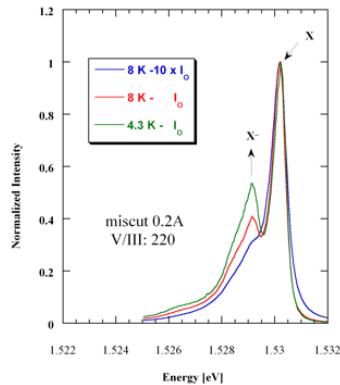


Vicinal surfaces: the case of AlGaAs/GaAs QWs

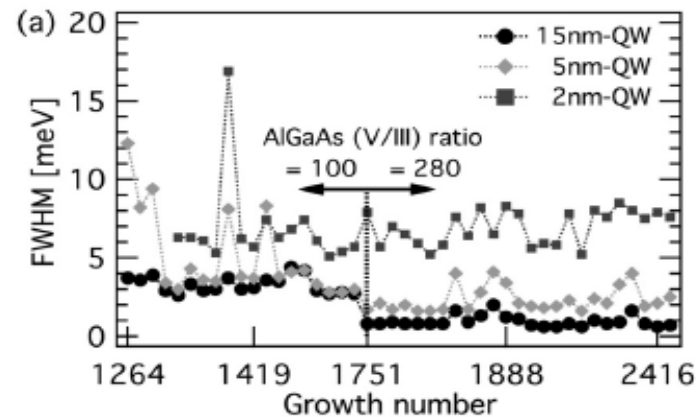
- A well studied III-V heterostructure: GaAs/AlGaAs
 - ✓ Strategic industrial and scientific importance
- A widely used characterization tool: low temperature PL
 - ✓ A probe of material purity and interface quality
- A lasting superiority of MBE over MOVPE in this area
 - ✓ PL linewidth considerably lower in MBE (sub-meV in MBE vs ~ 4 meV in MOVPE)

Vicinal surfaces: the case of AlGaAs/GaAs QWs

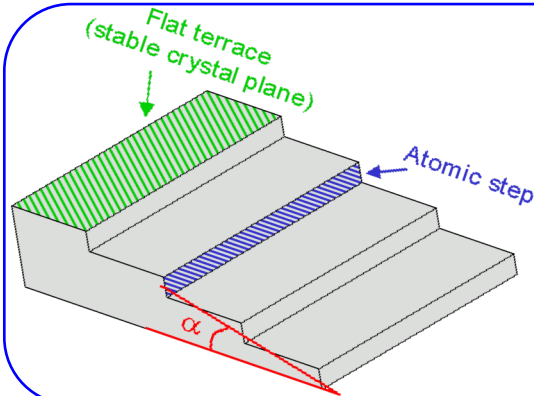
A probe of material purity
& interface smoothness



A probe of reactor status over time



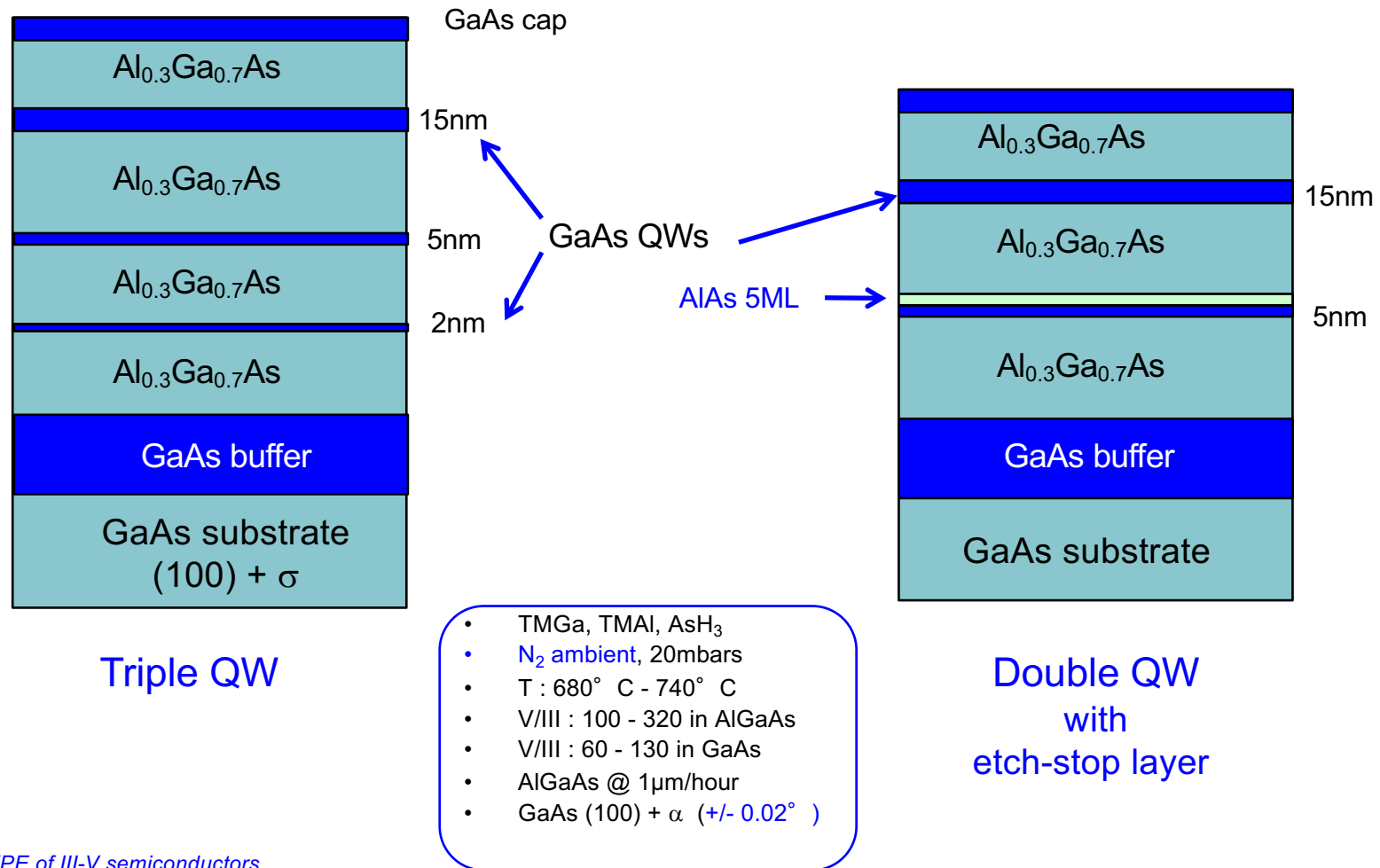
N. Moret,
PhD thesis (2008)



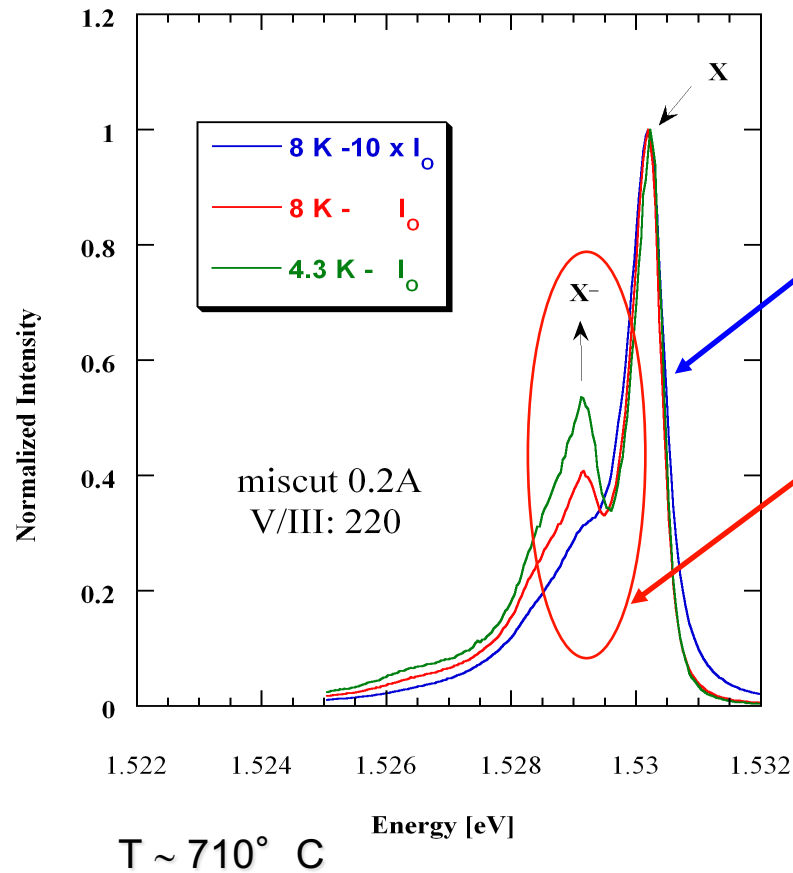
Influence of substrate miscut ($\alpha > 0.5^\circ$)

- Improved morphology : MBE AlGaAs (Tsui, APL 1986)
- Smoother surface under STM : MBE GaAs (Grousseau, PRB 1997)
- Reduced O and C uptake : MOVPE AlGaAs (Leu, JCG 1998)
- Reduced QW PL linewidth : MOVPE GaAs/AlGaAs (Bitz, PRB 1998)

PL & interface morphology of AlGaAs/GaAs QWs

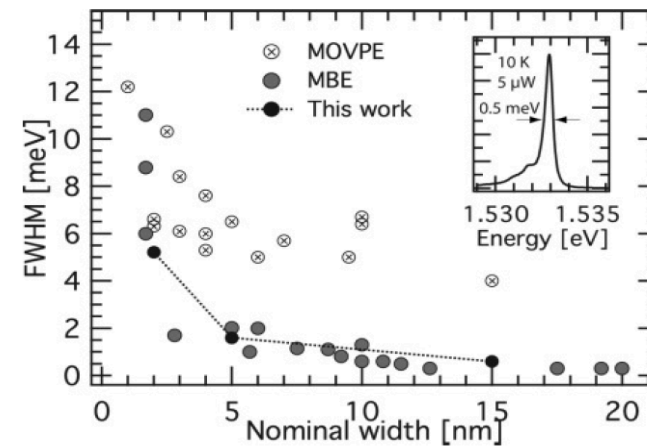


Photolumuminescence of GaAs/AlGaAs QWs

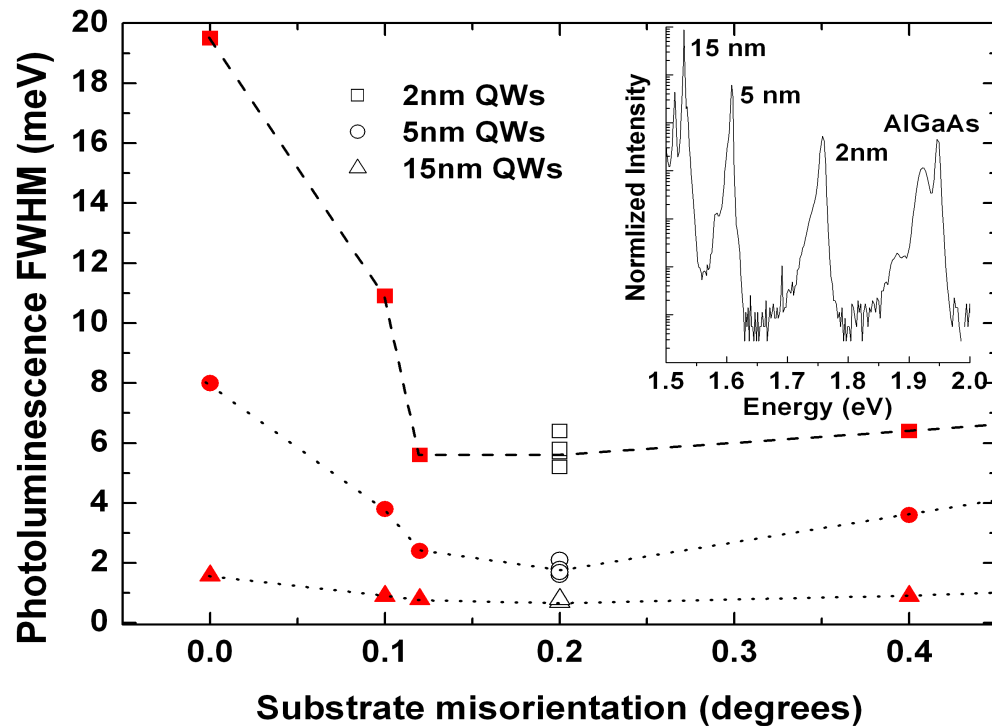


0.6 meV: lowest linewidth
reported on MOVPE grown
material

Negatively charged trion:
first unambiguous observation
on MOVPE grown material



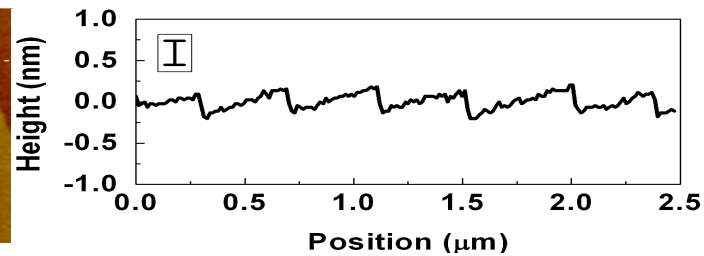
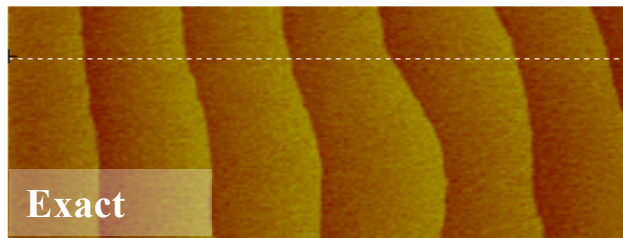
Influence of low substrate misorientations



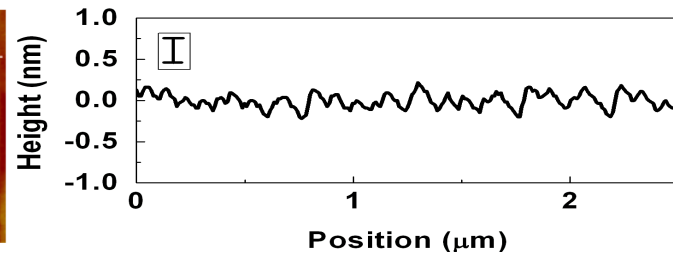
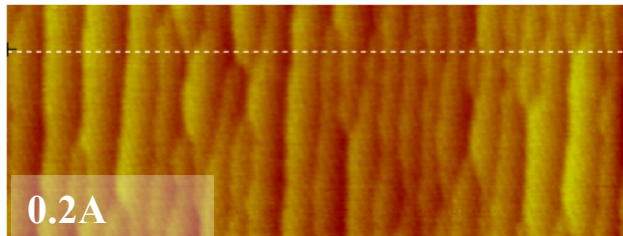
- 0.1° miscut dramatically reduces the PL linewidth
- Reproducible sub-meV linewidths
- Stronger effect on thin QWs points to growth front smoothing

$T \sim 710^\circ \text{ C}$, $V/\text{III} = 220 - 280$ in AlGaAs
 $V/\text{III} = 130$ in GaAs, miscut towards (111)A

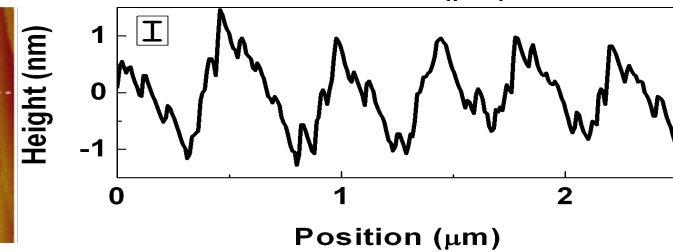
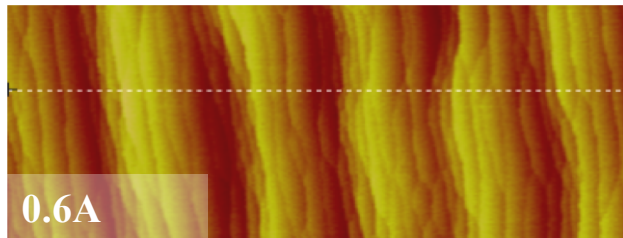
Surface morphology: “A” off-cut



Monolayer steps



Step bunching

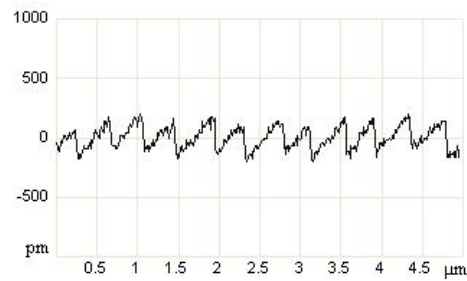
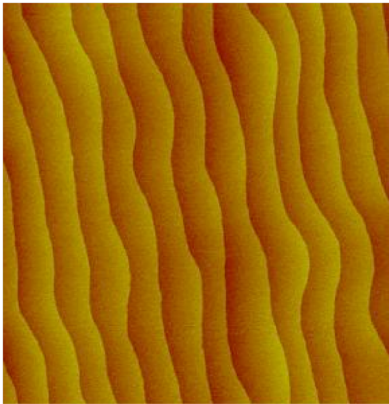


Step bunching
+
undulation

Surface morphology: “B” offcut

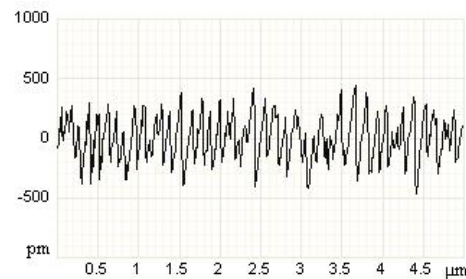
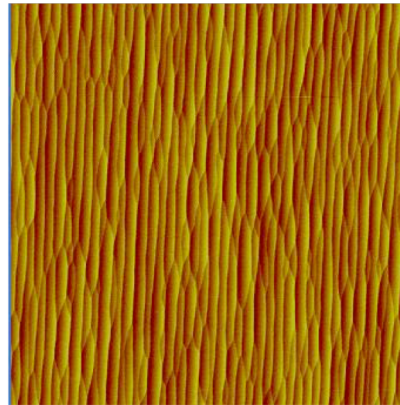
AFM

Exact



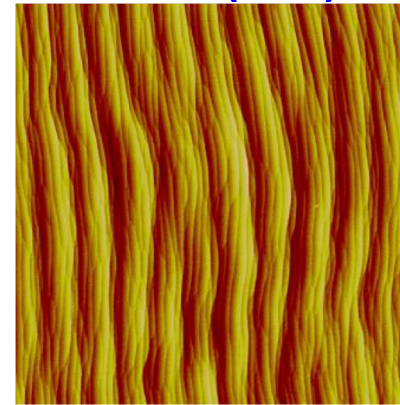
Monolayer steps

$0.3^\circ > (111)B$

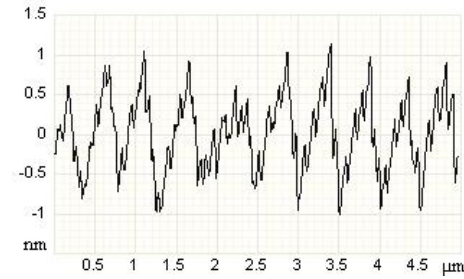


Step bunching

$0.6^\circ > (111)B$

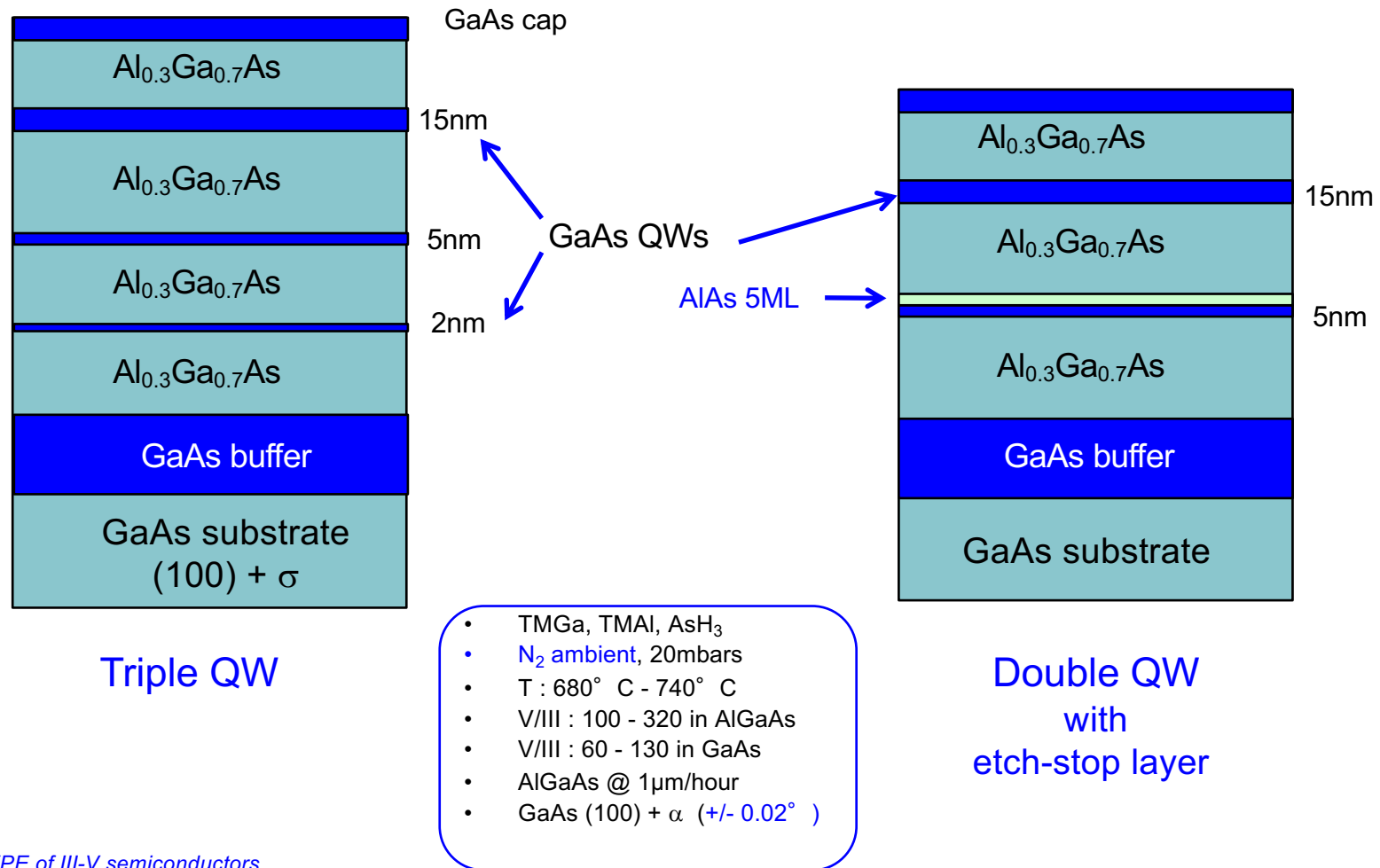


5μm



Step bunching
+ undulation

PL & interface morphology of AlGaAs/GaAs QWs



PL dependence on miscut points to 4 growth modes

PHYSICAL REVIEW B 84, 155311 (2011)

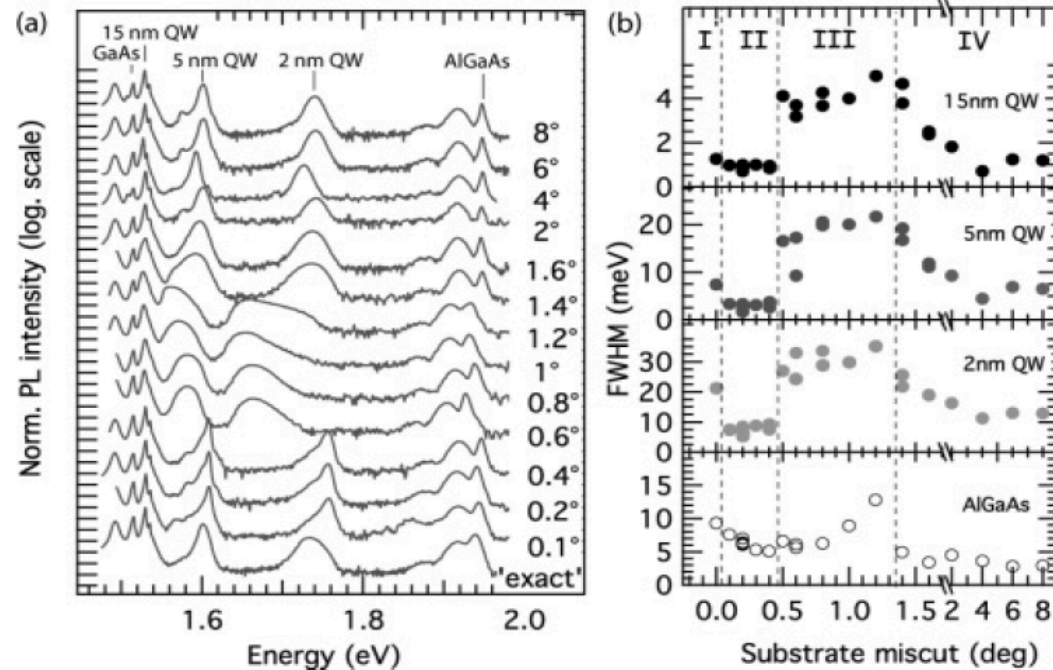
Optics, morphology, and growth kinetics of GaAs/Al_xGa_{1-x}As quantum wells grown on vicinal substrates by metalorganic vapor phase epitaxy

N. Moret, D. Y. Oberli, E. Pelucchi,^{*} N. Gogneau,[†] A. Rudra, and E. Kapon

Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Physics of Nanostructures, CH-1015 Lausanne, Switzerland

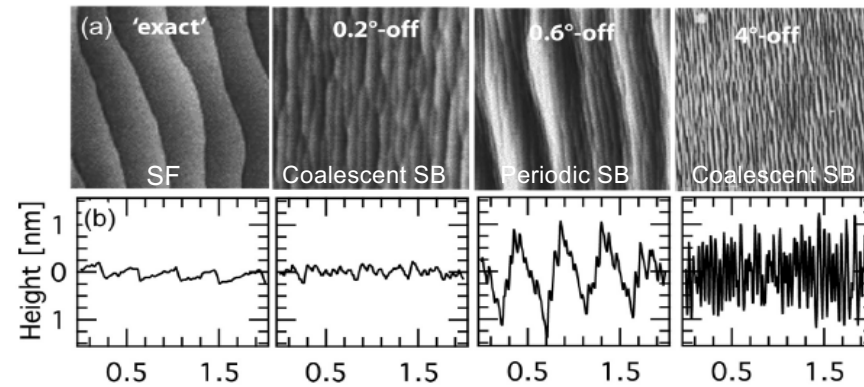
PL spectra of TQW samples grown on
substrates with different miscuts

FWHM of the 3 QWs
& the AlGaAs bound exciton line

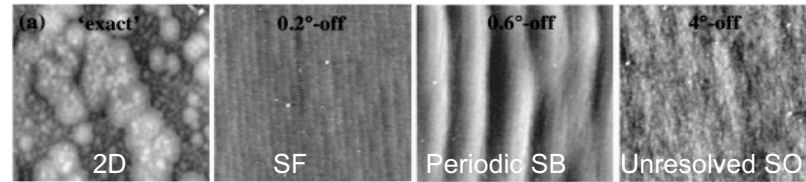


AFM of top surface and QW interfaces

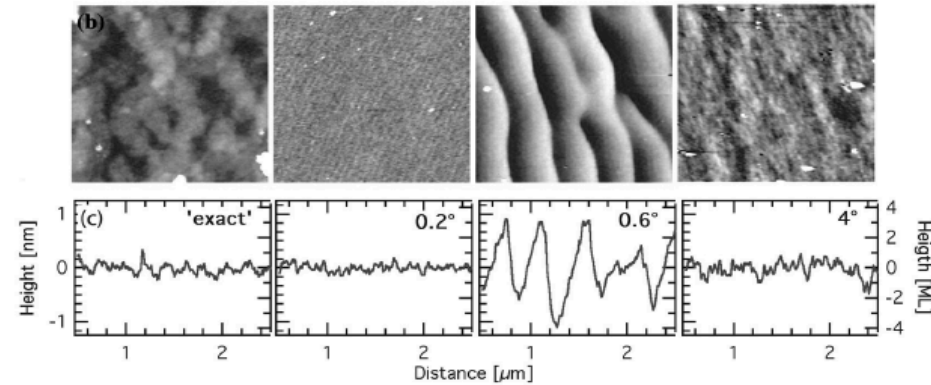
Top surface



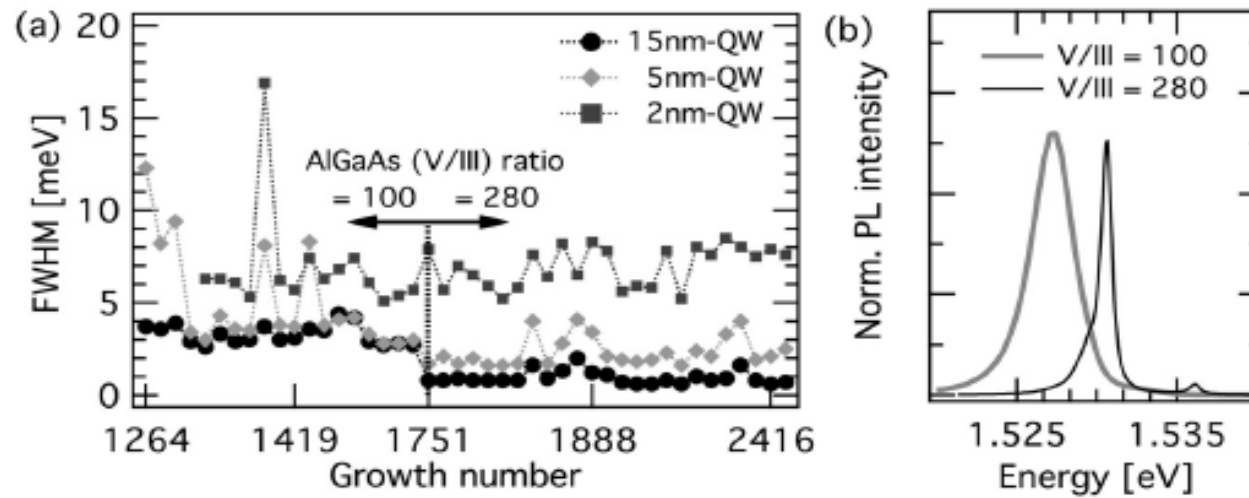
Upper QW surface



Lower QW surface



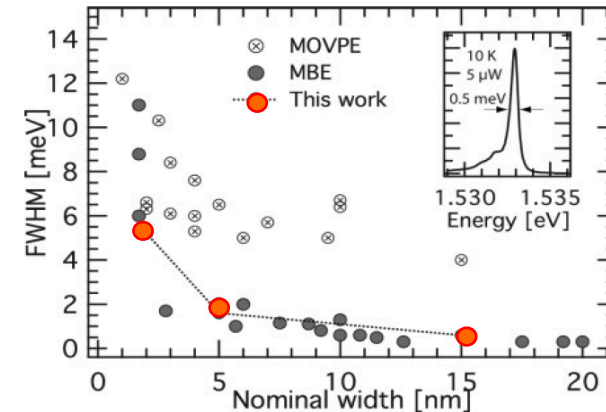
Probing reactor status with PL of AlGaAs/GaAs QWs



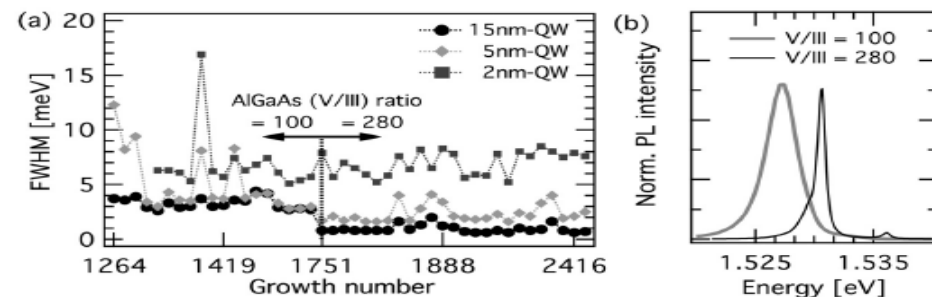
N. Moret, PhD thesis (EPFL, 1988)

AlGaAs/GaAs QWs on vicinals: a summary

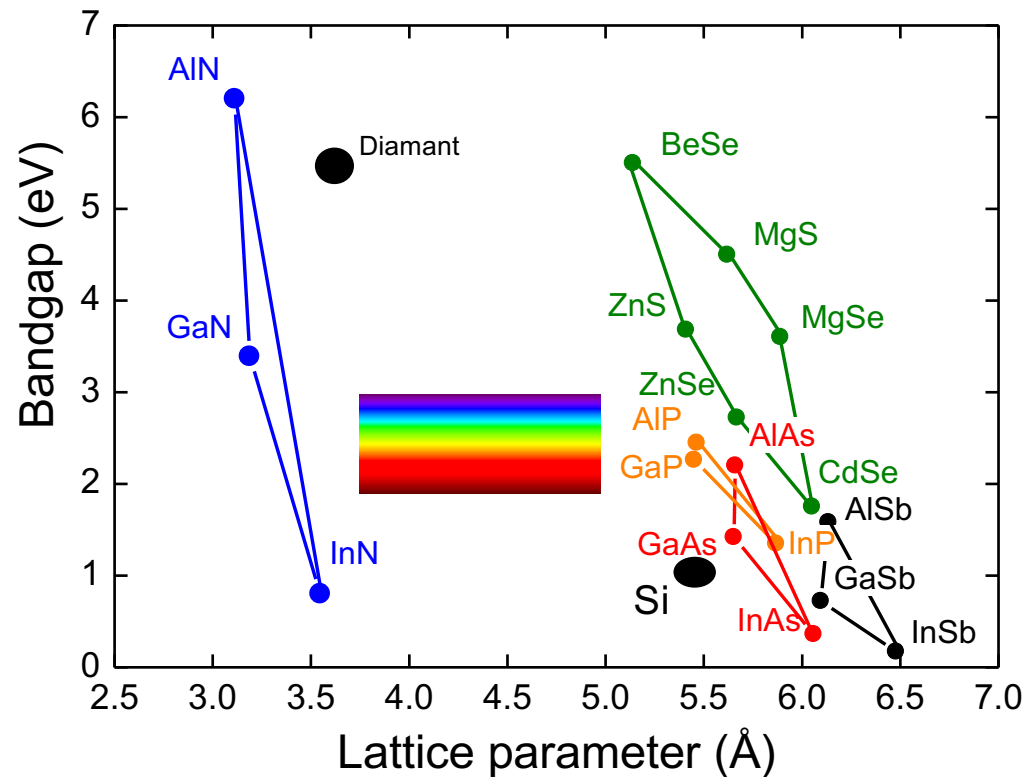
- Best combination:
 - $0.1 - 0.3^\circ$ towards (111)A
 - $T \sim 710^\circ \text{C}$
 - $V/\text{III} \sim 280$ in AlGaAs, $V/\text{III} \sim 130$ in GaAs
- Best optical properties reported:
 - Linewidth as low as 0.5 meV for 15 nm thick GaAs
 - Fine excitonic structures
- AFM on QW interfaces
 - Regular step flow surface gives lowest PL linewidth



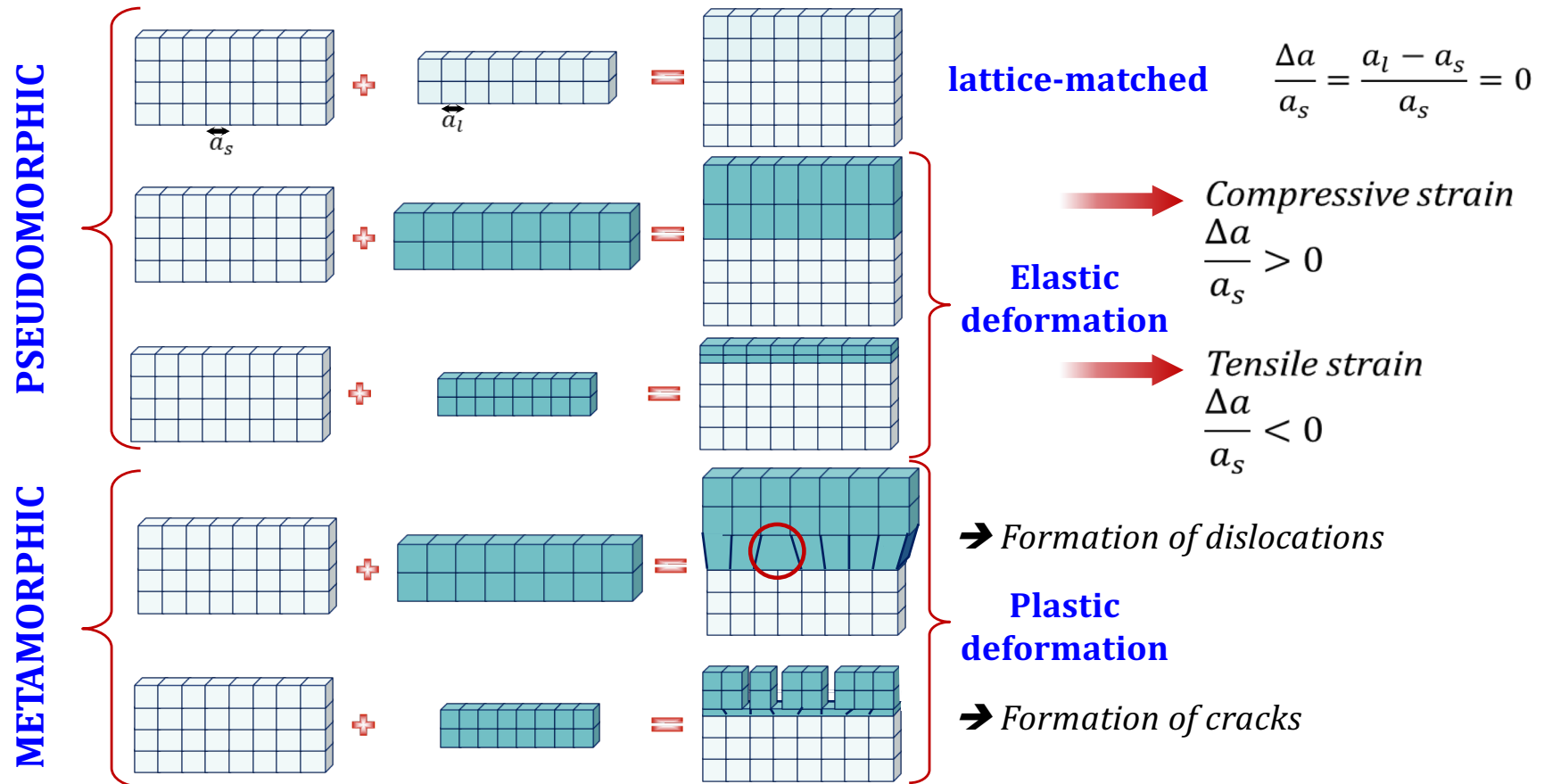
A sensitive tool to evaluate
the growth system over years:
PL of GaAs/AlGaAs QWs



Heteroepitaxy

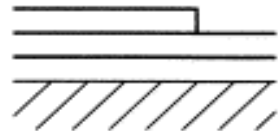
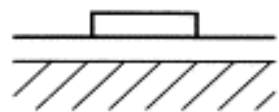
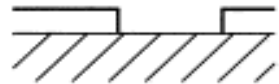


Heteroepitaxy



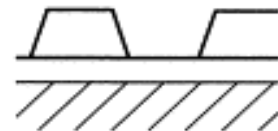
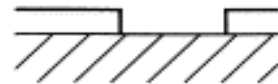
Heteroepitaxy

Layer by Layer
Growth



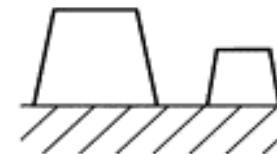
Frank-van der Merwe
2D

Layer plus
Island Growth



Stranski-Krastanov
2D-3D

Island Growth

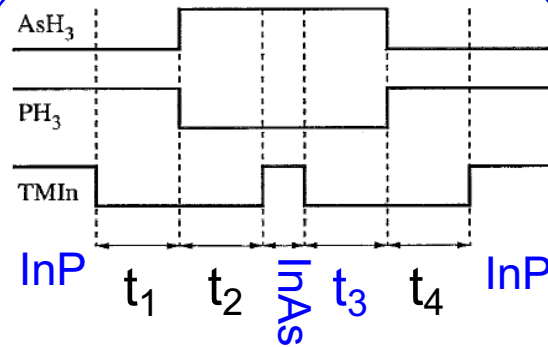
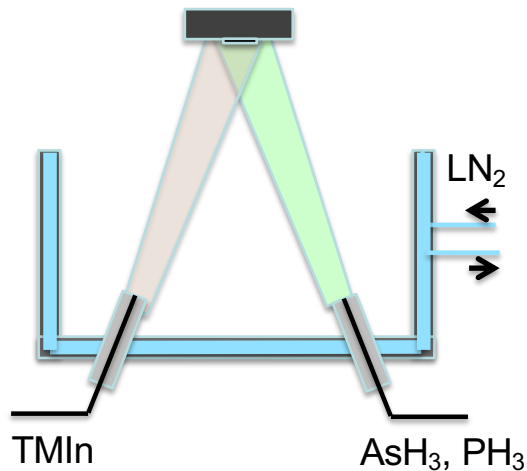


Volmer-Weber
3D

Dynamics of island formation in InAs/InP QWs

- Chemical Beam Epitaxy
- TMIn, AsH₃, PH₃
- InP (100)+/-0.1°
- 400nm InP buffer
- 2 ML InAs QW
- 50nm InP cap
- 1 ML/s

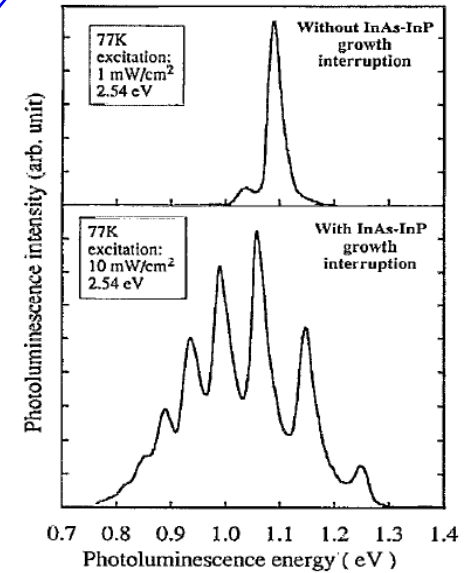
Holder/heater



t₁, t₂ and t₄: no effect

t₃ : 0 – 15"

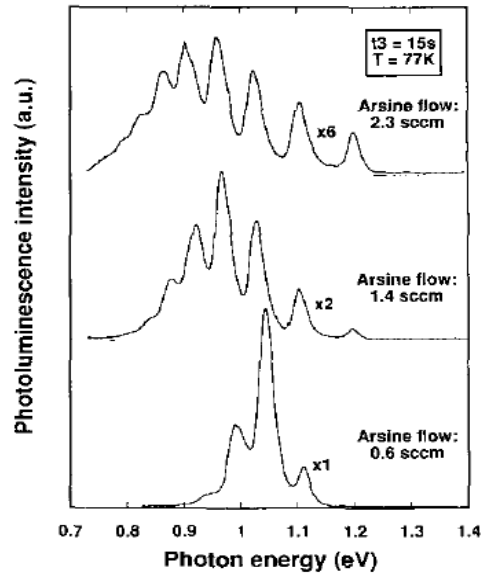
J.F. Carlin *et al.*
Appl. Phys. Lett. 1991



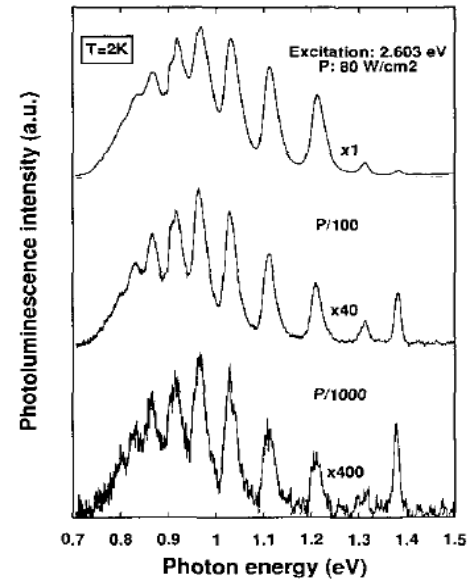
Multiple PL lines appear
if t₃ > 0

The QW structure transforms
during growth interrupt
under AsH₃

Dynamics of island formation in InAs/InP QWs



AsH_3 enhances surface transformation



PL emission shows linear dependency
on excitation $\gg$ islands are isolated

The as-grown InAs 2D layer is metastable:

- It transforms into isolated InAs islands during t_3
- This evolution is inhibited under low AsH_3 flux
- It is thermally activated

GaInAsN dilute nitride alloys

Motivations

- A surface science case study
- Long wavelength nanostructures
- Advanced light sources

Challenges

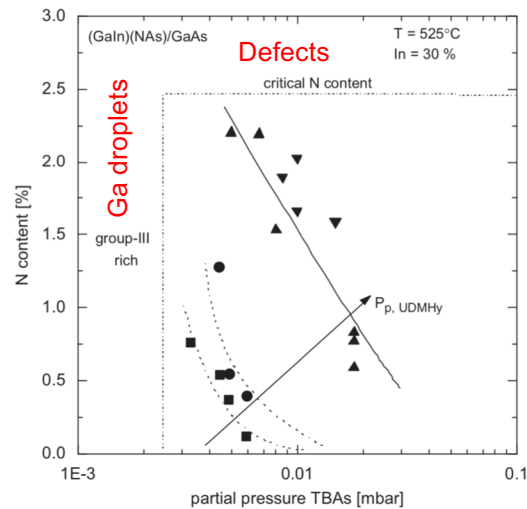
- High radiative efficiency
- Understanding surface kinetics

Keys

- Modulated growth
- Vicinal surfaces
- Non-planar growth

(GaIn)(AsN): N - As competition on group V sites

Series at constant DMHy partial pressure
(constant nominal $[N_{ad}]$ on the surface)

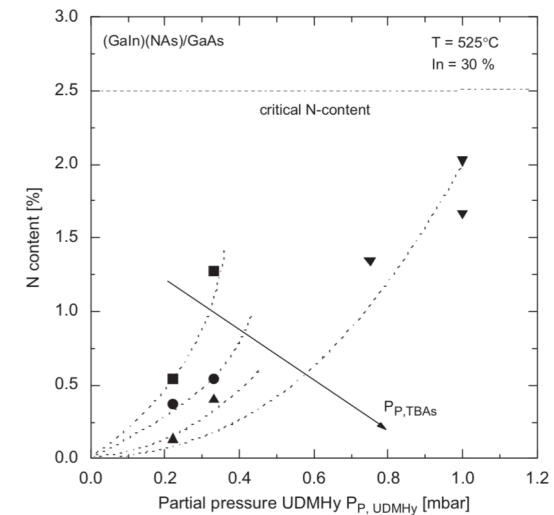


$P_{\text{TBAs}} \rightarrow [As_{ad}] \rightarrow [N] \downarrow$

$[N] > 2.5\%$:

Structural degradation
not due to As deficient
conditions

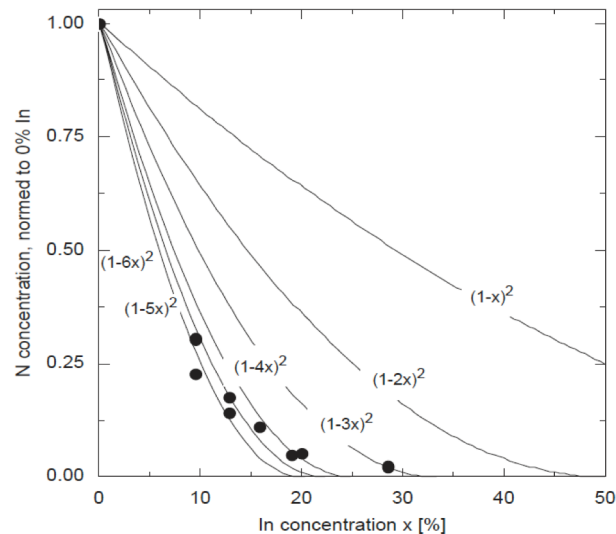
Series at constant TBAs partial pressure
(constant nominal $[As_{ad}]$ on the surface)



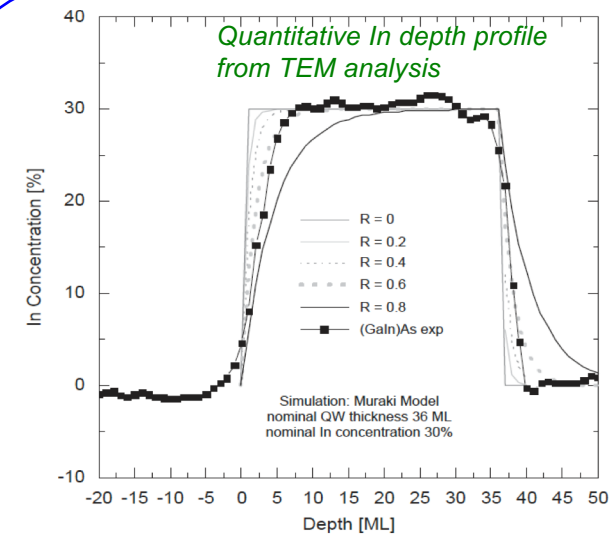
$P_{\text{DMHy}} \rightarrow [N]$

In-induced desorption of N

- In-N strongly repulsive on the surface
- N sticks to Ga, desorbs on In
- N « sees » 3-5 times more In than actually incorporated in the crystal



GaInAsN/GaAs MQWs



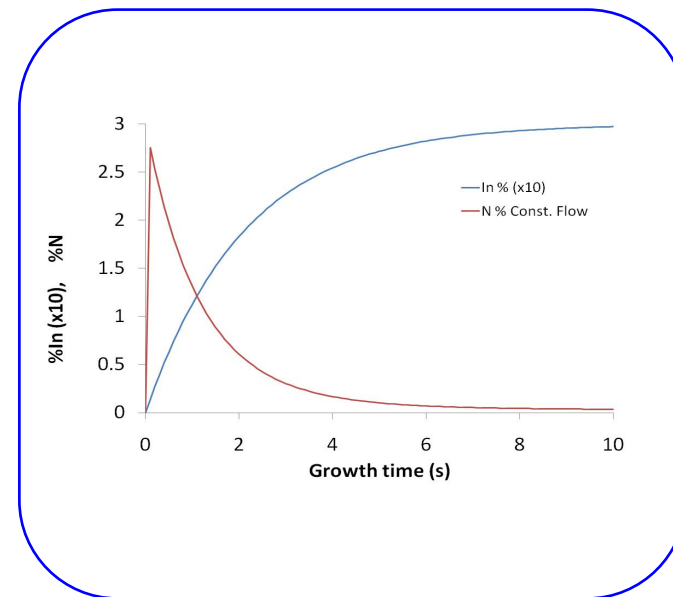
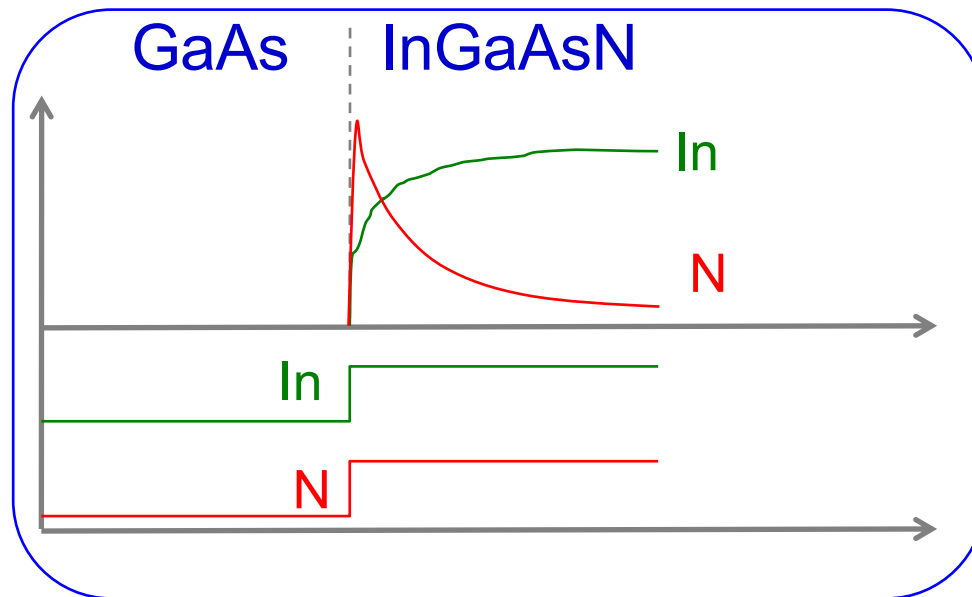
- 7 MLs [In] transient
- $[In]_{\text{surface}} = 2.5 [In]_{\text{volume}}$

Volz *et al.*, J. Crystal Growth 311 (2009) 2418
Rosenauer *et al.*, Ultramicroscopy 72 (1998) 121-133
Muraki *et al.*, Appl. Phys. Lett. 61, 557 (1992)
Albrecht *et al.*, Phys. Rev. Lett. 99, 206103 (2007)

N & In profiles through GaInNAs growth

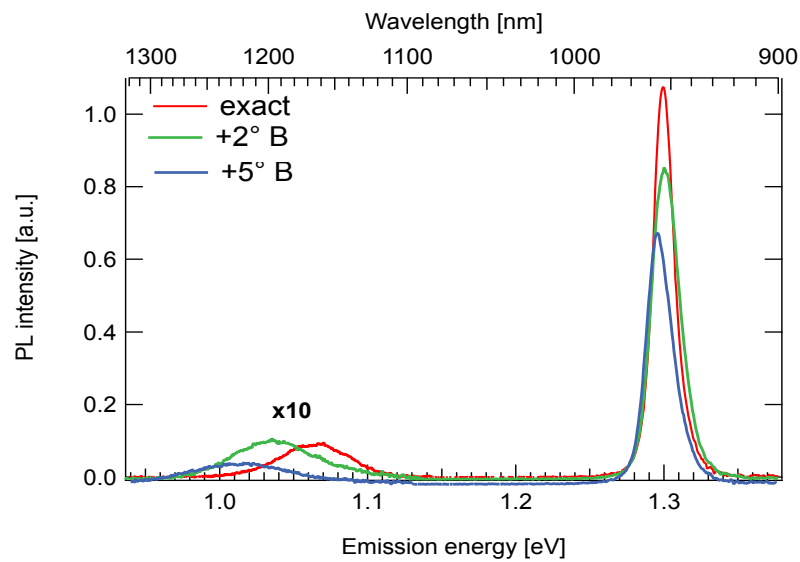
Nitrogen

- 1) accumulates at the lower interface
- 2) diffuses during growth
- 3) desorbs at the growth surface

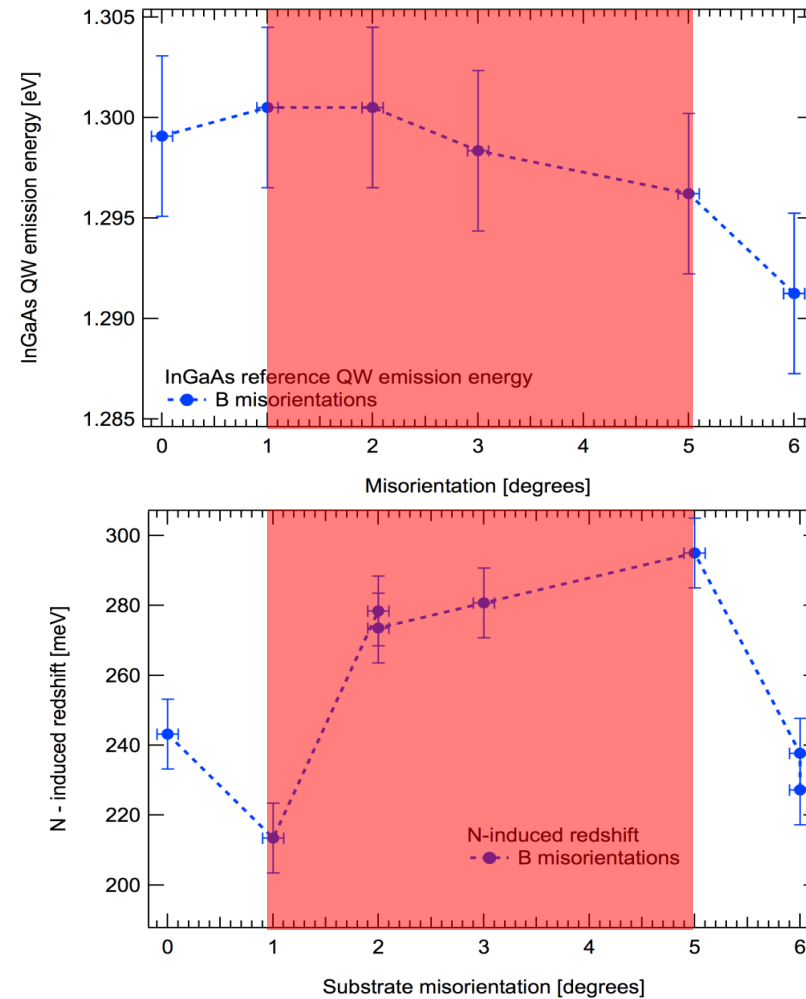


Albo *et al.*, Appl. Phys. Lett. 96, 141102 (2010)

Influence of substrate off-orientation



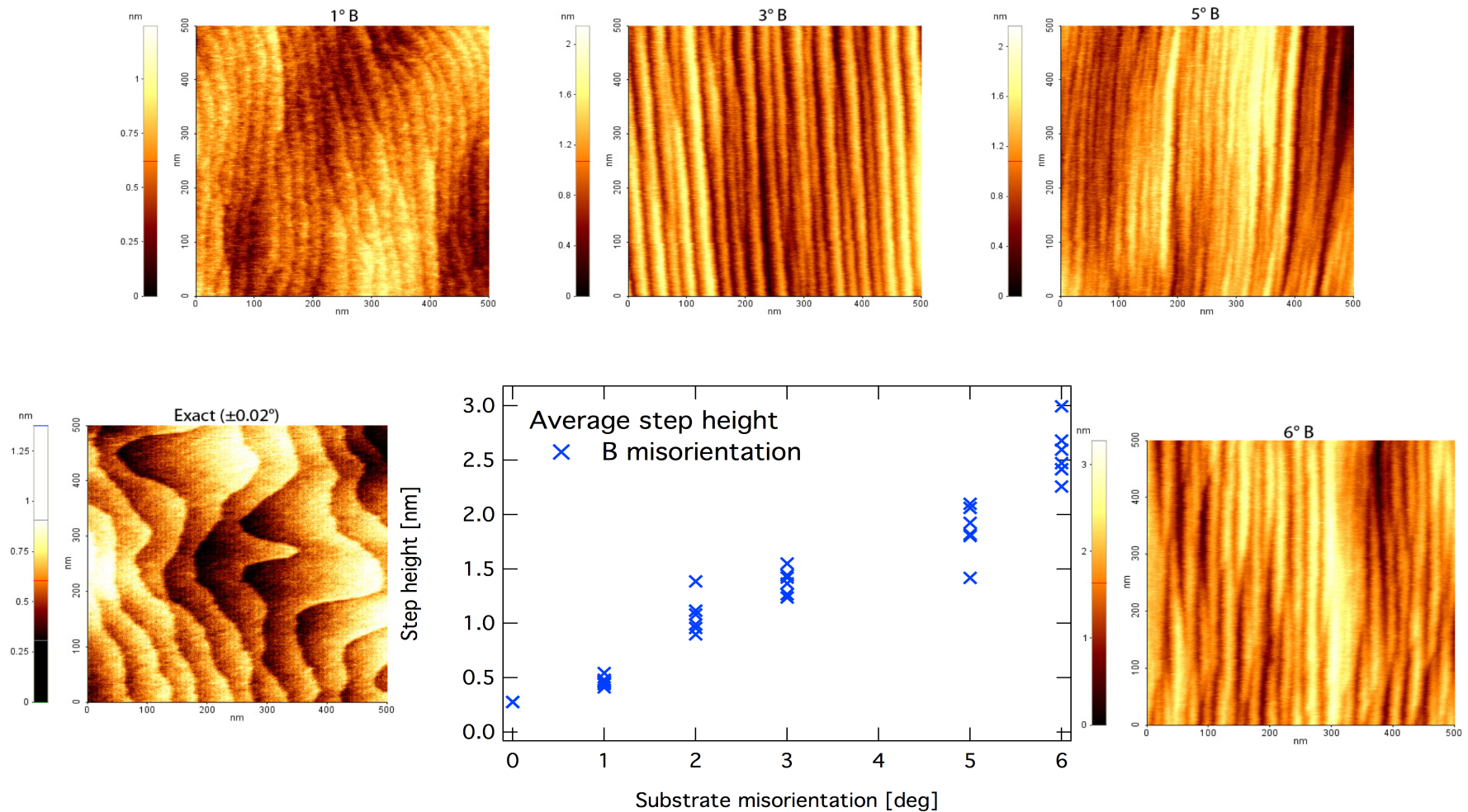
1-5° : [In] increases in InGaAs
 ΔE increases $\gg$ [N] increases



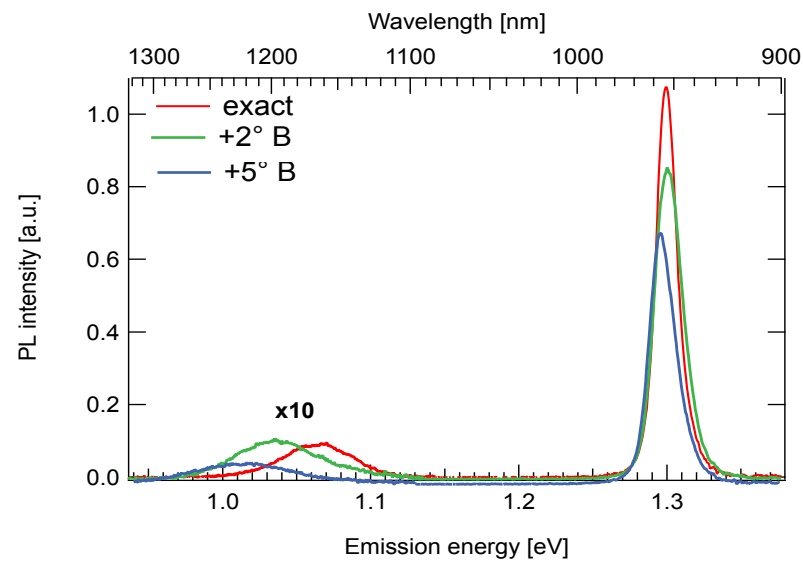
GaInAsN

dilute nitride alloys

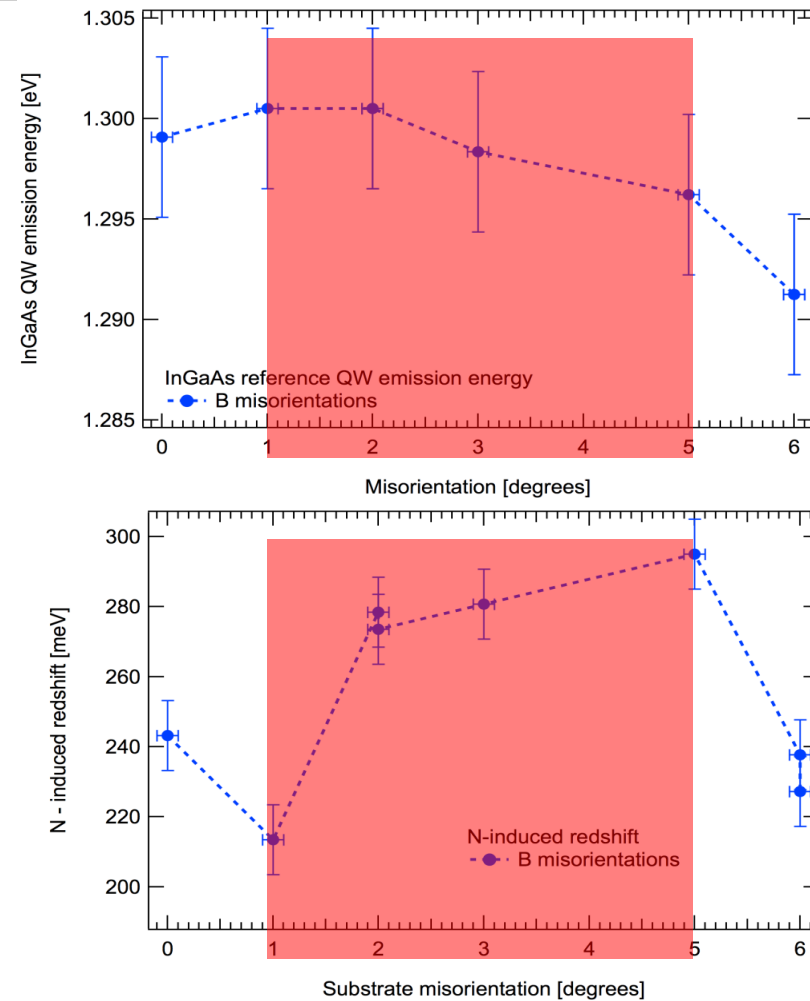
Vicinal « B » epitaxial surfaces step patterns



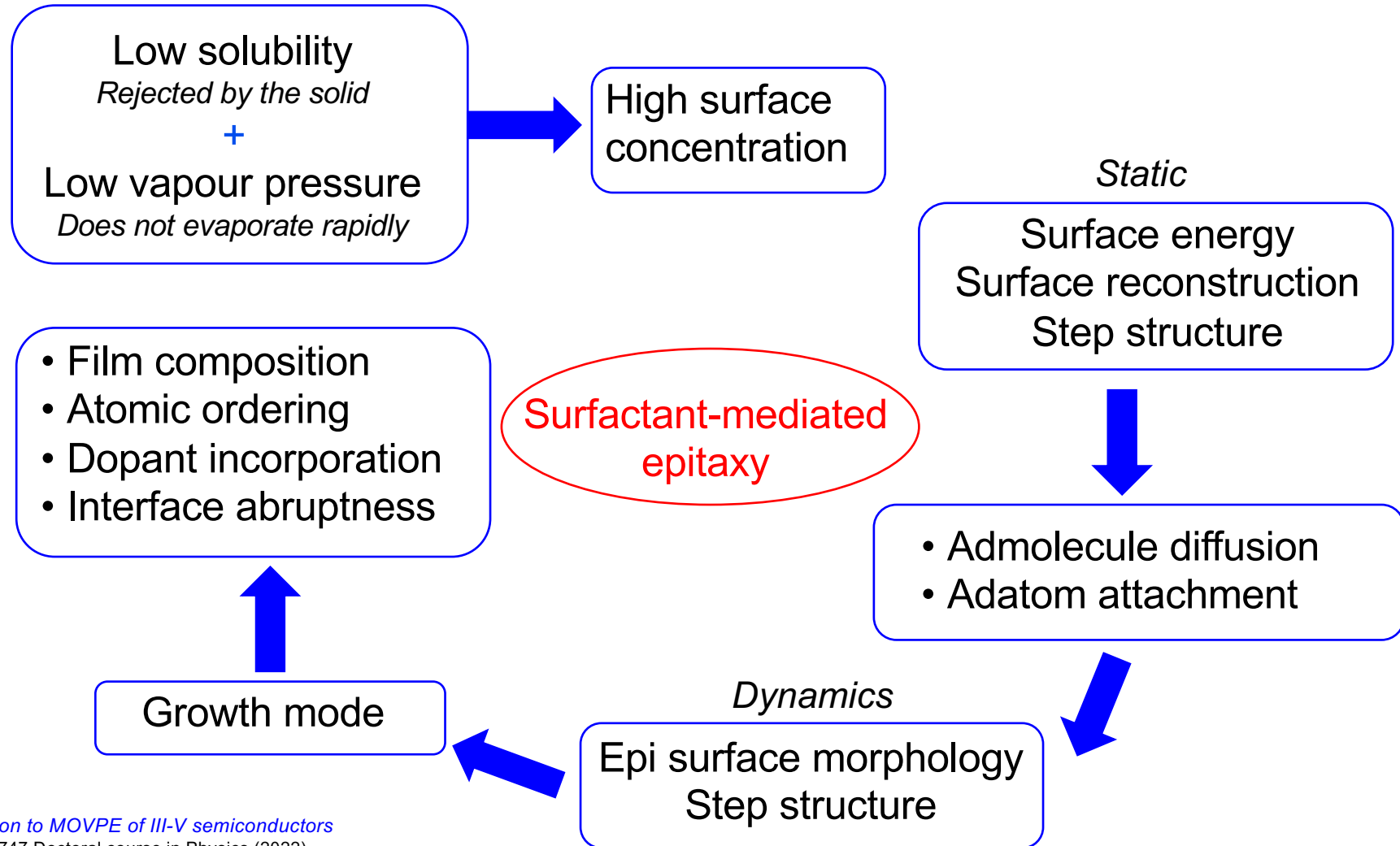
Influence of substrate off-orientation



1-5° : [In] increases in InGaAs
 ΔE increases $\gg$ [N] increases



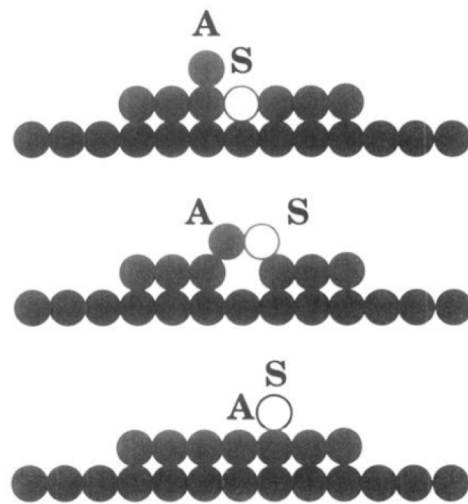
Surfactant: surface active agent



Atomistic model of surfactant behaviour in homoepitaxy

A: matrix atom / impinging adatom
 S: surfactant atom
 V_{X-Y} = bond strength of X and Y atoms

$$V_{A-A} > V_{A-S} \gg V_{S-S}$$

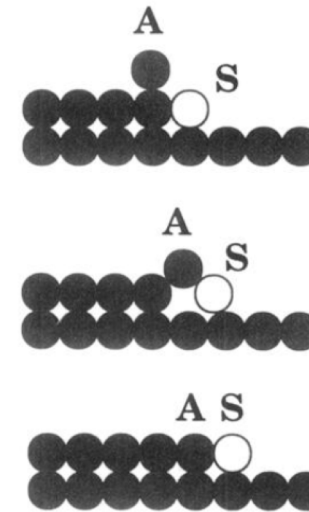


S/A exchange process
on island

Initial

Transient

Final



S/A exchange process
on step

Surfactants: selected examples

- Smoothens static homoepitaxial surface
- Enhances dopant incorporation
- Extends 2D growth thickness in strained epitaxy
- Reduces tapering & diameter of nanowires
- Reduces aspect ratio of nanowires

- ✓ MBE
- ✓ MOVPE
- ✓ CVD

Te as a surfactant in molecular beam epitaxy

PHYSICAL REVIEW B

VOLUME 53, NUMBER 20

15 MAY 1996-II

Kinetics of surfactant-mediated epitaxy of III-V semiconductors

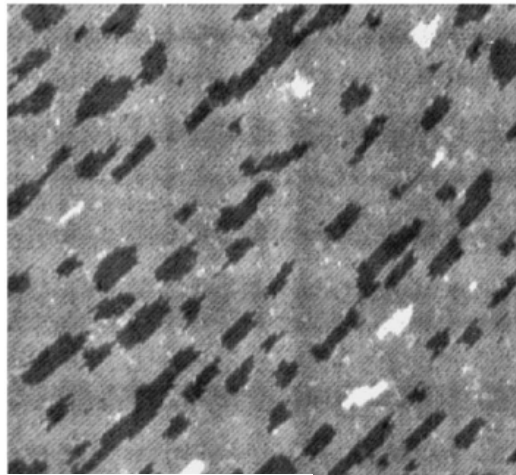
N. Grandjean and J. Massies

*Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique,
Rue B. Grégory-Sophia Antipolis, 06560 Valbonne, France*

- MBE (Ga & As sources)
- Scanning tunneling microscopy
- X-ray Photoelectron Spectroscopy
- n-GaAs:Si (100) substrates
- 1 μ m GaAs buffer grown at 590° C, annealed 45' at 600° C
- Te (0.5 ML) deposited at 580° C under As₄
- GaAs (10 MLs) epitaxial growth at 580° C, r = 0.3 ML/s
- Without / with preabsorbed Te
- As partial pressure $P_{\text{As}} = 5 \cdot 10^{-7} / 5 \cdot 10^{-6}$ Torrs
- Variable As coverage θ

Scanning Tunneling Microscopy of GaAs static surface

2x4 reconstructed GaAs surface



↗ [1 $\bar{1}$ 0]

+ Te
0.5 ML



3x1 reconstructed GaAs surface



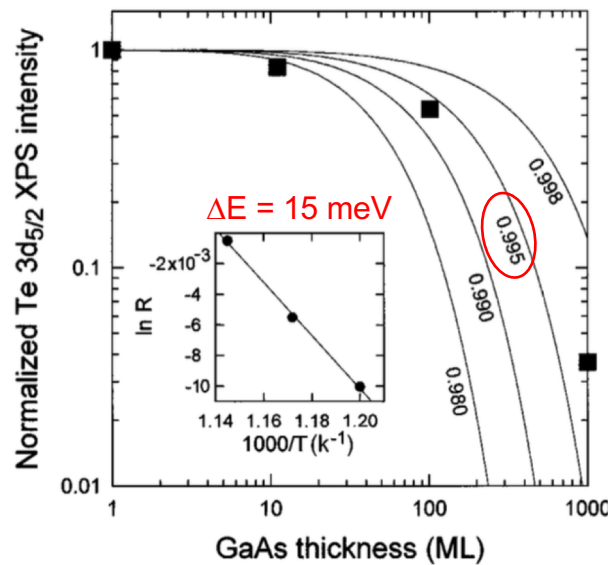
Large and smooth shaped terraces

Te chemisorption
reduces the GaAs
surface energy

- 180x180nm² STM scans
- Each grey level: 1 ML (2.83 Å)

Surface & subsurface processes

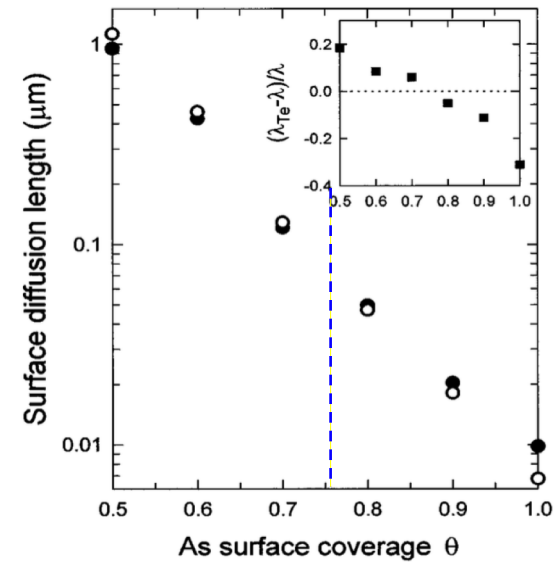
Te surface concentration
vs
GaAs epilayer thickness



Exchange coefficient R : $x_{n+1} = R x_n$

$x_n = [\text{Te}]$ on the n^{th} layer

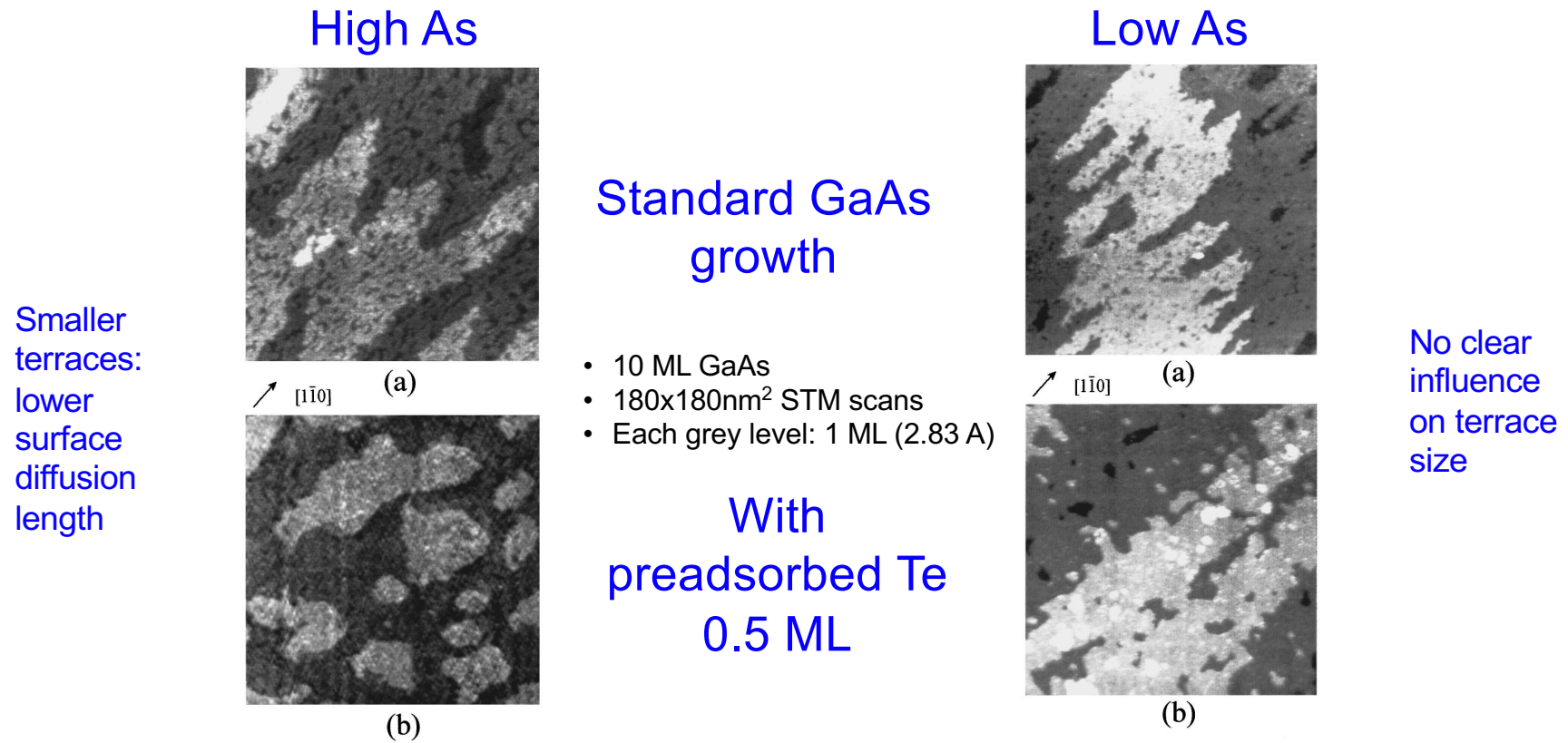
Calculated surface diffusion
length vs As coverage



$\theta < 0.75 : \lambda_{\text{Te}} > \lambda$

$\theta > 0.75 : \lambda_{\text{Te}} < \lambda$

Te assisted MBE of GaAs: influence of As flux



Surface diffusion length affected only at high As coverage

Surfactants & step bunching: GaAs + Te

APPLIED PHYSICS LETTERS

VOLUME 73, NUMBER 12

21 SEPTEMBER 1998

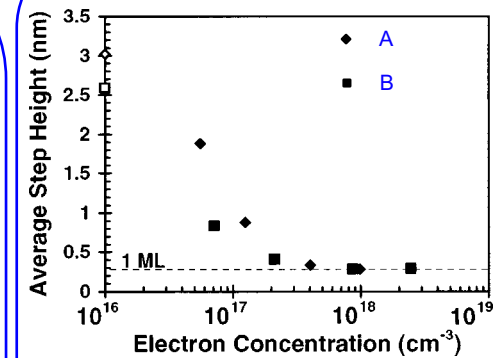
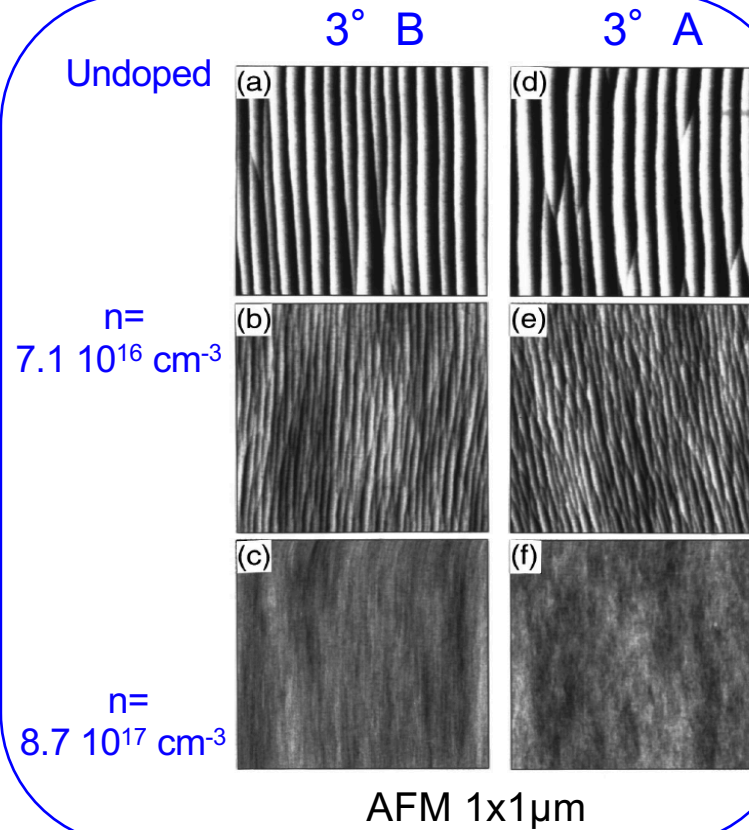
Influence of tellurium doping on step bunching of GaAs(001) vicinal surfaces grown by organometallic vapor phase epitaxy

S. H. Lee and G. B. Stringfellow^{a)}*Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112*

GaAs:Te

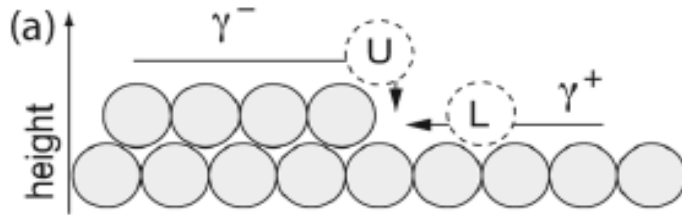
TMGa, AsH₃, DETe
 Carrier gas: H₂
 620° C, 0.6 μm/h
 250nm

- Reconstructed step edges free of dangling bonds
- Te attaches to step edges
- Changes the reconstruction
- Increases γ^+ (Ga_{ad} sticking probability from lower terrace)
- $\gamma^+ > \gamma^-$
- Step bunching disappears


 $n > 4 \times 10^{17} \text{ cm}^{-3}$


monolayer steps

Ehrlich & Schwoebel statistics

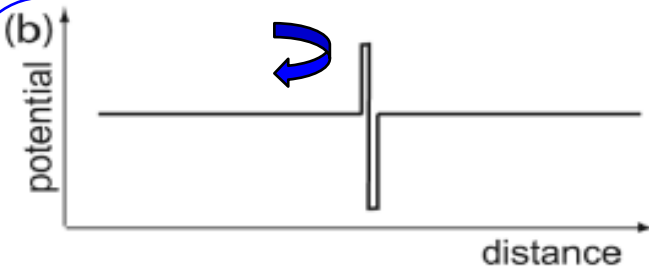


Adatom approaches surface step
from upper (U) or lower (L) terrace

Adatom to step sticking probability

γ^+ : from lower terrace

γ^- : from upper terrace



Difference of nearest neighbors seen by a
diffusing adatom creates a potential barrier
at the step upper edge

$$\gamma^+ > \gamma^-$$

- Repulsive step-step interaction
- Uniform step separation develops
- Step flow mode

$$\gamma^+ < \gamma^- :$$

- Attractive step-step interaction
- Large terraces grows faster and catch up with lower, smaller one
- Step bunching

Surfactants and doping: GaAs:Zn + Sb

APPLIED PHYSICS LETTERS

VOLUME 78, NUMBER 20

14 MAY 2001

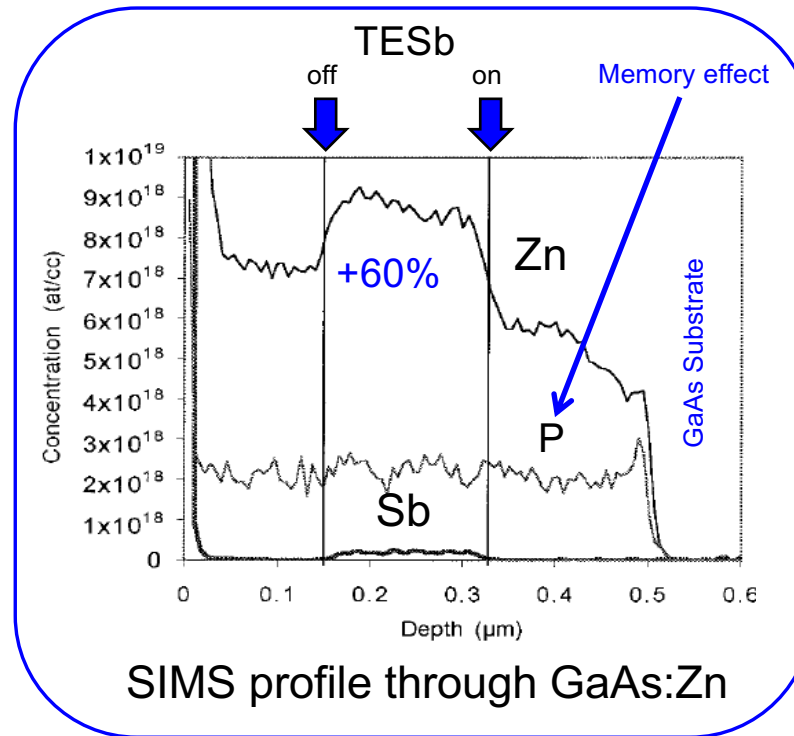
Surfactant effects on doping of GaAs grown by organometallic vapor phase epitaxy

J. K. Shurtleff, S. W. Jun, and G. B. Stringfellow^{a)}*Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112*

TMGa, TBA,
DMZn, DETe, TESb
Carrier gas: H₂
620° C, V/III=40, 1.3 μm/h
TESb/TMGa = 0.012

TESb:

↑ Zn & In uptake
↔ P, Te uptake



Surfactants and doping: GaAs:Zn + Sb

TESb:

↑ Zn & In uptake
↔ P, Te uptake

Sb increases

- Surface **diffusion** of Zn/In adatoms
- **Step attachment** of Zn/In adatoms at step edges
- Incorporation of Zn and In on Ga sites (As dangling bonds)

- Te & P should incorporate on group V sublattice
- Sb does NOT enhance the attachment to As sites
- Sb shows no influence on Te and P uptake

Surfactants and strain: InGaAs / InP + Sb

IEEE JOURNAL OF SELECTED TOPICS IN QUANTUM ELECTRONICS, VOL. 13, NO. 5, SEPTEMBER/OCTOBER 2007

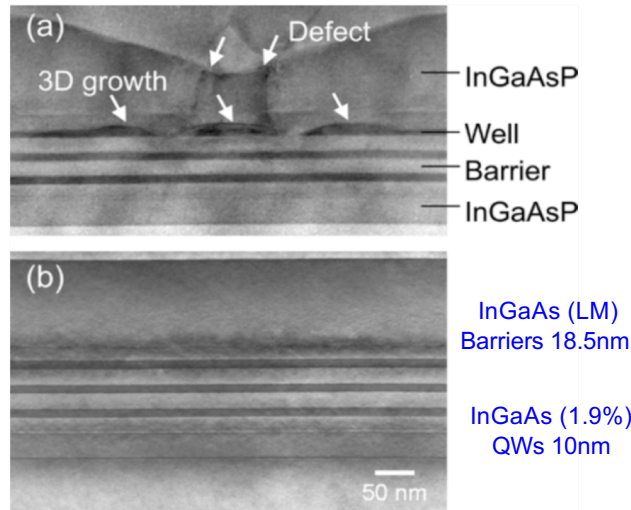
1079

2.1- μm -Wavelength InGaAs Multiple-Quantum-Well Distributed Feedback Lasers Grown by MOVPE Using Sb Surfactant

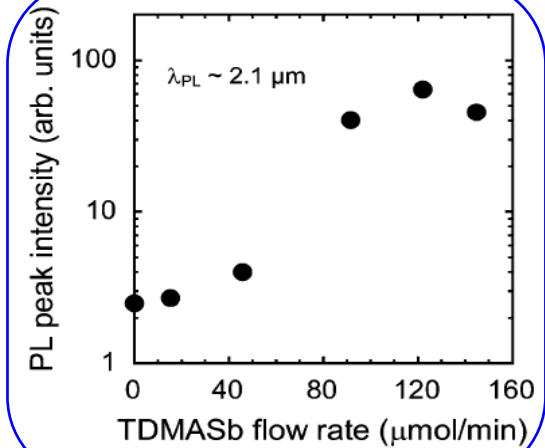
Tomonari Sato, Manabu Mitsuhashi, Takao Watanabe, Kazuo Kasaya, Tatsuya Takeshita, and Yasuhiro Kondo, *Member, IEEE*

- TEGa, TMIn, AsH₃, PH₃
- TDMASb (Tris-dimethyl-amino-antimony)
- 620° C, 50 Torr
- 4 barriers: InGaAs LM to InP
- 3 QWs : strained InGaAs (1.9%)

Without Sb



With Sb



- Stable 2D growth
- Improved PL intensity
- Stable laser operation

Surfactants & nanowires: GaSb + S (CVD)



ARTICLE

Received 29 Apr 2014 | Accepted 11 Sep 2014 | Published 16 Oct 2014

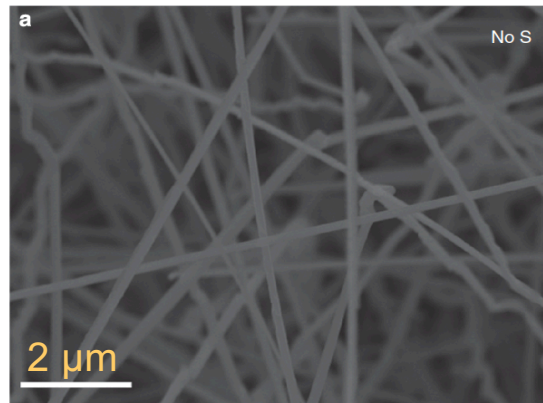
DOI: 10.1038/ncomms6249

Surfactant-assisted chemical vapour deposition of high-performance small-diameter GaSb nanowires

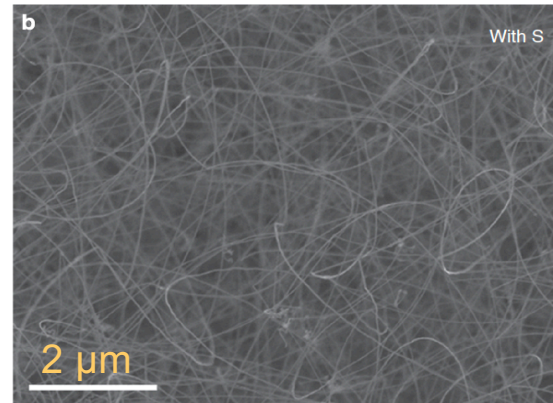
Zai-xing Yang^{1,*}, Ning Han^{1,2,*}, Ming Fang¹, Hao Lin¹, Ho-Yuen Cheung³, SenPo Yip¹, Er-Jun Wang¹, TakFu Hung¹, Chun-Yuen Wong³ & Johnny C. Ho^{1,2}

CVD of GaSb on Si :

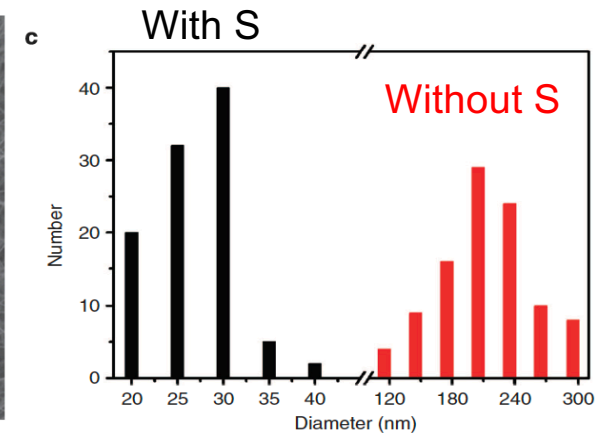
GaSb & S powder, H₂ carrier gas,
 $T_{\text{GaSb}} = 850^\circ \text{C}$, $T_{\text{substrate}} = 620^\circ \text{C}$
 Vapour-Liquid-Solid NW growth with
 Au catalyst



Without S



With S



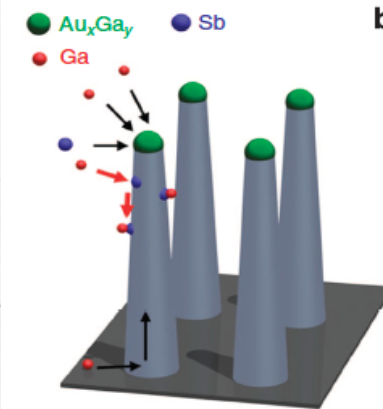
NW diameter distribution

Surfactants & nanowires: GaSb + S (CVD)

Unsaturated Sb terminated sidewalls



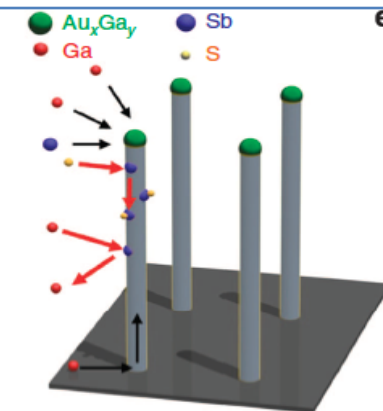
- Uncontrolled radial growth
- Tapered NWs



S stabilizes Sb surface atoms by creating stable S-Sb bonds

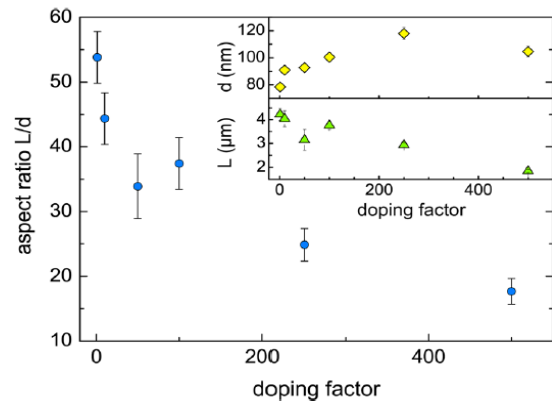
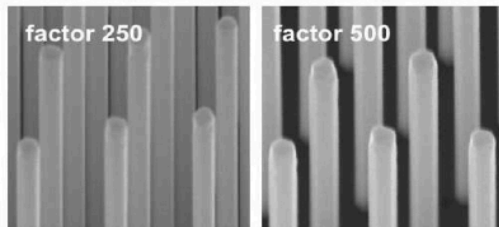
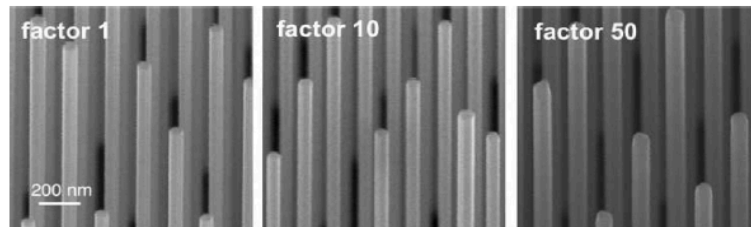


- Reduces radial growth
- Reduces tapering



Surfactants & nanowires: InAs, GaAs + Si

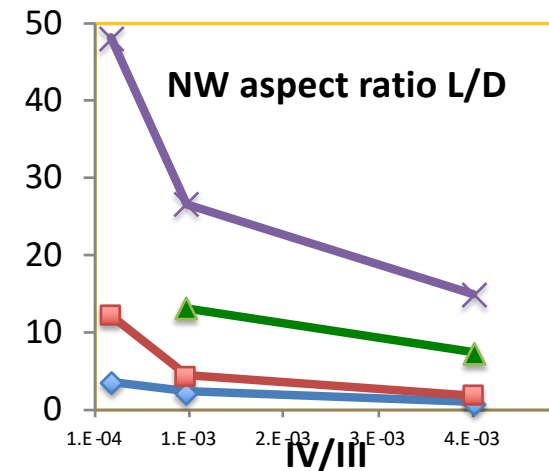
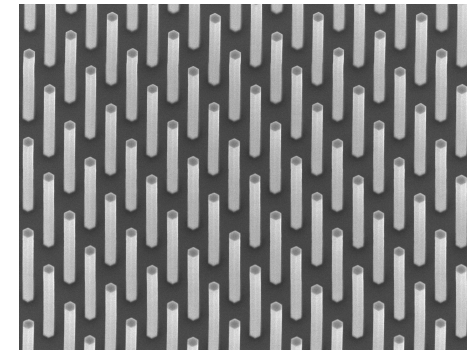
InAs



Si₂H₆ flow

- **reduces** the growth rate on the top (111)B facet
- **increases** the growth rate on the lateral {110} facets
- **reduces** the NW aspect ratio

GaAs



S. Wirths *et al.*, J. Appl. Phys. 110 (2011)

Introduction to MOVPE of III-V semiconductors

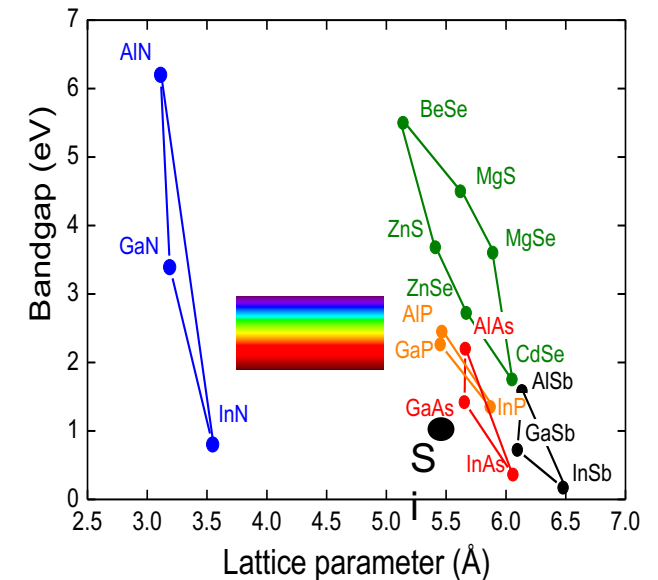
PHYS-747 Doctoral course in Physics (2022)

Surfactant mediated epitaxy: a summary

- 0.5ML Te smoothens GaAs surface (MBE + STM)
- Te (from DETe) suppresses step bunching in GaAs if $n > 4 \cdot 10^{17} \text{ cm}^{-2}$
- Sb (from TESb) increases Zn and In incorporation in GaAs
- Sb (from TDMASb) increases pseudomorphic thickness in InGaAs/InP MQWs
- S reduces diameter of GaSb nanowires (CVD)
- Si (from Si_2H_6) reduces the aspect ratio of GaAs nanowires

Selective area epitaxy – motivations

- **Functional integration, the smart way :**
 - Post-growth processing damages the materials – mechanically and chemically
 - Multiple processing steps are as many opportunities to kill the material
 - **Better: spatial modulation of surface kinetics** by pre-growth patterning
 - In-plane, growth engineered optical and electrical modulation
 - Cristallographic facet engineering
 - Strechable electronics for biological interfaces
- **Heteroepitaxy: broaden the range of accessible materials**
 - The dream: grow anything on anything: III-V on Si, GaN...
 - Lattice + thermal expansion mismatch > strain
 - Solutions through SAE
 - Epitaxial lateral overgrowth (ELO)
 - Aspect ratio trapping (ART)
 - Template assisted selective epitaxy (TASE)
- **Homoepitaxy**
 - Improve material properties in specific cases
 - Substrate recycling: patterning used to separate substrate from epi & recycle

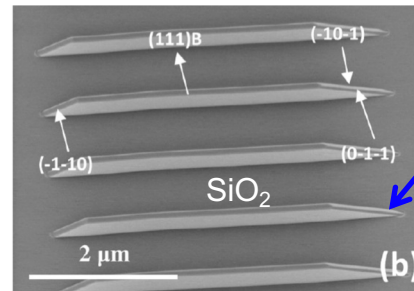
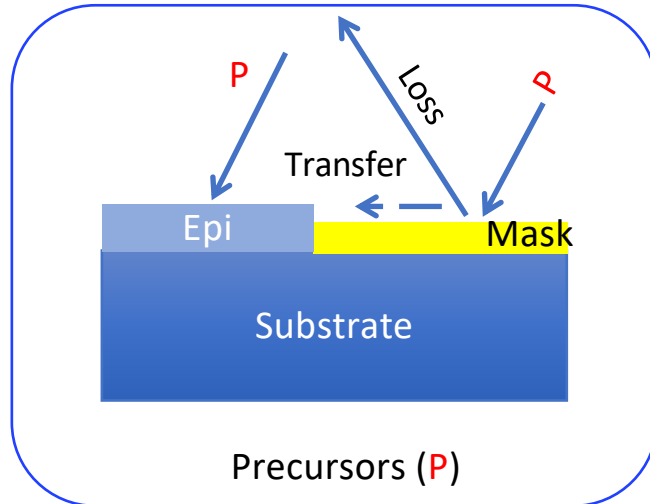


Selective area epitaxy : basics

Spatial modulation of surface kinetics:

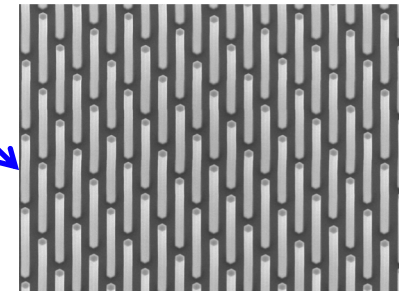
- • Partly cover surface with a **mask** material which has a different chemical reactivity to the growth precursors compared to the original substrate
- Modulate cristallographic orientation by **non-planar** patterning
- Build spatially localised **strain fields** below the growth surface that will modify the surface growth kinetics

→ Masked SAE

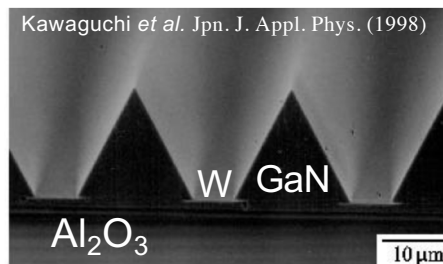


Chi *et al.*, Nano Lett. (2013)

GaAs

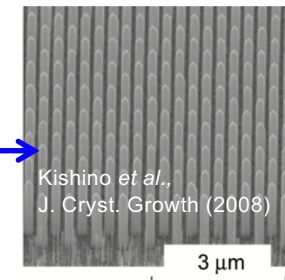


P.R. Gomez, LMSC (2019)



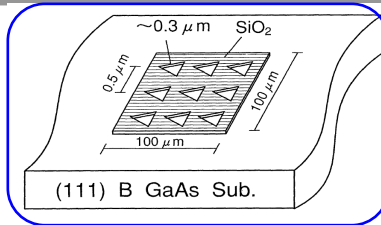
Kawaguchi *et al.* Jpn. J. Appl. Phys. (1998)

GaN →



Kishino *et al.*, J. Cryst. Growth (2008)

Selective area epitaxy: GaAs tetrahedral growth

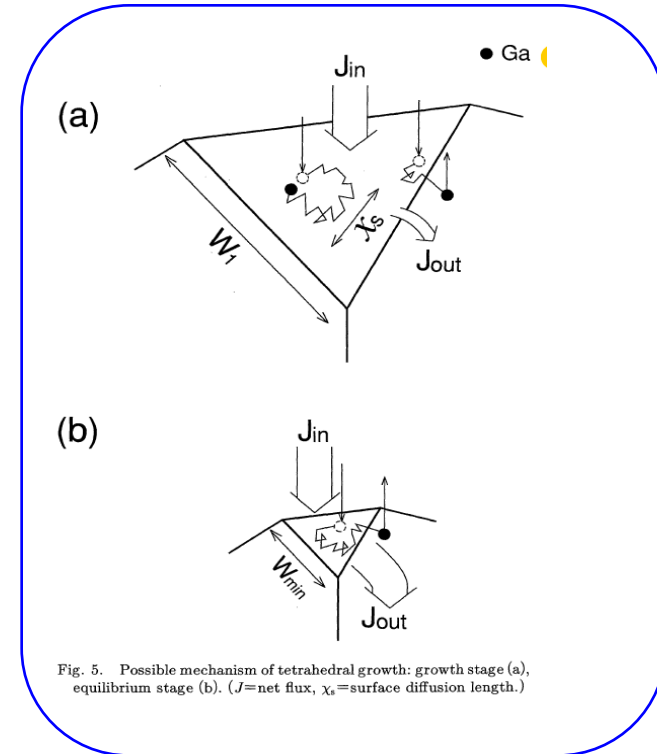
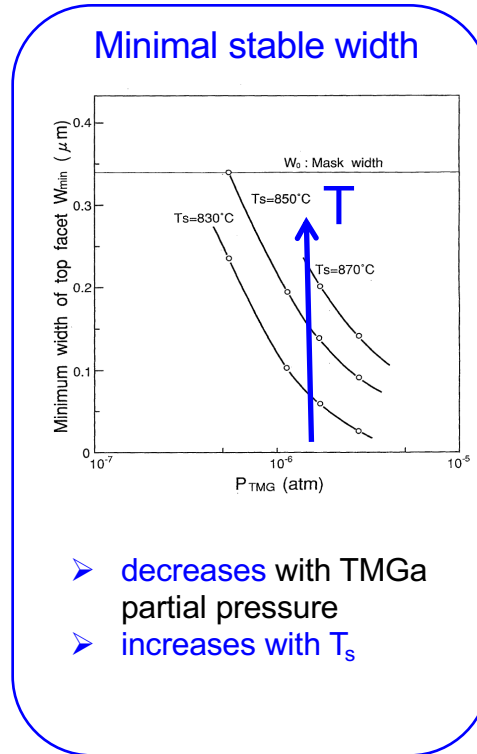
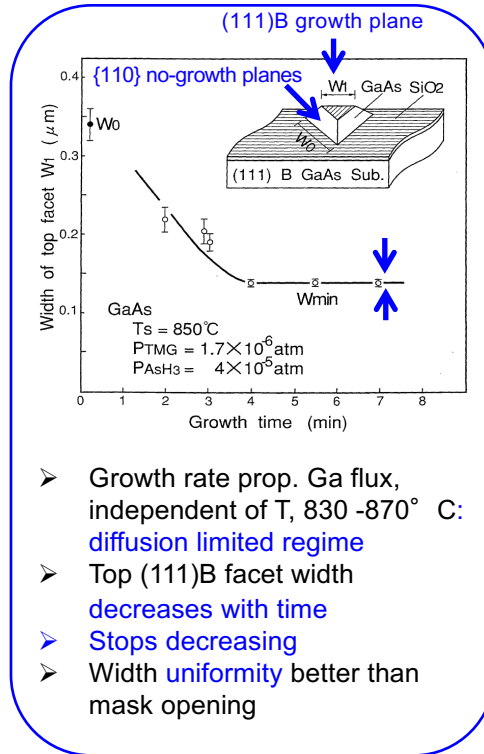


Jpn. J. Appl. Phys. Vol. 32 (1993) pp. L 104-L 106
Part 2, No. 1A/B, 15 January 1993

Self-Limited Facet Growth for GaAs Tetrahedral Quantum Dots

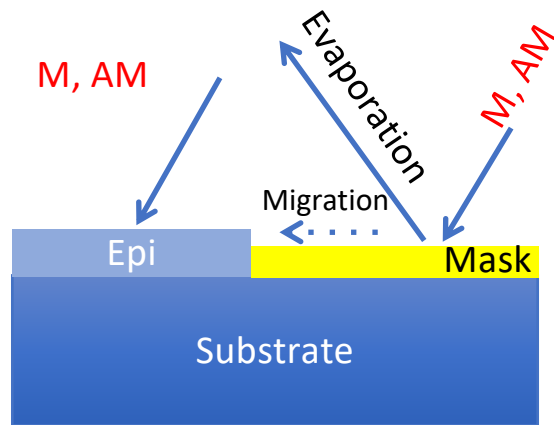
Seigo ANDO, Takashi HONDA and Naoki KOBAYASHI
NTT Basic Research Laboratories, 3-9-11 Musashino-shi, Tokyo 180

- TMGa, AsH₃
- Carrier gas: H₂
- (111)B +/-0.1°
- P=19 Torr
- 830 - 870° C



SAE: the influence of the gas phase

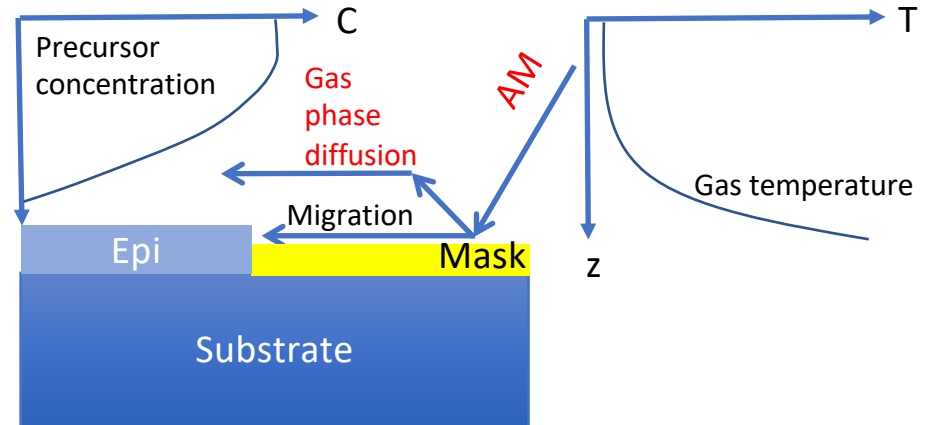
Vacuum Epitaxy (MBE, GSMBE, CBE)



Adatoms (**M**) or Admolecules (**AM**)

- migrate on the mask surface
- re-evaporate

Gas phase Epitaxy (HVPE, MOVPE)



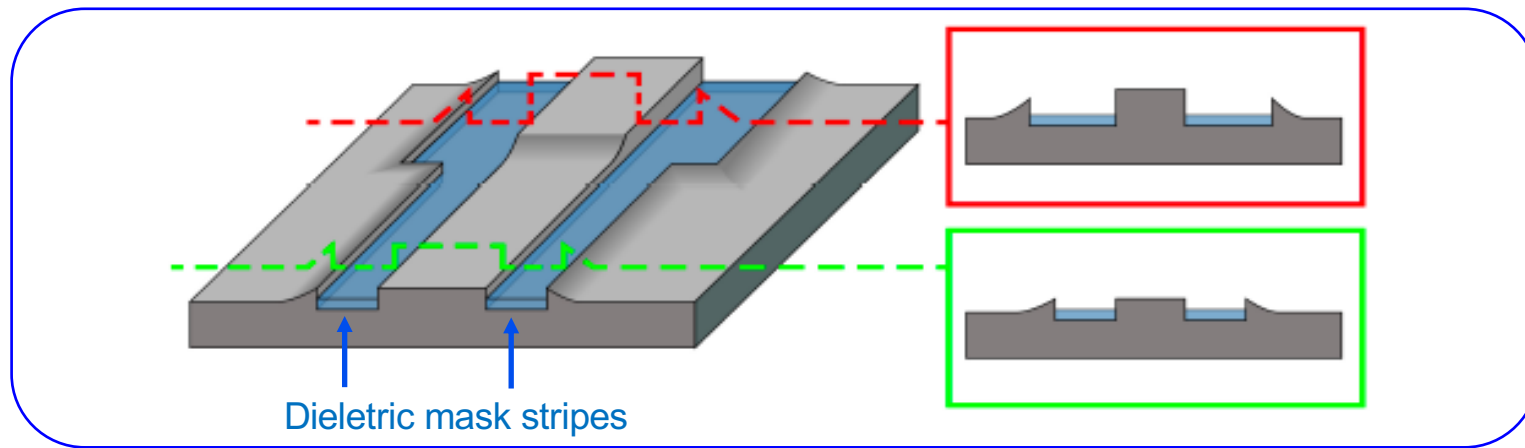
Admolecules (**AM**)

- migrate on the mask surface
- partly decompose in the gas phase boundary layer
- diffuse in the gas phase from the masked to the unmasked area

M: Ga, Al, In, Ge, Si, Be, As, P, Zn, etc...

AM: TMGa, TMAI, TMIIn, $C_4H_{12}Ge$, Si_2H_6 , CBr_4 , DEZn, etc...

Selective area epitaxy: growth rate enhancement



- No growth sites on the dielectric mask >> precursor desorption
- Concentration **gradient** in gas phase >> precursor **gas phase diffusion**
- Growth rate **enhancement** in the window area
- Growth **profile** depends on the masked area geometry
- Partial precursor **fragmentation** in the gas phase **above** the mask
- **Effective** gas phase diffusion depends on the precursor
- **Modulation** of thickness and alloy composition
- Issues with **strain** in alloys
- Applications to device **integration** on the surface

Ethyl- vs methyl- precursors: intrinsic C uptake

Inst. Phys. Conf. Ser. No. 63 : Chapter 3

Paper presented at Int. Symp. GaAs and Related Compounds, Japan, 1981

Acceptor incorporation in high-purity OMCVD grown GaAs using trimethyl and triethyl gallium sources

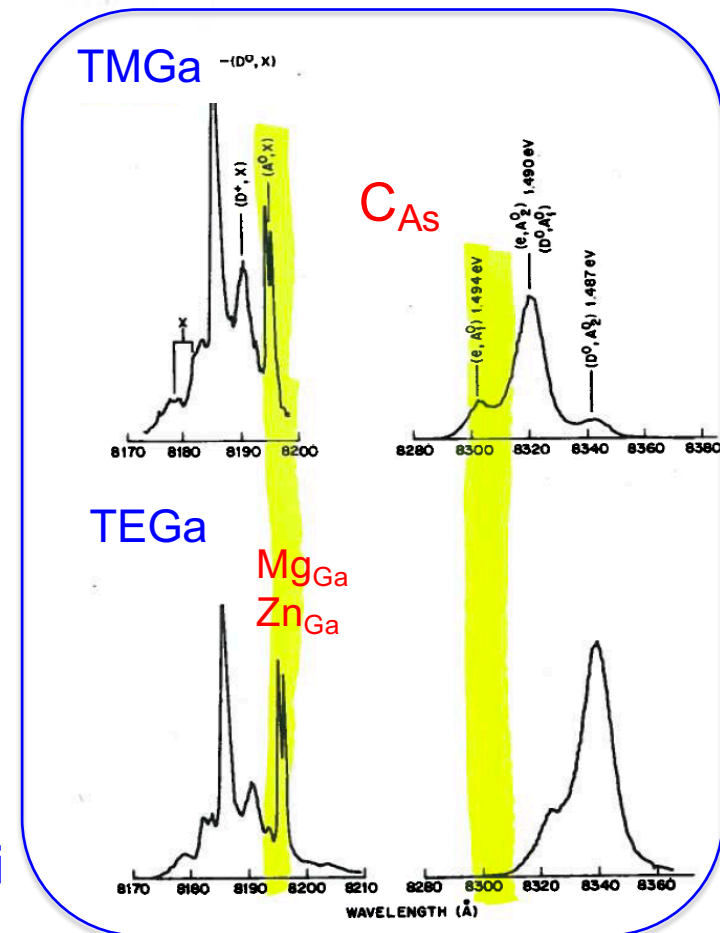
R. Bhat, P. O'Connor, H. Temkin, R. Dingle and V. G. Keramidas

Bell Laboratories, 600 Mountain Ave., Murray Hill, N.J. 07974, USA

- TMGa: $(\text{CH}_3)_3\text{Ga}$
- TEGa: $(\text{C}_2\text{H}_5)_3\text{Ga}$

- Extrinsic C present with both precursors
- C_{As} with TMGa, NOT with TEGa
- Reduced intrinsic C uptake in (Al)GaAs
- Ga-C bond stronger in TMGa than in TEGa
- TEGa decomposes at lower temperatures

8° K PL
GaAs epi



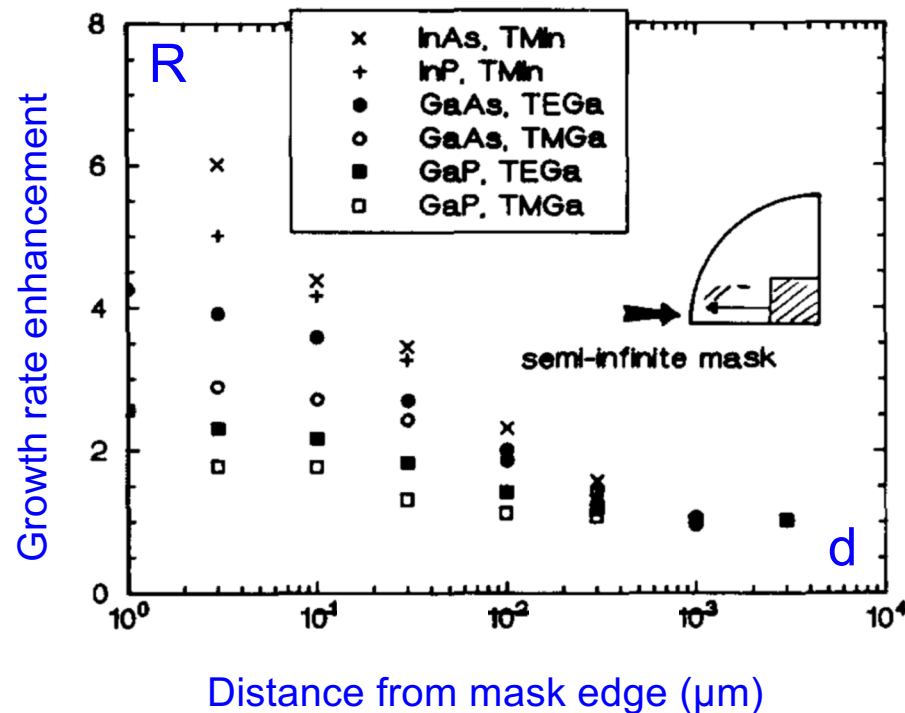
Ethyl- vs methyl: selective area growth of binary alloys

Selective organometallic vapor phase epitaxy of Ga and In compounds:
a comparison of TMIn and TEGa versus TMIn and TMGa

C. Caneau, R. Bhat, C.C. Chang, K. Kash and M.A. Koza

Bellcore 331 Newman Springs Road, Red Bank, New Jersey 07701-7040, U.S.A

Journal of Crystal Growth 132 (1993) 364–370



- (100) Substrates
- InAs, InP, GaAs, GaP
- TMIn, **TMGa/TEGa**, AsH₃, PH₃
- 2x2cm SiO₂ masked area
- 650°C (mass transport limited)
- H₂ carrier gas, 76 Torr

$$R_{\text{InAs}} > R_{\text{InP}} > R_{\text{GaAs}} > R_{\text{GaP}}$$

$$\text{Dec}(\text{TMIn}_{\text{AsH}_3}) > \text{Dec}(\text{TMIn}_{\text{PH}_3})$$

$$\text{Dec}(\text{TMGa}_{\text{AsH}_3}) > \text{Dec}(\text{TMGa}_{\text{PH}_3})$$

$$R_{\text{GaAs/TEGa}} > R_{\text{GaAs/TMGa}}$$

$$R_{\text{GaP/TEGa}} > R_{\text{GaP/TMGa}}$$

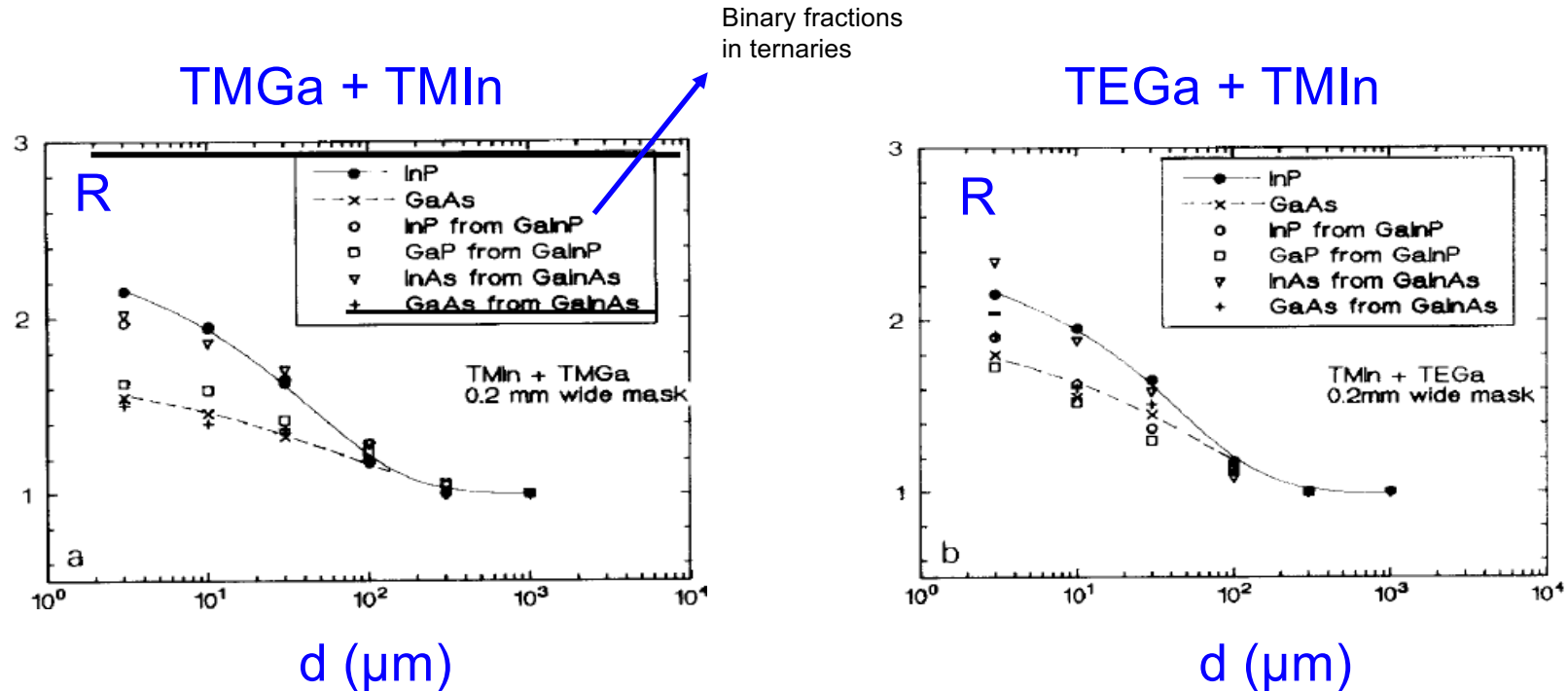
TEGa vs TMGa:

higher *effective* diffusion coefficient



Larger growth rate enhancement

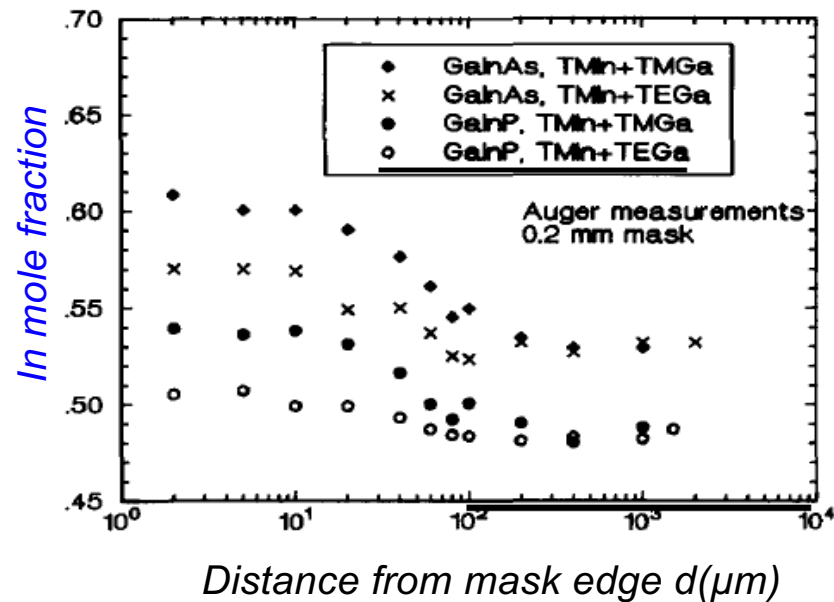
Ethyl- vs methyl- : InGaAs, InGaP selective area growth



- Increased growth rate enhancement using TEGa
- Difference between "pure binaries" and binary fractions of alloys

C. Caneau *et al.*, J. Crystal Growth (1993)

Ethyl- vs methyl : GaInAs & GaInP selective area growth



Reduced In content increase using TEGa

Change in In content:

- undesired > use TEGa
- desired > use TMGa