ANR O GaNex

Nanowires of III-nitride compounds

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10 nm







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Introduction

- GaN nanowire growth mechanisms
- Critical dimensions of nanowire heterostructures
- Nanowire characterization
- Nanowire applications

Scientific activity on semiconductor nanowires



Source : Web of Sciences

TS=((nanowire* OR nanowhisker* OR nanorod* OR nanocolumn* OR nanotube*) AND (semiconductor OR III-V OR II-VI OR Si OR Ge OR GaN OR GaP OR GaAs OR GaSb OR InN OR InAs OR InP OR InSb OR CdSe OR CdS OR ZnS OR ZnSe OR ZnO)) NOT TS=(carbon AND nanotube*)

Part of these publications related to III-nitrides nanowires

10 %

Contributions per country for III-N NWs



Where does the enthusiasm for NWs come from?

- > A general interest for nanosciences which really started in the 90's
- ID character (after quantum wells and quantum dots)
- Possibility to elaborate NWs on various substrates and by various methods (both chemists and physicists got involved in their elaboration)
- Flexibility to form original heterostructures (radial, axial, combination of both)
- Easy manipulation
 (possibility to isolate , address and study a single nano-object, fabrication of nanodevices)
- Collective effects of NWs ensembles (light trapping, light extraction)
- Exploitation of their high surface to volume ration in specific devices (sensors, thermoelectric devices)

Where does the enthusiasm for NWs come from?











What are the specific advantages of elaborating III-nitrides in the form of NWs?

- Integration of III-N on various substrates:
 Lattice mismatch and difference of thermal expansion are much less critical
 - \rightarrow Strain is relieved by elastic relaxation (free surfaces)
 - \rightarrow Crystal quality better than that of 2D layers (no threading dislocations, no cracks)
- > Expected impact on strategic markets: solid state lighting at low cost (white LEDs)
- > To overcome the non-miscibility gap in strategic alloys (InGaN)
- ➤ High surface/volume + inertness of GaN (does not degrade easily) → good for bio-sensing

What about 1D confinement?

Not really sought in III-N NWs
 Exciton Bohr radius in GaN is small (~3 nm)
 Thin GaN NWs are rarely elaborated (the typical range of diameters is 50 nm - 1 μm)

Growth of Self-Organized GaN Nanostructures on $Al_2O_3(0001)$ by RF-Radical Source Molecular Beam Epitaxy

Jpn. J. Appl. Phys. Vol. 36 (1997) pp. L 459-L 462 Part 2, No. 4B, 15 April 1997

1.5 2.0 2.5 3.0 3.5 4.0

N₂ Flow Rate (sccm)

60

1.0

Masaki YOSHIZAWA, Akihiko KIKUCHI, Masashi MORI, Nobuhiko FUJITA and Katsumi KISHINO Department of Electrical and Electronics Engineering, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan



MBE growth, N radicals, T=800°C

The effect of the III/V ratio and substrate temperature on the morphology and properties of GaN- and AlN-layers grown by molecular beam epitaxy on Si(1 1 1)

Journal of Crystal Growth 183 (1998) 23-30

M.A. Sanchez-Garcia*, E. Calleja, E. Monroy, F.J. Sanchez, F. Calle, E. Muñoz, R. Beresford¹



Later, it will be noticed that NW samples do not show defectrelated emission in the yellow band

Fig. 7. PL spectra of two GaN layers grown directly on Si(1 1 1) substrates: (a) N-rich condition and (b) Ga-rich condition.

Observation of well defined excitonic peaks in the NW sample

APPLIED PHYSICS LETTERS

VOLUME 75, NUMBER 16

18 OCTOBER 1999

Large-scale synthesis of single crystalline gallium nitride nanowires

G. S. Cheng,^{a)} L. D. Zhang,^{b)} Y. Zhu, G. T. Fei, and L. Li Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, People's Republic of China

C. M. Mo Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

Y. Q. Mao Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, People's Republic of China

Reaction of Ga₂O and NH₃ on anodic alumina membranes at T=1000°C

$4\operatorname{Ga}(l) + \operatorname{Ga}_2\operatorname{O}_3(s) \rightarrow 3\operatorname{Ga}_2\operatorname{O}(g),$	(1)
$Ga_2O(g) + 2NH_3(g) \rightarrow 2GaN(s) + H_2O(g) + 2H_2(g).$	(2)







Mono-crystalline GaN NWs WZ structure

Template porous membrane

Laser-Assisted Catalytic Growth of Single Crystal GaN Nanowires

Xiangfeng Duan and Charles M. Lieber*

Department of Chemistry and Chemical Biology Harvard University, Cambridge, Massachusetts 02138



a



Laser ablation GaN/Fe target is vaporized Catalyst-assisted VLS growth No epitaxial relationship with a substrate J. Am. Chem. Soc. 2000, 122, 188-189

Formation of GaN nanorods by a sublimation method

J.Y. Li^{a,b,*}, X.L. Chen^a, Z.Y. Qiao^b, Y.G. Cao^a, Y.C. Lan^a

^aInstitute of Physics and Center for Condensed Matter Physics, Group 401, Chinese Academy of Sciences, P.O. Box 603-33, Beijing 100080, People's Republic of China ^bDepartment of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

Journal of Crystal Growth 213 (2000) 408-410





Sublimation of ball-milled GaN in ammonia at 930°C straight and long NWs

A wide range of methods allow growing GaN nanowires

Molecular beam epitaxy

Vapor phase epitaxy

Chemical vapor deposition

In epitaxy with a substrate or not

Growth with templates

Various precursors

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Crystallography of hexagonal systems



The lower index planes

4-index notation: (h,k,i,l) coordinates in the (a_1, a_2, a_3, c) basis h, k, i are not independent: h+k+i=0





Crystallography of hexagonal systems



Polar planes:

c planes contain only one type of atoms (0001): Ga atoms (000-1): N atoms

Non-polar planes:

a planes and m planes contain equal numbers of N and Ga atoms

Semi-polar planes:

{10-11} planes contain the two types of atoms in inequal numbers

{ }: family of planes

- (): particular plane
- < >: family of directions
- []: particular direction

Various strategies to grow epitaxial GaN nanowires



What determines the crystal shape ? Situation at thermodynamic equilibrium: the Wulff construction



The energy of surfaces depend on their cristalline orientation. At thermodynamic equilibrium, the crystal shape is related to the anisotropy of the surface energies.

This anisotropy is represented by the equilibrium Wulff plot (γ -plot)

Wulff, G. Z. Kristallogr. Mineral. 1901, 34, 449–530.

Broken-bond model:



relaxation, buckling and surface reconstruction are not considered

Type of surface	Broken bond meV/Å ²	Ab initio meV/Å ²
{1-100}	136.7	118 ^a
{11-20}	158.8	123 ^a
(Ga terminated (0001)+N terminated (000-1))/2	128.9	
(N terminated (0001)+Ga terminated (000-1))/2	386.9	
$({1-101}+{1-10-1})/2$	181.2	
$({11-21}+{11-2-1})/2$	201.5	

The facets of lower energy develops

What determines the crystal shape ? Situation during growth: limitation by kinetics



The different surfaces have:

→ different kinetic barriers for adsorption/desorption, surface diffusion, nucleation and incorporation of atoms
 → different chemical potential and growth velocities

The crystal shape is related to the anisotropy of the growth velocity This anisotropy is represented by the kinetic Wulff plot (ν -plot)



Growth velocities are determined on crystals obtained by SAG on various substrate orientations (MOVPE, TMGa and NH₃ sources)

The low velocity facets develops, the high velocity facets disappear.

The influence of growth conditions



In SAG, the facets close to the dielectric mask can exhibit reduced growth velocities

MOVPE of GaN on masked r-sapphire substrates The v-plot is strongly dependent on growth conditions

Temperature: a key parameter

K. Kawasaki et al, J. Cryst. Growth 243, 129 (2002) Tokyo Institute of Technology, Yokohama



GSMBE of GaN nano-crystals on masked SiC (0001) Ga and NH_3 sources Effect of growth temperature on the crystal shape

Classification of typical growth regimes

V. Jindal et al, J. Appl. Phys. 106, 083115 (2009) University at Albany, New York)



Experimental results in SAG





 N_2 carrier gas H_2/N_2 carrier gas 1:2 H_2/N_2 carrier gas 2:1

Bergbauer et al, Nanotechnol. 21, 305201 (2010) Osram Opto Semiconductors, Regensburg



Experimental results in SAG



MOCVD SAG growth on SiO₂ masked substrates: Ga-polar GaN



Pérez-Solórzano, Appl. Phys. Lett. 87, 163121 (2005)



2-step growth to form NWs

X.J. Chen et al. , J. Cryst. Growth 322, 15 (2011) CEA-CNRS-UJF, Grenoble



Shape of the nanostructures can be changed by playing with the growth parameters:

Here, the NW shape is stabilized by a 2-step growth at different temperatures.

A more appropriate denomination here: **Microwire**

MOCVD GaN SAG on masked c-sapphire

Pulsed growth mode



GaN MOCVD SAG, pulsed growth mode

Initial step to fill the openings: 100 Torr H₂/N₂ carrier gas V/III=1500 Ts=1050°C

Pulsed mode after 10 nm TMGa, 10 sccm, 20 s NH3, 500 sccm, 30 s

Hersee et al. , Nano Lett . 6, 1808 (2006) UniVersity of New Mexico, Albuquerque



Summary of SAG experiments

Various strategies can be implemented to form NWs in small mask openings:

- Carrier gas mixture
- Multi-step growth at different temperatures
- Pulsed growth

MOCVD is the most popular technique for SAG Typical wire diameters: 100 nm - 1µm (microwires)

Catalyst-assisted growth

• Method

- catalyst deposition + dewetting to produce nanoparticles
- direct deposition of colloidal particles on the substrate

•Advantages:

- successful for growing NWs of many III-V compounds
- can promote NW growth in various crystallographic directions
- very high aspect ratio
- catalyst size defines the NW diameter
- Drawbacks:
 - possible contamination of the NW by catalyst atoms
 - can generate a lot of stacking faults



Catalyst-assisted growth: change of surface energies



L. Geelhaar, IEEE J. Select. Topics Quantum Electron. 17, 878 (2011) Paul-Drude-Institut für Festkörperelektronik, Berlin

Catalyst-assisted growth: change of kinetic barriers



VPE, Ni catalyst GaCl, NH₃ V/III=7, Ts=980°C

Lekhal et al, Nanotechnol . 23, 405601 (2012) Institut Pascal, Clermont-Ferrand

 \rightarrow The hierarchy of kinetics barriers is changed



Catalyst-assisted growth: elongation along other growth axis







Wang et al, Nanotechnol. 17, 5773 (2006) Sandia National Labs, USA

Ni-assisted CVD (TMGa+NH₃)

Drawbacks of catalyst-assisted growth

Ni-catalyzed GaN NWs: Many basal stacking faults



PL spectra of Ni-catalyzed GaN NWs compared to catalyst-free GaN NWs: D⁰X peak 25 times less intense for catalyzed NWs



C. Chèze et al, Nano Res. 3, 528 (2010) Paul-Drude-Institut für Festkörperelektronik, Berlin Catalyst-free growth: self-formation of NW



Growth diagram of PA-MBE

S. Fernandez-Garrido, J. Appl. Phys. 106, 126102 (2009) Universidad Politécnica de Madrid



Ga-rich conditions 2D layer Threading dislocations

The impact of evaporation geometry

E. Galopin et al, Nanotechnology 22, 245606 (2011) LPN, Marcoussis



In MBE, the N flux incidence angle has an impact on the shape of the GaN NWs: lateral growth is reduced at normal incidence / favoured at grazing angles

Kinetics of nanowire growth



3 competing growth rates:

- Axial growth
- Lateral growth
- Growth on the planar surface

These growth rates are governed by different nucleation rates.

Adatoms can be exchanged between droplet, sidewalls, and substrate via surface diffusion.
Nucleation barrier

Supersaturated phase (gas, liquid, adatoms) $\Delta \mu > 0$

2r

Classical nucleation theory

Venables et al, Rep. Prog. Phys. 47, 399 (1984)

Gibbs free energy of nucleus formation $\Delta G = -\pi r^2 h \Delta \mu + 2\pi r h \gamma$





Diffusion flows of adatoms

MBE case, adapted from Dubrovskii 's model, Phys. Rev. B 80, 205305 (2009)



$$\varepsilon_f = exp\left(\frac{(\mu_l - \mu_f)}{kT}\right) \qquad \varepsilon_s = exp\left(\frac{(\mu_l - \mu_s)}{kT}\right)$$
$$U(x) = \sinh x + \nu\delta(\cosh x - 1)$$

AlN markers to investigate growth kinetics

E. Galopin et al, Nanotechnology 22, 245606 (2011) LPN, Marcoussis



STEM-HAADF (11-20) zone axis







39 ml





Evidence Ga adatoms diffusion

E. Galopin et al, Nanotechnology 22, 245606 (2011) LPN, Marcoussis



Direct Ga flux equivalent to 0.04 nm/s V/III>1

 \rightarrow Surface diffusion of Ga is necessary to explain the elongation rate

 \rightarrow Collection of Ga by the NW sidewalls

The fit gives

- > Ga adatom diffusion length on the sidewalls \approx 40 nm
- Difference of chemical potentials between the sidewall facets and the top facet : 39 meV/atom
- Tacels and the top facel : 39 meV/
- Incubation time : 280 s



NW growth pursued at V/III <1

Fernandez-Garrido et al, to appear in Nano Lett. 2013 ISOM, Madrid

> PAMBE, 2 step growth 1st step, V/III=2 2nd step, variable Ga flux



Whatever the V/III is, the axial growth rate is limited by N flux



For the second step growth under Ga-rich condition, lateral growth is observed



How does lateral growth proceed

E. Galopin et al, Nanotechnology 22, 245606 (2011) LPN, Marcoussis



In parallel with the growth of the NW core, stacks of atomic layers progress on the sidewalls, from bottom to top, and eventually catch up the top.

- 1. Correlations are evidenced: growth rate of the core reduces when a layer starts growing longitudinally on a facet. Ga collection by the sidewalls is shared between the shell and the core
- 2. Core and shell merge







How does lateral growth proceed





Cross-section



Catalyst-free growth: the initial stage of NW formation

3 stages:

O. Landré, Nanotechnol. 20, 415602 (2009) CEA-CNRS, Grenoble



In situ GIXRD measurements (3030) Diffraction (the in plane parameter is probed)

Experiment at ESFR



GIXRD intensity of the (30-30) GaN diffraction peak during GaN NW growth

wetting layer deposition
 → coherent growth: relaxed GaN peak absent

- GaN islands growing laterally (super-linear regime) \rightarrow linear increase of the island diameter ($I_d \propto S \propto R^2 \propto t^2$)

- elongation of fully relaxed GaN NWs \rightarrow linear increase of the NW height (I_d \sim H \sim t)

Shape transitions

1000

Consonni et al, Phys Rev B 81, 085310 (2010), Paul Drude Institute, Berlin



GaN NW formation driven by strain relaxation at the interface

coherent spherical-cap

Another scenario of NW formation

Largeau et al, Cryst. Growth Des. 12, 2724 (2012) LPN-CNRS, Marcoussis





Deposition of Al on Si substrate Formation of Al-Si liquid droplets Formation of AlN pedestals

Exposure to N flux





GaN growth at 800 °C Formation of GaN NWs





N-polar AIN pedestals

[0001]

N-polar GaN nanowires

Tuning the NW composition: $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys

Elaboration of Al_xGa_{1-x}N NWs over a wide range of composition



the PL peak

Elaboration of In_xGa_{1-x}N NWs over a wide range of composition

Kuykendal et al, Nature Mat. (2007) Univ. California, Berkeley



NW morphology \rightarrow strain-relaxed growth \rightarrow less phase separation

NW growth



Solves a major issue of III-nitrides growth :

Lattice mismatch and difference of thermal expansion with the substrates are much less critical

Free sidewalls \rightarrow Elastic relaxation of strain

No threading dislocations, no cracks \rightarrow High crystalline quality on any substrate

Introduction

- GaN nanowire growth mechanisms
- Critical dimensions of nanowire heterostructures
- Nanowire characterization
- Nanowire applications

Hetero-epitaxial systems in general







material B on material A a_B≠a_A The lattice is strained to accomodate the misfit

Lost of coherence of the crystalline lattices Strain energy > dislocation energy Strain relaxation via formation of dislocations Due to the presence of free surfaces, the NW morphology allows accommodating larger lattice-mismatches as compared to 2D films

(the forces on any free surface cancel)



3 cases to be considered

The case of axial heterostructures

F. Glas, Phys. Rev. B 74, 121302 (2006) LPN-CNRS, Marcoussis



Axial heterostructure

Assumptions:

- elastic stiffness tensor is isotropic
- infinite nanowire length (material A)
- ε_0 : misfit of material B
- Circular cross-section





Calculate the total strain energy of the system, W_e , as a function of h (finite-element calculations and approximate analytical expression)



Introduction of dislocations

F. Glas, Phys. Rev. B 74, 121302 (2006) LPN-CNRS, Marcoussis

Dislocation formation:

A single pair of orthogonal dislocations is considered

The total energy is modified :

- W_e is reduced (partial relaxation)
 -Additionnal energy W_d (dislocation energy)

$$w_d = \frac{E(1-\nu\cos^2\theta)b^2}{8\pi(1-\nu^2)} \left(1+\ln\frac{\bar{h}}{b}\right)$$

h distance between the dislocation line and the free surface
b Burger vector
θ Angle between the dislocation line and the Burger vector
E Young modulus
v Poisson ratio

Pure edge ($\theta = \pi/2$, $b_{eff} = b$) or 60° type ($\theta = \pi/3$, $b_{eff} = b/2$)



Excess of energy of the state with the dislocation pair with respect to the coherently strained case

$$\Delta W(r_0,h) = \frac{Er_0}{1-\nu} \left[f_\nu \left(\frac{h}{2r_0}\right) \pi r_0 h \left(\frac{\alpha^2 b_{\text{eff}}^2}{4r_0^2} - \frac{\alpha b_{\text{eff}}}{r_0} \epsilon_0\right) \right. \\ \left. + C \left(1 + \ln\frac{\bar{h}(r_0,h)}{b}\right) \right]$$

with $C = (1 - \nu \cos^2 \theta) b^2 / [2\pi (1 + \nu)]$

 $\Delta W(r_{0},h)=0 \rightarrow \text{critical dimensions}$

Critical dimensions of axial heterostructures

F. Glas, Phys. Rev. B 74, 121302 (2006) LPN-CNRS, Marcoussis



Critical dimensions as function of the misfit Calculation based on GaAs parameters Calculation for III-N systems

The critical radius of axial III-N heterostructures

$$\frac{2\pi}{A_{\nu}} \left(\frac{\alpha^2 b_{\text{eff}}^2}{4} - \alpha b_{\text{eff}} \epsilon_0 r_0^c \right) + C \left(1 + \ln \frac{\beta r_0^c}{b} \right) = 0$$



8

The case of radial heterostructures

Raychaudhuri and Yu, J. Appl. Phys. 99, 114308 (2006) University of California, San Diego



Assumptions:

- elastic stiffness tensor is isotropic in a cross-sectional plane
- infinite nanowire length L
- Circular cross-section

Longitudinal (c) and tangential strain (a) at the interface for the core (i) and for the shell (ii)

$$f_c^{(i)} = \frac{c - c^{(i)}}{c^{(i)}} \qquad f_c^{(ii)} = \frac{c - c^{(ii)}}{c^{(ii)}}$$

$$f_a^{(i)} = \frac{a - a^{(i)}}{a^{(i)}} \qquad f_a^{(ii)} = \frac{a - a^{(ii)}}{a^{(ii)}}$$



Equilibrium parameters in a radial heterostructure

Raychaudhuri and Yu, J. Appl. Phys. 99, 114308 (2006)

Method:

Express the total strain energy of the system as a function of

- strain components
- elastic stiffness tensor elements

$$\begin{split} U^{(i)} &= \frac{[c_{11}^{(i)}f_a^{(i)}]^2 - [c_{12}^{(i)}f_a^{(i)} + c_{13}^{(i)}f_c^{(i)}]^2 + c_{11}^{(i)}f_c^{(i)}[c_{13}^{(i)}f_a^{(i)} + c_{33}^{(i)}f_c^{(i)}]^2}{2c_{11}^{(i)}} L\pi(r^2), \\ U^{(ii)} &= \frac{[c_{11}^{(ii)}f_a^{(ii)}]^2 - [c_{12}^{(ii)}f_a^{(ii)} + c_{13}^{(ii)}f_c^{(ii)}]^2 + c_{11}^{(ii)}f_c^{(ii)}[c_{13}^{(ii)}f_a^{(ii)} + c_{33}^{(ii)}f_c^{(ii)}]^2}{2c_{11}^{(ii)}} L\pi[(r+h)^2 - r^2] \end{split}$$

Find the equilibrium lattice parameters a and c which minimize this expression



Equilibrium lattice parameters of a coherent core-shell structure: 25 nm GaN core - Al_{0.2}Ga_{0.8}N shell

Strain fields calculated by the VFF model and their experimental observation

Hestroffer, Nanotechnology 21, 415702 (2010) CEA-CNRS, Grenoble

Valence Force Field (VFF) atomistic model







Strain along the axis



In-plane parameter

AIN shell has the same a as the relaxed AIN

Axial parameter GaN and AlN have almost the same c in the core-shell region

Geometrical phase analysis (GPA): Maps of the a and c parameters

Introduction of dislocations

Raychaudhuri and Yu, J. Appl. Phys. 99, 114308 (2006)



Critical dimensions of radial heterostructures

Raychaudhuri and Yu, J. Appl. Phys. 99, 114308 (2006)



The case of a NW on a planar substrate

X. Zhang et al, Cryst. Growth Des. 11, 5441 (2011) St. Petersburg Academic University



The critical radius of epitaxial GaN nanowires on misfitting substrates



Summary on the critical dimensions of nanowire heterostructures



In axial heterostructures, there are practical cases which really benefit from the NW morphology. Ex: AlN deposited on a GaN stem, r_c = 60 nm



In radial heterostructures, the advantage compared to the 2D case is less obvious.

Ex: GaN shell deposited on a $In_{0.15}Ga_{0.85}N$ core, r_c = 7 nm



In most practical cases, a few discolations might exist at the GaN NW/substrate interface. Ex: GaN NW grown on SiC, r_c = 20 nm Ex: GaN NW grown on Si, r_c = 2 nm

The real benefit here is to avoid threading dislocations.

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μ-PL on single GaN NWs

Brandt et al, Phys. Rev. B 81, 045302 (2010) Paul Drude Institute, Berlin

> MBE grown GaN NWs Catalyst-free Si (111) substrate

 $D^{0}X_{A} @ 3.4716 eV$ (FWHM 0.84 meV) ($D^{0}X_{A}$)^s @ 3.4749 eV : surface donor bound X (FWHM 0.28 meV) FX_A @ 3.4789 eV Chen et al, Appl. Phys. Lett. 99, 251910 (2011) CEA, Grenoble

> MOVPE grown GaN NWs Catalyst-free C-sapphire substrate

 $D^{0}X_{A} @ 3.470 eV (FWHM 0.95 meV)$ $D^{0}X_{B} @ 3.473 eV$ $FX_{A} @ 3.477 eV$ $FX_{R} @ 3.482 eV$



✓ No yellow band

✓ Degradation with time (sensitive to surface evolution)

Sensitivity to the environment

GaN NWs under illumination (He-Cd laser) and exposed to air → Progressive PL quenching at RT

- Intensity ÷ 10

- no spectral change

- reversible

Photoabsorption of oxygen

Absorbed O creates

- non radiative channels at the surface
- or strong band bending in the NW

P. Lefebvre et al., Superlattices and Microstruct. 52, 165 (2012) Lab. Charles Coulomb. Montpellier



μ PL of a GaN/AIN heterostructure

NW growth: Maria Tchernycheva, LPN, Marcoussis

μPL : Julien Renard, Bruno Gayral, CEA-DRFMC ,Grenoble



Nano-cathodoluminescence

Zagonel et al, Nanotechnol. 23, 455205 (2012) Laboratoire de Physique des solides, Orsay

GaN/AIN NW heterostructure





Quantum disc + unintentional quantum rods

- Ideal tool to identify the emission of nano-structures
- ➢ High spatial resolution due to strong carrier confinement



Q disc emission: affected by the disc thickness (confinement and QCSE)

Micro-PL of strained core-shell structures

Rigutti et al, Phys Rev B 83, 155320 (2011) IEF, Orsay





The strain modify the band structure: the optical transition of lower energy changes from X_A type to X_C type This kind of study necessitates micro-PL + TEM measurements on the very same objects

How to measure the electrical properties of nanowires

- Implementing Hall effect is very challenging
- Field effect is commonly used

Y. Huang et al, Nano Lett. 2, 101 (2002) Harvard Univ.




Field effect mobility

- L length of NW between the contacts
- **h** gate oxide thickness
- rNW radius





Y. Huang et al, Nano Lett. 2, 101 (2002) Harvard Univ.

1.0



Comparison with Hall effect measurements (case of InAs NWs)

Problems:

• In actual situations, the assumptions to derive the previous C formula are not verified

• C is very sensitive to interface charges! If the interface charges are neglected, μ_{FE} is underestimated n is overestimated

Ch. Blömers et al, Appl. Phys. Lett. 101, 152106 (2012) Peter Grünberg Institute, Jülich See

- Khanal and Wu, Nano Lett 7, 2778 (2007)
- Dayeh et al, Small, 3, 326 (2007)



"Hall bar" fabricated by e-beam lithography on InAs NWs

Measuring the minority carrier diffusion length by EBIC

Gutsche et al, Nano Lett. 12, 1453 (2012) Univ. Duisburg Essen



 $I = I_0 e^{-x/L}$

GaAs NWs

X distance to the junction*L* minority carrier diffusion length

Also possible with a Schottky contact

Allen et al, Nature Nanotechnol. 3, 168 (2008) Northwestern University, Evanston



Not yet applied to III-N nanowires

Alternative (but more questionable) technique applied to III-N heterostructures

Baird et al, Physica B 404, 4933 (2009). Baird et al, Appl. Phys. Lett. 98, 132104 (2011)







Near field scanning optical microscopy is used to visualize the radiative recombinations of e⁻/h pairs created by and incident e⁻ beam.

Wire	Diameter (nm)	Diffusion length (nm)
AlGaN/GaN-n-type	200	1100
	500	1200
	700	1100
GaN-n-type	300	130
	500	660
	700	830
InGaN/GaN-n-type	500	350
	700	430
	1000	470

Higher and radius-independent values are obtained with an AlGaN shell.

Structural properties and composition (2 lectures today)

TEM/STEM

X-ray diffraction







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Potential benefits of III-N NWs for LEDs

(NWs ensembles compared to 2D layers)

Less crystal defects (dislocations and cracks)
Operation at lower carrier density, reduced Auger effect

> Large choice of substrates (thermal management and cost issues)

More efficient light extraction

➤ Reduced quantum confined Stark effect in QW structures axial QWs: reduced strain → reduced piezoelectric fields Lateral QWs: non-polar facets

Good tuning of the InGaN or AlGaN composition (wavelength tuning, colorimetry)

Lower material consumption

NW structures for LEDs



More strain accommodation Easier wavelength tuning

Large emitting area Non-polar lateral QWs

Strategies to tune the emission wavelength

- GaInN discs or radial QWs of various composition
- GaInN discs radial QWs of various thicknesses
- NWs of different diameters

To get white emission

- GaInN segment with a gradual composition
- Stack different discs QWs

LED efficiency



In_xGa_{1-x}N discs of various thicknesses

(a) (b) Ni/Au Fi/Au Si(111) (c) p-GaN T_3 5 InGaN NDs 1 1 n-GaN

InGaN discs of different thicknesses (10-25 nm)

PAMBE, self organized NWs,

Lin et al, Appl. Phys. Lett. 97, 073101 (2010) National Tsing-Hua University, Taiwan



White emission is obtained

Only a small part of the NWs are contacted



blue-band @ 448 nm yellow-band @ 569 nm

Almost no spectral shift with increasing electrical injection (reduced QCSE)

No current density values

In_xGa_{1-x}N segments of various composition

Guo et al, Appl. Phys. Lett. 98, 193102 (2011) Univ. Michigan, Ann Arbor

PAMBE, self organized NWs, GaInN/GaN discs



In_xGa_{1-x}N dots in GaN NWs

Chang et al, Appl. Phys. Lett. 96, 013106 (2010) Nguyen et al, Nano Lett. 11, 1919 (2011) McGill Univ., Montreal

PAMBE, self organized NWs,



InGaN/GaN dots-in-a-wire heterostructures



Current Density (A/cm²

300

Good IQE in the « green gap » 45% @ 564 nm



White emission no efficiency droop @ 300 A/cm²

Estimated IQE at 300 K: 57%

P doped InGaN/GaN dots

Regular NW arrays of different diameters

PAMBE, regular NW arrays, Ti mask



K. Kishino et al, J. Cryst. Growth 311, 2063 (2009) Sophia Univ. Tokyo



77% IQE @ λ =487 nm

Sekiguchi et al, Appl. Phys. Lett. 231104 (2010) Sekiguchi , Kishino et al, Appl. Phys. Express 124002 (2008) K. Kishino et al, Appl. Phys. Express 6, 012101 (2013)

Radial InGaN/GaN heterostructures for LEDs

Koester et al, Nano Lett. 2011, 4839 CEA Grenoble (France)

Non-polar radial QWs Lateral growth on {1T00} *m*-plane sidewalls MOCVD

InGaN/GaN MQWs



Difficulty to get uniform thicknesses



InGaN well-GaN barrier thicknesses 1.0 nm / 7.5 nm



5.2 nm / 11.6 nm



Too thick radial InGaN QWs generate dislocations

Radial InGaN/GaN heterostructures for LEDs

Yong-Ho et al, Nano Lett. ASAP , 2013 Chonbuk National University, Korea

Au-catalyzed MOCVD



EQE ≈ 28%



InGaN QWs on m planes and r planes No dislocations

Ga(In)N nanowires for LEDs

LEDs based on GaN microwires on 200-mm Si substrates

http://www.aledia.com/en/ LETI, Grenoble (France)



e e e e e Standard (100) n-Si

Objective : \$/lumen divided by 10

3D (Microwire) LEDs:

- Large, economical substrate
- Fast MOCVD growth process (low capital expenditure)
- Low materials consumption
- Existing high-volume silicon wafer fabs
- Light emission area = up to 3X the 2D area = more light/mm² or less current density, less efficiency droop
- Multiple colors on one wafer or even on one chip

Potential benefits of III-N NWs for Photovoltaics

(NWs ensembles compared to 2D layers)

Less crystal defects (dislocations and cracks) less carrier recombination

- Large choice of substrates (cost issue)
- Lower material consumption (cost issue, exhaustible elements)
- Good tuning of the InGaN composition
- More flexibility in designing heterostructures
- Reduced reflection of light and light trapping effect (improves absorption)
- Charge separation over short distances in radial junctions

Three possible junction designs





Surface recombination

Best design:

Large junction area Short distance for minority carrier transport Large contact area possible on the p-shell

Optimal shape for absorption

B. Wang et al, Nanotechnology 2012, 194003 University of Pittsburgh, USA

Array of small diameter NWs \rightarrow low reflection but high transmission

Array of large diameter NWs \rightarrow low transmission but high reflection

Array of nanocones: good trade-off





Enhanced absorption in silicon nanocone arrays

Light trapping and enhanced absorption



GaN(p) NWs on Si(n) substrate

Tang et al, Nano Lett. 8, 4191 (2008) City UniVersity of Hong Kong,

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Some comparative references

Today, the best efficiency of InGaN solar cells is obtained with 2D layers cell: $\eta \approx 6\%$

B. W. Liou, Thin Solid Films 520, 1084 (2011) WuFeng University, Taiwan



Today, the best NW solar cell is based on InP NWs (pin axial structure): η=13.8%

Wallentin et al, Science 339, 1057 (2013) Univ. Lund



Single NW photovoltaic device core-shell n-p junction



Dong et al, Nano Lett. 9 (5), 2183 (2009)





Green cell (EL peak at 556 nm) 1-sun illumination $J_{sc}=58pA$ $V_{oc}=1V$ Conversion efficiency =0.2% (very weak absorption)

\rightarrow nano-photodetector

Nanolasers and nano-photodetectors

J.C. Johnson et al, Nature Mat. 1, 106 (2002) Univ. California, Berkeley

Single GaN NW





PL under CW optical excitation (1mW) Lasing under pulsed excitation (1µJ.cm⁻²)

GaN n-i-n device Wavelength (nm)

IEF, Orsay



Rigutti et al, Nano Lett. 10, 2939 (2010)

Application \rightarrow nanodevices on bio-chips / nano-sensors

Device with GaN/AIN Qdiscs

Piezo electric nano-generators



Z. L. Wang et al 2006 Science 312 242 (2006) Georgia Inst. Technol. , Atlanta Xu et al, Nanotechnology 22, 105704 (2011) IMEP, Grenoble



Power generation from bending NWs

Spontaneous electric potential measured in GaN nanowires

Application \rightarrow self-powering of nano-systems

Photonic properties

Kölper , Phys. Status Solidi C 8, 2305 (2011) Osram Opto Semiconductors, Regensburg



a NW can act as a monomode waveguide for r/ $\lambda{<}0.2$



Purcell factor and light extraction efficiency



Directivity of the light emission

Brief outlook on III-N NW devices

NW ensembles

- A few promising characteristics
- Very challenging competition with established technologies based 2D layers
- Advantage of the large choice of substrates
- Uniform injection/collection in NW ensembles is necessary (regular arrays)

Single NWs

- More academic studies
- Single photon emitter
- Sensors in micro-systems