





Heterogeneous integration and applications in electronics





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What kind of functionnalities can be addresses by nanomaterials and nanostructures grown on a substrate ?

How to integrate nanomaterials in devices with an added value ?





□ Nanocrystals for memory devices

□ Nanowires for low power devices, capacitors and sensors

Thin films : SiGe (D. Dutartre) and III-V (B. Kunert) on a Si platform for NMOS and PMOS FET



OUTLINE

Nanocrystals for memory devices

- Principle
- Nanocrystal growth
- Integration in devices

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□ SiGe and InGaAs thin films for NMOS and PMOS FET



□ Flash memory = MOSFET + floating gate

□ Electron storage in floating gate → shift Id-Vg characteristic



Two different states due to the presence of charges in the floating gate



Standard Flash memories :

Limitation of reducing the thicknesses of dielectric [1] :

- ✓ tunnel oxide t > 6nm (SILC)
- Control oxide EOT > 10nm

Spacing reduction between memory cells :
Parasitic coupling between floating gate [2]
Decrease of the capacitive coupling between the floating gate and the channel (lateral extension of the gate)





[1] S. Lai et al., Int. non volatile memory conf. 1998 [2] K. Kim, IEEE Proc. Of IEDM 2005



Decrease of the tunnel oxide without compromise with charge retention :



- Decrease of the parasitic capacitive coupling between cells [1]
- Multilevels storage
- Decrease of the fabrication cost by decreasing the number of lithographic masks needed
- □ NC advantages : more robust devices against defects



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Choice of CVD for nanocrystal growth

Uniform distribution over large areas

Uniform thickness and composition over large areas

Selective area deposition because of different activation energies for reaction with different surfaces

Objectives : high nc density and low size dispersion
For high charge storage and low device variability











Si deposition by CVD on amorphous substrates

Silane dissociation reactions :

$$\begin{array}{l} \operatorname{SiH}_4(\operatorname{g}) \to \operatorname{SiH}_4(\operatorname{ad}) \\ \operatorname{SiH}_4(\operatorname{ad}) \to \operatorname{SiH}_2(\operatorname{ad}) + \operatorname{H}_2(\operatorname{ad}) \\ \operatorname{SiH}_2(\operatorname{ad}) \to \operatorname{Si} + \operatorname{H}_2(\operatorname{ad}) \\ \operatorname{H}_2(\operatorname{ad}) \to \operatorname{H}_2(\operatorname{g}) \end{array} \end{array}$$

 \Box V_{dépôt} = C P^a exp(-E_a/kT)

Si nanocrystals nucleation study on amorphous substrate:

- Experimental parameters (T, P_{SiH4})
- > Chemical nature of the substrate (SiO₂, Si₃N₄, Al₂O₃)



Si deposition by CVD on SiO₂

Volmer Weber 3D growth mode











T = 30s



120s



P_{SiH4} and growth temperature constants

- 1. Nucleation
- 2. Growth
- **3.** Coalescence
- 4. Formation of continuous Si film

F. Mazen, PhD Thesis 2003



- □ Low effect of temperature on Si nucleation (range 570-620°C)
- P_{SiH4} promotes Si nucleation



² 3x10¹¹ Si-Ncs/cm²

9.5x10¹¹ Si-Ncs/cm²

10¹² Si-Ncs/cm²

□ Thermal SiO₂ is not favourable for a high Si-Ncs density (strong Si-O bonds)

□ On deposited Si₃N₄, strong nucleation (rugosity, defects...)

□ On Al₂O₃ deposited by Atomic Layer Deposition, OH groups favour Si nucleation





H

0

Si

Ħ

Si

Η

Si





Influence of OH groups on SiO₂ substrate





HF treatment Density : 10¹² Si-Ncs/cm² As grown SiO₂ Density : 7 10¹⁰ Si-Ncs/cm²

□ Si-OH groups govern the Si nucleation on SiO₂

JECS 150, G203 (2003)



Structural characterization by TEM



nc-Si are crystalline









Step 1 influence

60 mTorr SiH₄



 $5 \times 10^9 \text{ nc-Si/cm}^2$

200 mTorr SiH_4



 $3 \times 10^{11} nc$ -Si/cm²

200 mTorr SiH₄ With HF treatment



 $7 \times 10^{11} nc$ -Si/cm²

Step 1, exposition of the surface to SiH_4 for a short time, control the nanocrystal density



Step 2 influence



Step 2, exposition of the Si nuclei to SiH_2CI_2 control the growth rate and hence the size of the nc (0.001 à 13 nm/minute)



Size dispersion

1 step SiH₄

Density: 2.8 10¹¹/cm² Diameter : 9 nm



30 nm







Possibility to elaborate Ge nanocrystals

GeH₄ : almost no Ge nucleation on SiO₂



Density : $2x10^{11}$ Diameter : 12 nm

Density : $6x10^{11}$ Diameter : 7 nm



Structural characterization of nc-Ge

XRD



Nc-Ge cristallins with GeO_x shell





Si-nc double layers – Basics

Objective: deposition of 2 layers of Si-ncs to improve the nc-Si density











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Passivation of Si-nc by nitridation

- □ Nitridation effects
 - > $Si_3N_4 O_2$ diffusion¹ is imited
 - \succ NO et NH₃



¹ M.L. Green *et al.*, APL 67(11), p 1600, (1995) ² K. C. Scheer *et al.*, APL 93 (9), p 5637, (2003) Thèse J. Dufourcq P. Mur, O. Renault, CEA-Leti S. Bodnar, ATMEL,



Selective deposition of SiN on Si-nc



Si-ncs capped with SiN shell : hybrid Si-nc SiN trapping layer G. Molas et al., IEDM 2007



XPS simple description





XPS analysis of nitrided NC-Si

□ XPS VUV ELETTRA Synchrotron :

- > Energy resolution (0.05 eV/0.5 eV for laboratory equipment)
- Energy screening (depth profil)





Si (2p) e-, hv = 160 eV



* O. Renault et al., APL 87, 163119 (2005)



TEM analysis of nitrided Si-nc

Density : 8x10¹¹ cm⁻²,

EFTEM 50 nm



Reference,

nitridation at 750°C

Conclusion :

- > Si nanocrystals density reduction
- > N located preferentially at the surface
- J. Dufourcq, PhD thesis 2008

4x10¹¹ cm⁻² S. Lombardo et al., IMM



<u>10 nm</u>

Cross section TEM









*Thèse de doctorat Stéphanie Jacob, 2008



Industrial ncs-Si memories

Freescale

Split gate structure

STMicroelectronics

Architecture NOR 4Mb



Kang et al., VLSI 2008, IMW 2009, IMW 2012

<u>Commercial products:</u> Embedded memories for microcontrolers in 90nm technology



Gerardi et al., IEDM2008


□ W advantages :

- ✓ refractory material (T_{fusion} = 3410°C)
- ✓ Stable with SiO₂
- □ Precursors : WF_{6 (g)} et SiH_{4 (g)}





MEB, tilt 40°



TEM

Density : 7.10¹¹ cm⁻² Diameter moyen : 6 nm



Memory devices integrating metallic nanocrystals:

Floating gate = TiN NCs + DCS passivation + SiN encapsulation



G. Gay, PhD, 2011



Functional devices

Gain in writing speed, and memory windows







Conclusions

- CVD allows to grow directly Si, Ge and metallic nanodots
- Control of density and size dispersion possible if nucleation and growth decoupled
- Selective growth possible
- Core / shell nanostructured and passivation possible
- Large scale integration of nanolayers and nanostructures unable by CVD
- Semiconductors, metals, oxydes nanodots





VLS growth and applications of Si/Si_{1-x}Ge_x nanowires



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- > Objective
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- Other applications

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Introduction : CVD – VLS nanowires growth

Ellis et Wagner, 1964



[Oehler10]

- Crystalline growth possible without any epitaxy relation
- Nanometric diameter without lithographic steps
- Low temperature synthesis < 450°C compatible with back-end process</p>
- ➢ High aspect ratio
- High surface/Volume ratio





Source

Gate

Transistors

b

SiO₂

Si <111> Drain

[Schmidt06]



[Garnett09]

Sensors



Solar cells



[Cui01]





High density capacitors in Back End ?

Use the high surface area available from an assembly of NWs

$$C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot S}{e}$$

 \Rightarrow Challenge



Vertical NWFET

- Gate all around
 - Improve electrostatic control
- Compact
- Integration in interconnection lines





Reconfigurable interconnection







• CMOS subthreshold swing (SS): limitation

 $\frac{k_BT}{q}\ln(10)\sim 60 \text{mV/dec at } 300 \text{K}$

 Scaling down of supply voltage increases the leakage current of MOSFETs (I_{OFF})



Increased power consumption

Interest of steep slope devices. It allows

 Low threshold voltage
 Low I_{OFF}



Potential candidate: Gate all around vertical Tunnel FET



- TFET is a reverse biased p-i-n gated diode
- The gate voltage V_G modifies channel E_C and E_V enabling tunneling at source/channel junction





TFET heterostructures in NWs

Prerequisites for TFET material

- Low Eg (source) and wide Eg (drain)
- Abrupt source-channel junctions
- High source doping

Proposed TFET structures





How to grow Si-SiGe NWs

A. TOP DOWN METHOD

Deposition of Si-SiGe multilayers+Etching

?? Strain relaxation, roughness, defects

- **B. BOTTOM UP METHOD**
- Vapor Liquid Solid mechanism (CVD, MBE, Solid phase synthesis..)



CVD-VLS mechanism allows

- strain relaxation
- low defects

CVD Equipment



RP-CVD reactor



SiNaPs/CEA/INAC/LTM

- Gas sources : SiH₄, GeH₄, HCl, H₂, PH₃ (n type), B₂H₆ (p type)
- **Temperature** : up to 1100° C
- **Pressure** : from 1 to 10 torr

HAADF-STEM image





P. Periwal, PhD 2014

Effect of temperature on NW morphology



- T_G for Si= 600°C
- T_G for SiGe=450°C

Growth of Si and SiGe at two different temperatures are not favourable





Growth of both segments at 450°C produces high density of NWs

Effect of growth stop on NW morphology





- Growth stop stabilizes
 Growth stop stabilizes
 Sige
 Growth stop stabilizes
 Sige
- It should be for optime.
- Destabilization in the droplet induces kinks or twin boundary.

E=+++=**E**=++=**E** 540 560 580 600 620 640 Distance (nm)



P. Periwal et al JVST A 32 (3) 031101 (2014)

Effect of NW diameter on Si/SiGe and SiGe/Si interface





- Si_{0.7}Ge_{0.3}/Si interface: linear relation
- Si/Si_{0.7}Ge_{0.3} interface abruptness does not exceed 30 nm.



P. Periwal et al NanoLetters 14, 5140 (2014)

Effect of Ge composition in Si_{1-x}Ge_x part (0.3<x<0.8)

In collaboration with Gilles Patriarche, LPN-Paris

$Si_{0.4}Ge_{0.6}$ -Si-Si_{0.4}Ge_{0.6} for D=50-60 nm



Asymmetric heterointerfaces: $Si_{1-x}Ge_x/Si$ is always broader than $Si/Si_{1-x}Ge_x$



P. Periwal et al NanoLetters 14, 5140 (2014)

Modeling & Experimental results



- Experimental data fits well with the Model
- High Ge & small dia = sharp Si/SiGe interface



P. Periwal et al NanoLetters 14, 5140 (2014)

Two step growth process: B doped Si_{0.7}Ge_{0.3} NWs

SiH₄+ GeH₄ + B2H6

11111

SiH₄ + GeH₄

Two step process:

- Continuous flow of SiH₄, GeH₄ and HCl but no exposure of diborane for few minutes.





Passivation effect by PH₃ in Ge NWs: Modeling



Mechanism~MBE occurs.



Perspectives: Integration of heterostructure NW in TFET

DE LA MICROÉLECTRONIQUE









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Sensors

□ SiGe and InGaAs thin films for NMOS and PMOS FET





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DC/DC convertor



- Decoupling capacitor is a <u>capacitor</u> used to <u>decouple</u> one part of an <u>electrical network</u> (circuit) from another. Noise caused by other circuit elements is shunted through the capacitor, reducing the effect it has on the rest of the circuit.
 - \checkmark high capacitance value (1 nF 1 $\mu F)$
 - ✓ Low leakage current
 - ✓ High breakdown voltage (> 10 V)
 - ✓ Low series resistance





Technologies for high density capacitors

Back-End





T. Ernst et al., CEA-Leti



Process integration

Materials choice

- Dielectric : ALD alumina
 - \checkmark Conformal deposition
 - ✓ high-κ, $ε_r = 9$
 - ✓ High breakdown voltage : 7-10 MV / cm
 - ✓ Large band gap : 8,7 eV
- Electrodes : CVD TiN
 - \checkmark Conformal deposition
 - ✓ Thermodynamically inert with alumina
 - ✓ High workfunction : 4,8 eV
 - × <u>High resistivity</u> > 200 μΩ.cm
 - rightarrow put AlSi for top electrode (2,7 μΩ.cm)

Requirements

- High capacitance density
- Low serie resistance





Morphological characterization

- TiN, 20 nm conformal
- Al₂O₃, 20 nm conformal





SEM cross section

MOS capacitors



High capacitance density

- 10 nm alumina
- SI NWs surface cleaning and passivation before ALD deposition
- ➢ leakage for NWs capacitors
 ➢ NWs : 49 µA/cm² à -1V
 ➢ Reference : 6,3 nA/cm²
- Lower breakdown voltage











C(V) @ 20 Hz with 15 nm d'alumine

- ➢ Gain in capacitance : 16
- decrease of the capacitance from 20 Hz
 - \rightarrow High serie resistance
 - \rightarrow Technological parameters to

control



References	[Black04] Gravure	[Choi10] Nanotubes	[Banerjee09] Alum. nanop	Al ₂ O ₃ 15 nm
Density of Capacitance (µF/cm²) F	3,13	0,62	10	9,6
Density of leakage current de fuite à 1V (nA/cm²) A	2 500	5 000	5	11
(F/A)	1,25	0,124	2000	873

Industrial requirements for DC/DC converter and decoupling capacitors



	I / C @ 3,6 V	Breakdown V
Specifications Ipdia	< 7 x 10 ⁻¹² A / nF	> 10 V
NW cap 15 nm Al_2O_3	3,5 x 10 ⁻¹¹ A / nF	9 V



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Silicon nanonets, Sensors



P. Serre, PhD 2014

UNIVERSITÉ DE GRENOBLE





Nanonet = NANOstructured NETwork Network of 1D (NFs or NTs) randomly oriented

Nanonets






Introduction : Si 2D nanonets

Characteristics

- High aspect ratio
- High specific area
- Electrical conductor
- Optical transparency
- Mechanical flexibility
- Functionnalisation possible
- Versatile
- Reproductible

Applications

- Conductive, transparent, flexible electrodes,
 - → Solar cells
 - → OLED
 - → touch screen
- Photodetection
- Chemical and biological sensors

Si Nanonets for detection





Nanonets fabrication by filtration method

NWs elaboration



C. Ternon et al., LTM-LMGP



Nanonet morphology



Randomly oriented Well interconnected Percolation path Uniform Large scale Good adherence with substrate





Precise control of NWs density



ADN hybridation detection by fluorescence







P. Serre et al,



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1 V

Need of SiGe alloys for future devices and III-V exploration on a Si platform

Ge, SiGe or III-V



SiGe

SiGe



Epitaxy = mono-crystalline layer grown on a mono-crystalline substrate; homo-epitaxy : layer A (Si) on substrate A (Si); hetero-epitaxy : layer B (SiGe) on substrate A (Si) a (Si_{1-x}Ge_x) = $5.43105 + 0.20050x + 0.0263x^2 \text{ Å} > a(Si) = 5.43105 \text{ Å} =>$ Strain accumulation inside the SiGe layer when grown on Si. 2 scenarii :



Courtesy of JM Hartmann, CEA-Leti

DE L



Si channels

Tunable Width

Courtesy of JM Hartmann, CEA-Leti

- 1 Growth of SiGe/Si superlattices on SOI
- 2 Anisotropic etching of those SL
- **3 selective plasma etching of SiGe**
- 4 gate stack formation
- 5 gate etch

Superior I_{on}/I_{off} trade-offs in MBCFETs : nMOS : 2.27 mA/µm ⇔ 16 pA/µm pMOS : 1.32 mA/µm ⇔ 16 pA/µm

Sol. State Electron. 52 (2008) 519; VLSI Tech. 2008 (16); IEDM 2008 (749)

NW ENGINEERING THANKS TO EPITAXY



(b) SiGe NW (a) SiGe NWs Ge NW C Long L_{NW} SiN HM (001)~600nm 500nm (d)_{1nm} SiGe NWs SiGe NWs Short L_{NW} ~250nm 500nm Unstrained (e) SiGe NWs Long L_{NW} Long L_{NW} ~600nm 500nm 50nm ~600nm 10nm

70 nm Si:B (2x10¹⁹ cm⁻³) Courtesy of JM Hartmann, CEA-Leti SEG Courtesy of JM Hartmann, CEA-Leti IMOSIC PUCES Tr6 IMOSIC PUCES Tr6 x70. 0k' 29'n'm XZ0.0K 429nm

H₂ bake of squarebased Si NWs rounding. Combined self-limiting with oxydation => very small diameter NWs.

H₂ bake of squarebased SiGe NWs : hexagonal section. SEG of thin Si cap improve hole to mobility.

Selective thickening of the access regions of Si NWs

APL 91, 233502 (2007); ECS Trans. 13 (1), 195 (2008) & 27 (7) 471 (2009)





Room temperature properties	Si	Ge	GaAs	InAs	InP	InSb
Electron mobility (cm ² V ⁻¹ s ⁻¹)	1 400	3 900	8 500	40 000	5 400	77 000
Hole mobility (cm ² V ⁻¹ s ⁻¹)	450	1 900	400	500	200	850
Bandgap (eV)	1.12	0.66	1.42	0.35	1.34	0.17
Lattice parameter (Å) Diamond or blende- zinc structure	5.431	5.658	5.653	6.058	5.869	6.749

 \Rightarrow Conduction channel (nMOS) : InGaAs ([In] : 30-70%) on GaAs / Ge / Si when thinking of a monolithic integration on Si



Challenges : Growth of InGaAs channel on Si(100)

Lattice mismatch (Si-GaAs 4%, Si-InAs 10%)

Polarity induces antiphase domains

Thermal expansion coefficient limits the total thickness before cracks appearing



Antiphase domains



Figure 3: Schematic diagram of the formation of anti-phase disorder due to III-V heteroepitaxy on a Si(100) substrate. Single-layer steps of the Si(100) surface induce anti-phase boundaries (APBs) which penetrate through the film and can be subject to self-annihilation, while double-layer steps on the substrate prevent the formation of APBs during nucleation.

DOESCHER PhD,



(002) Dark field TEM image in [110] cross section of the GaP/Si heterolayer. Self-annihilation of all antiphase domains leads to antiphase disorder free GaP layer after about 50 nm of overgrowth B. Kunert et al. / Thin Solid Films 517 (2008) 140–143



Optimization of GaAs buffer on nominal Si(100)

Growth of InP on GaAs/Si(100)

Development of InGaAs growth on InP(100) substrates



GaAs RMS roughness : 1,4 nm APB density = 1,83 μ m⁻¹ Optimized GaAs RMS roughness : 0,9 nm Optimized GaAs RMS roughness : 0,8 nm





Evaluation of dislocation density, 10⁹ cm⁻²





¹ μm Signal A = InLens EHT = 5.00 kV 18 Mar 2015 8:54:31 Mag = 15.23 K X WD = 3.1 mm Uitra Plus



STEM/TEM characterisation









GaAs/AIAs/GaAs QW/AIAs/GaAs/InGaAs QW/GaAs/AIAs/GaAs/Si(100)



□ High dislocation density (10⁹ cm⁻²), to be improved



Aspect Ratio Trapping : selective epitaxial growth

GaAs selective epitaxial growth in SiO₂ patterns (STEM cross sectional views)





Annihilation of anti-phase boundaries, emerging dislocations, stacking fault



Optical measurements

 $\hfill\square$ μPL at room temperature



R. Cipro et al., Appl. Phys. Lett. 104, 262103 (2014)
Cathodolum. mapping at low temperature (top view)



- □ Room temperature µPL signal with FWHM of 60 meV is seen on pattern with dimension <200 nm
- Non radiative recombination centers degrade the luminescence



InGaAs MOSFET on 300 mm wafers







M.L. Huang et al., TSMC, VLSI Symposium 2015



Fig. 8 The (a) SS and (b) I_{on}/I_{off} ratio map across 300mm wafer, respectively. The good uniformity with low SS(AVE) of 93 mV/dec and high I_{on}/I_{off} (AVE) ratio of 1.2×10^5 .



InAs/InGaSb/OI NMOS and PMOSFET



Fig. 10 Fabrication process flow of the front-gate InAs/InGaSb-OI CMOS on Si with single-layer InGaSb, InAs/InGaSb/InAs QW, and InAs/InGaSb hetero-channel.



Fig. 15 Band diagram of the (a) QW and (b) Fi hetero channel InGaSb-OI under $V_{FG} < 0$ and V_{BG} In = 0V. as



K. Nishi, et al. University of Tokyo, VLSI Symposium 2015



InGaAs-OI FinFET by selective + lateral epitaxy



a



direction SIN. -n+ Concern-In. -GaAs CELO InGaAs <111> Si seed W (b) ILD HK and W gate SiN, cap In_{n 7}GaAs CELO SiO₂ BOX SiO. In_{o 7}GaAs fins Si substrate (c) Si

Al_O_/HfO_



Fig. 9: Cross-sectional TEM images of a self-aligned InGaAs-OI FinFET Fig. 10: Transfer an InGaAs FinFET integrated on Si by CELO. Views are (a,c) across the gate and (b) across the 25nm x 35nm fins. Standard gate-first process [8] with raised source/drain could Ion/IoFF ratio above 10⁴ decades be applied seamlessly thanks to the excellent InGaAs thermal stability.

without RSD showing an excellent suggesting a low background doping.

L. Czornomaz, et al. IBM Zurich, VLSI Symposium 2015



CNRS-LTM staff

- M. Martin, J. Moeyart, F. Bassani, B. Salem, S. David, C. Ternon...
- CEA -Leti, T. Ernst, H. Boutry, P. Mur, F. Martin, JM. Hartmann ...
- CNRS, UJF, Renatech, PTA, ANR, European founding,

PhD works :

- > NCS : F. Mazen, J. Dufourcq, G. Gay
- NWS / F. Dhalluin, A. Potié, G. Rosaz, P. Periwal, PH Morel, F. Oelher, P. Serre
- > III-V/Si : R. Cipro, R. Alcotte, V. Gorbenko, M. Billaud,