

Selected experiments in MOVPE

- Overview
 - History & importance
 - Materials, devices, applications
 - Basic architecture & growth process
 - Growth modes
 - Precursors and carrier gas
- Vicinal surfaces
 - Probing AlGaAs/GaAs QWs
- Surfactants
 - Step bunching
 - Doping
 - Strain management
- Non-planar growth
 - GaInAsN dilute nitride alloys
 - InGaAs / GaAs QDs
- Selective area growth
 - In content modulation of InGaAs
 - Self-limited GaAs facet growth

Brief history

- 1954 : T.R. Scott: Patent on InSb epi
- 1968 : H.M. Manasevit (Rockwell, USA)
- 1970s : Work on home made reactors
Intuitive, trial and error development, « Black box »
- 1980s : First commercial reactors
- 1981 : International Conference **ICMOVPE I** in Ajaccio
- 2014 :
Lausanne, July 2014
- 
- 2020 : Major industrial fabrication technique

Materials, devices, applications

Consumer electronics, displays, TVs, cell phones, tablets, lighting, automotive, datacom, telecom, power management, photovoltaics, ...

- GaAs, InAs, AlGaAs, AlInAs, GaInAlAs
- GaAsN, InGaAsN
- InP, GaP, AlInP, GaInP, GaInAsP, AlGaInP
- GaN, AlN, InN, InGaN, AlGaN ←
- InSb, GaSb, InAsSb, AlGaSb
- ZnSe, ZnS, HgCdTe
- GeSi
- Oxides, metals
- 2D materials

LEDs, lasers, solar cells, photodetectors, HBTs, FETs...

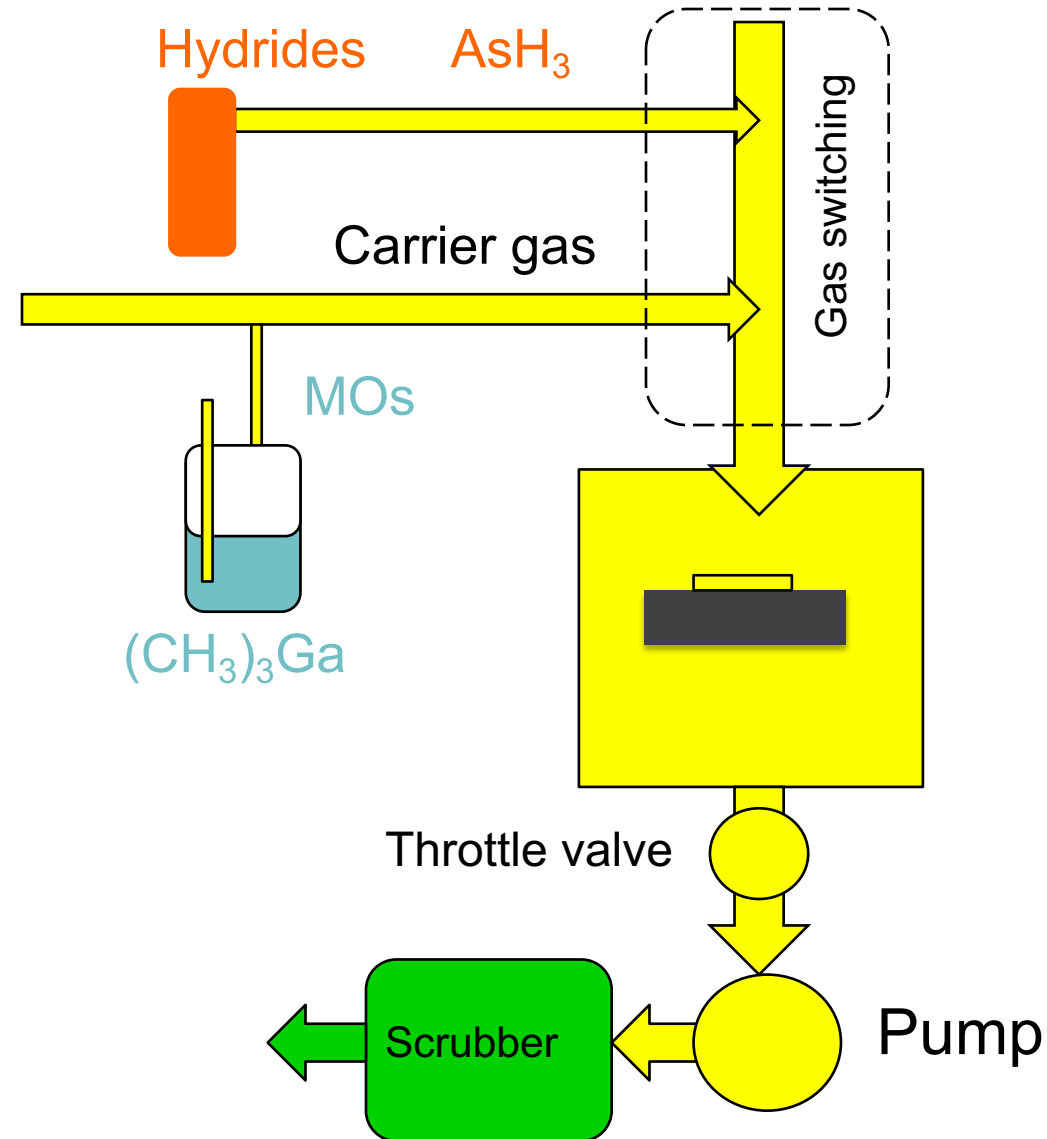
Surface science

Vicinal surfaces, surfactants
non-planar & selective growth...

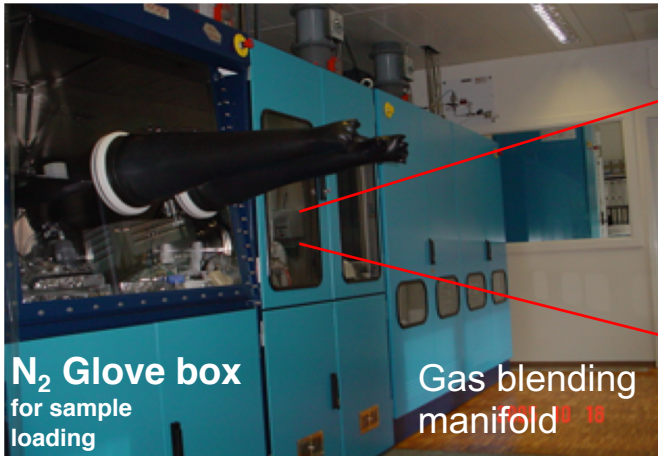
Nanoscale engineering
QWs, QDs, NWs...

MOVPE basic architecture

- Cold wall, open reactor:
Gas mixture flows in and out
Loading through glove box
- Susceptor: 500° C – 1500° C
- P: 5 – 800mbars
Variable throughput pumping system
- Chemical sources (precursors)
MOs from bubblers, hydrides from pressurized cylinders
- Carrier gas: usually H₂ , preferably N₂
Transports the sources from storage point to reactor
- Gas mixing & switching system
Fast gas composition switching for abrupt interfaces
- Scrubbers
Reduce toxic exhaust to acceptable levels
- Safety concept
Survive your growth runs until your PhD

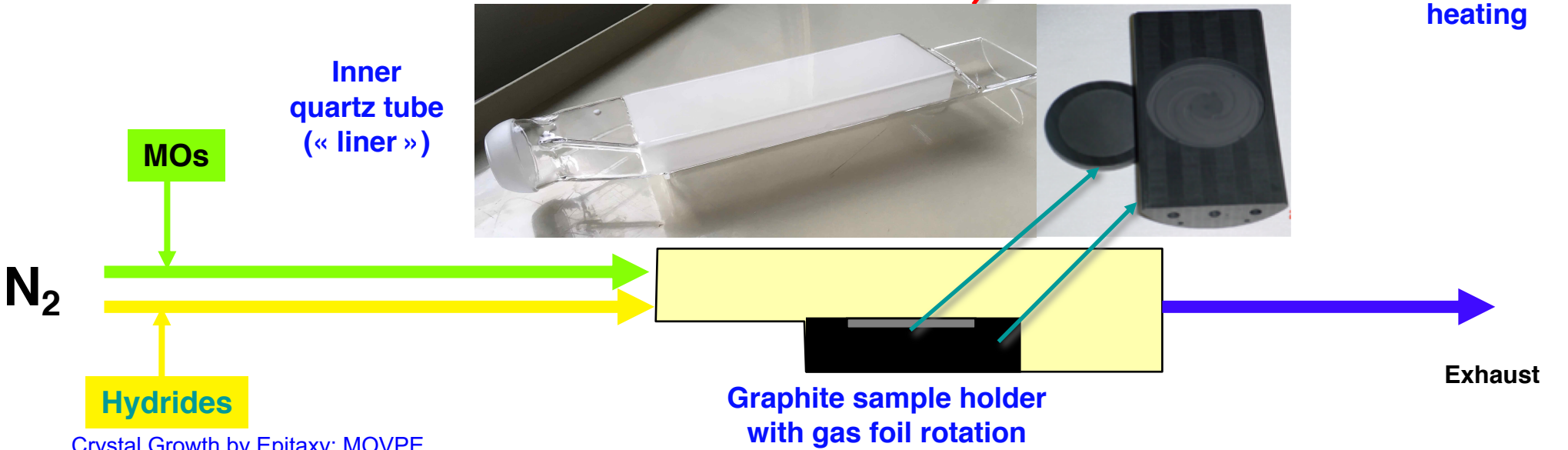
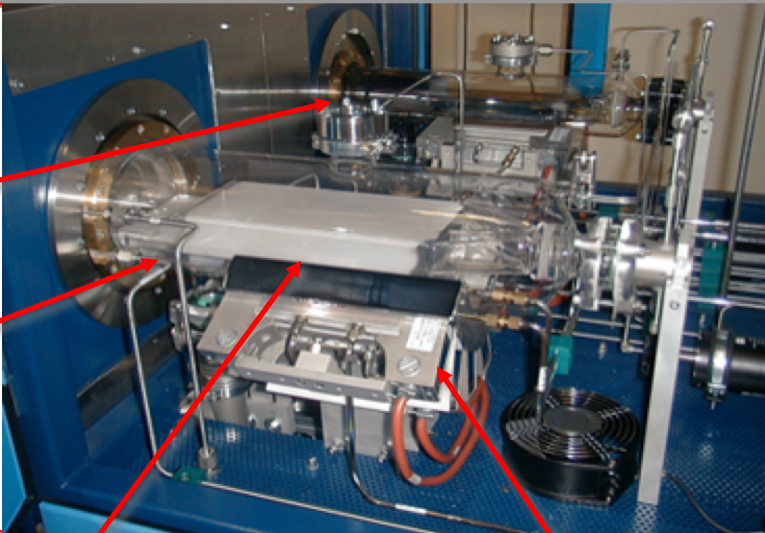


The III-V MOVPE facility @ LMSC2

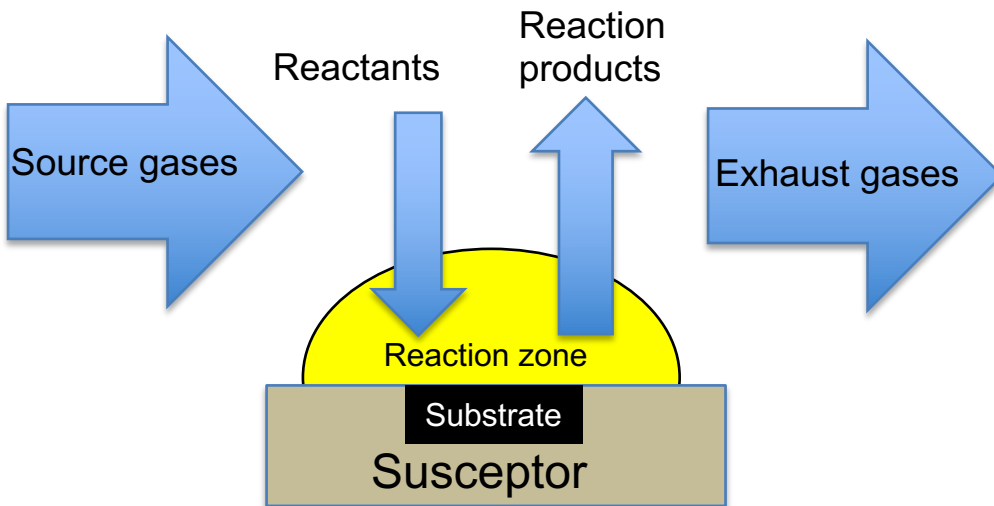


Single 2" wafer chamber

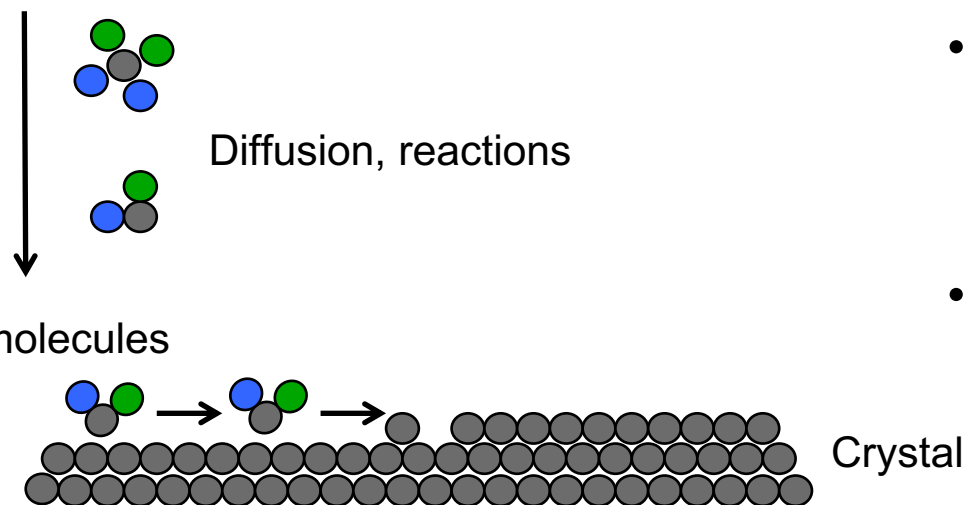
Three 2" wafers chamber



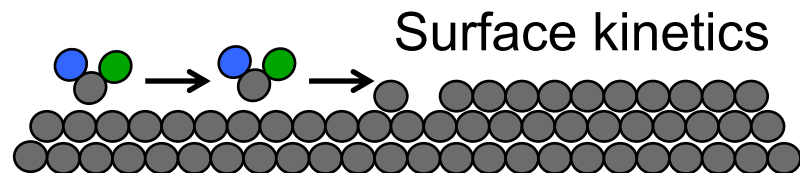
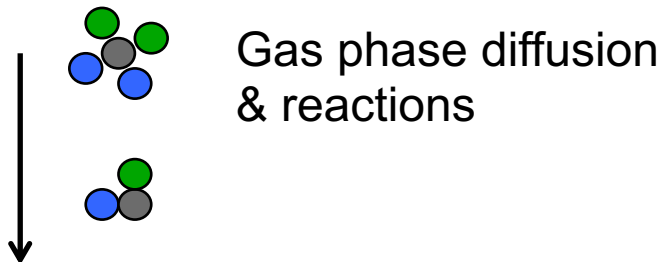
The MOVPE growth process



- Thermodynamics
 - Driving force for epitaxial growth
 - Precursors unstable at growth temperatures
- Gas phase reactions
- Mass transport
 - Diffusion through the gas phase to the growth surface
- Surface processes
 - Physical processes: physical adsorption, diffusion, evaporation
 - Chemical reactions: chemical adsorption, fragmentation, incorporation
- Subsurface processes



The main growth regimes

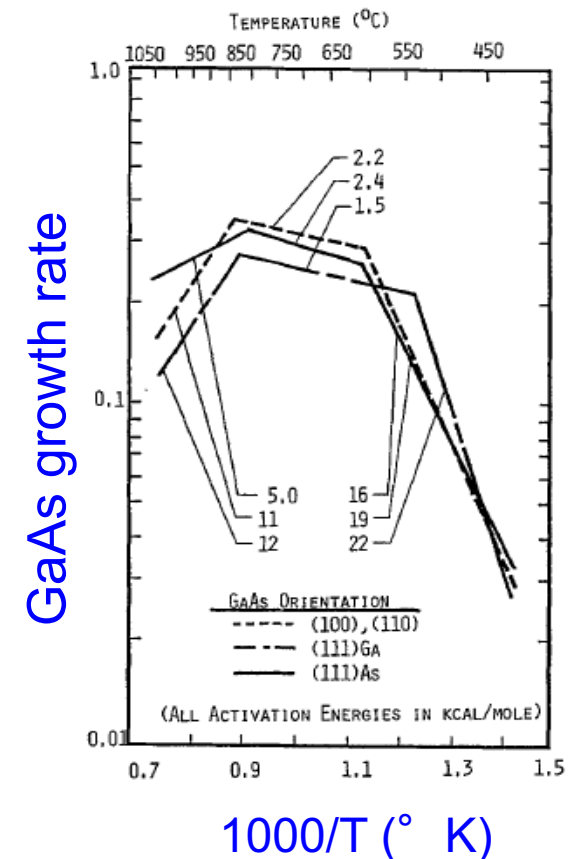


Diffusion limited growth:

- Surface kinetics faster than diffusion
- Near equilibrium at the interface
- Growth rate almost temperature insensitive
- Growth rate varies linearly with input group III flow
- $550^{\circ}\text{C} < T < 850^{\circ}\text{C}$ for TMGa + AsH₃

Kinetically limited growth

- Diffusion faster than surface processes
- Growth rate increases with temperature
- $T < 550^{\circ}\text{C}$ for TMGa + AsH₃



Main MOVPE precursors

Wish list

- Suitable vapour pressure: 0.01 - 10 μ/h
- Stable at room temperature
- Unstable at growth conditions
- No *intrinsic* doping (C !)
- Pure (no *extrinsic* doping)
- No *memory* effect (short & long term)
- Dopants:
large *doping range*, low *diffusion* coefficient,
low growth parameters dependence
- **Safe...!**

Group V

As: AsH_3 , $\text{C}_4\text{H}_{11}\text{As}$ (TBA)
 P: PH_3 , $\text{C}_4\text{H}_{11}\text{P}$ (TBP)
 Sb: SbH_3
 N: NH_3 , DMHy

Group III

Ga : $(\text{CH}_3)_3\text{Ga}$, $(\text{C}_2\text{H}_5)_3\text{Ga}$ (TMGa, TEGa)
 Al : $(\text{CH}_3)_3\text{Al}$ (TMAI)
 In : $(\text{CH}_3)_3\text{In}$ (TMIn); $(\text{C}_2\text{H}_5)_3\text{In}$ (TEIn)

Dopants

Donors:
 Si, S, Se, Te, Sn Si_2H_6 , SiH_4 , H_2S
 $(\text{C}_2\text{H}_5)_2\text{Te}$ (DETe)
 $(\text{C}_2\text{H}_5)_4\text{Sn}$ (TESn)

Acceptors:

C, Zn, Mg

(Al)GaAs

InP

GaN

CBr_4

$(\text{CH}_3)_2\text{Zn}$ (DMZn)

DMZn

Cp_2Mg

Cp_2Mg

Main hazards

Sources

Hydrides
(pressurized
gases)

- **Arsine** (AsH_3 , 15 Bars): most toxic form of As, flammable
 - LC50 = 5-50 ppm, IDLH = 2 ppm, TLV = 50 ppb
- **Phosphine** (PH_3 , 40 Bars): toxic, flammable,
 - LC50 = 11-50 ppm, IDLH = 7 ppm, TLV = 300 ppb

Metalorganics
(mostly liquids)

- Generally pyrophoric, violent exothermic reaction with moisture or oxygen, toxic fumes
- Tertiarybutylarsine: LC50 = 70 ppm, TLV = 500 ppb

Operation

- High temperature, low pressure process: reactor strain
- H_2 as carrier gas: explosion hazard
- Exhaust gases contains toxic & flammable gases

Maintenance

- Servicing and cleaning of contaminated parts is hazardous
Decomposition products are toxic, sometimes flammable
- Source exchange
- Scrubber cartridge exchange

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

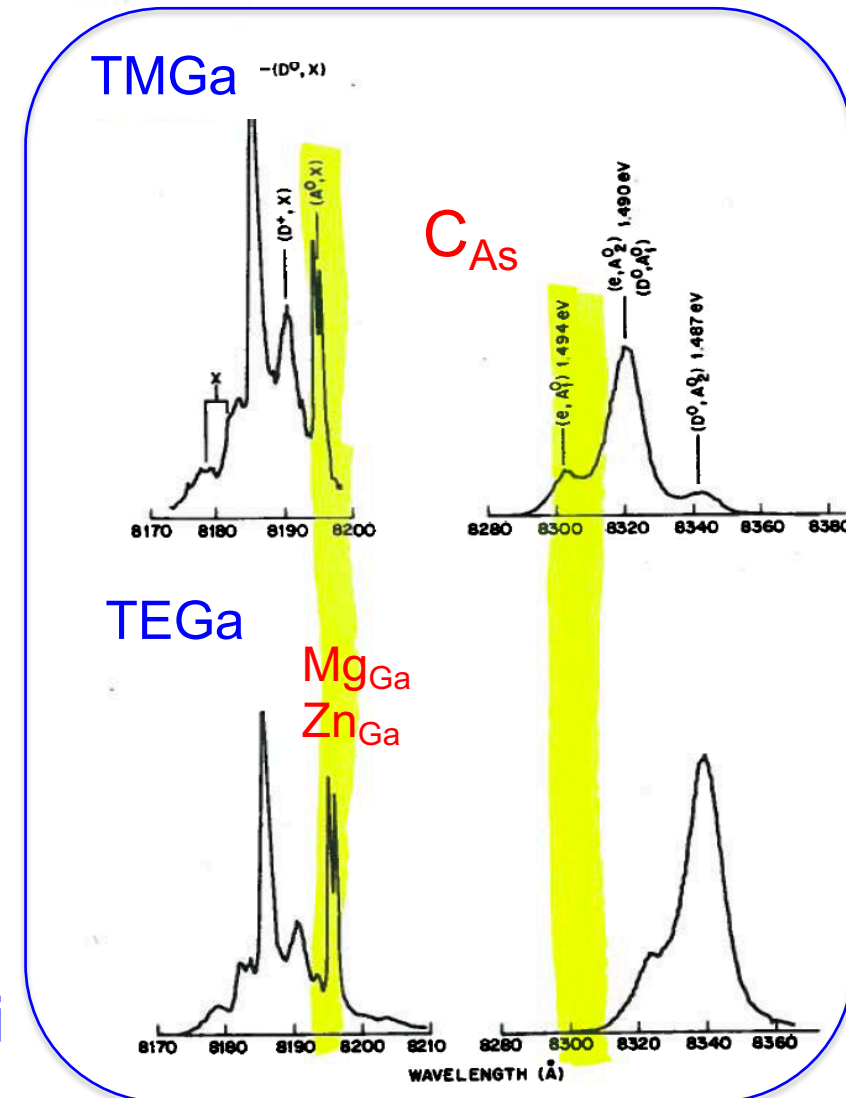
R. Bhat, P. O'Connor, H. Temkin, R. Dingle and V. G. Keramidas

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

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

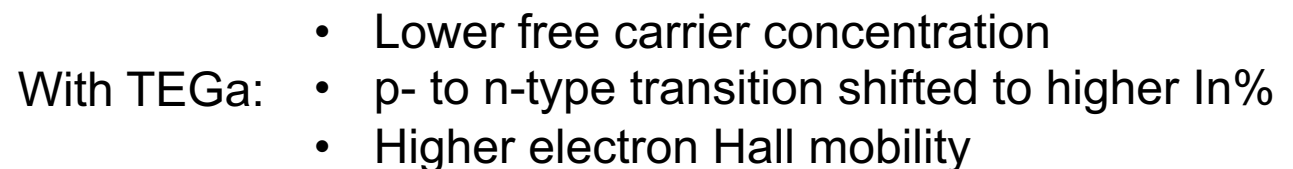
- Extrinsic C present with both precursors
- C_{As} with TMGa, NOT with TEGa
- Reduced intrinsic C uptake in (Al)GaAs
- Ga-C bond stronger in TMGa than in TEGa
- TEGa decomposes at lower temperatures

8° K PL
GaAs epi

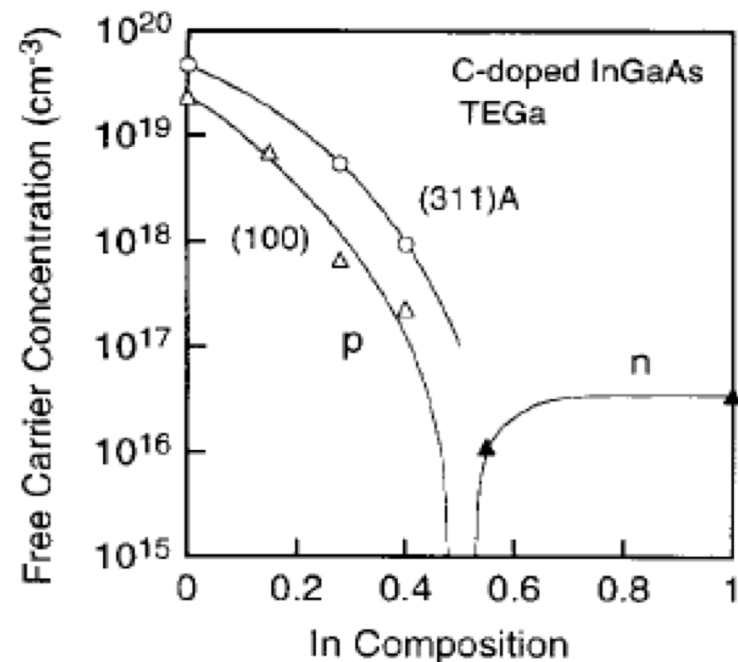
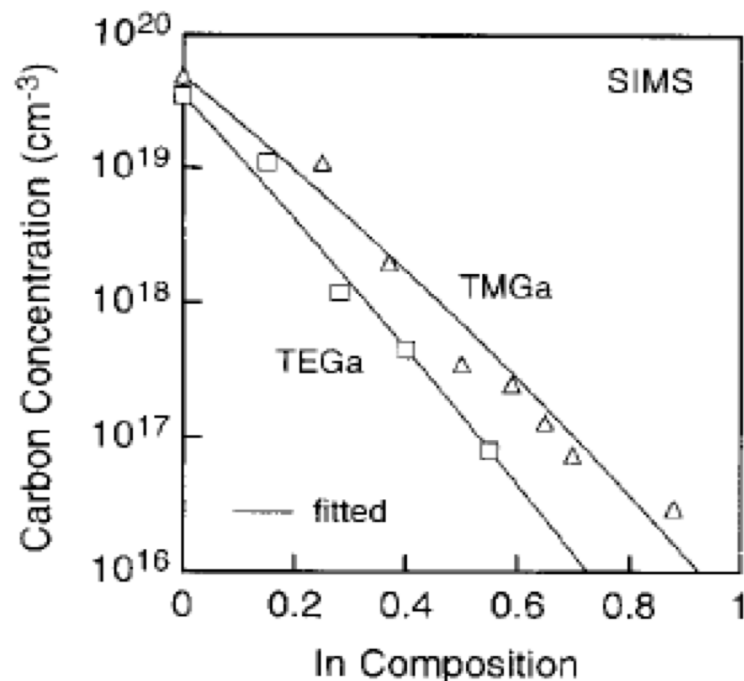


NTT LSI Laboratories, 3-1, Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01, Japan

- ## InGaAs:C free carrier concentration and Hall mobilities



Ethyl- vs methyl- sources and doping: InGaAs:C



- ✓ [C] decreases with [In]
- ✓ More [C] with TMGa vs TEGa

- C-Ga bond stronger than C-In bond
- CBr_4 dissociates at step edges
- C « lost » in presence of In

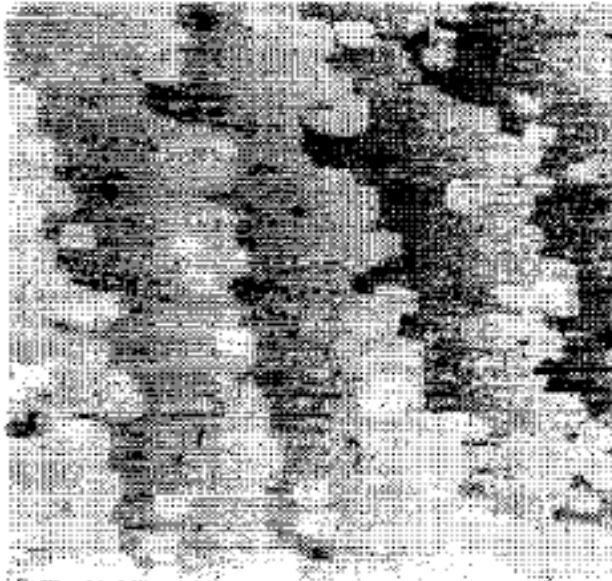
- ✓ More [C] on (311)A vs (100) surfaces

- Higher step density on (311)A

Growth mode, step structure and C incorporation

AFM of GaAs:C surfaces

TEGa

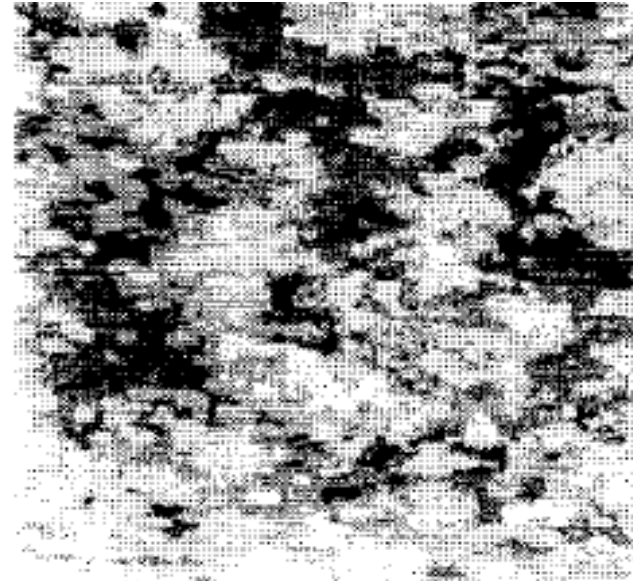


Monolayer stepped terraces



Mass transport limited regime

TMGa



2D islands

- ✓ Higher step density
- ✓ Enhanced CBr_4 dissociation
- ✓ Increased C incorporation



Kinetically limited regime

The choice of carrier gas: N₂ vs H₂

Wish list

- Enables laminar flow in growth chamber
- < 10⁻⁸ impurities
- Inert towards the transported chemicals
- Inexpensive
- Safe

H₂

- H₂ enables laminar flow at atm. pressure
- Mature H₂ purifier technique (Pd foil diffusion)
- H₂ selected against N₂, He and Ar from tests in early atmospheric reactors
- Most widely used, mandatory for nitrides
- **Explosion hazard**

N₂

- Low pressure (<100 hPa) > laminar flow
- Getter purifiers developed in the 90s
- Improved uniformity in AlGaAs/GaAs ¹ and InGaAsP/InP ²
- Lower O, C uptake in (Al)GaAs ³
- Improved N uptake in InGaAsN ⁴
- Higher p-(In)GaAs doping (TMGa+CBr₄) ⁵
- **Lower growth rates**

N₂ vs H₂

- Higher density: N₂: 28g/mole; H₂: 2g/mole
 - > Lower diffusion through the more viscous N₂ gas phase
 - > Lower (x0.6) group III concentration on surface
 - > Lower growth rates
- Higher viscosity
- Lower thermal conductivity
 - > lower heat transfer
 - > steeper temperature profiles

(1) Dauelsberg *et al.*, J. Crystal Growth (2001)

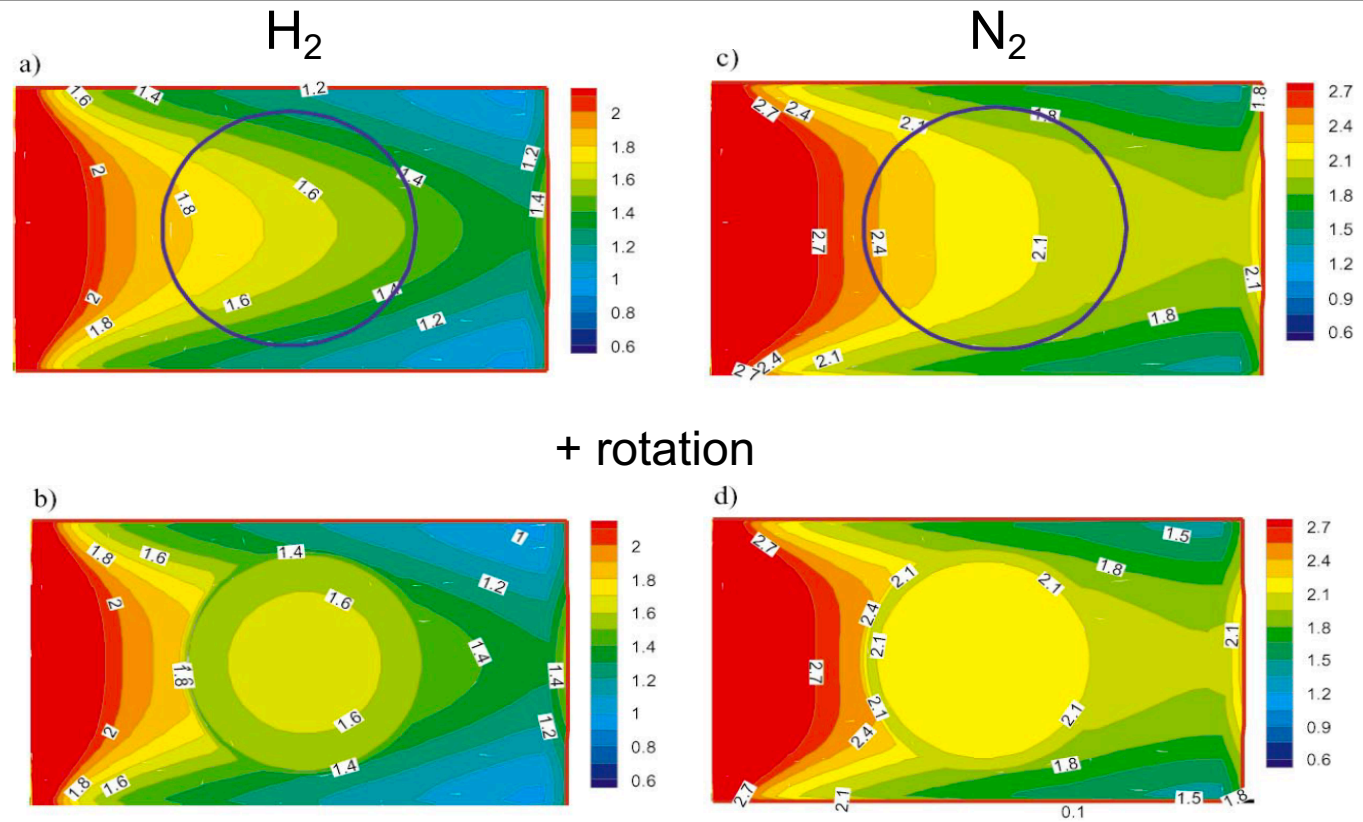
(2) Roehle *et al.*, J. Crystal Growth 170 (1997) 109-112

(3) Hardtdegen *et al.*, III-Vs review (2001)

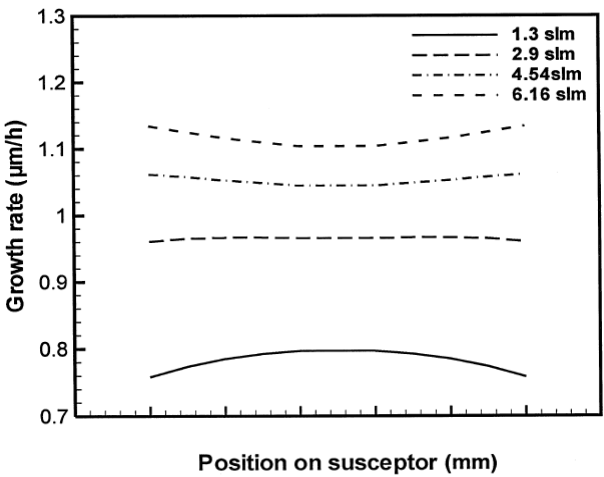
(4) Ougazzaden *et al.*, Jpn. J. Appl. Phys. Vol. 38 (1999) 1019-1021

(5) Keiper *et al.*, J. Crystal Growth 197 (1999) 25-30

AlGaAs growth rate profiles: N₂ vs H₂



TMAI, TMGa, AsH₃,
700° C, 20 hPa



Fully developed parabolic profile,
steep gradient
orthogonal to reactor axis

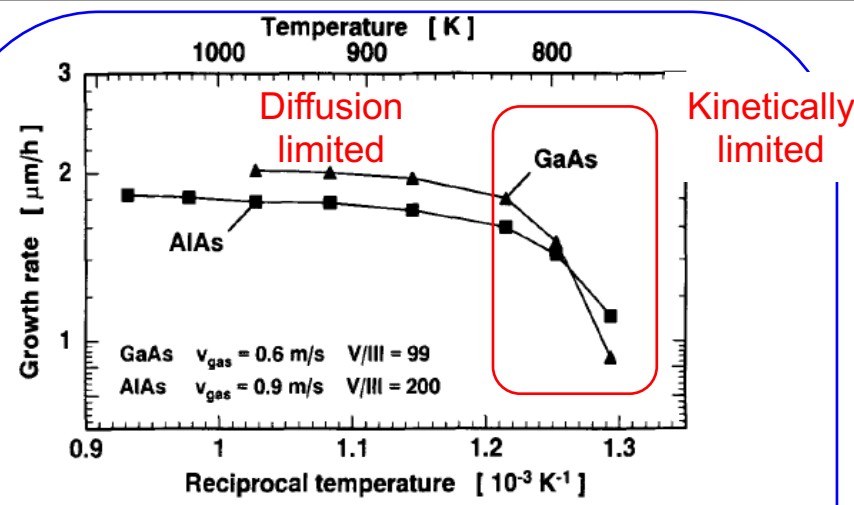
Bloc-like profile
reduced orthogonal gradient

Optimized uniformity
through total flow
adjustment

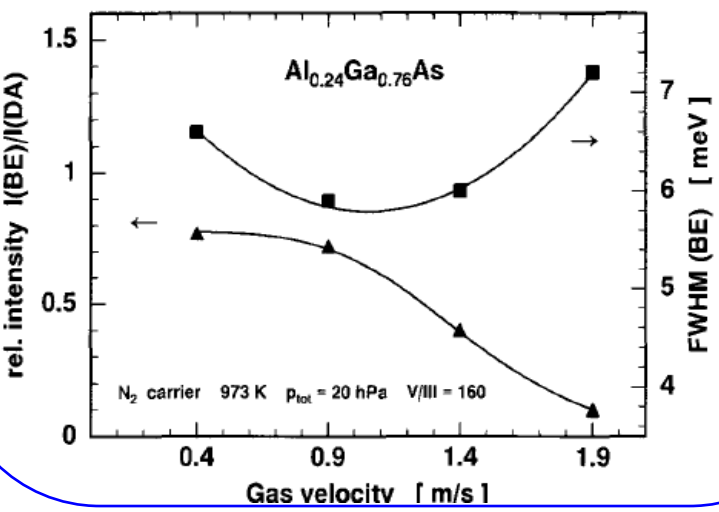
Rotation does not compensate
for orthogonal gradient

Rotation compensates
for axial gradient

Growth of AlGaAs using N₂ as carrier gas



M. Hollfelder *et al.*,
J. Electron. Materials (1994)



Crystal Growth by Epitaxy: MOVPE
MSE-649 (2020)

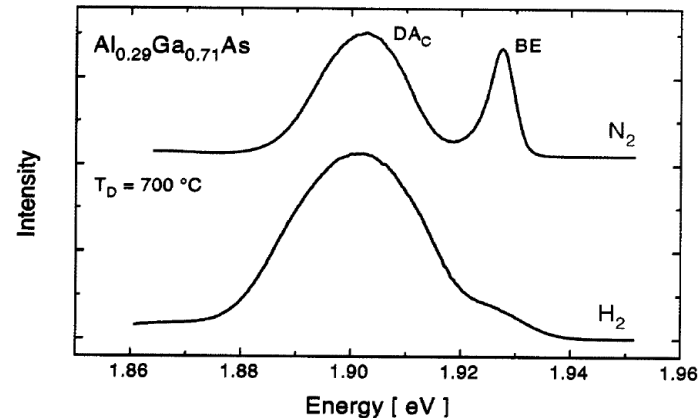


Figure 4. 2K photoluminescence spectra of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ deposited by the nitrogen (upper spectrum) and hydrogen (lower spectrum) processes at 20 mbar and 700°C . The higher intensity ratio of the bound exciton transition (BE) to donor acceptor transition (DA)_c indicates the lower carbon and deep level impurity concentration in the layers, when N_2 is used as the carrier.

H.Hardtdegen *et al.*,
III-Vs reviews (1005)

Higher As and H⁺ surface coverage from AsH₃ decomposition (not from H₂)

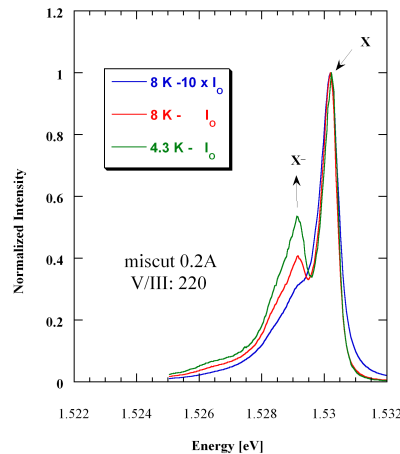


Lower C and O incorporation

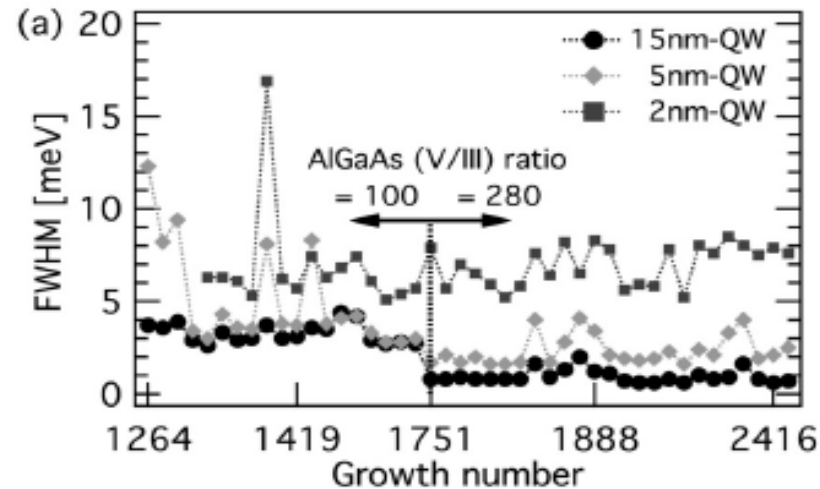
Improved optical and transport properties

Vicinal surfaces: the case of AlGaAs/GaAs QWs

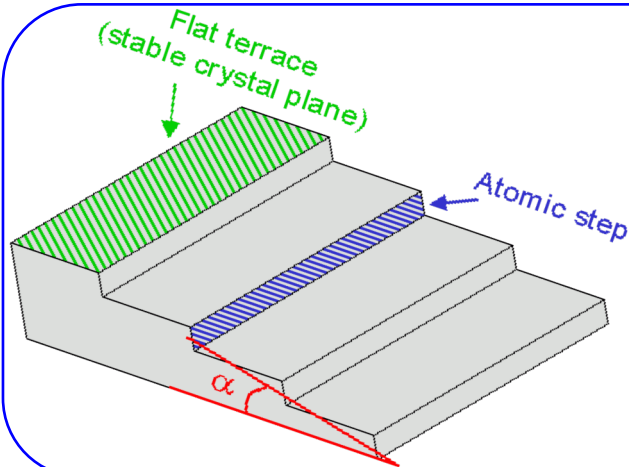
A probe of material purity & interface smoothness



A probe of reactor status over time



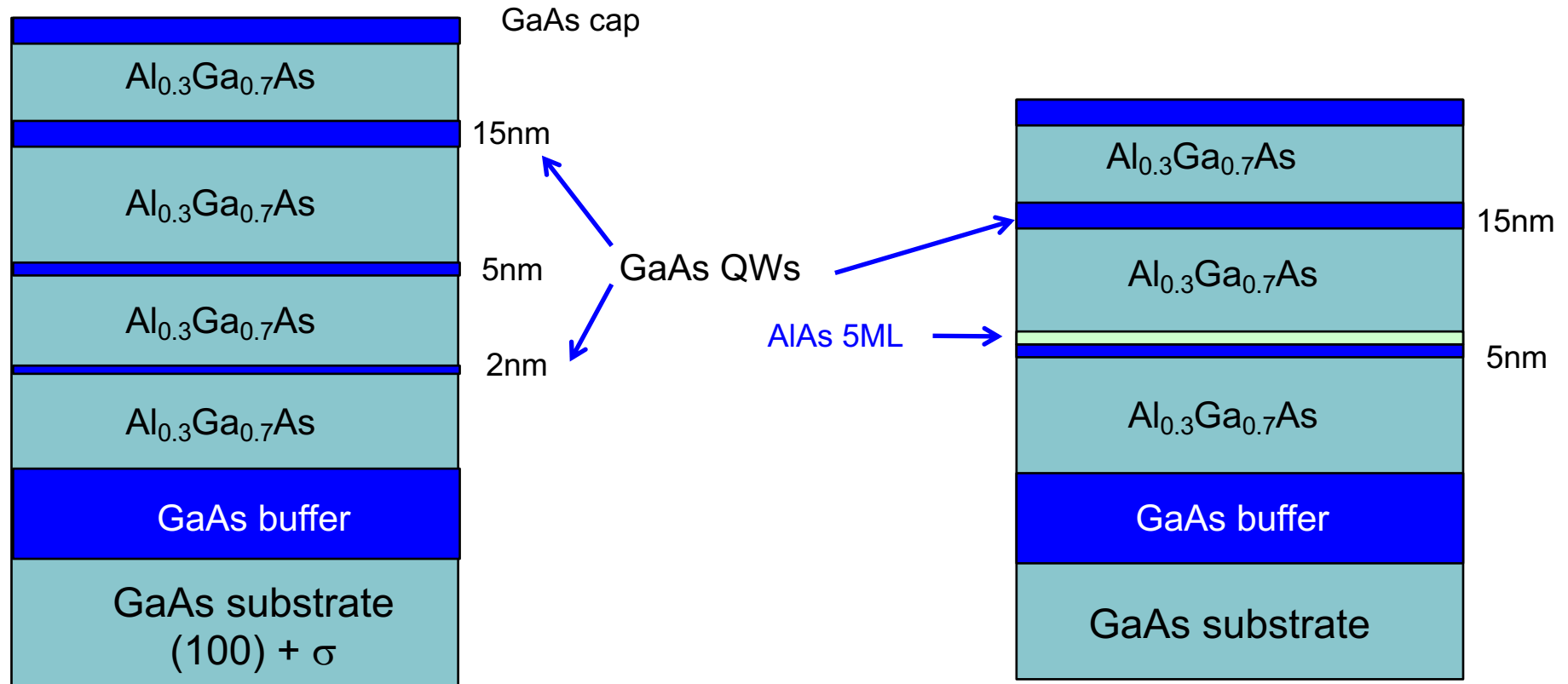
N. Moret,
PhD thesis (2008)



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

- Improved morphology : MBE AlGaAs (Tsui, APL 1986)
- Smoother surface under STM : MBE GaAs (Grousion, 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



Triple QW

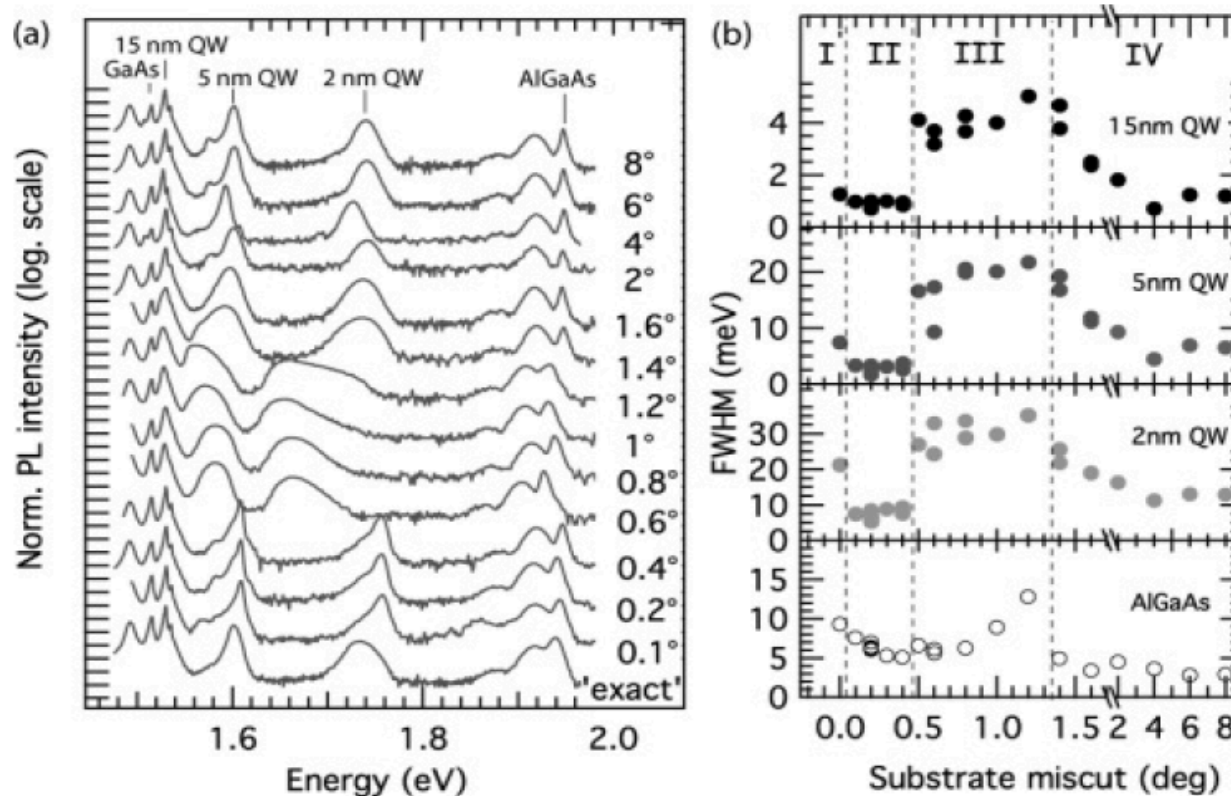
Double QW
with
etch-stop layer

- TMGa, TMAI, AsH₃
- N₂ ambient, 20mbars
- T : 680° C - 740° C
- V/III : 100 - 320 in AlGaAs
- V/III : 60 - 130 in GaAs
- AlGaAs @ 1 μ m/hour
- GaAs (100) + α (+/- 0.02°)

PL dependence on miscut points to 4 growth modes

PL spectra of TQW samples grown on
substrates with different miscuts

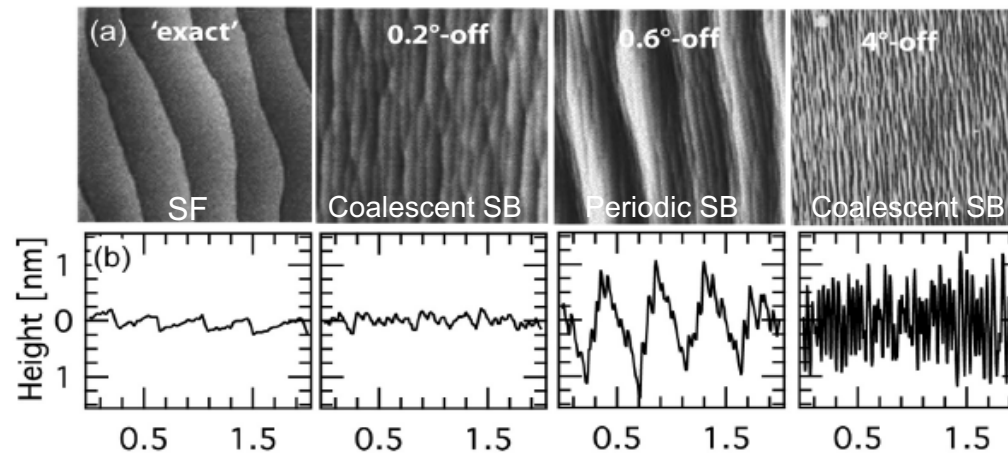
FWHM of the 3 QWs
& the AlGaAs bound exciton line



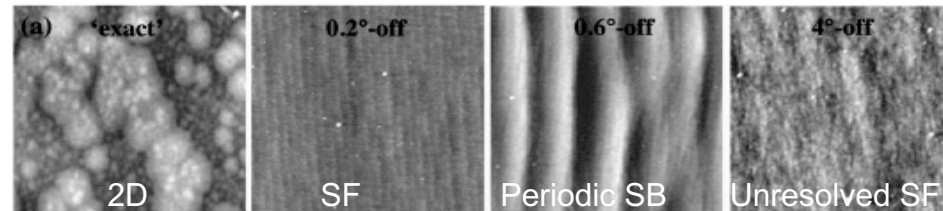
N. Moret *et al.* Phys. Rev. B 84 (2011)

AFM of top surface and QW interfaces

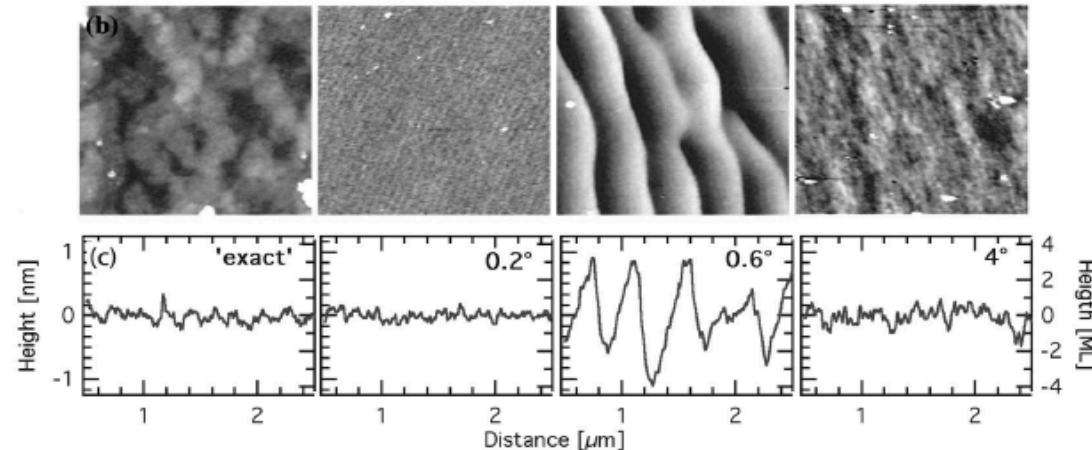
Top surface



Upper QW surface

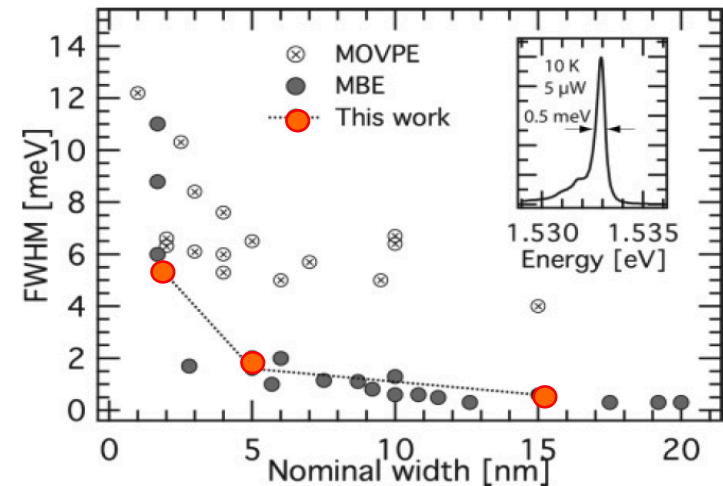


Lower QW surface

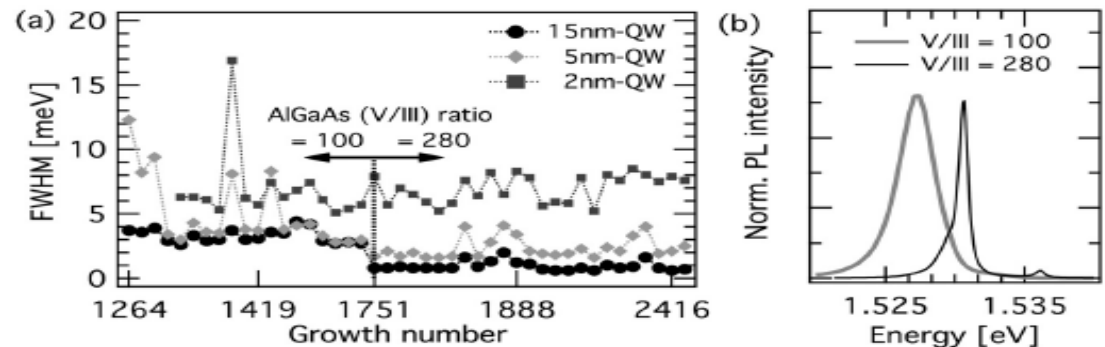


AlGaAs/GaAs QWs on vicinals: a summary

- Best combination:
 - $0.1 - 0.3^\circ$ towards (111)A
 - $T \sim 710^\circ \text{C}$
 - $V/III \sim 280$ in AlGaAs, $V/III \sim 130$ 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



Surfactants: surface active agents

Low solubility
Rejected by the solid

Low vapour pressure
Does not evaporate rapidly

High surface
concentration

- Film composition
- Atomic ordering
- Dopant incorporation
- Interface abruptness

Surfactant-mediated
epitaxy

Surface energy
Surface reconstruction
Step structure

- Admolecule diffusion
- Adatom attachment

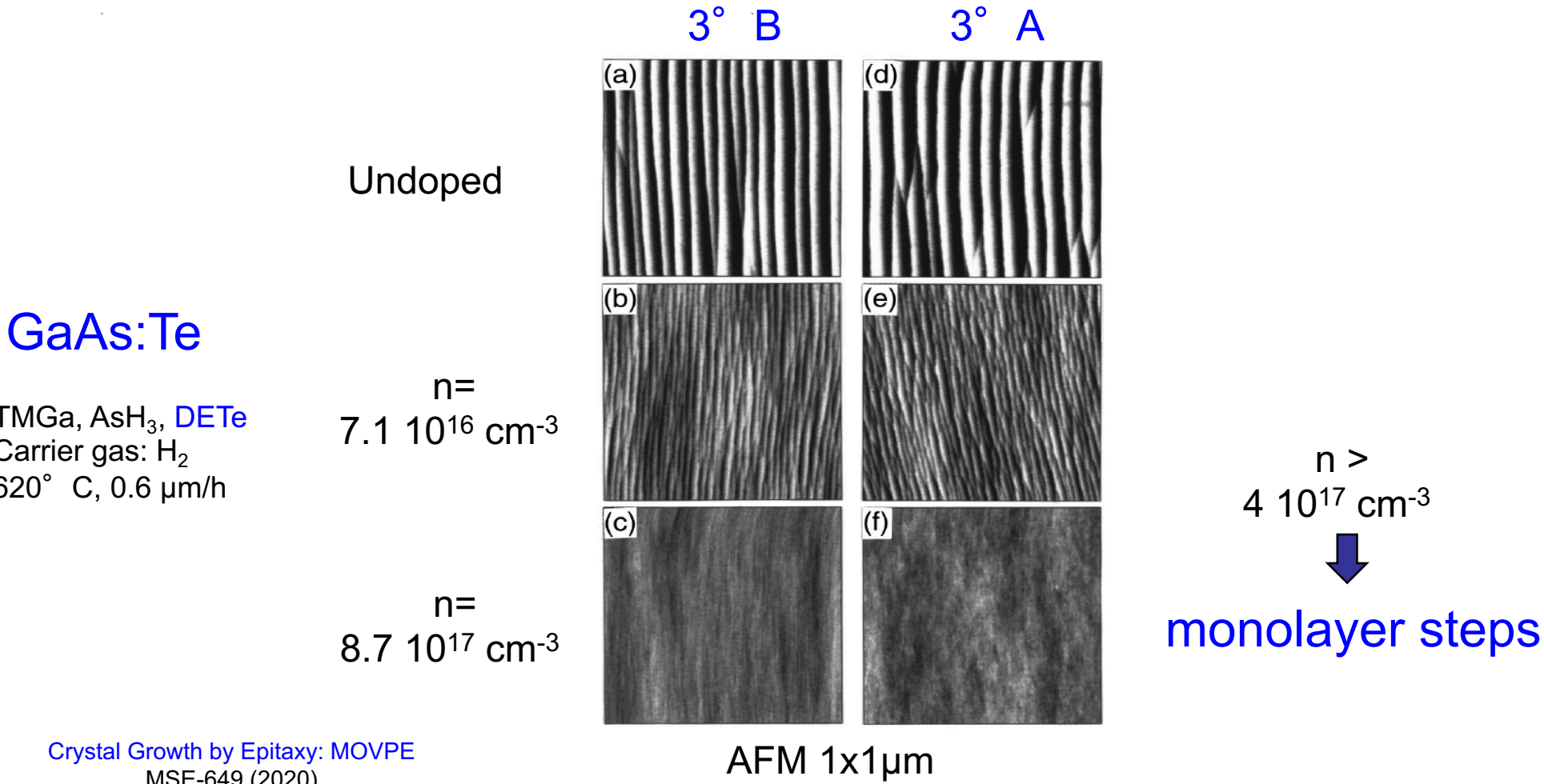
Growth mode

Epi surface morphology
Step structure

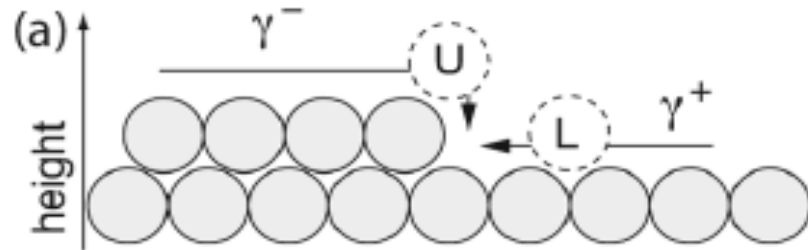
Surfactants & step bunching: GaAs + Te

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



Ehrlich & Schwoebel statistics

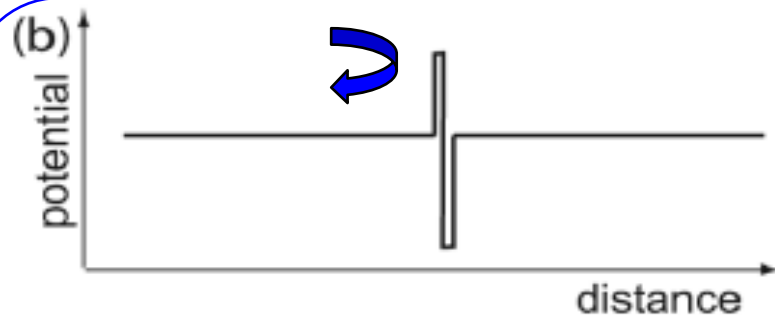


Adatom approaches surface step
from upper (U) or lower (L) terrace

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 catches up with lower, smaller one
- **Step bunching**

Surfactants and doping: GaAs:Zn + Sb

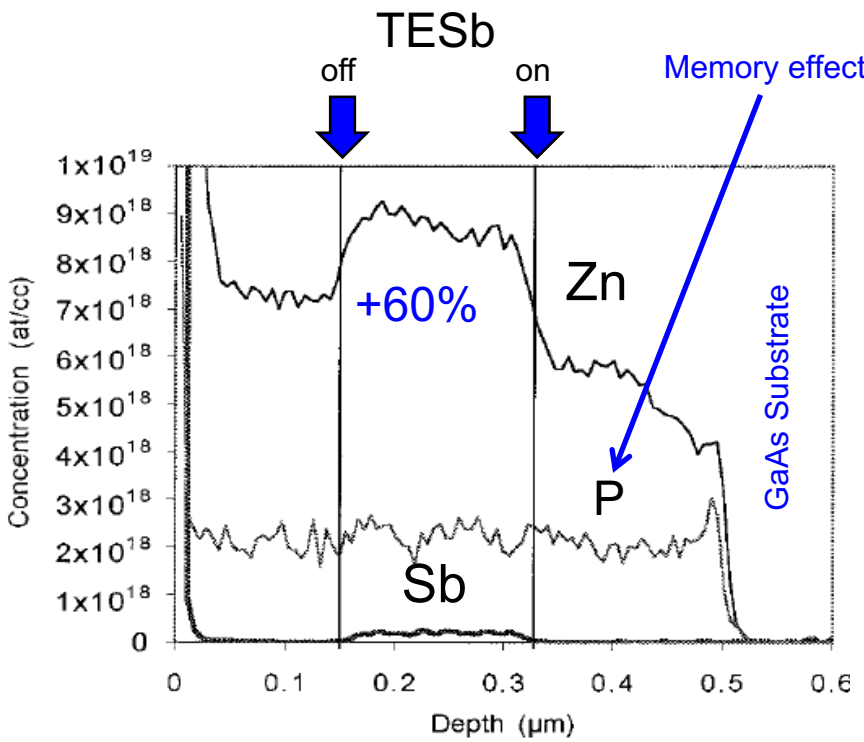
Surfactant effects on doping of GaAs grown by organometallic vapor phase epitaxy

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, 1.3µm/h
DMZn/TMGa = 0.08
TESb/TMGa = 0.012

TESb:
↑ Zn & In uptake (Ga sites)
↔ P, Te uptake (As sites)

- Sb increases the surface diffusion of Zn/In adatoms
- Sb may substitute on V sites at step edges and enhance sticking coefficient of Zn/In adatoms

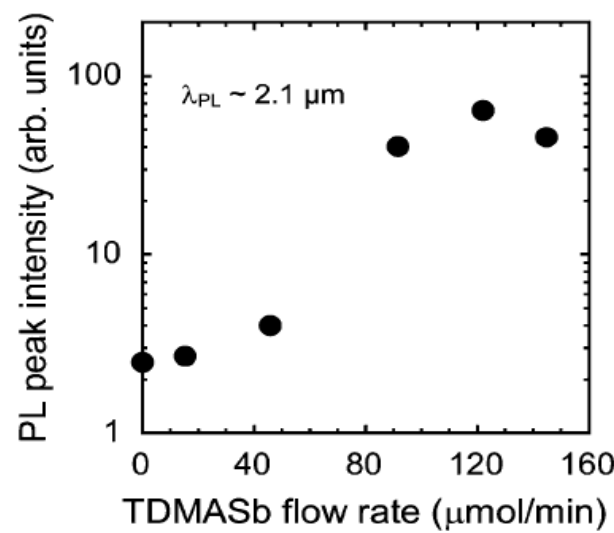


SIMS profile through GaAs:Zn

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

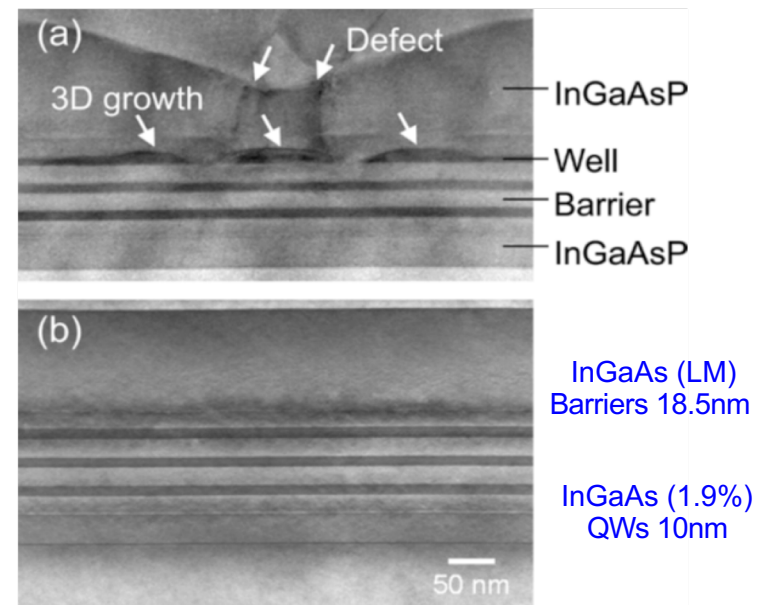
Tomonari Sato, Manabu Mitsuhashi, Takao Watanabe, Kazuo Kasaya, Tatsuya Takeshita, and Yasuhiro Kondo, *Member, IEEE*

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



- 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%)

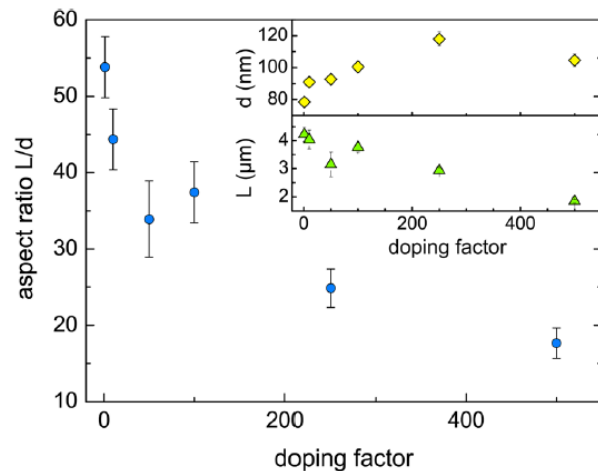
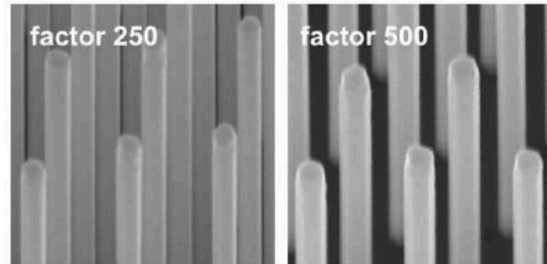
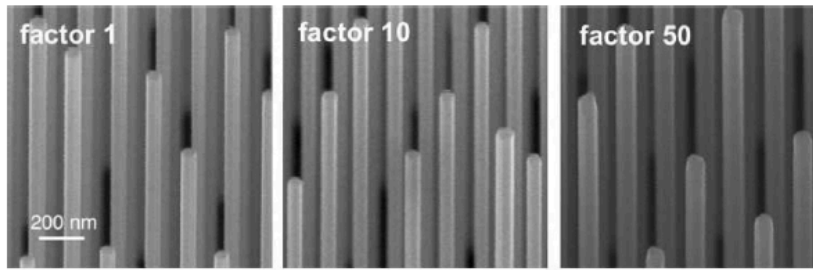
Without Sb



With Sb

Surfactants & nanowires: InAs, GaAs + Si

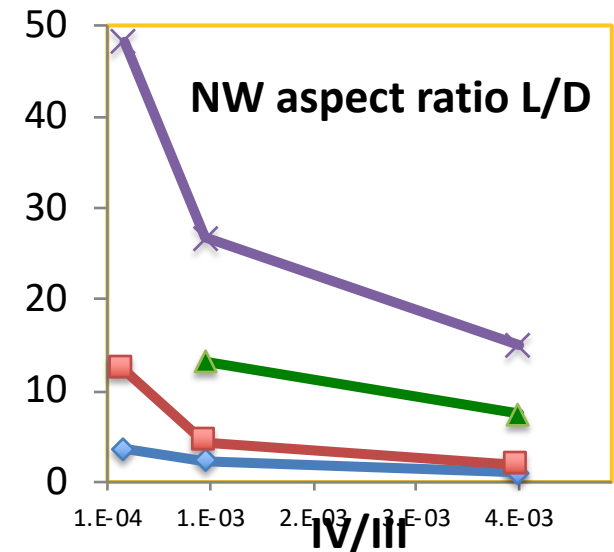
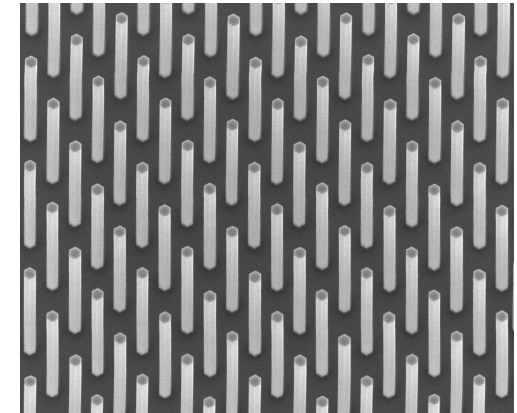
InAs



Si_2H_6 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)

Crystal Growth by Epitaxy: MOVPE

MSE-649 (2020)

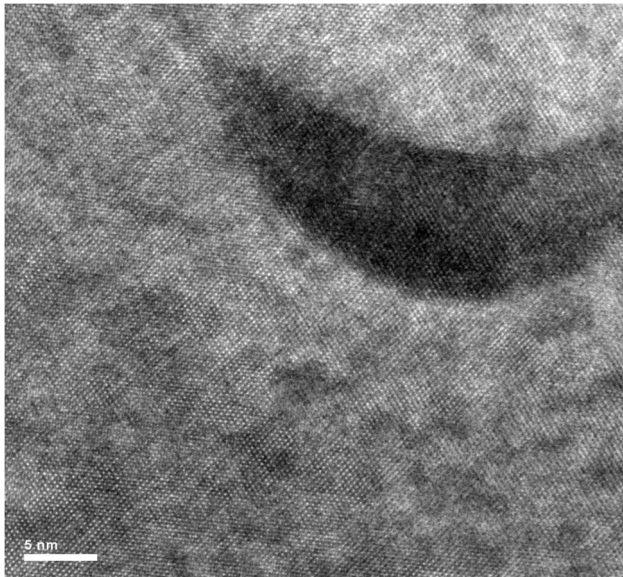
Surfactant mediated epitaxy: a summary

- **Te** (from DETe) suppresses step bunching in GaAs if $n > 4 \times 10^{17} \text{ cm}^{-2}$
- **Sb** (from TESb) increases Zn and In incorporation in GaAs
- **Sb** (from TDMASb) increases pseudomorphic thickness in InGaAs/InP MQWs
- **Si** (from Si_2H_6) reduces the aspect ratio of GaAs nanowires

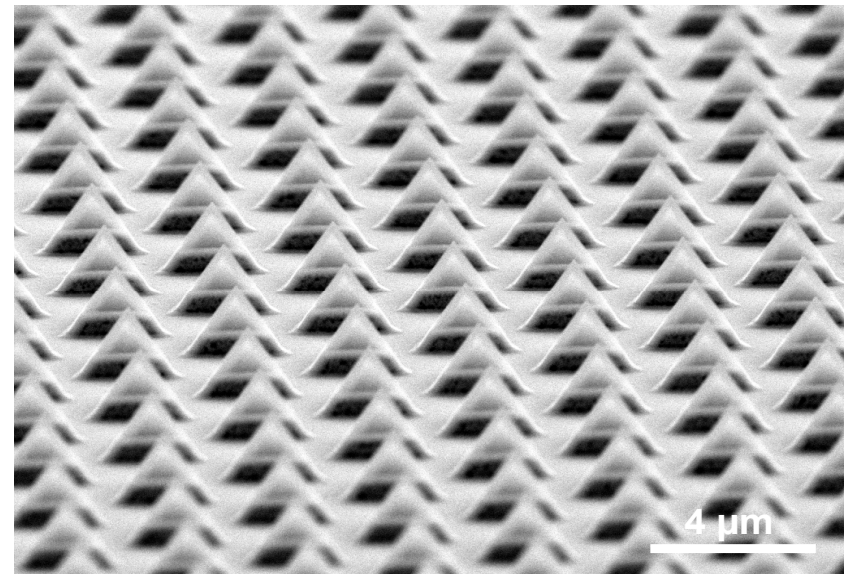
GaInAsN dilute nitride alloys

- N incorporation
- Modulated growth

Non-planar epitaxy



Quantum wires



Quantum dots

GaInAsN dilute nitride alloys

Motivations

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

Challenges

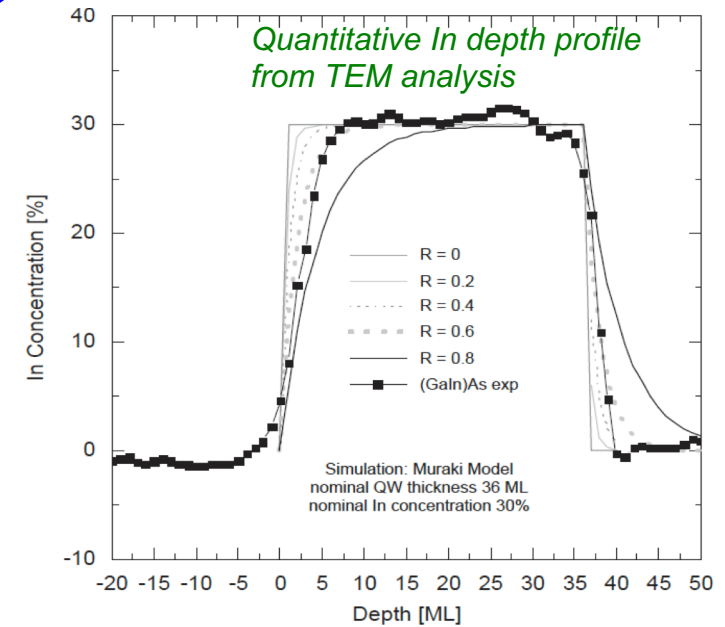
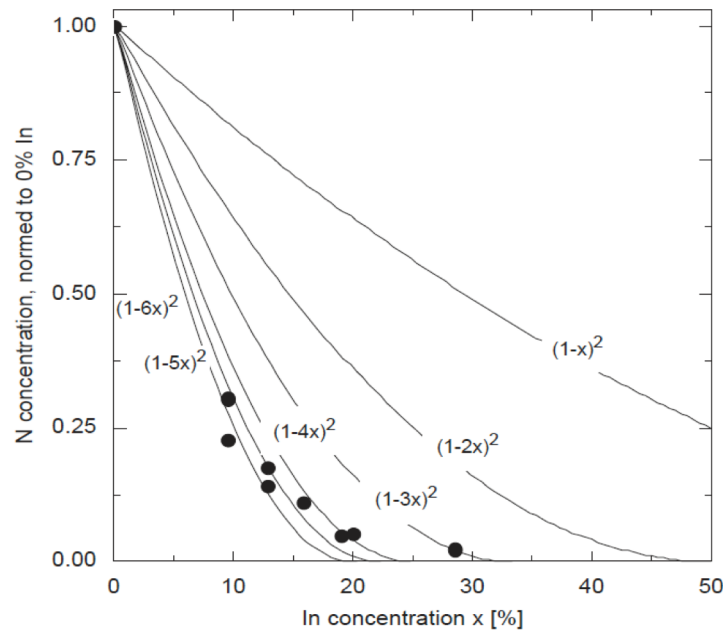
- High radiative efficiency
- Understanding Surface Kinetics

Keys

- Modulated growth
- Vicinal surfaces
- Non-planar growth

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

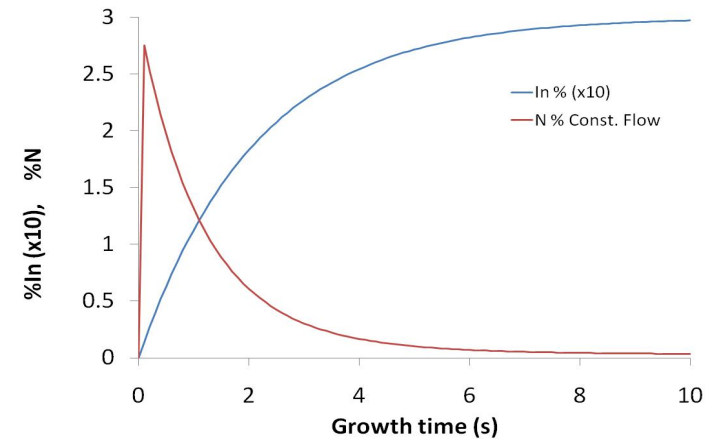
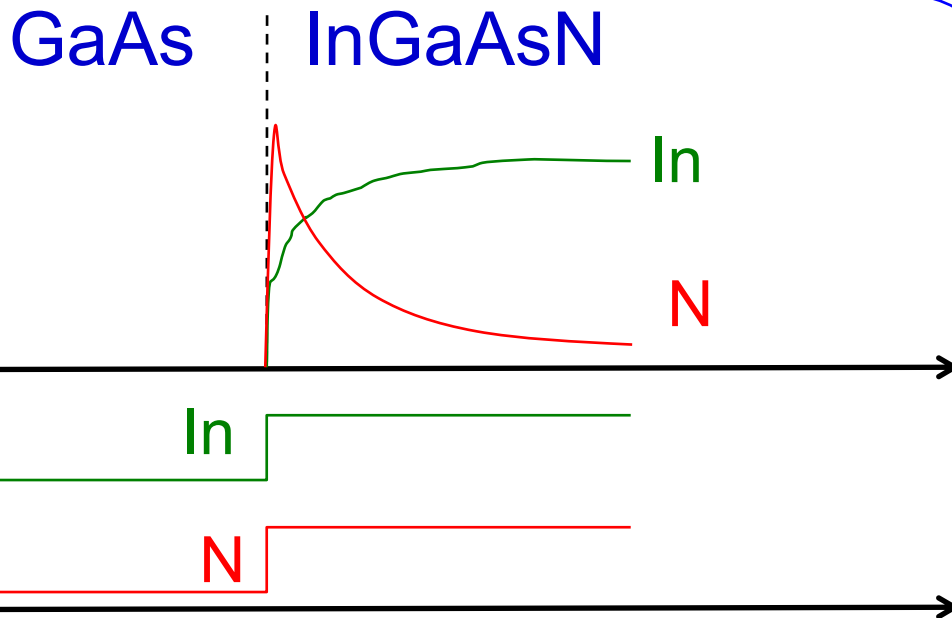


- 7 MLs [In] transient
- $[In]_{\text{surface}} = 2.5 [In]_{\text{volume}}$

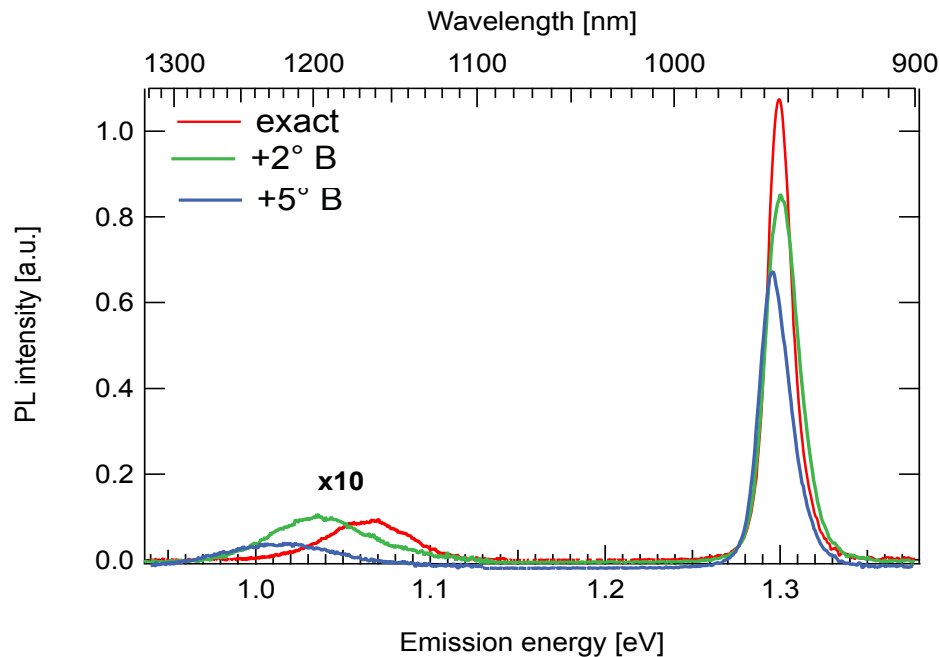
N & In profiles through GaInNAs growth

Nitrogen

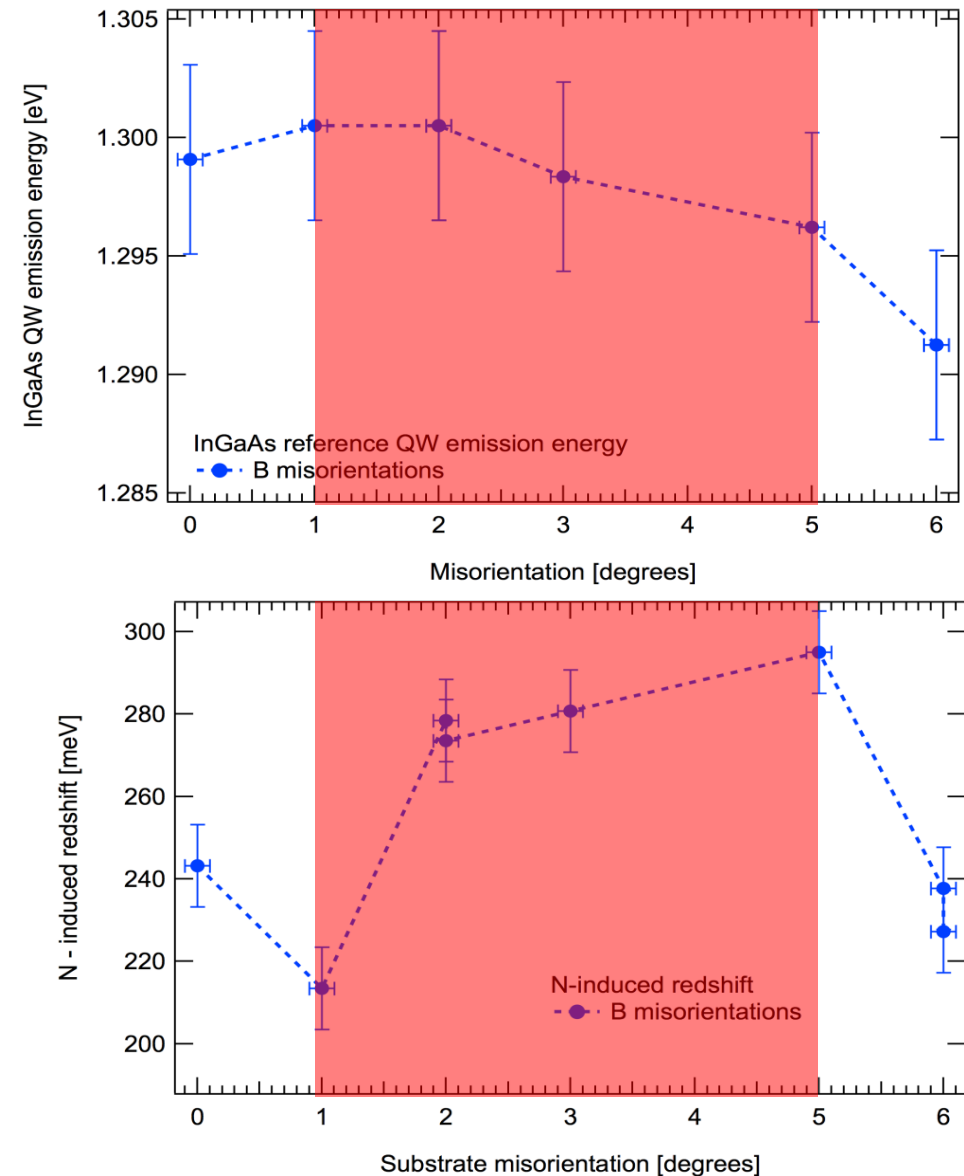
- 1) accumulates at the lower interface
- 2) diffuses during growth
- 3) desorbs at the growth surface



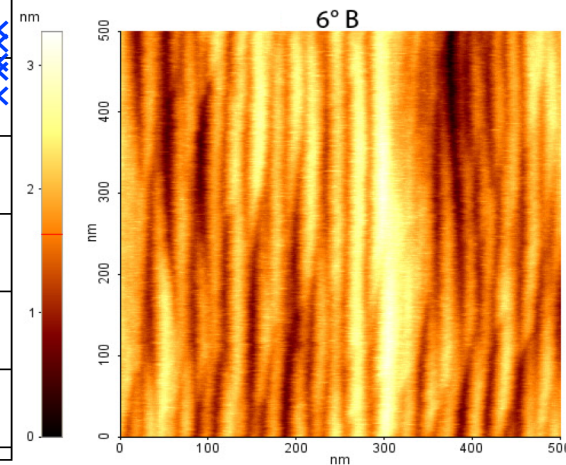
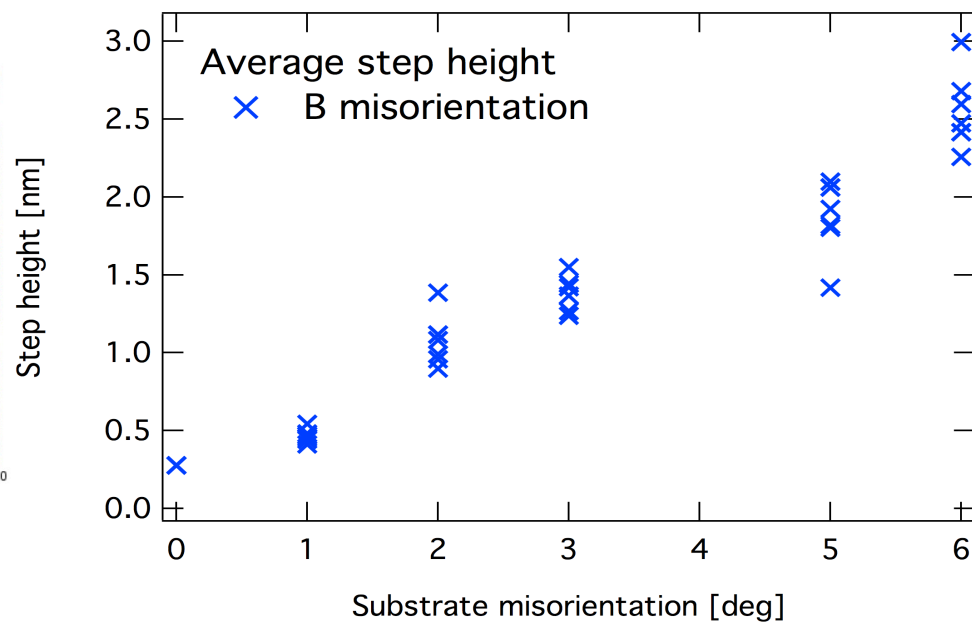
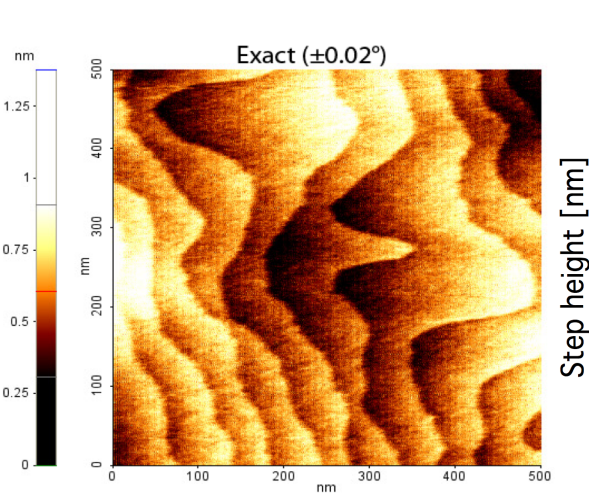
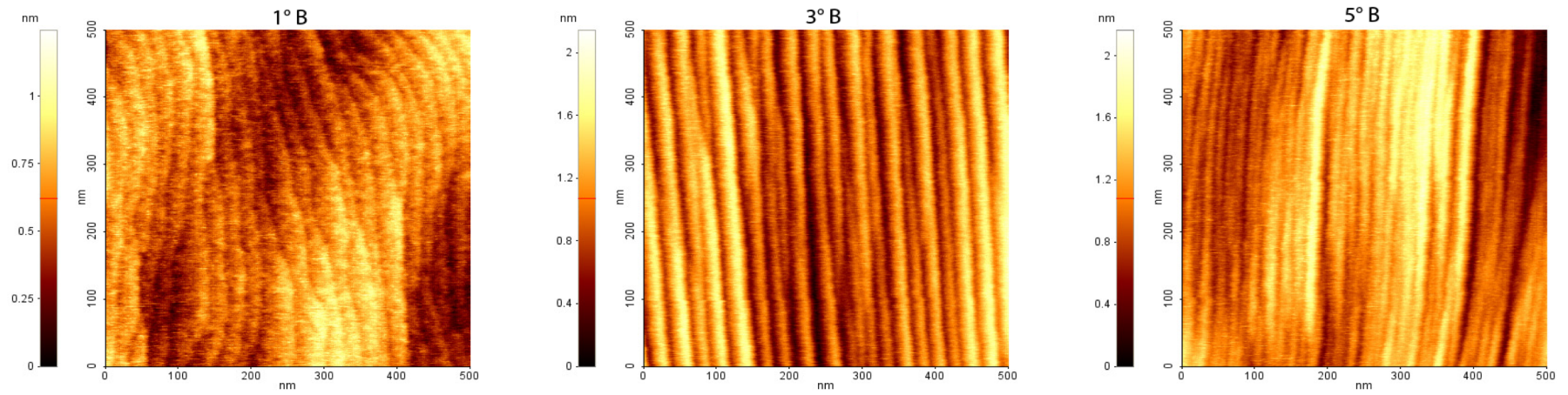
GaInAsN *dilute nitride alloys* Influence of substrate off-orientation



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



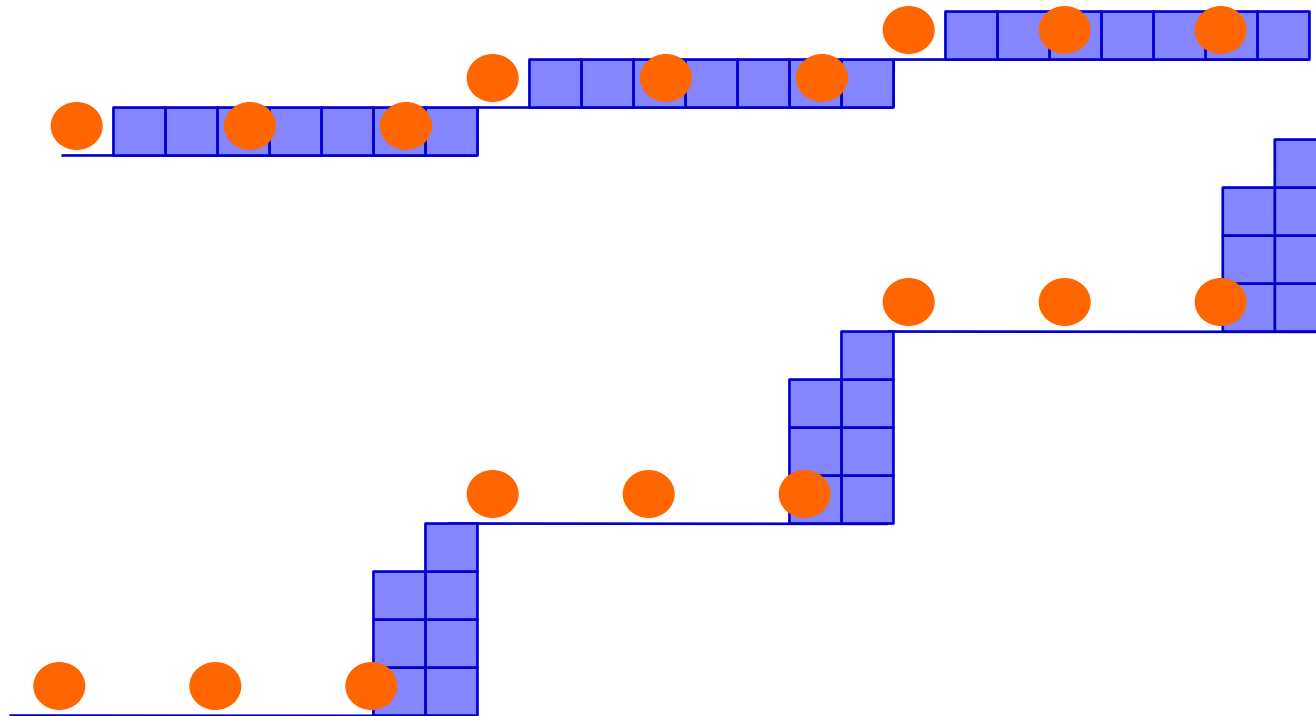
GaInAsN *dilute nitride alloys* Vicinal « B » epitaxial surfaces step patterns



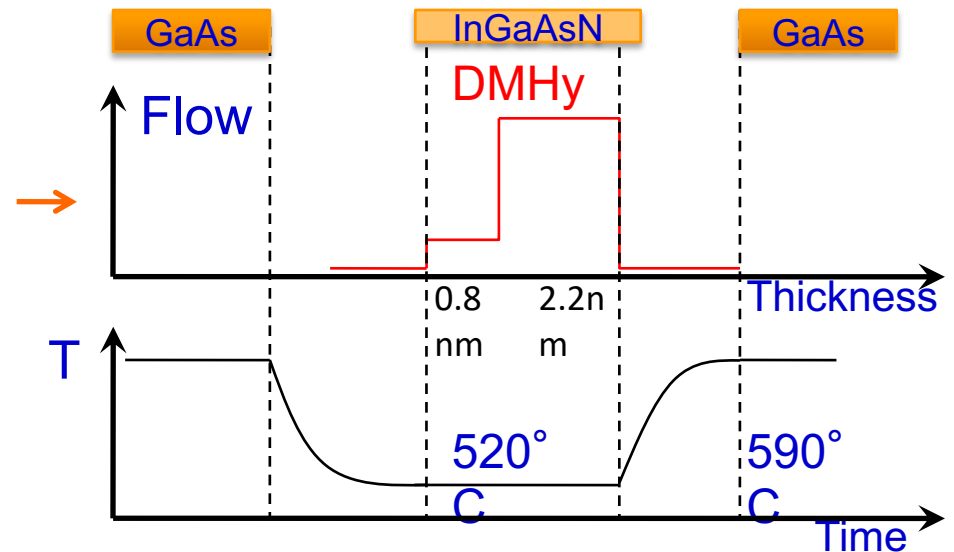
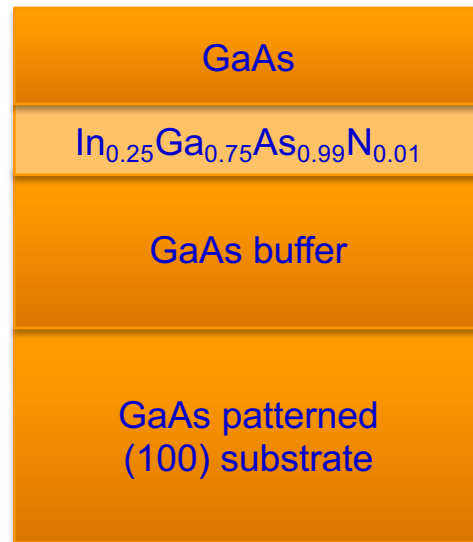
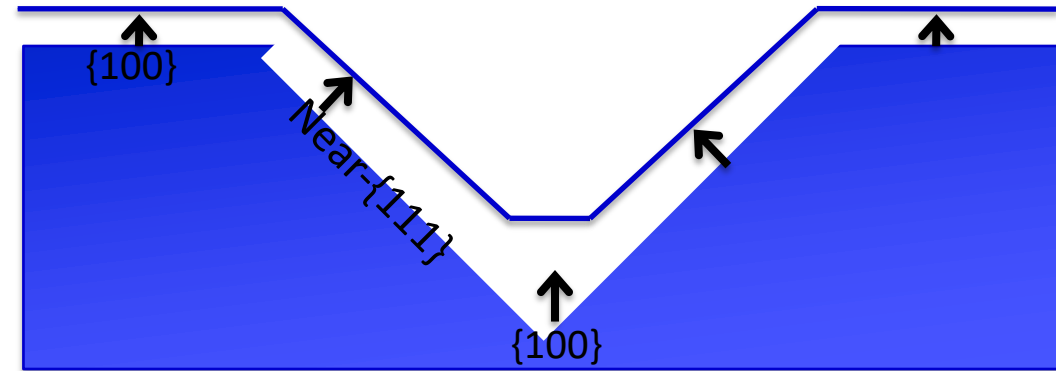
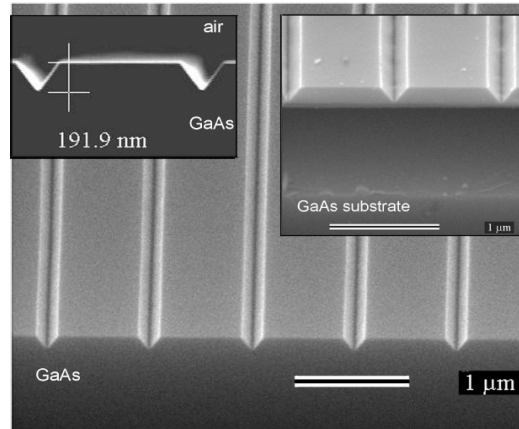
N desorption on vicinal surfaces

■ InGaAs

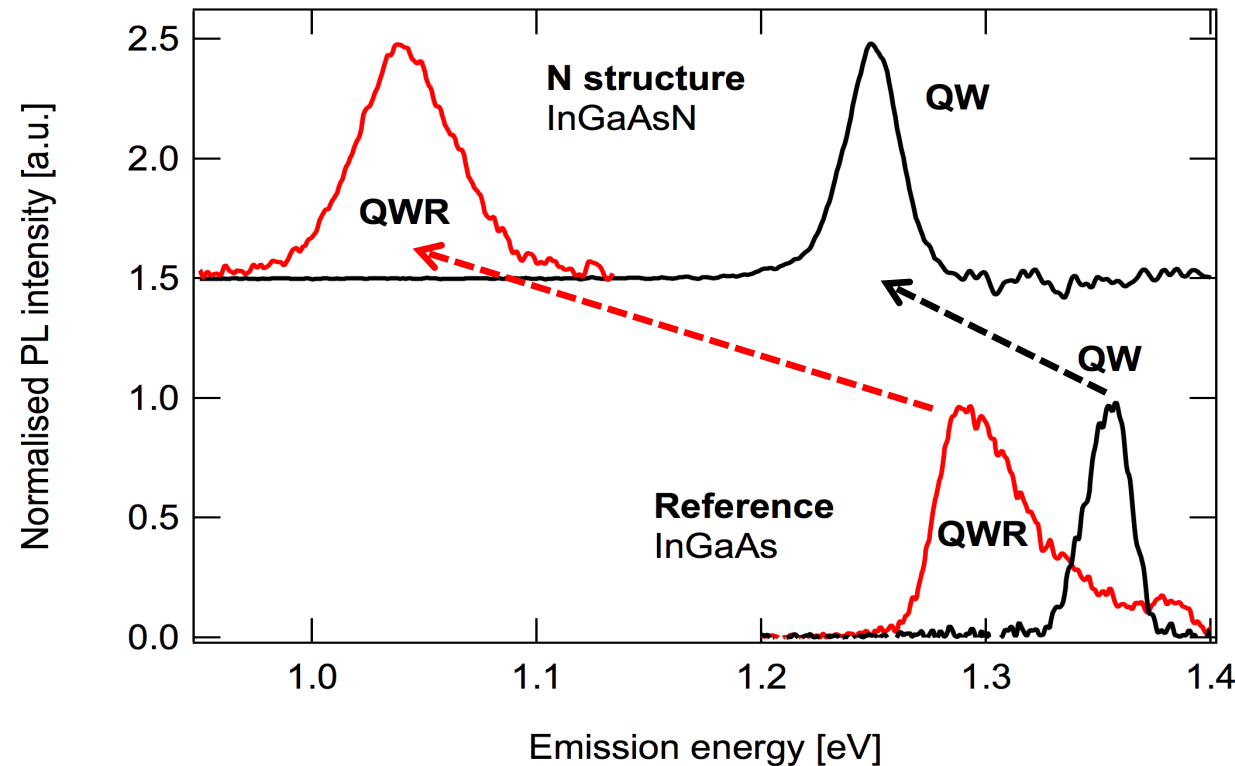
● N



Growth of GaInAsN/GaAs on non-planar surfaces



N incorporation in QWs and QWRs

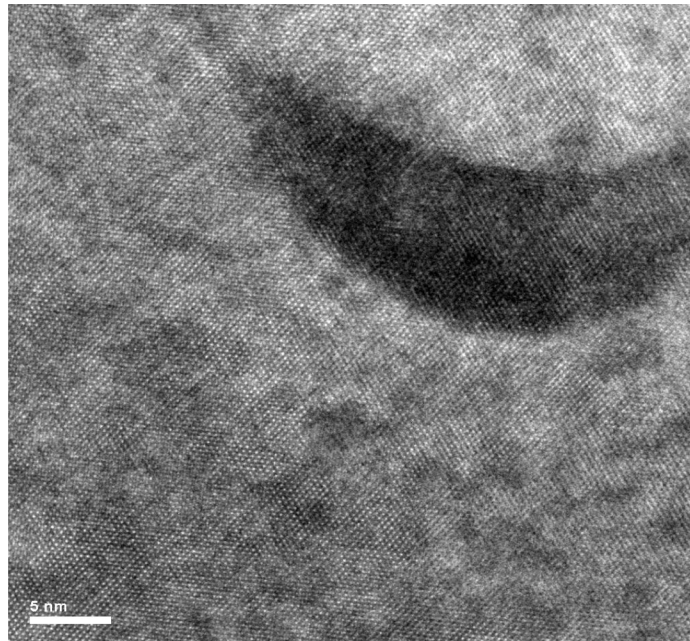


R. Carron, PhD (2013)

- Higher growth rate for the QWR
- Decrease of N desorption from the surface
- Larger energy shift for the QWRs

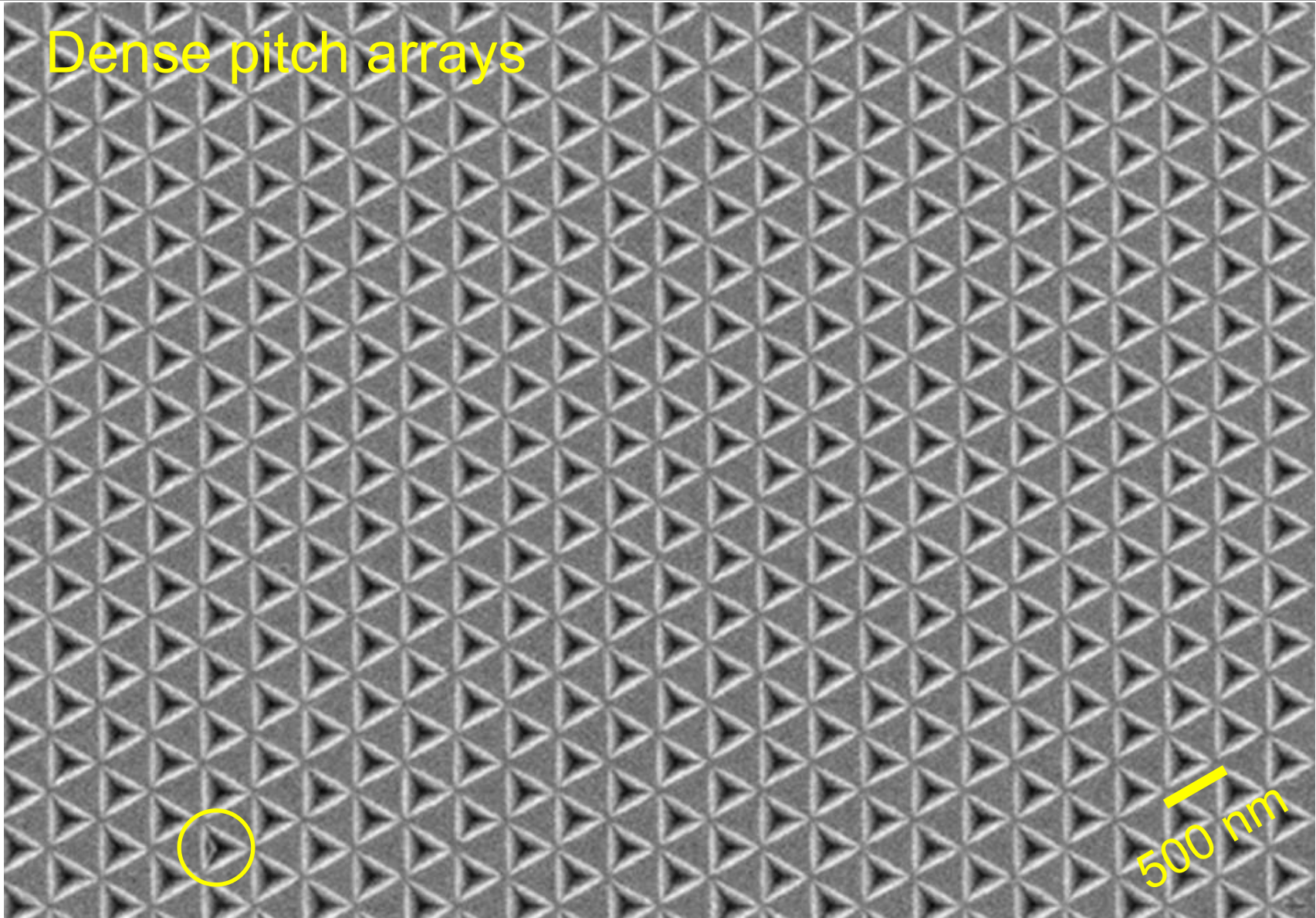
Summary - InGaAsN QWs & QWrs

- Enhanced N uptake on vicinal (100) substrates
- Enhanced N incorporation on non-planar substrates
- V-groove QWRs emitting at $1.3\mu\text{m}$ at room temperature



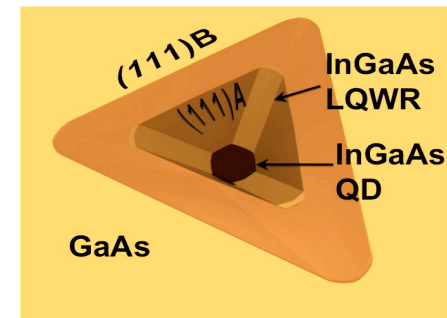
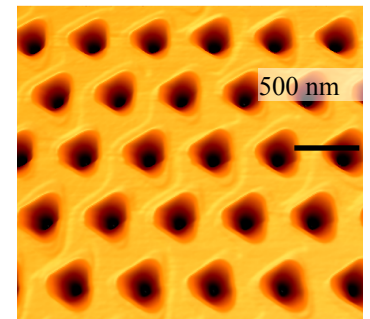
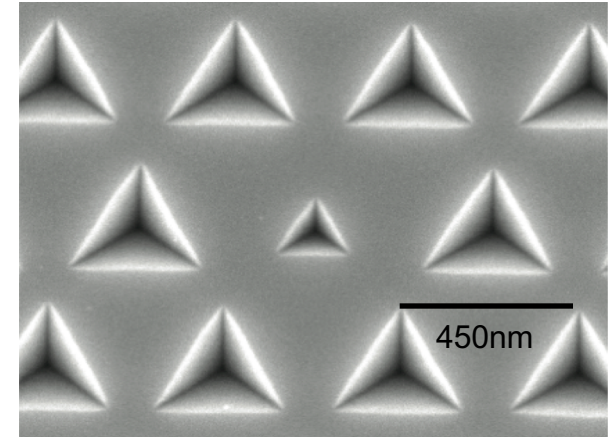
Non-planar epitaxy on 2D patterns

Dense pitch arrays



Multiwavelength InGaAs quantum dot arrays

- Motivations & challenges
- MOVPE of “pyramidal” Quantum Dots
- Spectral & spatial control of QDs
- Spectral & spatial isolation of QDs
- Summary and perspectives



NANOPHOTONICS

Electron + photon confinement >> integrated nano-photonics

Quantum information

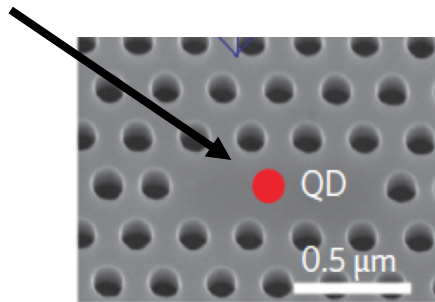
- Storage
- Transmission
- Treatment

Quantum devices

Single-photon emitters
Quantum-entangled photon sources
Low-current and high-speed lasers
Integrated photonic devices

Quantum logic gate

InAs QD coupled
to cavity

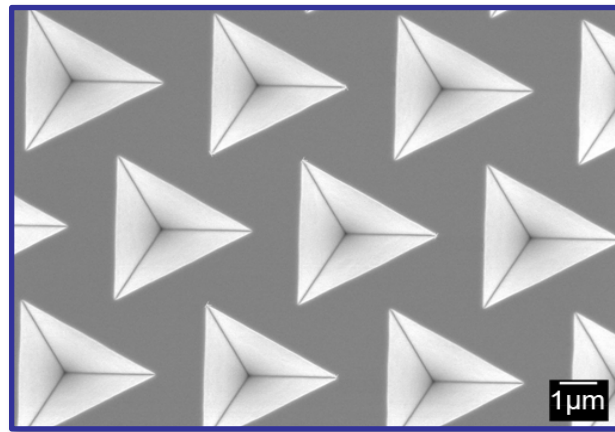


Kim et al., Nature Photonics (2013)

Stransky-Krastanov QDs

SK dots : random nucleation
“Soft” site control not accurate
enough
“Hard” site control damages the
QDs

MOVPE of pyramidal quantum dots: localized growth controlled by substrate patterning

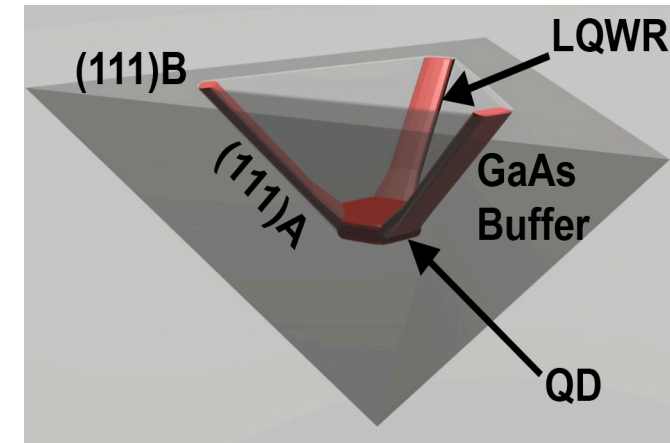


Patterned GaAs substrate (Top View SEM)

(111)B, As-terminated :
quasi inert

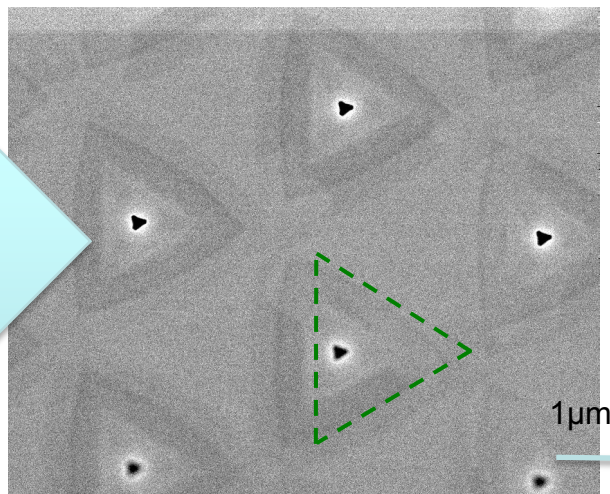
(111)A : Ga-terminated:
Adatom incorporation

- Adatom migration
- Capillarity

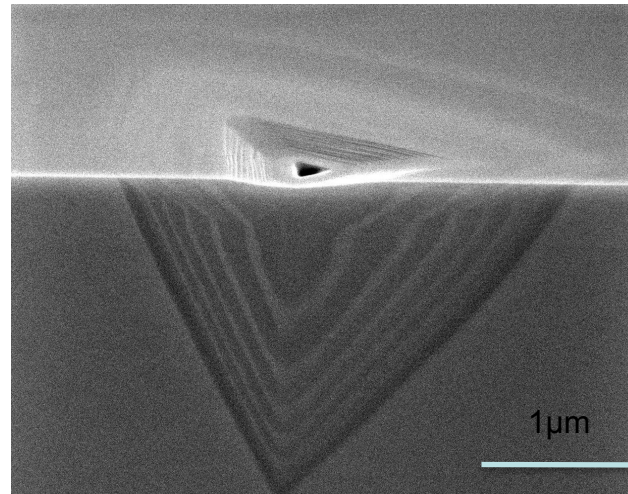


E. Kapon et al., APL 50, 347 (1987)
G. Biasiol et al., PRL 81, 2962 (1998)

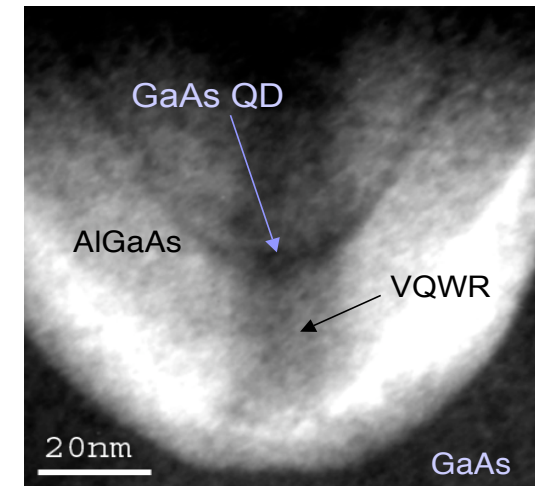
MOVPE
growth



SEM Top View

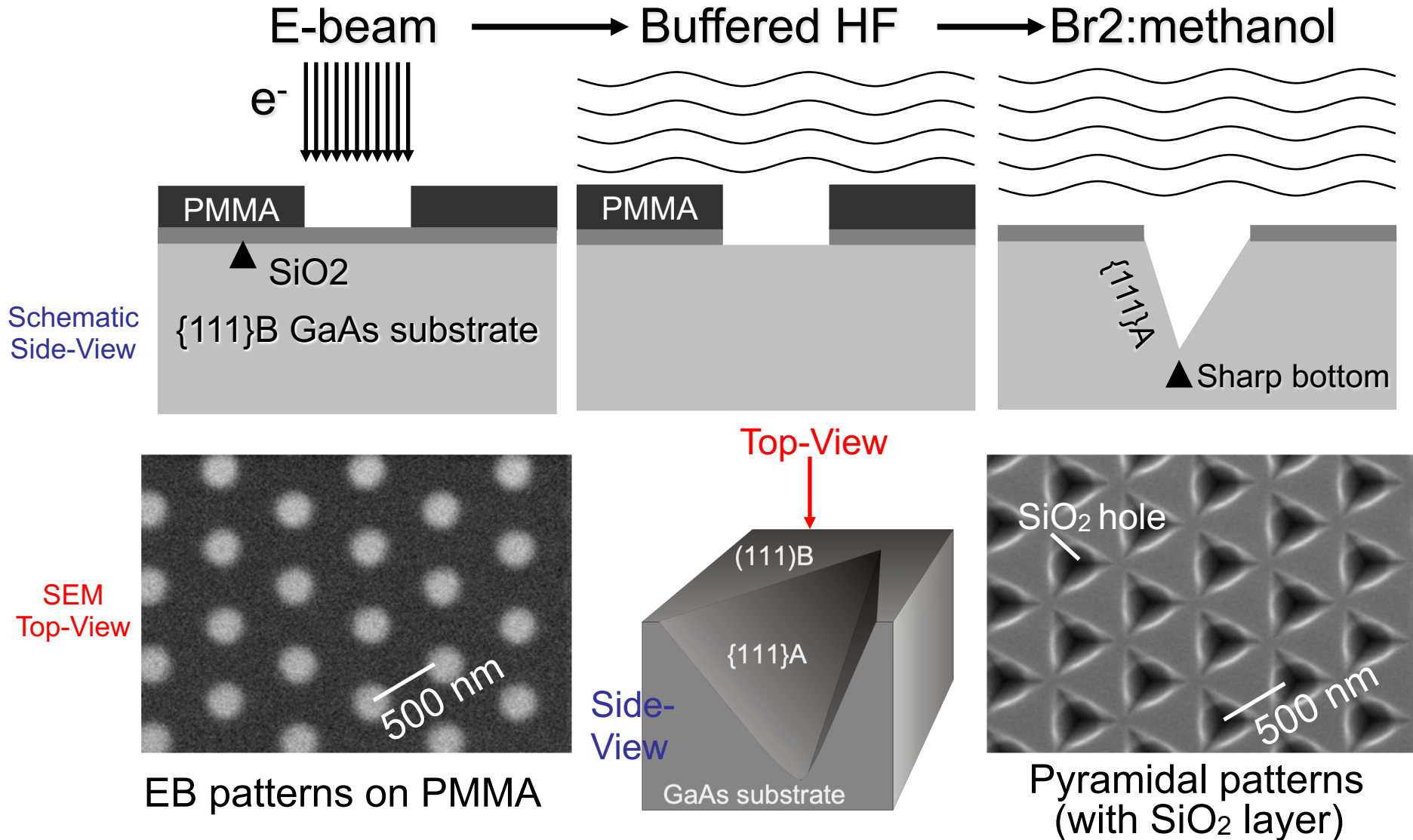


SEM cross-section

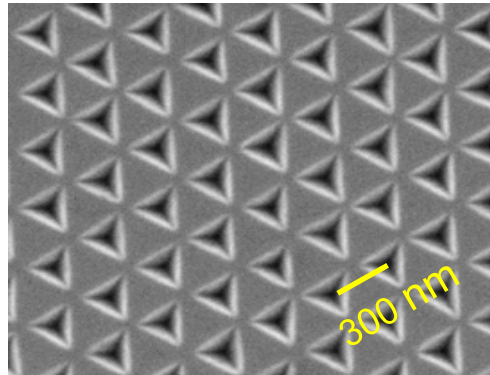


TEM Cross Section

Substrate Preparation: e-beam lithography + selective wet etching

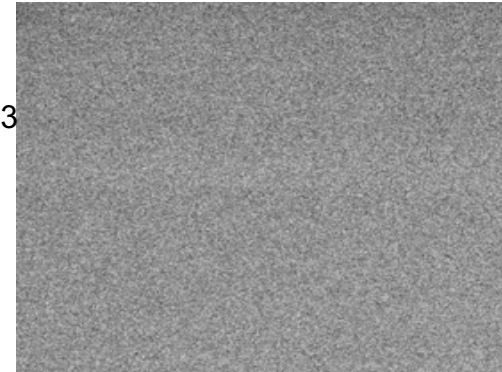


GROWTH PARAMETERS

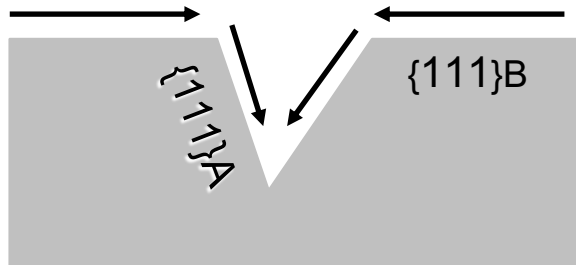


Original substrate

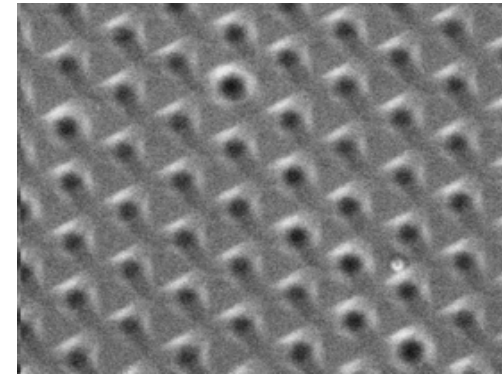
Deoxidize under AsH_3
at 730°C



Surface mass transport

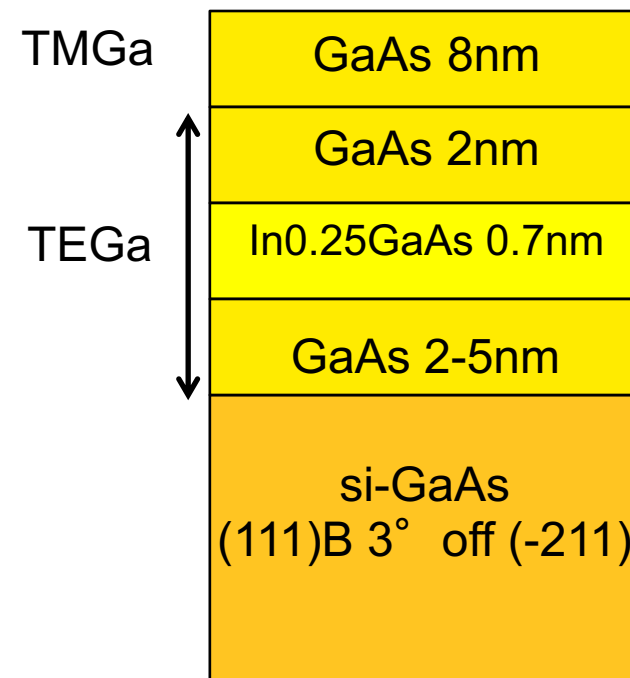
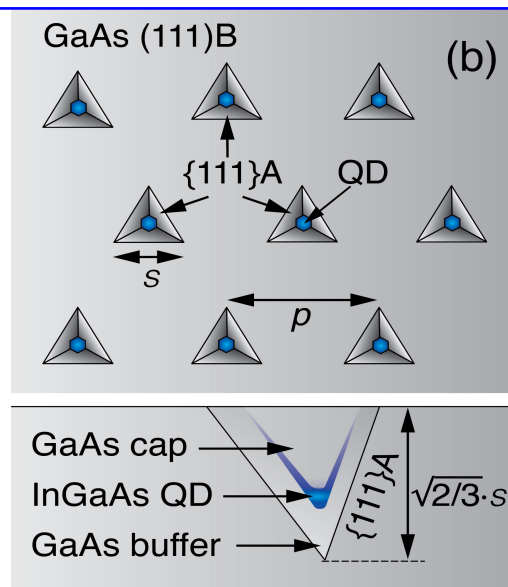
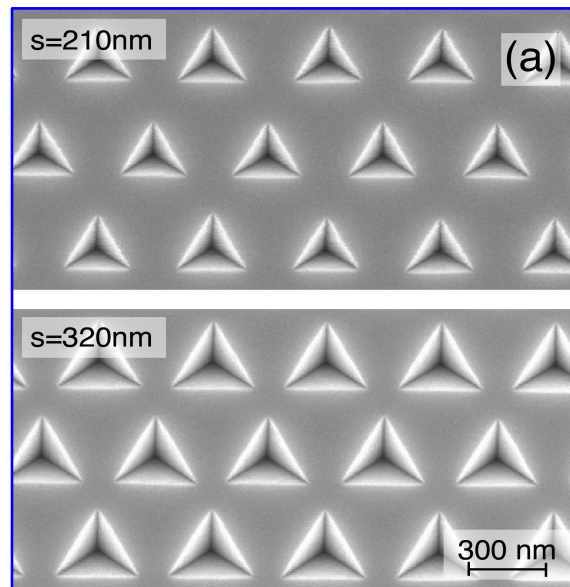


At $\sim 620^\circ \text{C}$



- Deoxidation under AsH_3 : 4mn @ 600°C
- si-GaAs (111)B + 3° towards (-211)
- 20mbars, $550\text{-}600^\circ \text{C}$, N_2 ambient (total flow 7l/mn)
- TEGa, TMGa, TMIIn, TEIn, AsH_3
- 0.01nm/s on (100)

MOVPE OVER SETS OF UNIFORM ARRAYS OF PYRAMIDS



Varying pyramidal size s at constant pitch p

affects

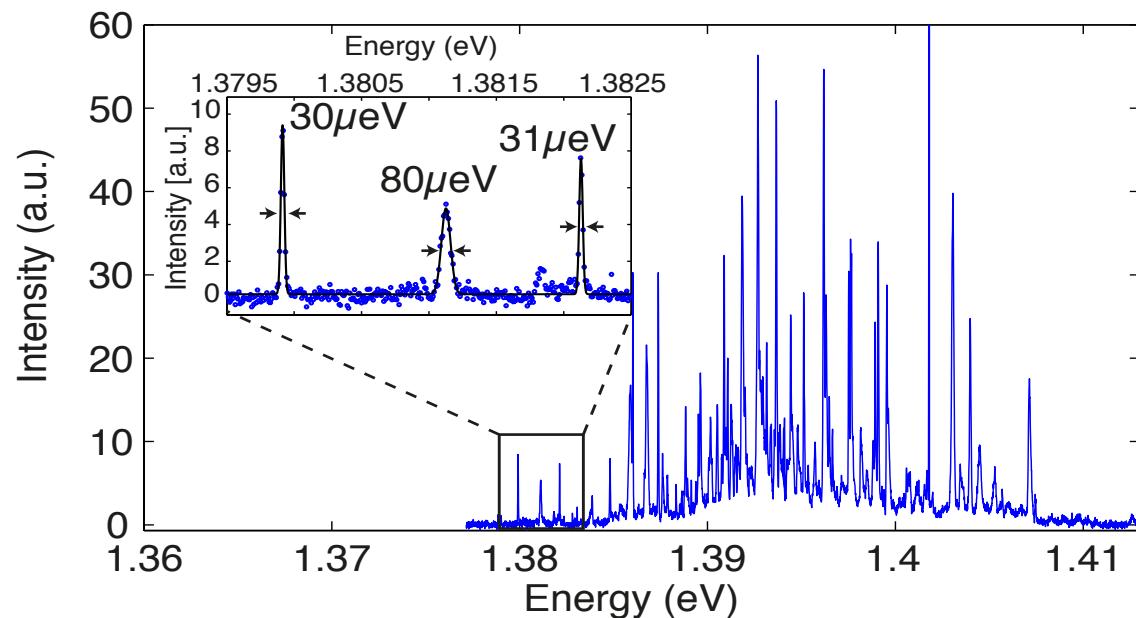
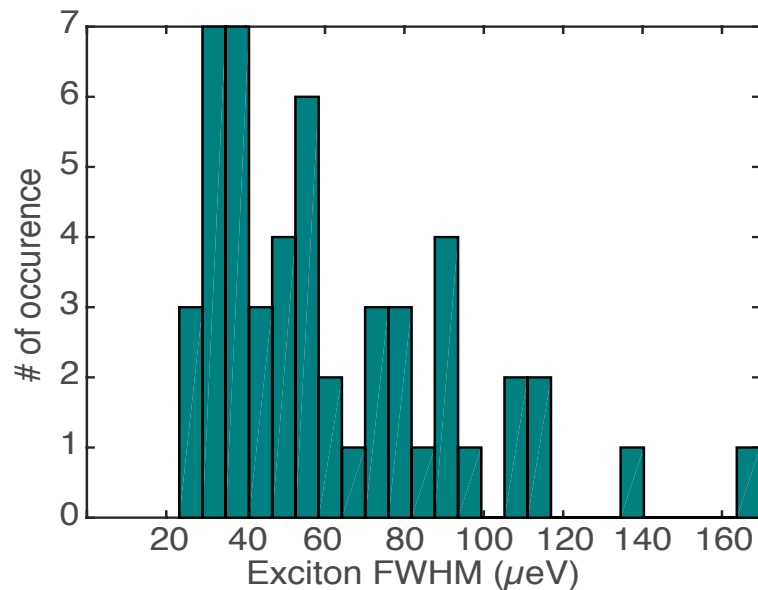
- metalorganic decomposition
- adatom population

*Modifies
the QD*

growth rate
thickness and In %
emission energy

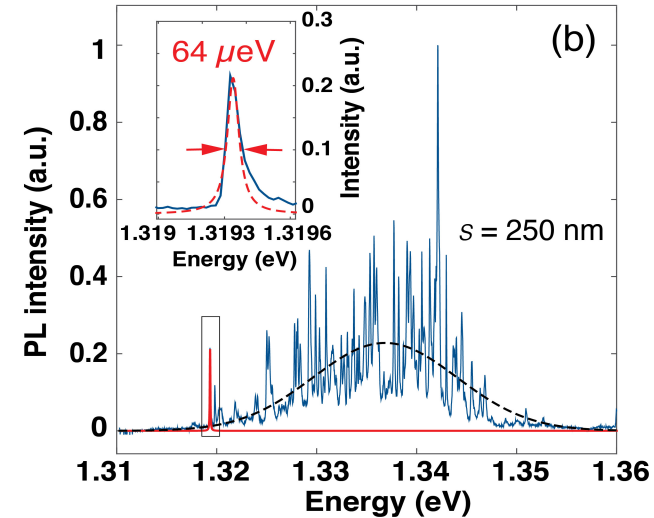
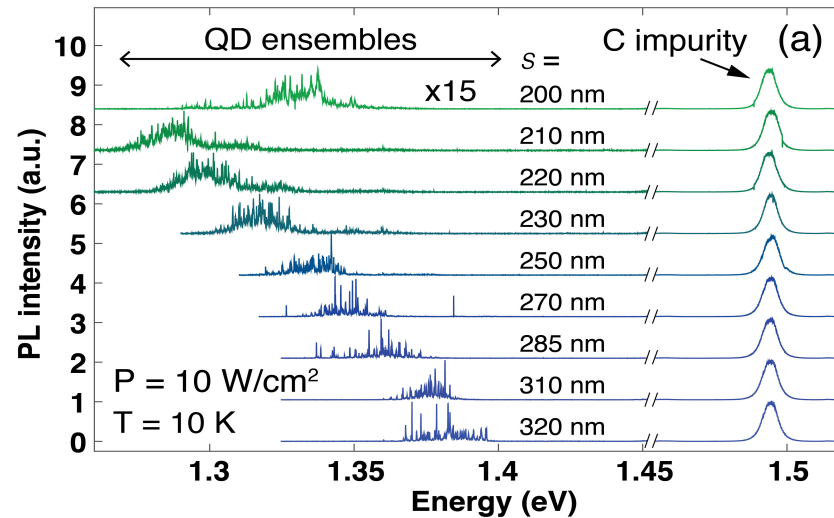
Site-controlled QDs with narrow PL emission

Micro-PL of an ensemble of
30-40 QDs



InGaAs QDs excitonic
linewidth < 30 μeV

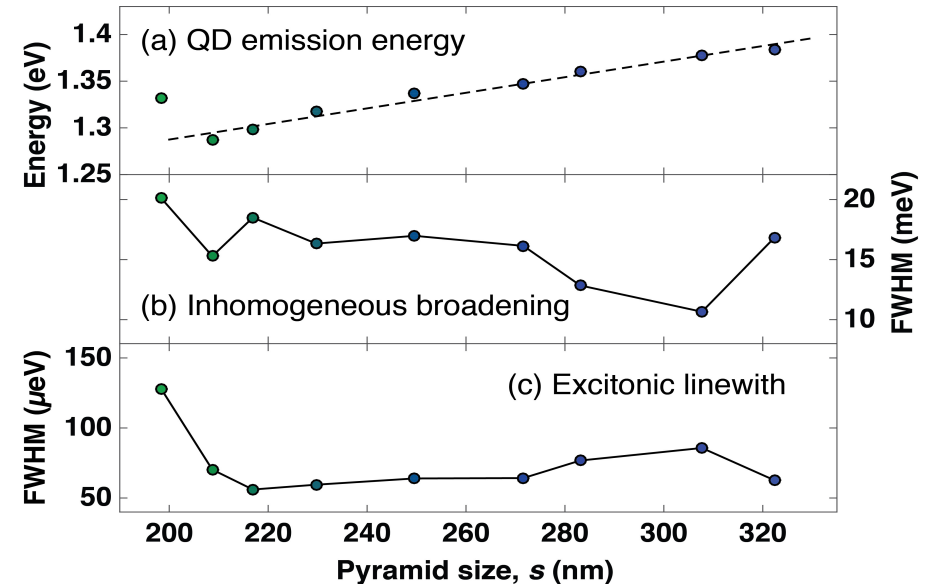
Controlling QD energy through pyramid size



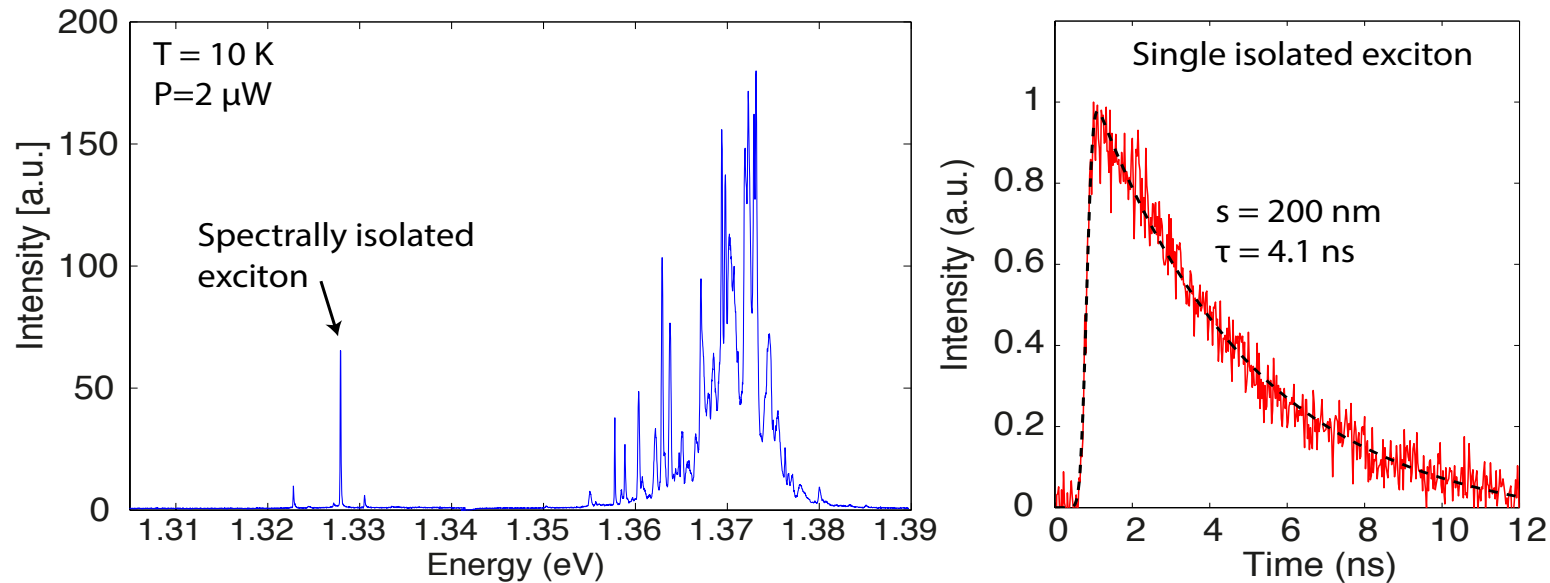
I.V. Kulkova *et al.*, J. Crystal Growth (2017)

With larger pyramid size:

- ✓ Higher QD emission energy
- ✓ Lower inhomogeneous broadening
- ✓ Comparable excitonic linewidth

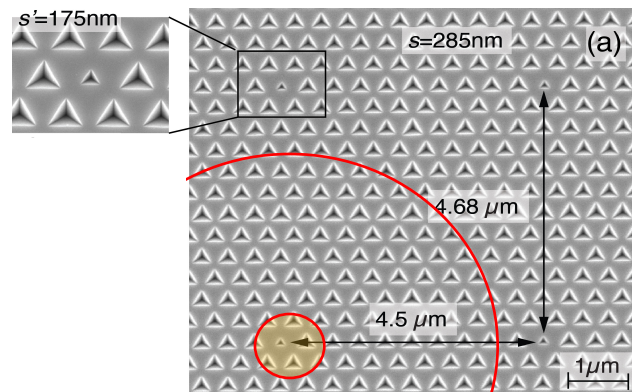


Time resolved photoluminescence on single QD



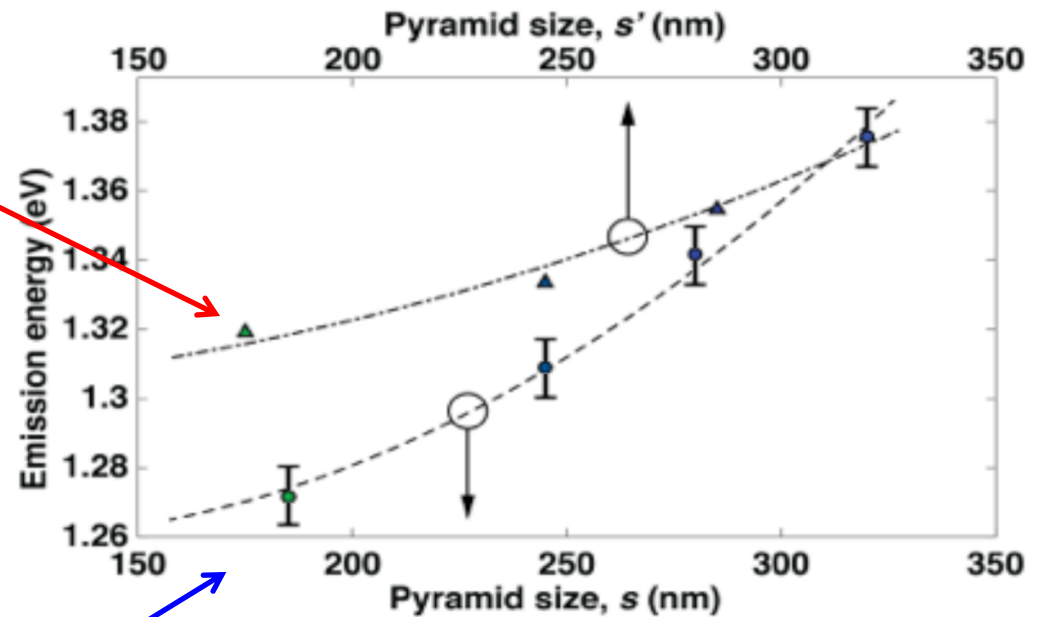
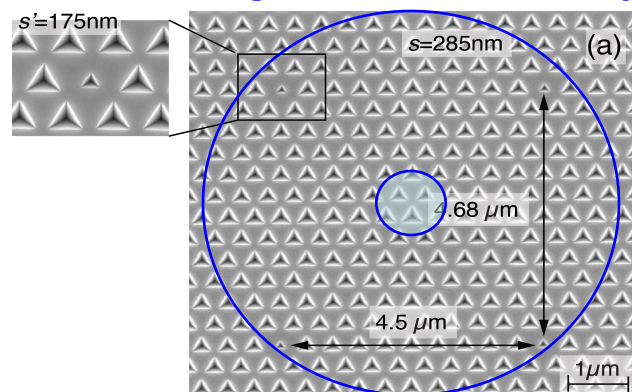
- PL decay measured on single spectrally isolated QD
- Valuable tool for cavity design

Controlling isolated QD emission energy through pyramid size



Isolated QDs

Homogeneous array



QD energy increases with pyramid size:
 Strong dependence in homogeneous array (100meV)
 Weaker dependence in isolated QDs (40 meV)
 QD energy span sufficiently large for WDM source

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

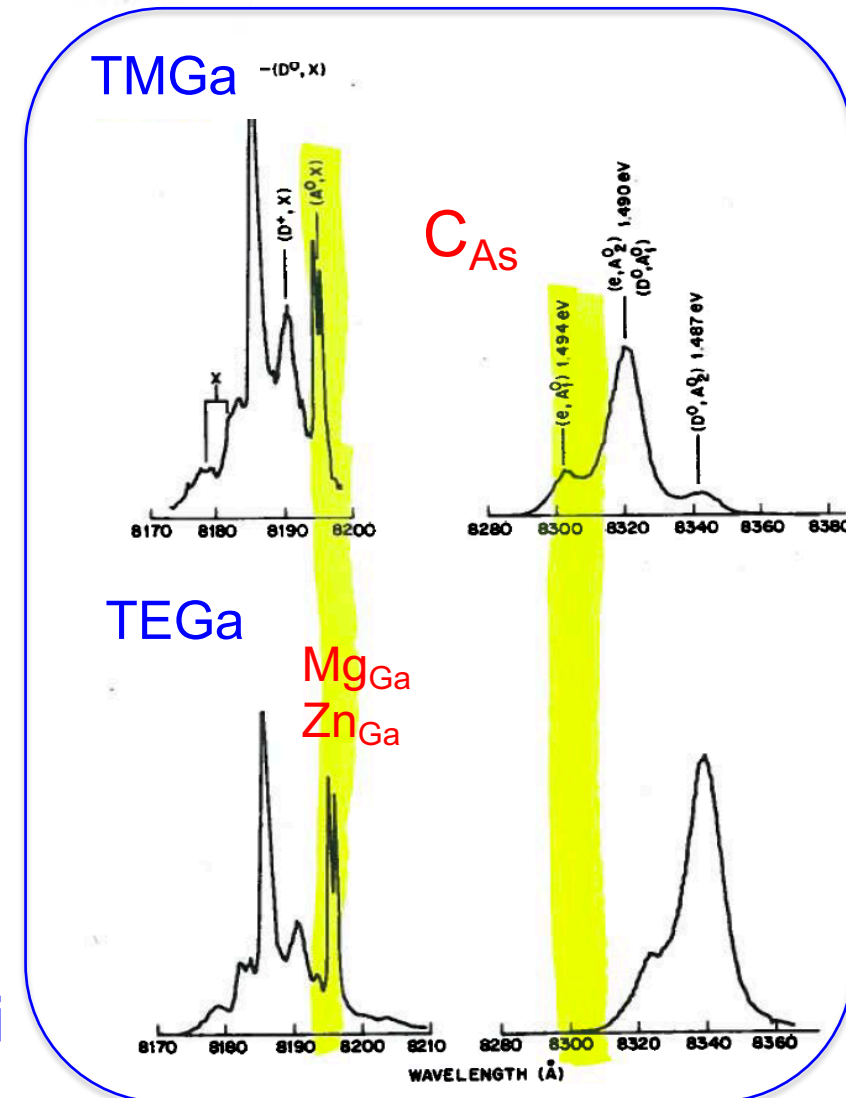
R. Bhat, P. O'Connor, H. Temkin, R. Dingle and V. G. Keramidas

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

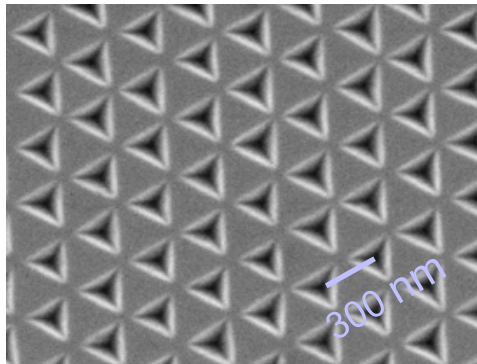
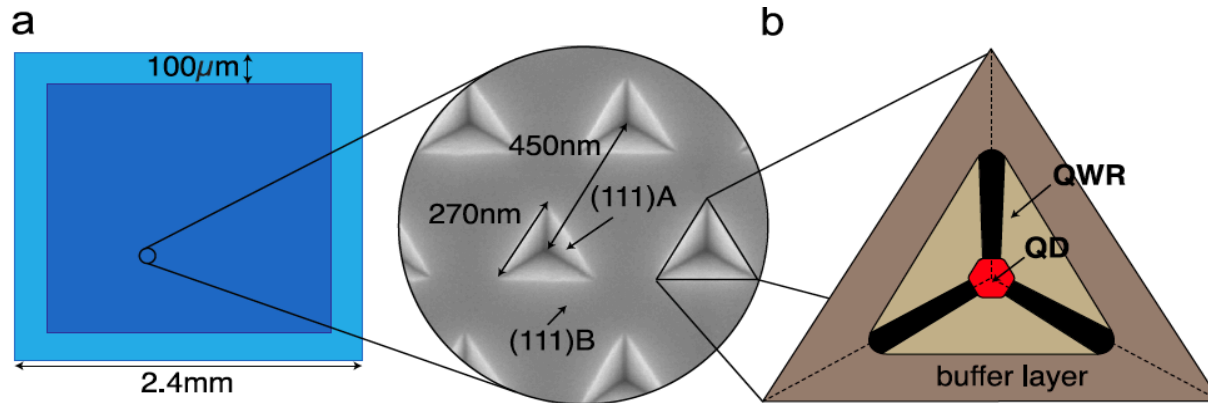
- TMGa: $(\text{CH}_3)_3\text{Ga}$
- TEGa: $(\text{C}_2\text{H}_5)_3\text{Ga}$

- 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

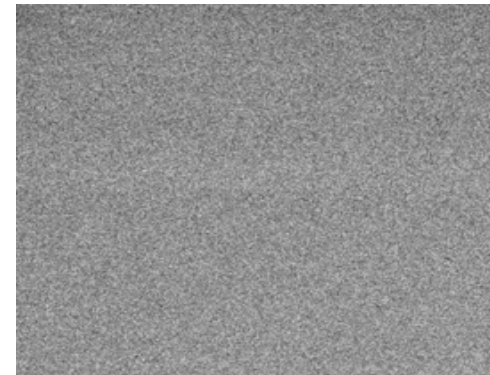
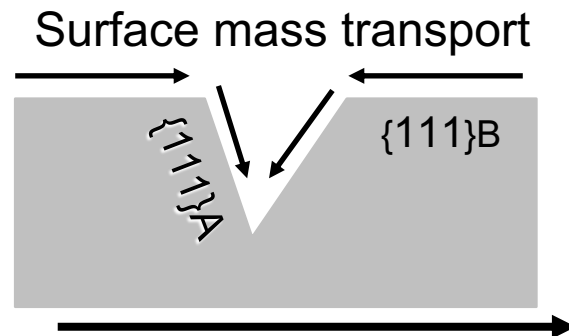
8° K PL
GaAs epi



Methyl- vs ethyl- precursors in QDs



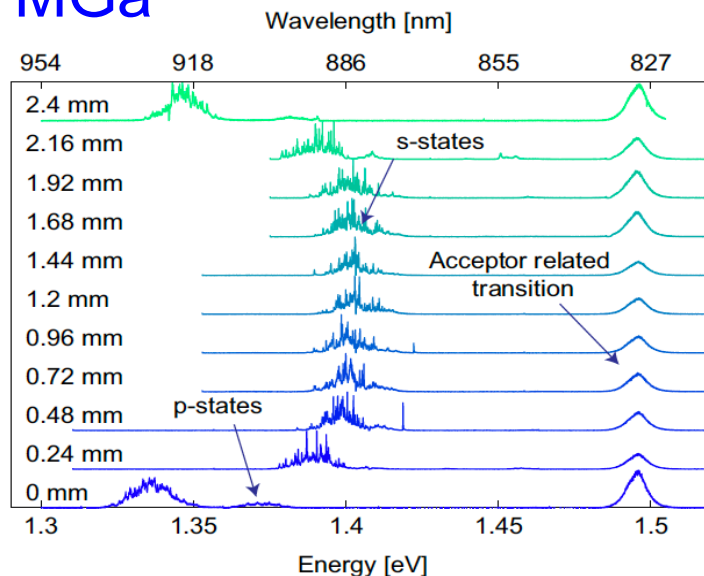
Original substrate



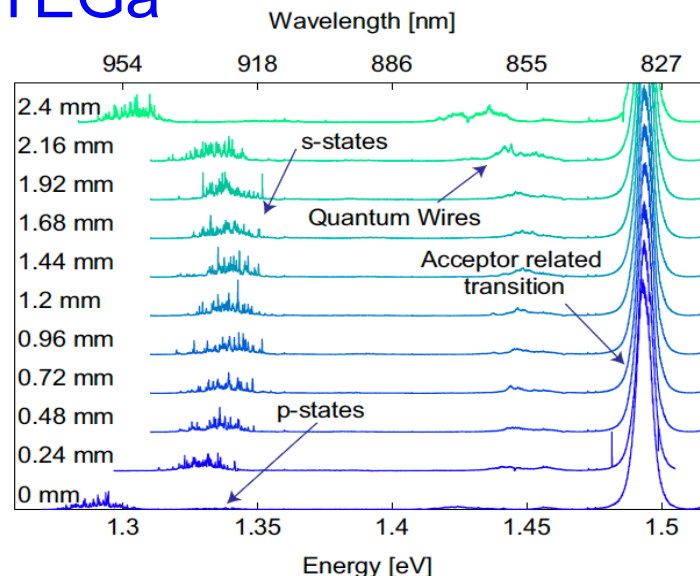
- Membrane 265nm: $s < 300\text{nm}$
- $T < 620^\circ\text{C}$ (otherwise planarization)
- TMGa growth rate varies with T below 600°C – not TEGa
- TMGa decomposes on 111A, **not** on 111B
- TEGa decomposes **on both surfaces** > edge effect is reduced
- Reduced C acceptor: **improved optical properties**

InGaAs/GaAs pyramidal dots: TMGa vs TEGa

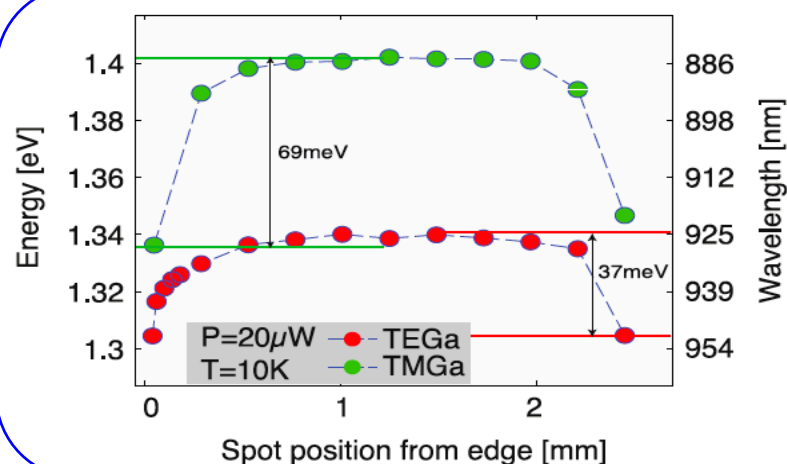
TMGa



TEGa



(+ TMIn)



With TEGa

- Longer emission wavelength
- Reduced edge effect : shorter diffusion length
- Better reproducibility : gas diffusion limited

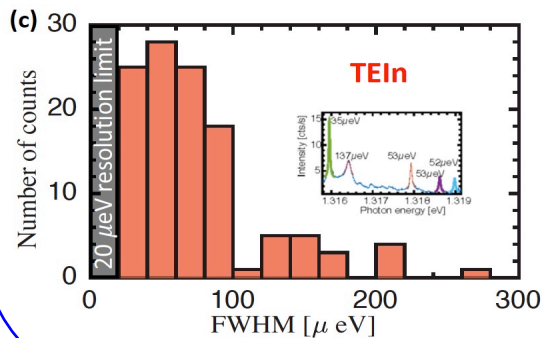
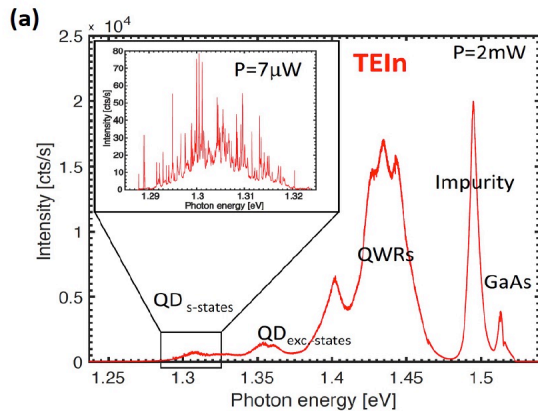
Site-controlled InGaAs/GaAs pyramidal quantum dots grown by MOVPE
on patterned substrates using TEGa

B. Rigal et al., J. Crystal Growth 414 (2015) 187-191

InGaAs/GaAs pyramidal dots: TMIn vs TEIn (+TEGa)

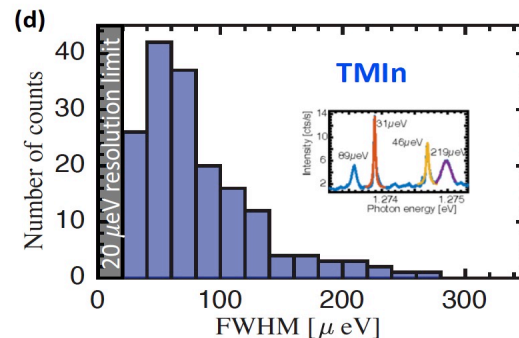
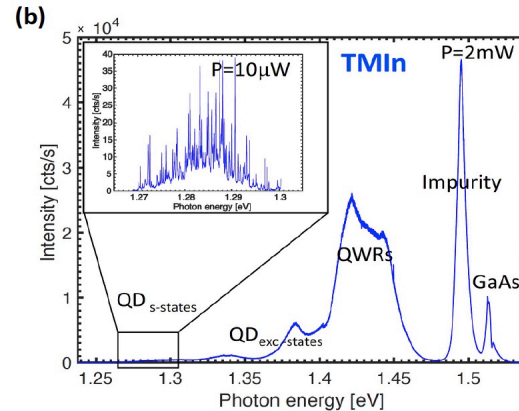
TEIn

$t_{\text{QD}}=0.5\text{nm}$, $\lambda_{\text{QD}}\sim 950\text{nm}$

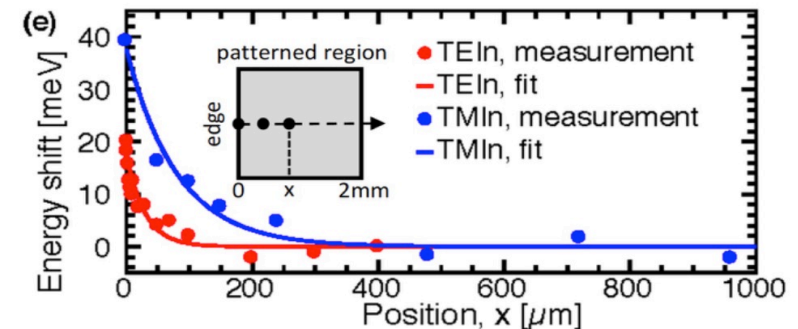


TMIn

$t_{\text{QD}}=0.75\text{nm}$, $\lambda_{\text{QD}}\sim 960\text{nm}$



Variation of QD emission energy across patterned area

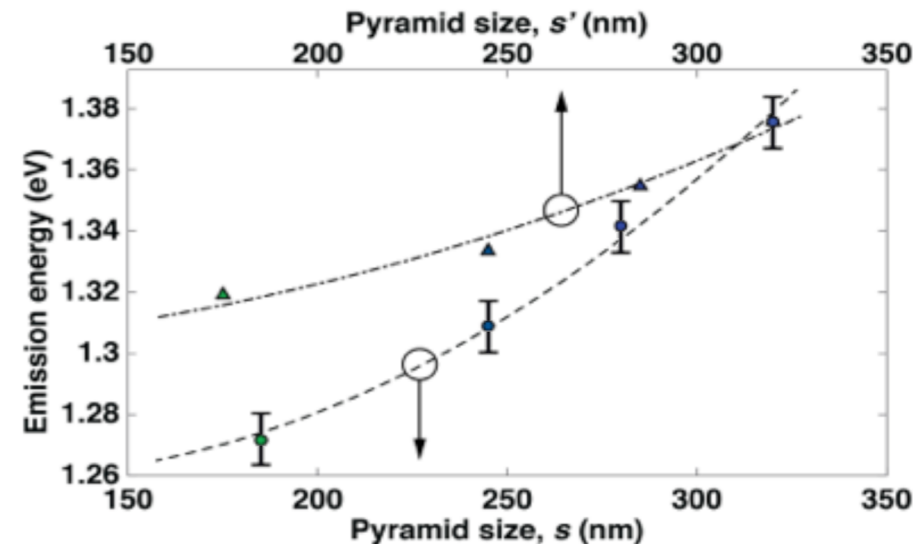
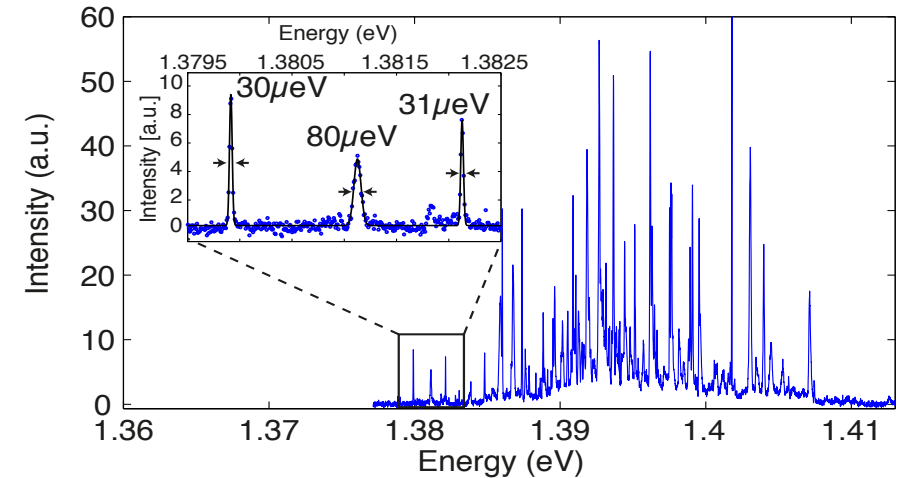


With TEIn:

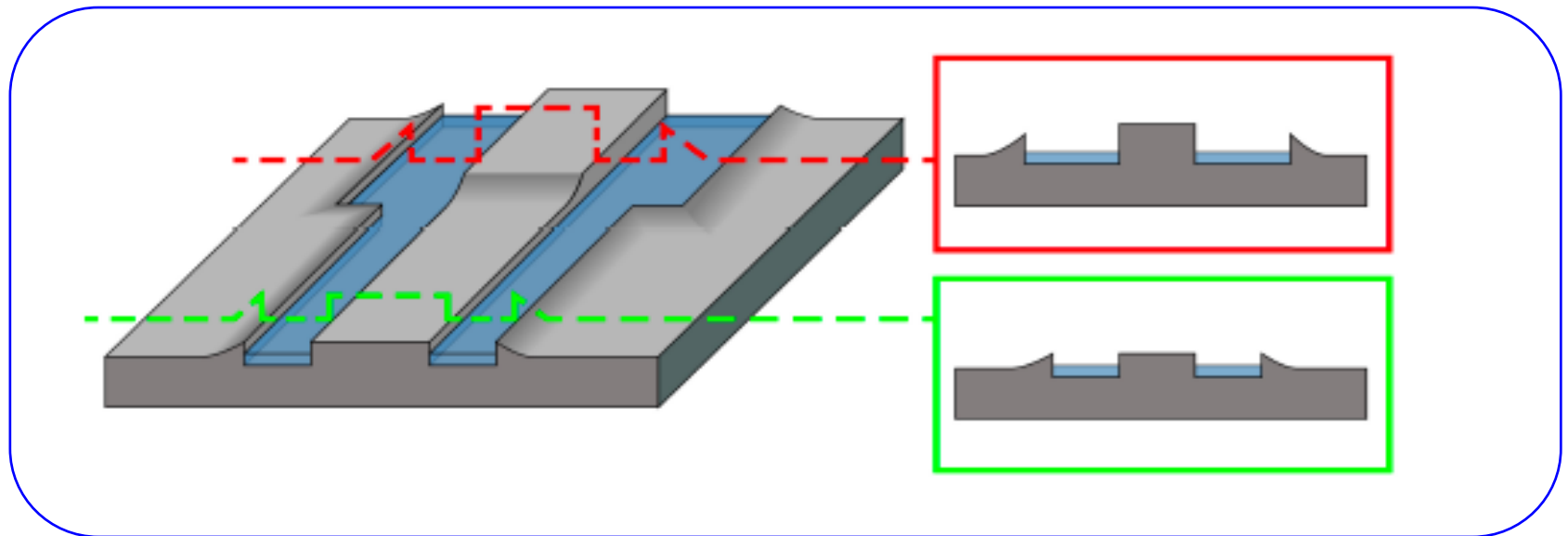
- Higher incorporation rate of In (compared to TMIn)
- Narrower margins of patterned QD array
- Longer emission wavelengths ($>1\mu\text{m}$) possible

InGaAs QDs arrays - summary

- InGaAs / GaAs QD arrays with 30 μeV PL emission lines & 7 meV inhomogeneous broadening (ensemble of 30-40 QDs)
- 100 meV wavelength tuning through pyramid size variation (210-320nm)
- Spectrally and spatially isolated QDs in uniform matrix
- 40 meV wavelength tuning of isolated QDs
- >>> Multi-wavelength QDs for integrated nanophotonics



Selective area epitaxy: growth rate enhancement

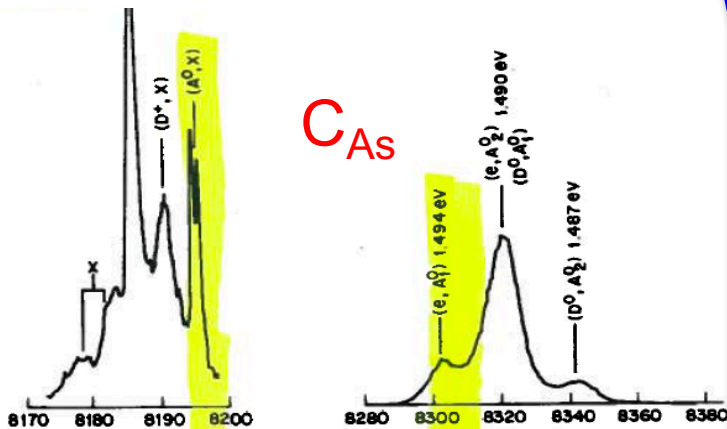


- No growth sites on the dielectric mask
- Gas phase concentration $\gg$ precursor **gas phase diffusion**
- Partial precursor **fragmentation**
- **Effective** gas phase diffusion depends on the precursor
- Growth rate **enhancement** in the window area
- Depends on the window **width**
- **Modulation** of thickness and composition
- Applications to device **integration** on the surface

Selective area growth: ethyl- vs methyl- sources

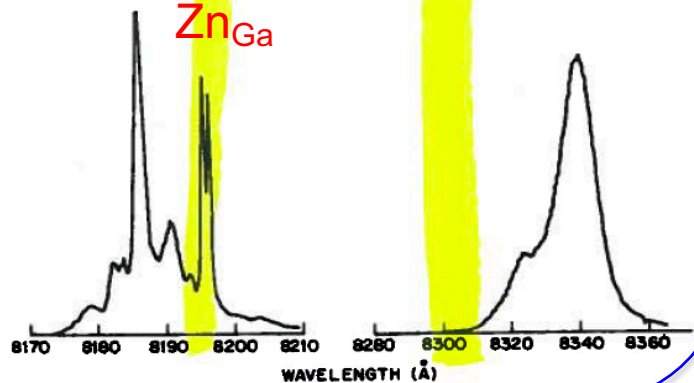
8° K PL of GaAs epi

TMGa $-(D^0, X)$



TEGa

Mg_{Ga}
Zn_{Ga}



- TMGa: $(CH_3)_3Ga$
- TEGa: $(C_2H_5)_3Ga$

- *Ga-C bond stronger in TMGa than in TEGa*
- *TEGa decomposes at lower temperatures*
- *Reduced C uptake in (Al)GaAs*
- Different gas phase and surface diffusion

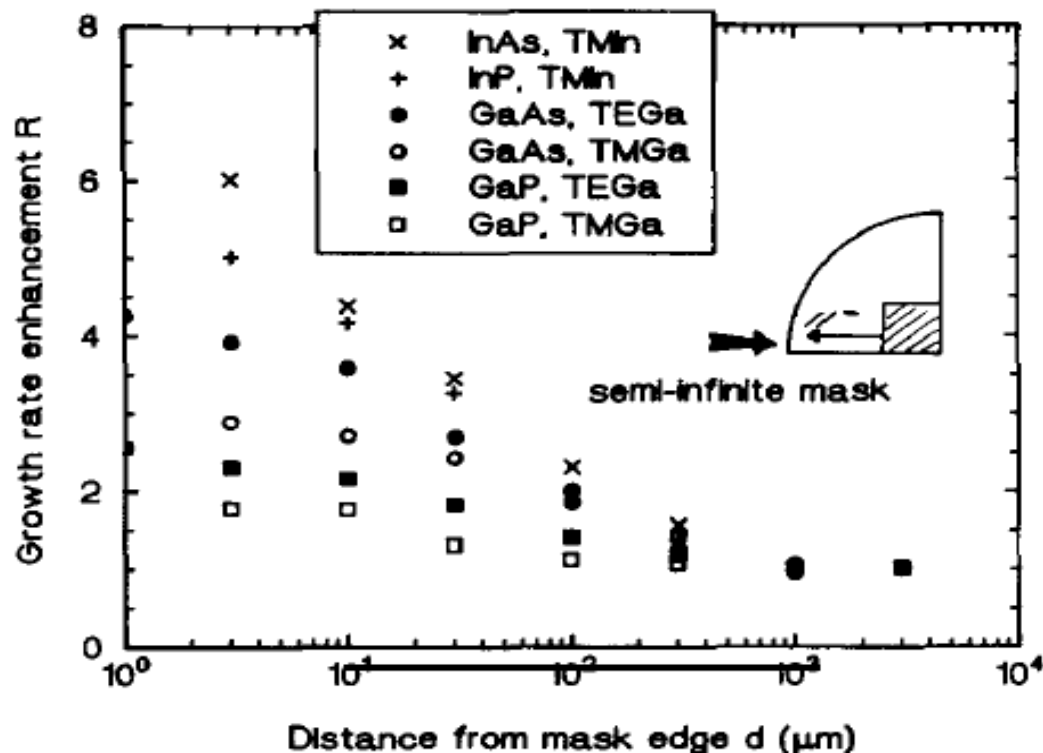
Ethyl- vs methyl : InGaAs selective area growth

Selective organometallic vapor phase epitaxy of Ga and In compounds:
a comparison of TMI_n and TEGa versus TMI_n 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, USA

Growth rate enhancement in binary alloys:



TEGa vs TMGa:
higher *effective* diffusion coefficient

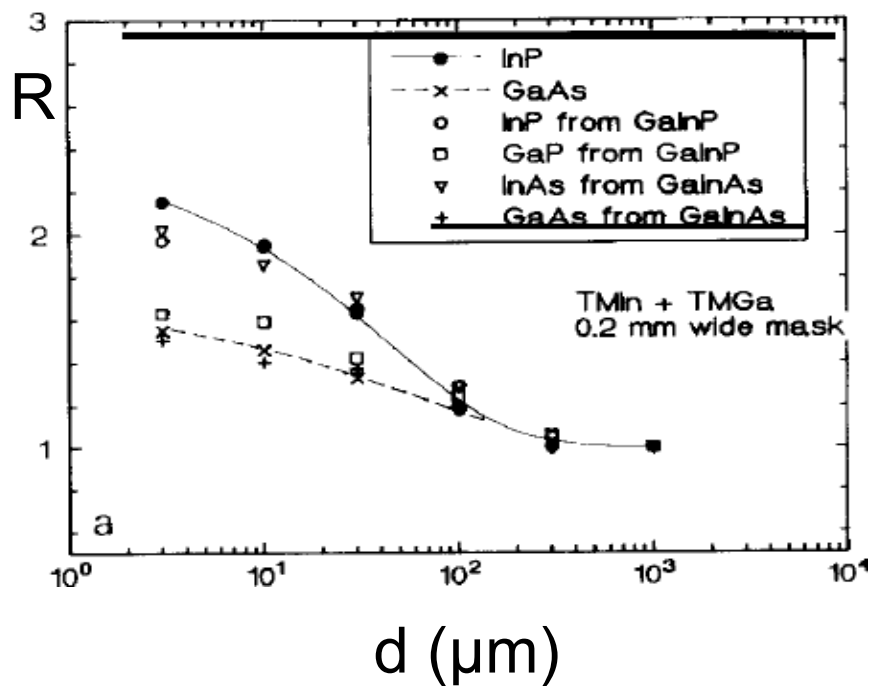


Larger growth rate enhancement

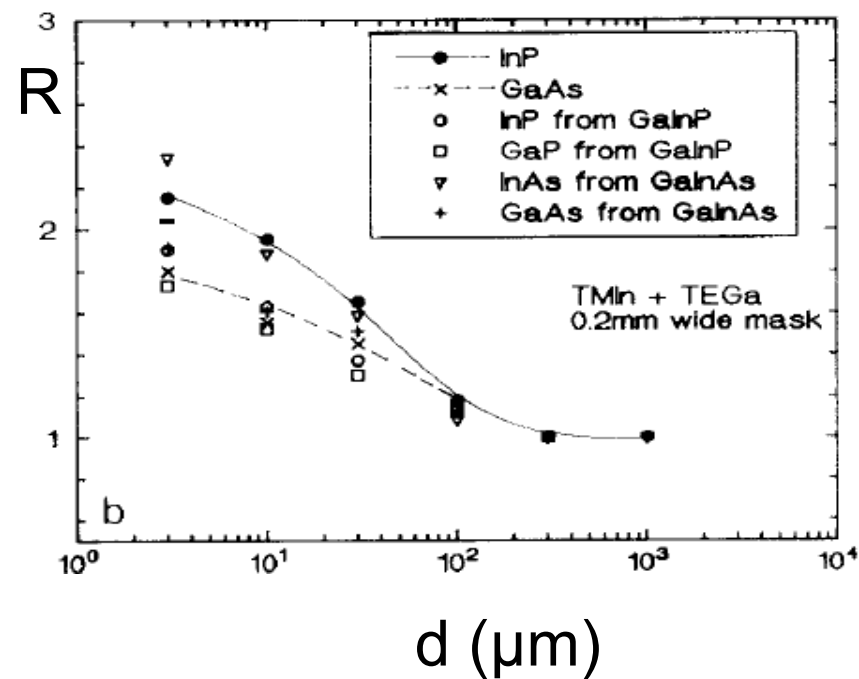
H_2 carrier gas, 76 Torr
 650°C (mass transport limited)
 TMI_n, TMGa/TEGa, AsH₃, PH₃

Ethyl- vs methyl- : InGaAs Selective area growth

TMGa + TMIIn



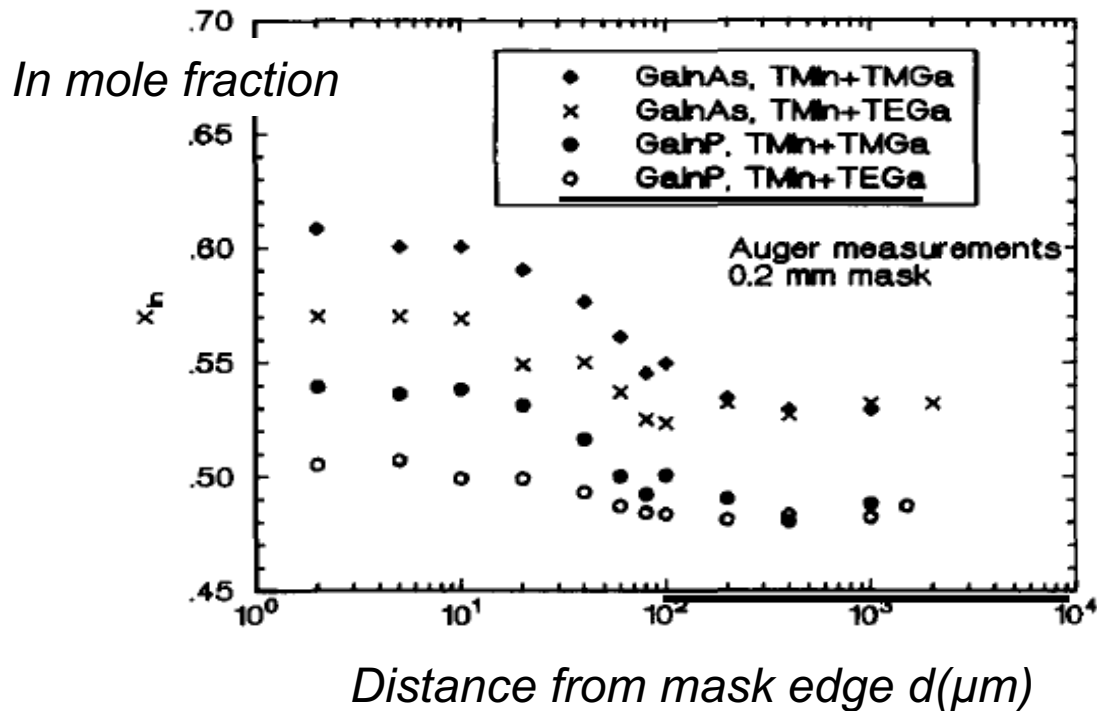
TEGa + TMIIn



Increased growth rate enhancement using TEGa

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

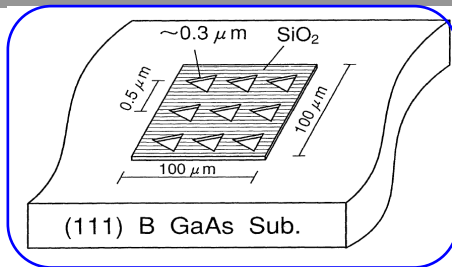
Ethyl- vs methyl : InGaAs selective area growth



Reduced In content increase using TEGa

- Change in In composition:
- undesired > use TEGa
 - desired > use TMGa

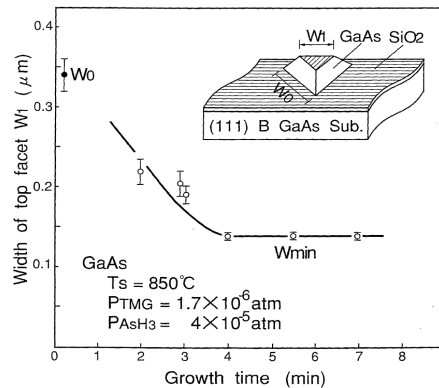
Selective area epitaxy : GaAs tetrahedral growth



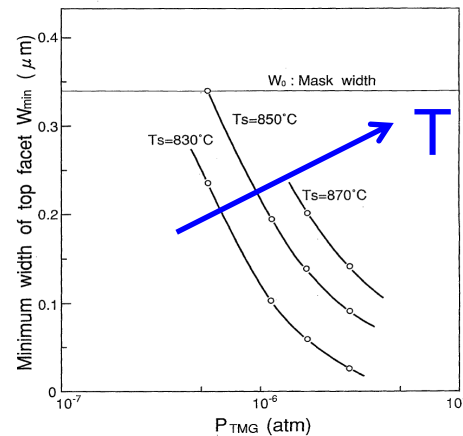
Jpn. J. Appl. Phys. Vol. 32 (1993) pp. L 104-L 106
Part 2, No. 1A/B, 15 January 1993

Self-Limited Facet Growth for GaAs Tetrahedral Quantum Dots

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- Top (111)B facet width decreases with time
- Stops decreasing
- Width uniformity better than mask opening
- Growth rate prop. Ga flux, independent of T: diffusion limited regime



- Minimal stable width larger at higher T

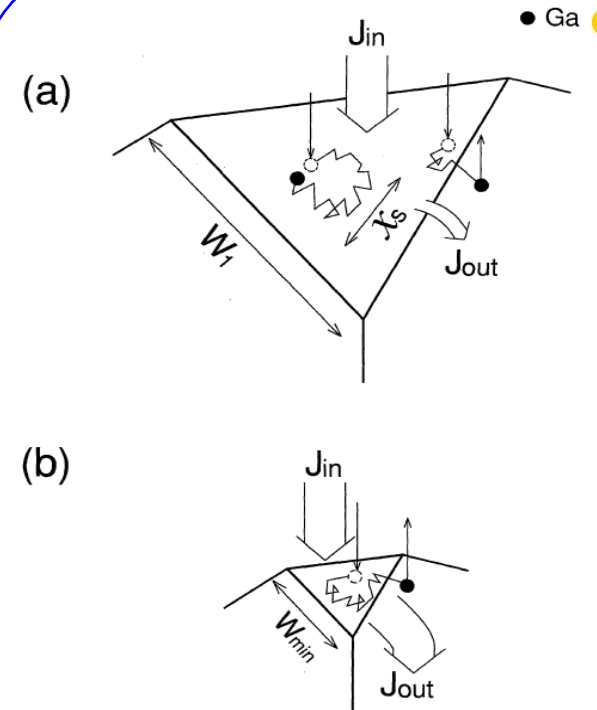


Fig. 5. Possible mechanism of tetrahedral growth: growth stage (a), equilibrium stage (b). (J =net flux, x_s =surface diffusion length.)

Quantum Cascade lasers

$$\lambda = 30\text{-}300\mu\text{m}$$

$$f = 1 - 5 \text{ THz}$$

- Over 1300 layers
- Over 13 μm thickness
- Low n-type background
- Low n-type doping

L. Sirigu *et al.* , Appl. Phys. Letters (2008)
M. Amanti *et al.* New Journal of Physics (2009)

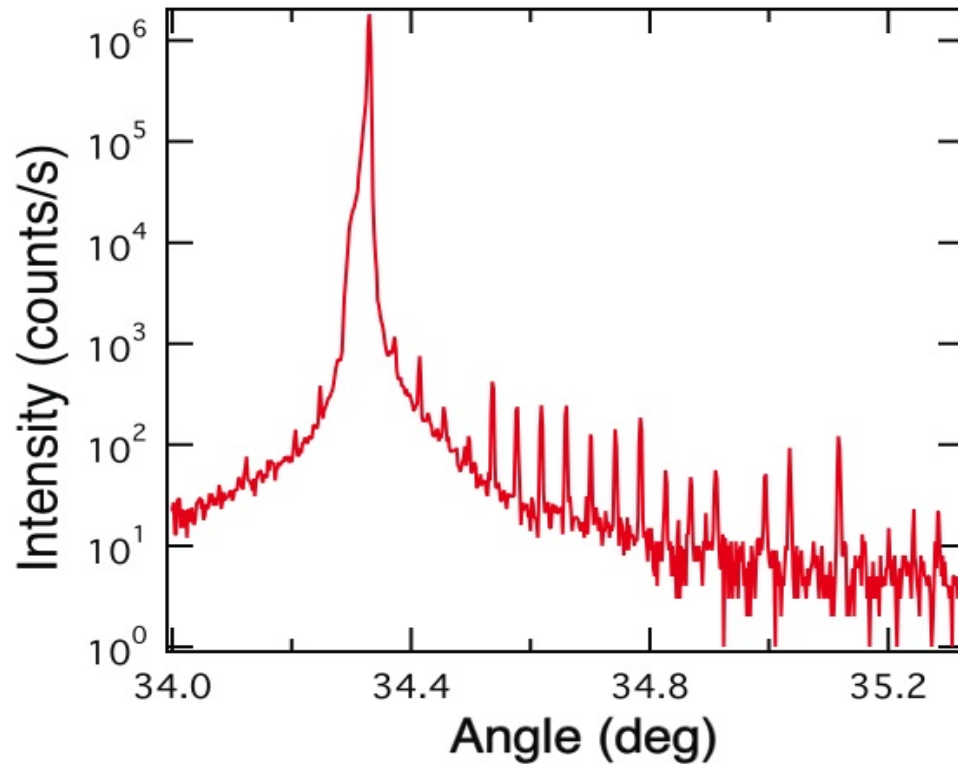
x 100

GaAs:Si	20nm
n=4x10 ¹⁸ cm ⁻³	
AlGaAs	10nm
AlGaAs 0-15%	290nm
GaAs	20nm
AlGaAs	3.7nm
GaAs	10nm
AlGaAs	0.7nm
GaAs	18.3nm
AlGaAs	1nm
GaAs	15.2nm
AlGaAs	1.3nm
GaAs	12.7nm
AlGaAs	1.7nm
GaAs	10.5nm
AlGaAs	2.7nm
GaAs:Si	21.1nm
n=4x10 ¹⁶ cm ⁻³	
AlGaAs	2.4nm
GaAs	16.5nm
AlGaAs	3.7nm
GaAs	20nm
AlGaAs 15-0%	290nm
AlGaAs	15nm
GaAs:Si	800nm
n=1.7x10 ¹⁸ cm ⁻³	
AlGaAs	300nm
GaAs	250nm
GaAs	350 μm
semi-insulating substrate	

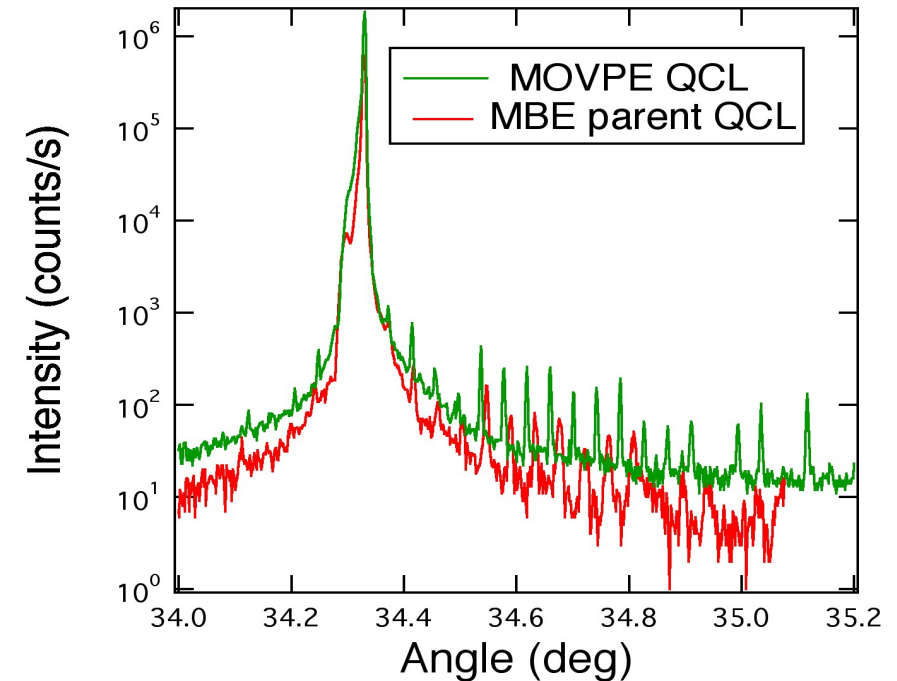
x 170

GaAs:Si	60nm
n=5x10 ¹⁸ cm ⁻³	
GaAs	20nm
AlGaAs	3.9nm
GaAs:Si	18.4nm
n=2.6x10 ¹⁶ cm ⁻³	
AlGaAs	4.8nm
GaAs	11nm
AlGaAs	1.8nm
GaAs	11.5nm
AlGaAs	3.5nm
GaAs	9.4nm
AlGaAs	3.9nm
GaAs:Si	18.4nm
n=4x10 ¹⁶ cm ⁻³	
AlGaAs	4.8nm
GaAs	20nm
GaAs:Si	300nm
n=1.7x10 ¹⁸ cm ⁻³	
AlGaAs	300nm
GaAs	250nm
GaAs	350 μm
semi-insulating substrate	

Vertical uniformity

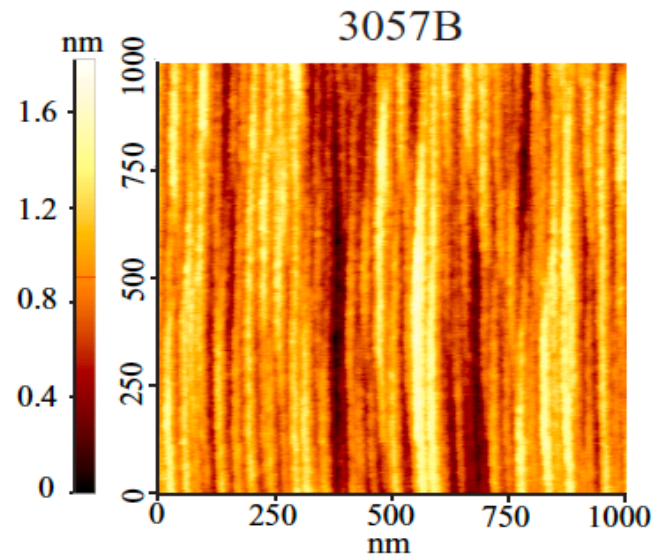
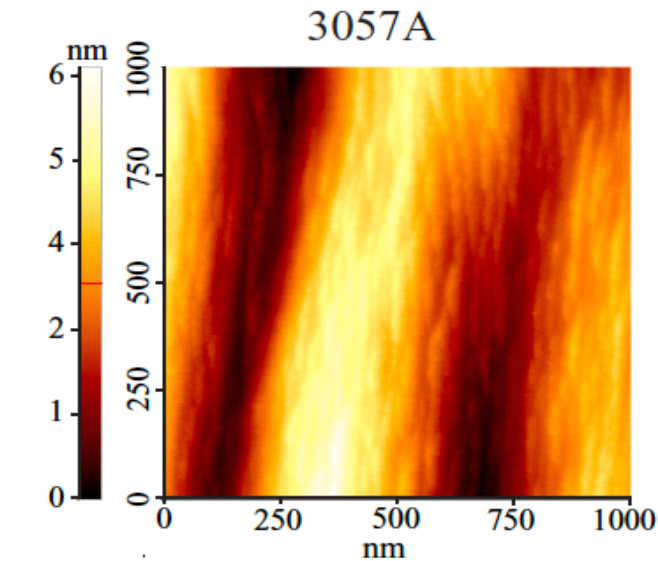


- Very sharp GaAs/ $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ interfaces.
- Satellite peaks visible up to the 15th-order



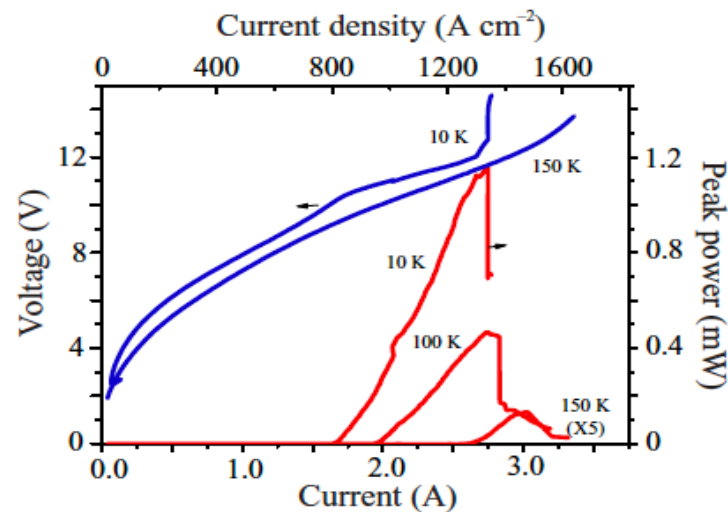
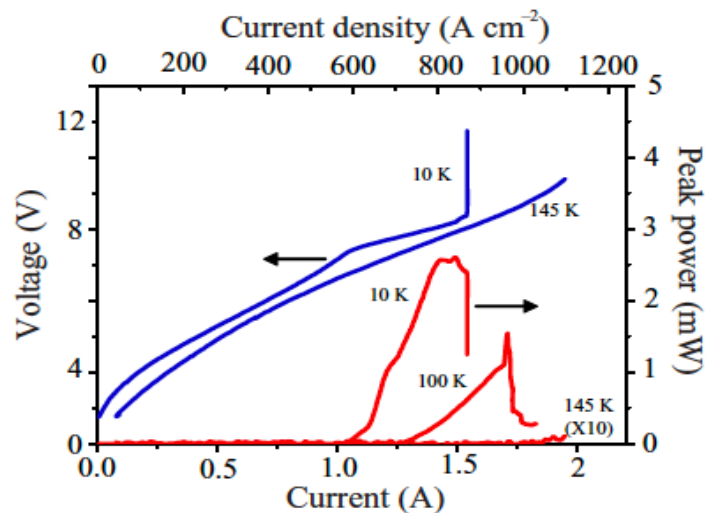
Comparison with the parent
MBE-grown QCL
(with 120 active periods)

Improved QCL performance on vicinal substrates



on the B vicinal:

- Smoother growth
- Higher $T_{\max}$



Selected experiments in MOVPE

Summary

- Understand and choose the proper **growth regime**
- **Mass transport** limits the growth rate in a **large** temperature range
- Use the right **precursors** and **carrier gas**
- Understand the **dynamics** of the growth process
- Taylor **smart surfaces** (vicinals, planar or non-planar patterns...)
- Make use of **surfactants**

Master the science & **art** of building new crystals atom
by atom:
Epitaxy