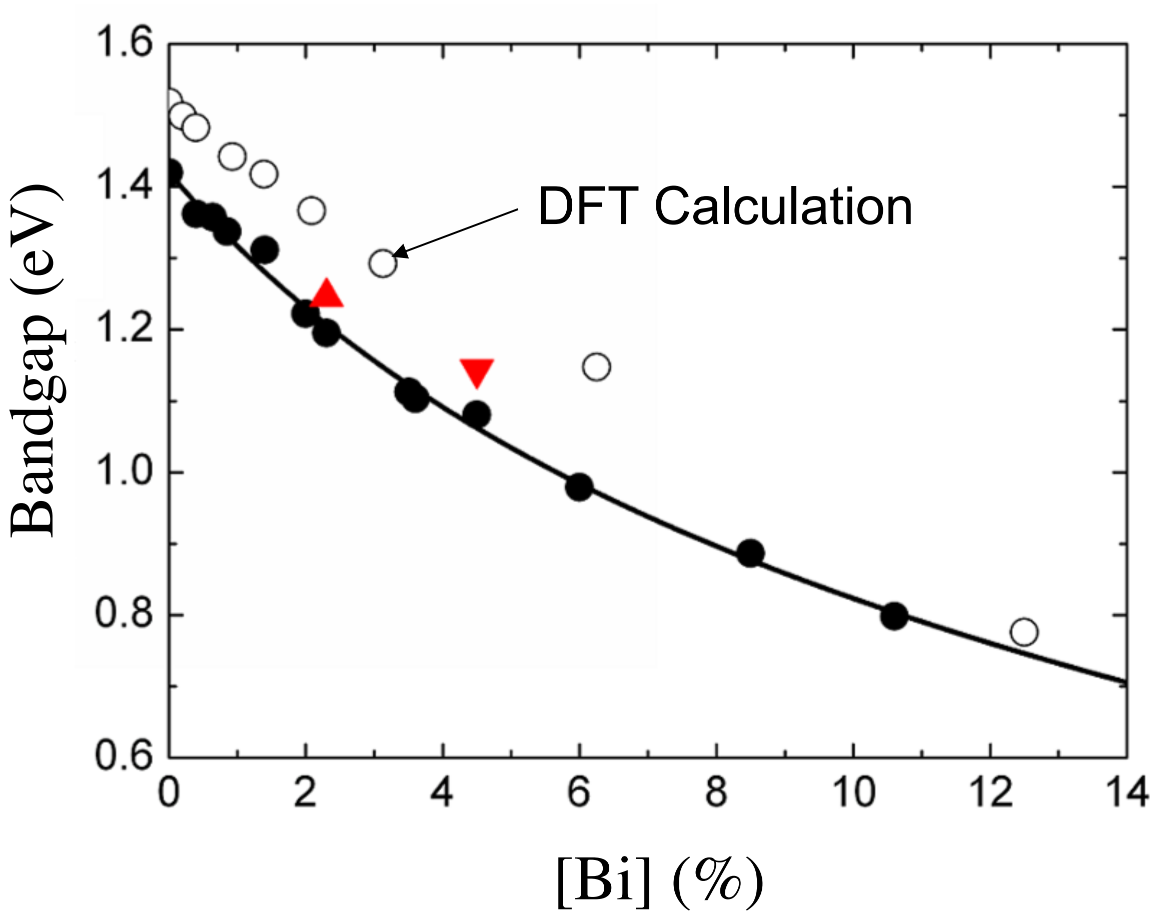


PL shows shift in bandgap to IR with [Bi]

“White” IR emission spectra, broader than kT

Composition dependence of GaAs$_{1-x}$Bi$_x$ bandgap

Xianfeng Lu APL (2009)

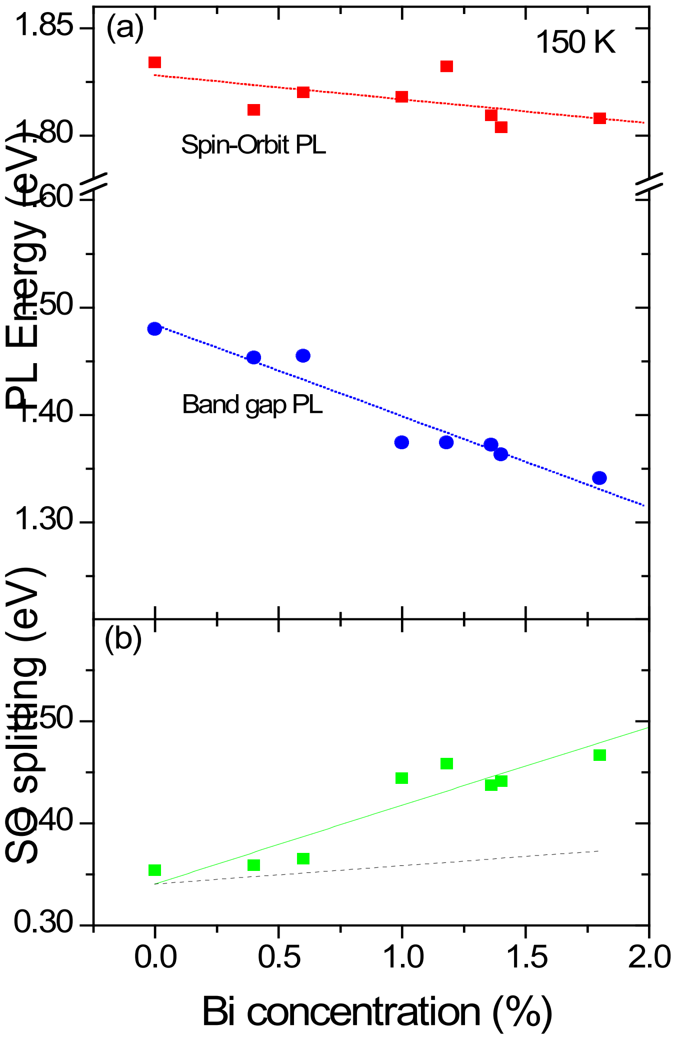


1.5 µm

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

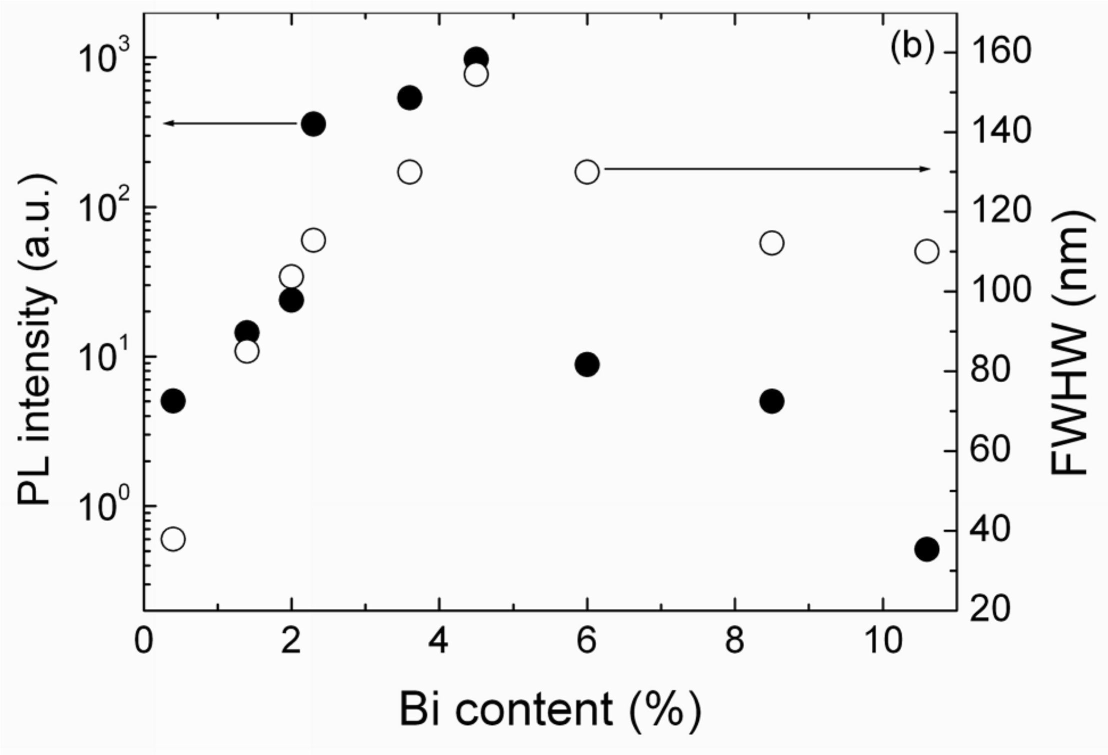


Increase in spin-orbit splitting in parallel with reduction in bandgap

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

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

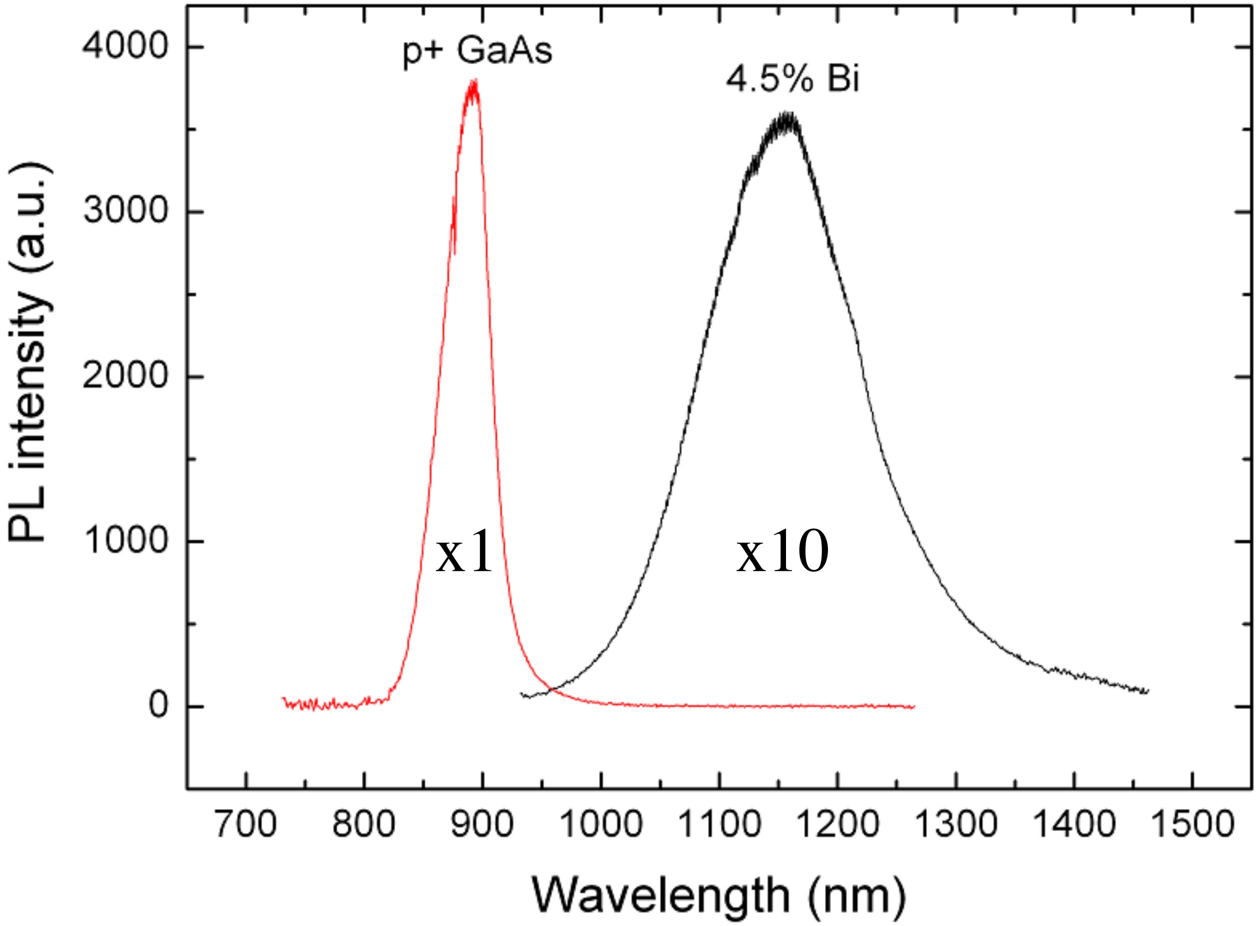
PL intensity increases with Bi at low concentration



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

Xianfeng Lu et al APL, 2009

Photoluminescence Intensity Comparison



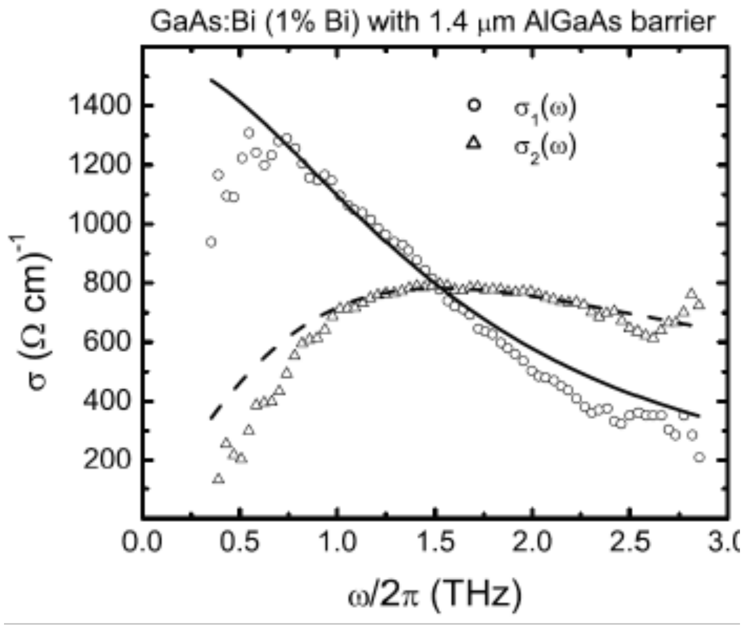
GaAs capped 50 nm $GaAs_{0.955}Bi_{0.045}$ layer shows comparable PL intensity to p^+ GaAs wafer

Frequency Dependent Conductivity

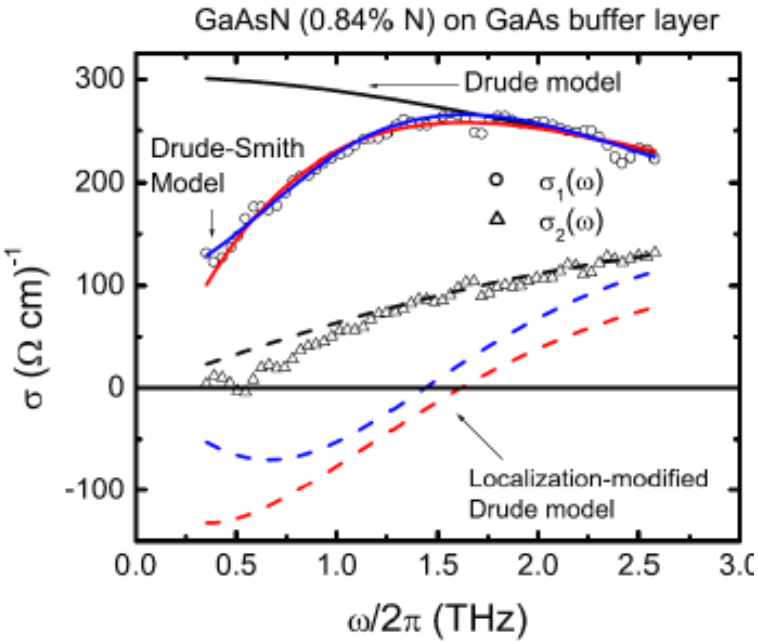
(Cooke, Hegmann U. Alberta)

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

Bismide: Drude-like

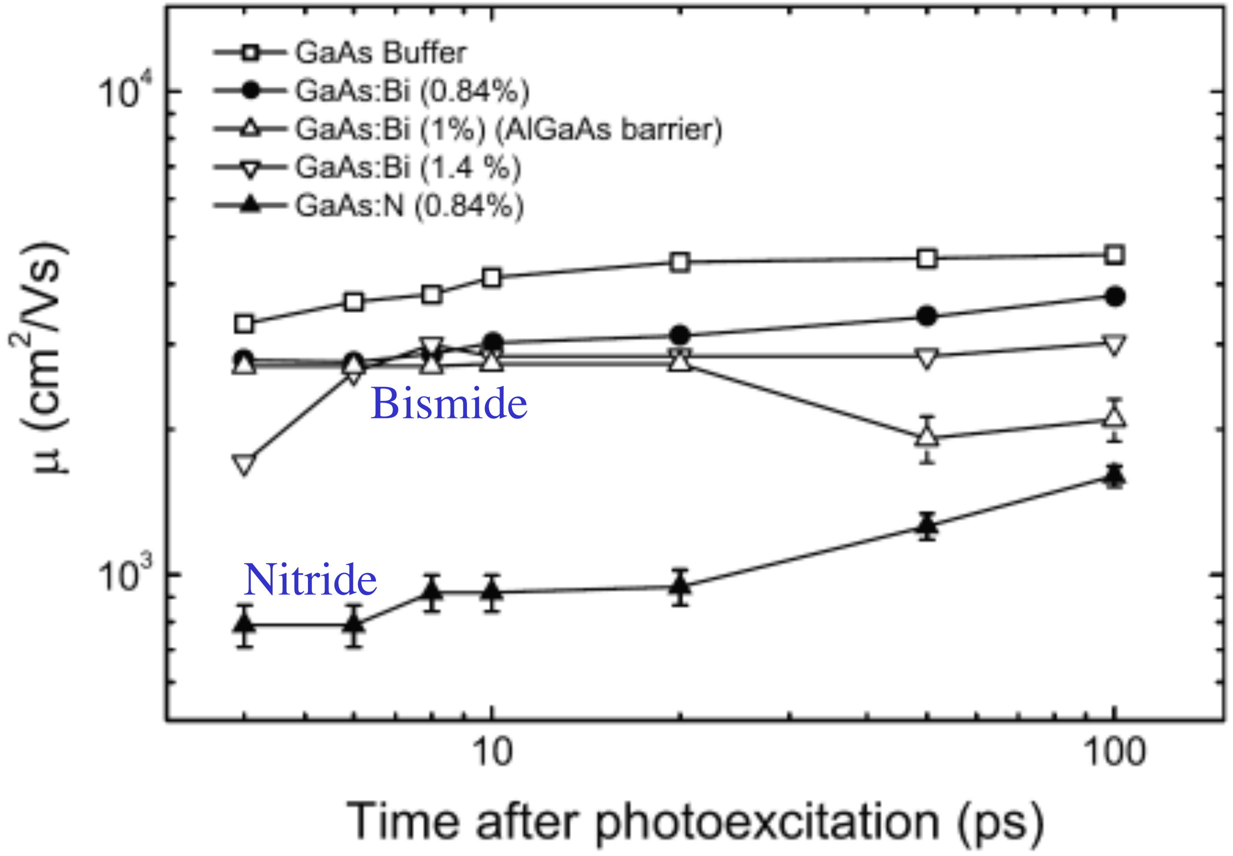


Nitride: non-Drude



- Optically induced conductivity dominated by electrons
- Bismide, nitride behave differently, N affects conduction band, Bi val. band

Terahertz Measurements of Electron Mobility

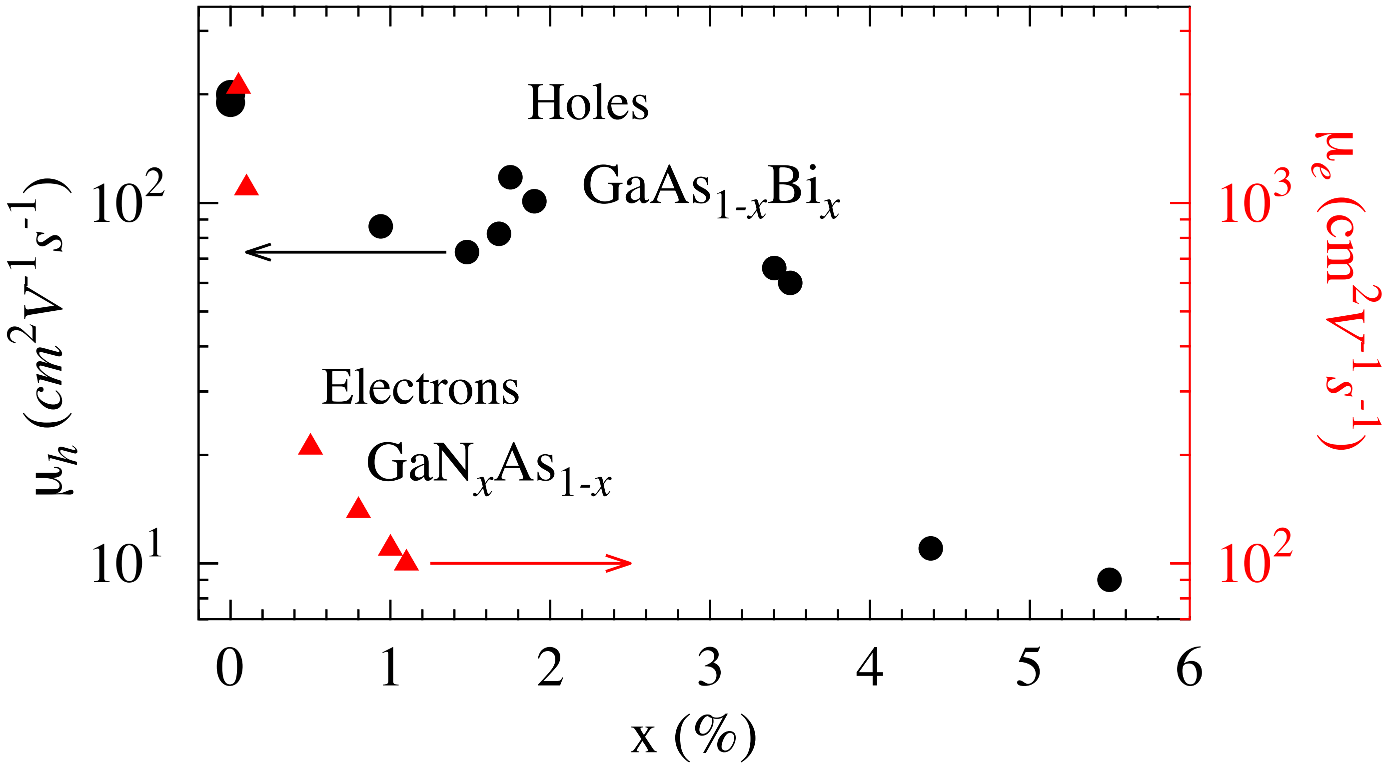


1% N has drastic effect on electron mobility, 1% Bi has comparatively little effect

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

Hall mobility of holes in $GaAs_{1-x}Bi_x$ at room temperature

(Dan Beaton talk on Friday)



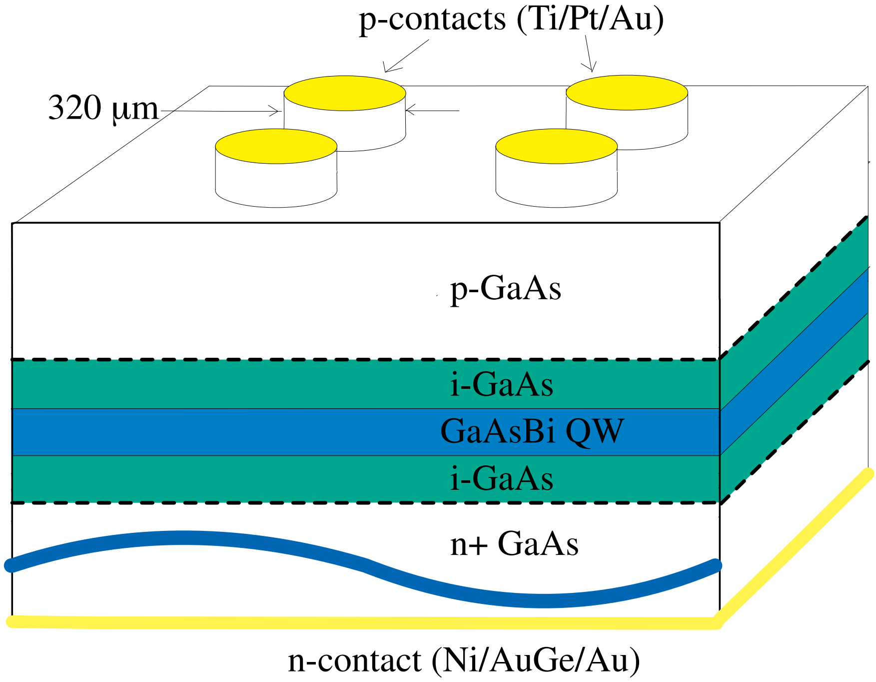
Sample design

200 nm p-type film

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

D. A. Beaton et al, (in preparation 2010)

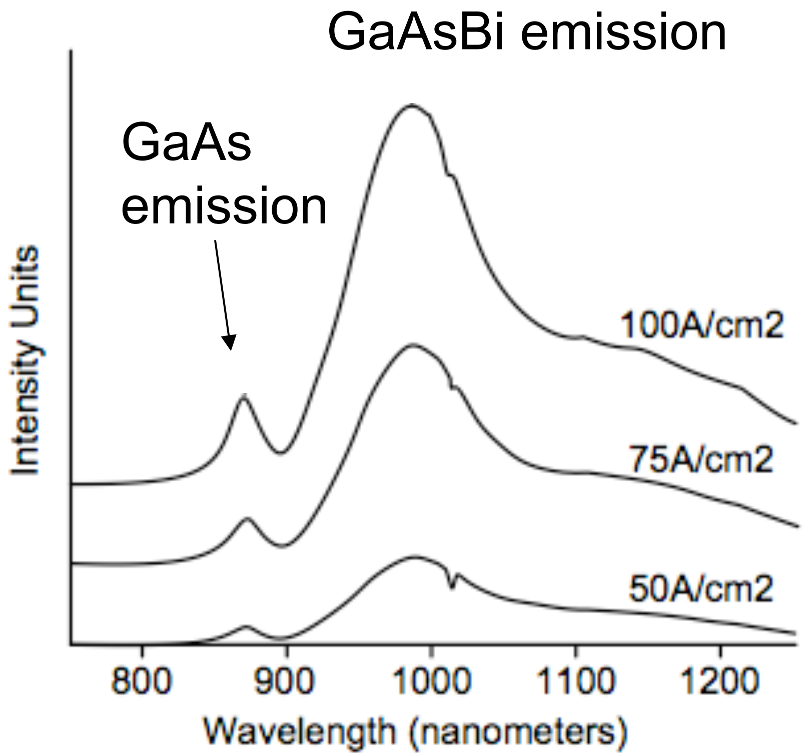
Light emitting diode structure



Light collected from the top around the periphery of the metal dots

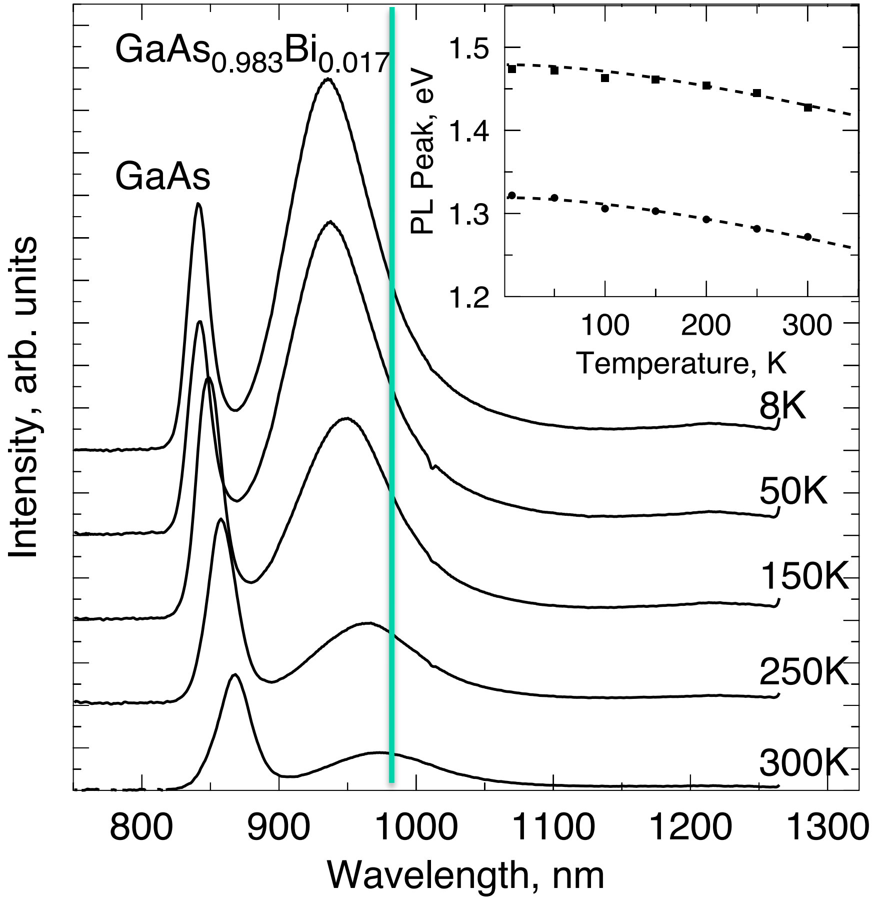
- not an efficient device design!

Light emitting diode emission spectrum



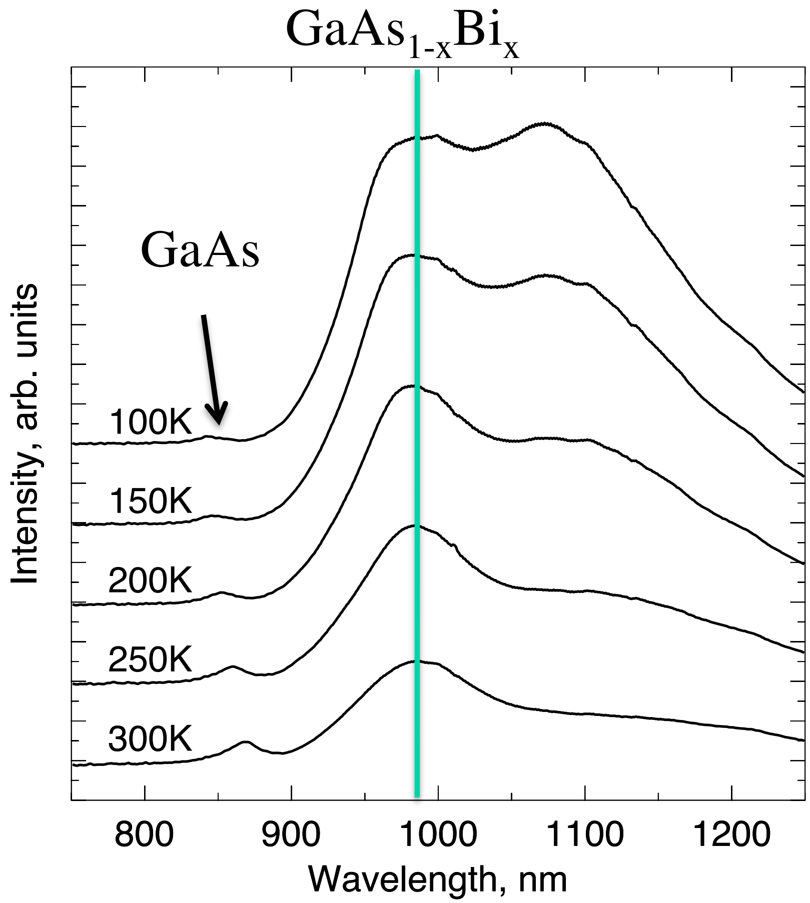
R. B. Lewis, MSc Thesis, UBC, 2008 and JCG 2009

LED emission temperature dependence #1



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?