Substrate preparation for selective area growth of III-V nanostructures

Ludovic Desplanque

Institute of Electronics, Microelectronics and Nanotechnology (IEMN),

CNRS and University of Lille, France

ludovic.desplanque@iemn.univ-lille1.fr

Epitaxy: A.Bucamp, M.Fahed, C.Coinon, J.-L. Codron, X.Wallart

Lithograhy: F.Vaurette, M.François, Y.Deblock

InAs MOSFET device fabrication: M.Pastorek, N.Wichmann, S.Bollaert

Electrical characterization: S.Lepilliet, E.Okada

TEM and FIB-STEM: G.Patriarche (C2N), P.Ruterana (CIMAP), A.Addad (UMET), D.Troadec (IEMN)



Outline

- Selective Area Growth: definition, motivation and method?
- Opportunities for Selective Area Growth (SAG) for III-V nanostructures
 - Optoelectronics
 - III-V MOSFET development
 - Quantum technologies
- Review of nano-SAG development (mainly MOCVD)
- Development of MBE-SAG for in-plane III-V nanostructures
 - Mask preparation
 - Surface deoxidation
 - Growth conditions
 - Atomic H assisted MBE
 - Examples of III-V nano-SAG using MBE
- Conclusion and prospects



Selective Area Growth (SAG) ?



- Selective area growth with respect to a passivation layer (where no deposition occurs)
- Need to open patterns in the passivation layer where the nucleation will happen
- Need to find the conditions for which growth occurs in the patterns whereas no material is deposited on the mask
- Preparation of patterns? Surface inside patterns? What kind of substrate (material, orientation) for what kind of applications?



Why SAG?

Nanodevice fabrication

- Quantum confinement (nanowires and nanowire arrays)
- Avoid dry etching
- Catalyst free growth
- Position controled nanostructures
- Ease device processing
- Core-shell and in-line heterojunctions



Ex: « 4D MOSFET » Gu et al, IEEE IEDM (2012)

Accommodate dissimilar materials

- Strain relaxation in nano-islands
- Integration of III-V on Silicon:
 - CMOS ??? (MOSFET, TFET)
 - RF ?
 - Opto ?



Ex: GaSb nano-island on GaP (>11% mismatch) free from TD S.El Kazzi et al, J. Appl. Phys. 111, 123506 (2012)



How to achieve SAG?

By Metal Organic Chemical Vapor Deposition (MOCVD) or Chemical Beam Epitaxy (CBE)

© Selectivity of Metal organic decomposition between oxyde mask and semiconductor surface

☺ High growth temperature needed for efficient decomposition and to avoid carbon incorporation

By Molecular Beam Epitaxy (MBE) ?

- © Lower temperature / dopant activation
- © Carbon incorporation
- ☺ Selectivity ??
- ☺ Directivity of the molecular beam (shadow effect)
- ☺ Temperature control



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III-V SAG for optoelectronics

 Co-integration of III-V based sources and detectors on CMOS platform



Richardson et al., MRS Bulletin 41, p193 (2016)

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• Single photon source emitters ?





Ex: Single InAs/InP QD grown by SAG

N. Gogneau et al., JCG 310 (2008) 3143

III-V SAG for microelectronics



Challenges for III-V CMOS:

J.Del Alamo, Nature 479, 318 (2011)

 Fundamental issues: Low DOS in low effective mass material => degradation of gate control efficiency Quantum confined nanostructures and high-k dielectrics are needed.

Technological issues: nanoscale fabrication and co-integration with pMOS (Ge?) on Si (001)
 low thermal budget, gate length < 20 nm, low resistance ohmic contacts, low parasitic capacitances



Architecture for efficient In(Ga)As MOSFET

Complexity



III-V SAG for quantum technologies ?



 Majorana fermions in 1D semiconductor with large spinorbit coupling (InSb, InAs) nanowire proximity coupled with a superconductor

H.Zhang et al, Nature 556, p. 74 (2018)



 Needs for branched ballistic nanostructures for complex quantum circuit architectures

Ex: Elaboration of InSb NW networks by VLS Nature 548 p434 (2017)

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Devices based on VLS growth + transfer on a host substrate: Interest of SAG for position controlled nanowires and nano-crosses and avoid gold assisted growth

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III-V integration on Silicon using SAG Vertical NW on Si (111): SAG or VLS ?

\succ GaAs on Si (111)



Noborisaka et al, Appl. Phys. Lett. 86, 213102 (2005)



➢ InAs on Si (111)



Threading dislocation filter using <u>aspect ratio trapping (ART)</u>

<u>Idea</u>: blocking the threading dislocations propagating in (111) planes by SiO_2 sidewalls



E. A. Fitzgerald et al, J. Electronic Materials 20, p. 839 (1991)

Micro-scale



Li et al, Appl. Phys. Lett. 91, 021114 (2007)

Nano-scale

Aspect Ratio Trapping using Shalow Trench Isolation process developed for CMOS technology



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- Process developed for 250 nm nodes and below
- Optical lithography (immersion)
- Trenches as narrow as 20 nm for a SiO₂ thickness of 250 nm can be achieved on 300 mm wafers
- Dense patterns can be obtained
- Silicon is etched between the trenches using vapor HCI

Aspect Ratio Trapping using Shalow Trench Isolation: Impact of Si surface preparation for InP deposition (IMEC)

or

- Si native oxide inside trenches removed using SiCoNi process: High temperature bake above 800°C in H₂ at 50 millibars
- « Rounded » Ge deposit before InP growth



Wang et al, Appl. Phys. Lett. 97, 121913 (2010)



Paladugu et al, Cryst. Growth Des. 12, p. 4696-4702 (2012)



Aspect Ratio Trapping using Shalow Trench Isolation: InGaAs in-plane nanowire MOSFET fabrication on Si (IMEC)

InP SAG + CMP + InGaAs SAG to avoid ternary InGaAs stoichiometry variation at inter-facets region when growth is initiated on (111) InP facets



Aspect Ratio Trapping using Shalow Trench Isolation: Other III-V materials

InAs on InP on Si



Doornbos et al, JEDS 4, p253 (2016)

InGaAs on GaAs on Si



GaSb on GaAs on Si



Li et al, Appl. Phys. Lett. 111, 172103 (2017)

Confined Epitaxial Lateral Overgrowth (CELO) developed by IBM





Template Assisted Epitaxy (TASE) developed by IBM

InGaAs in-plane NW on Si



Super-imposed GaAs in-plane NW on Si



Schmidt et al, Appl. Phys. Lett. 106, 233101 (2015)

Gate all-around InAs NW MOSFET on Si



20 nm

(b)

InAs -



High mobility GaSb on Si and cointegration with InAs



Borg et al, ACS Nano 2017, 11, 2554-2560

Template Assisted Epitaxy (TASE) developed by IBM

InAs/Si and GaSb/InAs in-plane heterojunctions for TFET fabrication



Cutaia et al, VLSI (2016)



TiN

TEOS

Template Assisted Epitaxy (TASE) of vertical NW

InAs/Si vertical heterojunctions (IBM - MOCVD)



InSb/InAs/Si vertical NW (IBM - MOCVD)



Kanungo et al, Nanotechnology 24 (2013) 225304

InAs/Si vertical NW (EPFL – MBE VLS)



Substrats Si (111)

Before introduction into the MBE growth chamber, samples were dipped for 2 s in poly-silicon etch solution [HNO3(70%):HF(49%):H2O]

Vukajlovic-Plestina et al, Nanotechnology 27 (2016) 455601

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VLS SAG (one Indroplet/nanotube)

VLS (several Indroplet/nanotube)



Impact of growth mode on yield

What about optoelectronic applications?



Kunert et al, APL 109, 091101 (2016)

SAG for III-V planar MOSFET with ultra-short gate



SAG for III-V MOSFET with ultra-short gate

Process using HSQ dummy gate



 $HSQ = hydrogen silesquioxane = inorganic compounds (H_8Si_8O_{12})$ Can be deposited by spin-coating and cross-linked with e-beam or EUV radiation Pattern width down to 10 nm achievable

Fabrication of InGaAs MOSFET on InP with 30 nm gate length (UCSB)



Double step MOCVD regrowth => optimization of the gate stack to achieve f_t =420 GHz



Wu et al, EDL IEEE EDL 39, p. 472 (2018)

SAG for III-V MOSFET with ultra-short gate

Process using HSQ dummy gate

Fabrication of single suspended InGaAs NW MOSFET on InP (Lund University)





Zota et al, IEDM 2016



SAG for ballistic nano-devices

Observation of quantum conductance plateaus in InGaAs nanowire grown using HSQ process





Zota et al, ACS Nano 9, p. 9892 (2015)

Observation of quantum conductance plateaus in InAs NW and cross-junction using TASE



Gooth et al, Nano Lett. 2017, 17, 2596–2602 Gooth et al, Appl. Phys. Lett. 110, 083105 (2017)



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What about SAG with MBE?

- Low thermal budget compared to MOCVD (lower growth temperature)
- Higher active doping density at low temperature
- Possibility of in-situ supraconductor deposition (ex: Al)

Challenges:

- Surface cleaning and deoxidation before regrowth
- Find growth conditions for selectivity: temperature, growth rate, V/III ratio



Our mask preparation for SA-MBE

Process for large area mask with small aperture



Process for large area mask with small aperture

Plasma Enhanced Chemical Vapor deposition Oxford Plasmalab 80+ chamber

- Sample heated at 300 °C under vacuum
- N₂ purge
- RF Plasma with SiH_4 and N_2O
- Ex-situ thickness control

30 nm SiO₂ Epitaxial layer (if needed)

(001) substrate



Process for large area mask with small aperture

E-beam lithography EBPG 5000plus (100kV)

- Spin coating PMMA (thickness 100 nm)
- E-beam exposure
- Development with MIBK/IPA
- Pattern width down to 50 nm achieved







Process for large area mask with small aperture

Reactive Ion Etching Oxford Plasmalab 80+ chamber

- Short O₂ plasma etching to remove PMMA residues in openings

- CHF3/CF4/Ar plasma etching
- Etching depth \approx 15-20 nm (SiO₂ not fully opened)





Process for large area mask with small aperture

SiO₂ opening before growth

- Dilute HydroFluoric acid
 Be careful if the top surface is GaSb (etched by HF!)
- Final thickness of the mask \approx 10 nm

SiO₂ Epitaxial layer (if needed) (001) substrate

Sample is then introduced rapidly in MBE outgasing chamber for 200° C annealing before growth



Process for small area mask (HSQ process)



Process for small area mask (HSQ process)

E-beam cross-linking + Development

- E-beam exposure (100 kV)
- Development:
- 300° C annealing for densification

HSQ Epitaxial layer (if needed)

(001) substrate



Width of 25 nm for a height of 200 nm can be achieved on InP substrate



M.Pastorek, PhD thesis (IEMN, 2017)

IEMN MBE systems

Riber Compact 21 TM

Riber 32P



As valved cracker (Riber VAC 500) Sb valved cracker (Veeco RB 200) Ga, In, Al Si, Te

CBr₄ gas injector for C doping RF plasma cell for atomic H flux



AsH₃ and PH₃ gas injector Sb valved cracker (Veeco RB 200) Ga, In, Al Si, Be CBr₄ gas injector for C doping

UHV connected systems + connection with ESCA for surface analysis

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How minimizing surface roughness and carbon contamination whithout any buffer ?

GaAs surface deoxidization before regrowth

Comparison of 3 different preparations:

- « Classical » thermal deoxydization under As₄ flux up to 620° C
- Deoxydization under As₄ + H atomic flux up to 450° C
- Deoxydization under Sb₂ flux + H atomic flux up to 450° C

RF power = 400 W $H_2 = 3 \text{ sccm}$



Surface preparation for SA-MBE GaAs surface analysis

GaAs surface deoxidization before regrowth: surface analysis with XPS



Deoxidization complete on the 3 samples, no carbon detectable



GaAs surface analysis

GaAs surface deoxidization before regrowth: roughness analysis



Reduced roughness for sampes deoxidized at 450° C under H atomic flux



InP surface preparation

Different InP surface preparation before InGaAs/InP QW epitaxy:

InP buffer (70 nm) In_{0,53}Ga_{0,47}As (30 nm) InP buffer (300 nm)

InP SI substrate

Reference (deoxidized under P2 flux @ 520°C)

InP buffer (70 nm)

In_{0,53}Ga_{0,47}As (30 nm)

No buffer

InP SI substrate

(deoxidized under As₄ flux @ 520° C)

InP buffer (70 nm)

In_{0,53}Ga_{0,47}As (30 nm)

No buffer

InP SI substrate

(deoxidized under P2 flux @ 520° C)

InP buffer (70 nm)

In_{0.53}Ga_{0.47}As (30 nm)

No buffer

InP SI substrate

(deoxidized under As₄ flux + atomic H @ 480° C)



InP surface preparation

300K Photoluminescence of InGaAs/InP QW



2 to 3 order of magnitude lower PL intensity than reference sample for buffer free epitaxy... ...except for the one with atomic H flux during deoxidation (same order of magnitude)

Probably reduced carbon incorporation in InGaAs QW using atomic H flux

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Growth conditions for SA-MBE Homoepitaxy



GaAs homoepitaxy

GaAs nanopillars on (111) GaAs substrate



Yoshiba et al, JCG301–302 (2007) 190

In-plane GaAs nanowires on (001) GaAs



Growth temperature = 595° C (**580°** C< T_G< **620°** C) Growth rate= 0,1 ML.s⁻¹



Growth conditions for SA-MBE InP homoepitaxy



⇒ Possibility to control the shape of the nanostructure playing with V/III ratio

M.Fahed et al, Nanotechnology 26 (2015) 295301



InAs homoepitaxy







L.Desplanque et al, Nanotechnology 25,46 (2014) 465302

.

On (001) substrate, strong impact of stripe orientation on faceting!

How to reach selectivity for InGaAs?



M.A. Wistey et al, JVST B 33 p011208 (2015)

Atomic H assisted MBE ?

Selective growth of InGaAs/InP layers by GS-MBE using H atomic irradiation



Kuroda et al, IEEE IPRM (1993)



Atomic hydrogen-assisted MBE growth

Selective area growth of GaAs by ECR-MBE





Fig. 3. Schematic diagram to explain the mechanism in the selective area growth by ECR-MBE: (a) migration process and (b) desorption process. The open and closed circles show the impinging atoms to the unmasked GaAs surface and those to the Si₃N₄ mask surface, respectively.

Yamamoto et al, JCG 93 p705 (1989)



Atomic H flux during the growth reduces Ga nucleation on the SiO_2 mask: same mechanism than for GaO_x removal?

⇒ the growth selectivity can be obtained at lower temperature



Atomic H-assisted MBE growth of InGaAs

With no atomic H during growth

With atomic H during growth



low growth rate (0.2 ML.s⁻¹) + H atomic hydrogen ⇒ InGaAs MBE selective growth down to 490° C



Atomic H-assisted MBE growth of InGaAs

Impact of atomic H on InGaAs properties ?



WD = 4.1 mm Stage at T = 0.0° EHT = 7.00 kV Mag = 15.74 K X Signal A = InLen

WD = 12.8 mm Stage at T = 30.0 -

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100 nm

200 nm

EHT = 7.00 kV Mag = 21.06 K X **Growth conditions for SA-MBE** Lattice mismatched materials



Growth conditions for SA-MBE InAs on InP

150 nm InAs:Si (10¹⁹ cm⁻³) on QW layer **@ 450° C** under atomic Hydrogen, V_{growth}=0.2 ML.s-1, As/In=5 Strain induced InAs 3D growth mode









- ⇒ Pinholes are still visible on large area
- ⇒ No pinholes in µm scaled area
- Small angle facets result in edge roughness
- ➡ Reduced roughness in confined area (formation of larger angle facets)





Raised InGaAs:n+ Source and Drain for QW MOSFET



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CNR5 0520

Growth conditions for SA-MBE InAs:n+ raised source-drain contacts for QW MOSFET on InP



⇒ Improvement of the access resistances using InAs rather than InGaAs (reduced R metal/SC)



M.Pastorek, PhD Thesis IEMN (2017)

Growth conditions for SA-MBE GaSb on GaAs



Growth conditions:

- Thermal annealing to 620° C under As₄ for GaAs deoxidation
- Deposition of 25 nm (nominal thickness) of GaAs @ 590° C to smooth the surface after deoxidation
- Deposition of 20 nm (nominal thickness) of GaSb with low growth rate and various Tg
- No H atomic flux during growth



Need to get selectivity at low temperature to fill the aperture !
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Growth conditions for SA-MBE GaSb on GaAs

65 nm GaSb inside 100 nm wide apertures; T_g =470° C; Sb/Ga=10; V_{Ga} =0,1 ML.s⁻¹





Seletive growth of GaSb on GaAs using atomic H assisted MBE

M.Fahed et al, Nanotechnology 27, 505301 (2016)

Without atomic hydrogen

With atomic hydrogen

> Atomic hydrogen flux improves the selectivity of GaSb growth w.r.t. SiO_2 mask

10 nm InAs on 150 nm GaSb inside 100 nm wide apertures; **T**_a=470° **C**; Sb/Ga=2; V_{Ga}=0,1 ML.s⁻¹



TEM analysis from G.Patriarche (C2N)



M.Fahed et al, Journal of Crystal Growth (2016)

> TD free relaxed GaSb nanotemplates can be obtained on GaAs (with a few stalking faults)



InAs on GaSb nanotemplates on GaAs



High quality InAs nanowires can be formed on top of the GaSb nanotemplates



InAs NW can be realeased after GaSb selective under-etching (ammonia based solution)



Selective area growth for in-plane nanowire fabrication InAs NW on GaSb/InP nanotemplates



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- ⇒ 100 or 200 nm wide / 12 µm long stripes opened in SiO₂ on InP
- \Rightarrow Deoxidization under As₄ + atomic H fluxes

$$\Rightarrow$$
 15 nm InAs (V_{growth}=0.2 ML.s⁻¹).

After GaSb selective chemical etching + supercritical drying

⇒ InAs NWs can be released

Selective area growth for in-plane nanowire fabrication InAs NWs with raised Source and Drain contact on InP



1. Selective growth of InAs (15 nm) / GaSb(150 nm) on InP



2. HSQ dummy gate and pillars maintaining InAs NWs after development



3. Second regrowth of 150 InAs:Si



4. HSQ removal



5. Metal contacts deposition

M.Pastorek, PhD Thesis IEMN (2017)



Selective area growth for in-plane nanowire fabrication InAs NWs with raised Source and Drain contact on InP

HAADF and EDX analysis in the access area (Collab. A. Addad, UMET)





M.Pastorek, PhD Thesis IEMN (2017)

Selective area growth for in-plane nanowire FET InAs NWs with raised Source and Drain contact on InP







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Desplanque et al, Nanotechnology 29 (2018) 305705

Selective area growth of InSb on GaAs Using AlGaSb buffer



Growth inside 100 nm wide 2,6 µm long apertures





Growth inside 50 nm wide 5 µm long apertures



Growth inside 100 nm wide 2,6 µm long cross

Desplanque et al, Nanotechnology 29 (2018) 305705

Selective area growth of InSb on GaAs Using AlGaSb buffer



 \rightarrow P has been removed in the aperture during deoxidization under Sb₂ flux + H



- → Mismatch is accomodated at the regrown interface by misfit dislocations without any TD in the InSb nanostructure
- → Regrown interface more rough than for GaSb/GaAs (effect of P replacement?)

EDX and GPA from G.Patriarche (C2N)

Desplanque et al, Nanotechnology 29 (2018) 305705

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Conclusion

- NanoSAG can address several technological issues
- MOCVD combined to advanced mask preparation using Si technology is the « natural » way but...
- SAG with MBE works also...
- Increasing interest for Selective area grown in-plane nanostructures for quantum technologies...



MBE SAG for quantum devices

MBE SAG of in-plane InAs NW (EPFL)

20 mV
 15 mV

• 10 mV

-4 -2 -6

ż

4

0

B (T)

6 8

• 5 mV • 0 mV

0.6

0.5

10 12



300K, No InAs

80 -• 4K • 300K

20

emn

0+0

2 4 6 8

Contact Spacing (µm)

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ĝ 60 to Add

- \rightarrow MBE SAG on GaAs (111)_B substrate masked with SiO₂
- \rightarrow InAs NW grown GaAs on top of nanomembranes thanks to In migration on side-wall
- \rightarrow Transport measurements (TLM) reaveal quasi-1D electronic transport

Friedl et al, Nano Lett. 2018, 18, 2666-2671

SAG for quantum devices

SAG-based topological networks (Niels Bohr Institute, QuTech Delft and StationQ)

SAG of InAs NW networks using MBE



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ID topological superconductors with proximity coupled InAs/AI



*B*_⊥ (mT)

Vaitiekenas et al, arXiv:1802.04210v2 (2018)

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